A Parametric Study on the Synthesis of Graphene Using Piranha-like Thermal Exfoliation

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Abstract. The remarkable physical properties of graphene has drawn the global attention of scientists and researchers. In order to harvest these intrinsic properties, a scalable, efficient synthesis method has to exist. Whilst conventional chemical synthesis of graphene oxide (GO) can be reduced to form reduced GO (rGO) or functionalised graphene. rGO is defective and sacrifices a portion of the intrinsic properties of graphene. On the other hand, direct exfoliation of graphite in solvents has been successful in synthesizing unfunctionalised graphene, but the yield is very low. As such, efforts need to be invested to synthesize unfunctionalised graphene, but with a higher yield. A combination of thermal and facile exfoliation of graphite intercalated compounds (GICs) is thus, proposed. Graphite was intercalated in a mixture of sulfuric acid and hydrogen peroxide before being subjected to a rapid heat treatment in excess of 900°C. The thermally expanded graphite was then exfoliated in solvents to produce graphene sheets. An optimisation of the limiting parameters was also carried out to determine the best approach. Results showed that an increase in the amount of oxidiser, extension of the thermal expansion time as well as an increase in the starting graphite flake size resulted in larger, thinner flakes. Tapping mode AFM analysis showed that the as produced flakes had average thicknesses ranging between $4 - 30$nm with average lengths ranging from 0.5 μm to 10 μm.

Keywords: Graphene, Thermal exfoliation, Piranha solution, Facile exfoliation, Optimization

1. Introduction

Graphene, a 2D monolayer of sp^2 hybridized carbon atoms arranged in a honeycomb lattice structure has sparked global interest in many disciplines due to its exotic and superior physical properties that were not previously observed at the nanoscale. Some of the important properties of graphene are quantum Hall Effect at room temperature, ultrahigh electron mobility and ballistic transport, long electron mean free paths, superior thermal conductivity, fascinating mechanical strength, and remarkable flexibility [1-4]. As such, graphene exhibits wide potential applicability in biosensing [5], various energy storage related devices [6-7], electronic displays and more. To date, the development and widespread application of graphene are mainly hampered by the lack of methods for controllable, reproducible and scalable mass production. While many synthesis methods have been reported [8-11], the most popular is by chemical reduction of graphene oxide (GO) via the Hummer's method [12]. This method involves the use of harsh acid mixtures at long processing times. Graphene from reduced GO is also known as functionalised graphene sheets due to its abundance of functional groups, such as hydroxyls and epoxides. While these functional groups can be removed by

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annealing and reduction, a significant number of residuals and defects still remain [13]. To produce defect-free, unoxidised graphene, Hernandez et. al. proposed a facile exfoliation of graphite in organic solvent method, resulting in graphene concentrations up to ~0.01 mg/ml [15].

Although the results showed promising production of unfunctionalised and defect-free graphene, the yield is a far cry from mass production. Recent research on the exfoliation of graphene from worm-like exfoliated graphite (WEG) serves as the basis of this work [16]. In order to achieve a higher yield compared to merely sonicating raw graphite flakes in organic solvents, it is necessary to first expand the interlayer distance between the graphitic flakes. In this paper, an improved synthesis method by thermal expansion of intercalated graphite (GIC), followed by facile exfoliation is presented. For process optimisation, the effects of varying various key synthesis parameters are reported.
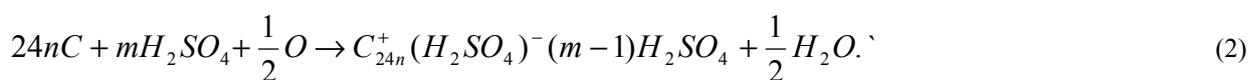
2. Methods

Graphite (Bay Carbon) was intercalated by stirring in a mixture of concentrated sulfuric acid, H_2SO_4 (96%) and hydrogen peroxide, H_2O_2 (30%). The intercalated graphite was then washed with distilled water until a pH of 7 is reached and dried at 100°C for 24 hours. Thermal expansion was carried out in a muffler furnace at 950°C, forming worm-like exfoliated graphite (WEG). WEG was then sonicated in a mixture of water and NMP for 30 minutes, forming a stable dispersion of few layered graphene (FLG) flakes. The parametric study was conducted by varying key parameters at each synthesis stage. Of these, the acid-oxidizer ratio was varied from 5:1 to 40:1. Thermal expansion times were varied at 5, 10 and 60 seconds and different starting flake sizes with average of 2 μm, 45 μm and 350 μm were used respectively.

The as-prepared graphene were examined using scanning electron microscopy (FEI Quanta-400 FESEM). WEG samples were scanned as powders whilst the final exfoliated multi-layered graphene were deposited from dispersion onto silicon wafers and the solvent was left to evaporate overnight at 37°C. Atomic force microscopy (AFM) analysis on samples drop casted on Si wafers was carried out on the NTEGRA Spectra (NT-MDT).

3. Results and Discussion

3.1. Effect of Acid Ratio to Intercalation.

The use of H_2O_2 as an oxidizing agent makes this process much more environmental friendly in comparison to the Hummer's or Brodie method whereby toxic gases are released as by-products. In contrast to this, water is the only by product from the reaction of sulphuric acid with hydrogen peroxide as shown in Eq. 1 and Eq. 2 below [17].

$$H_2O_2 \rightarrow H_2O + O. \tag{1}$$

$$24nC + mH_2SO_4 + \frac{1}{2}O \rightarrow C_{24n}^+ (H_2SO_4)^- (m-1)H_2SO_4 + \frac{1}{2}H_2O.` \tag{2}$$

The SEM images in Fig. 1 show that graphite flakes are subjected to a pre-expansion right after the intercalation stage is completed. In an effort to investigate the effect of the intercalation ratio, the acid to oxidizer ratio was varied from 5:1 to 40:1. SEM results show that an intercalant to oxidizer ratio of 5:1 gives the most efficient expansion ratio. This is attributed to the fact that more oxidizer are allowed to react with the intercalant present in the mixture. This is supported by past research on the effect of H_2O_2 as more than a catalyst, but also a co-intercalant during the intercalation stage, thereby improving the efficiency of expansion [17]. A comparison between the results obtained from the intercalation ratio of 5:1 (Fig. 1C) to that obtained from an intercalation ratio of 40:1 (Fig. 1F) distinctly illustrates the difference of these two extremes in the final FLG structure. Complete exfoliation is discernible in the thinner flakes as shown in Fig. 1C compared to the thicker flakes produced by an intercalation ratio of 40:1 (Fig. 1F)

Observing results obtained from an intercalation ratio of 40:1, the lower degree of expansion leads to an incomplete exfoliation of the final product. Therefore, lower intercalation ratio will improve the process effectiveness as the GICs are well pre-expanded before subjected to rapid thermal expansion.
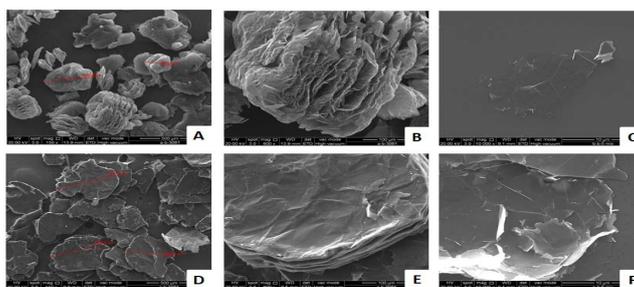
Fig. 1: (A) and (B) Intercalated graphite treated at a $H_2SO_4 : H_2O_2$ ratio of 5 : 1 (C) 5:1 Final exfoliated product on silicon substrate. (D) and (E) Intercalated graphite treated at a $H_2SO_4 : H_2O_2$ ratio of 40 : 1 (F) 40:1 Final exfoliated product on silicon substrate

3.2. Effect of Thermal Expansion Time

It is essential that GICs be subjected to a rapid thermal shock treatment in order to release the intercalants, thereby creating the pressure required to overcome the Van der Waals force holding the layers together. However, nanomaterials tend to sinter and agglomerate when subjected to high temperatures for prolonged periods. Although thermal expansion of intercalated graphite usually takes place in a matter of seconds [17], it is difficult to control the preciseness of this measure of time. The results in Fig. 2 show that by increasing the thermal expansion time from 5 seconds to 60 seconds, a vast increase in volume can be observed (Fig. 2A; left to right). Furthermore, a mere increase of 5 seconds in thermal expansion is found to vastly improved the expansion ratio and thus the interlayer distance of individual flakes (Fig. 2B and Fig. 2D *(x 600 magnification)*.
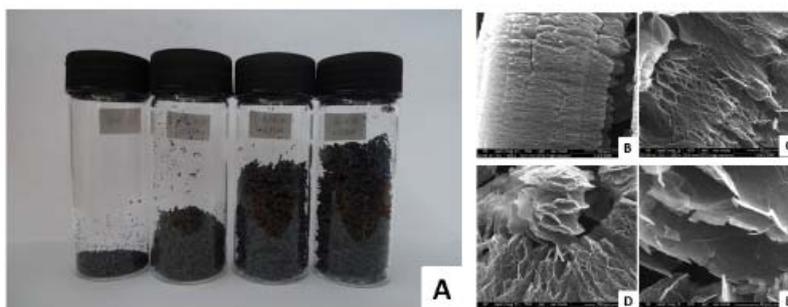

Fig. 2: *(A)* Glass vials containing raw GIC before expansion and WEG thermally expanded at 5 seconds, 10 seconds, and 60 seconds from left to right. (B) and (C) SEM image of intercalated graphite expanded at 900 C for 5 seconds . (D) and (E) SEM image of intercalated graphite expanded at 900 C for 10 seconds.

Comparing Fig. 2C with Fig. 2E, it can also be seen that apart from a larger interlayer distance, the WEG produced by a 10 second thermal expansion is less compact and much more flake-like. It is expected that with larger interlayer distance, WEG exfoliation efficiency will be improved, thus producing thinner graphene flakes/structure. The increment of time from 5 seconds to 60 seconds also allows precise standardization over the time for the thermal expansion treatment. The extended thermal expansion time of 60 seconds allows enough time for the dispersion of heat across all surfaces, thereby allowing all intercalated compounds to evaporate out of the graphitic layers. This proves that the heat dispersion was sufficient to expel all intercalants from within the graphitic layers, which in turn results in more pressure expanding the graphitic layers.

3.3. Effect of Starting Flake Size

Previous study on the effect of the starting flake size in the synthesis of graphite oxide (GO) has reported that the end product is independent of the starting flake size but instead affected by the amount of oxidation the flakes are exposed to [18]. However, from a theoretical point of view, larger graphite flakes provide a larger platform for intercalation between the graphitic layers. When these flakes are subjected to rapid thermal expansion, the pressure released by the decomposition of the intercalants is much higher

compared to the pressure build-up from intercalants trapped within smaller graphite flakes. This is illustrated in Fig. 3 whereby 350 μm graphite features a well-formed accordion structure due to the pressure released when trapped intercalants escape at rapid thermal shocks.
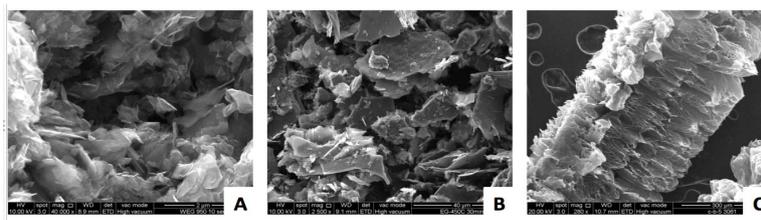

Fig. 3: (A) WEG obtained from 1-2 μm graphite (B) WEG obtained from 45 μm graphite (C) WEG obtained from 350 μm graphite

On contrary to [18], the results obtained showed that the starting flake size is important, where larger starting flake size results in larger as produced graphene sheets, with thicknesses comparable to that of smaller starting flake sizes (Fig. 4).
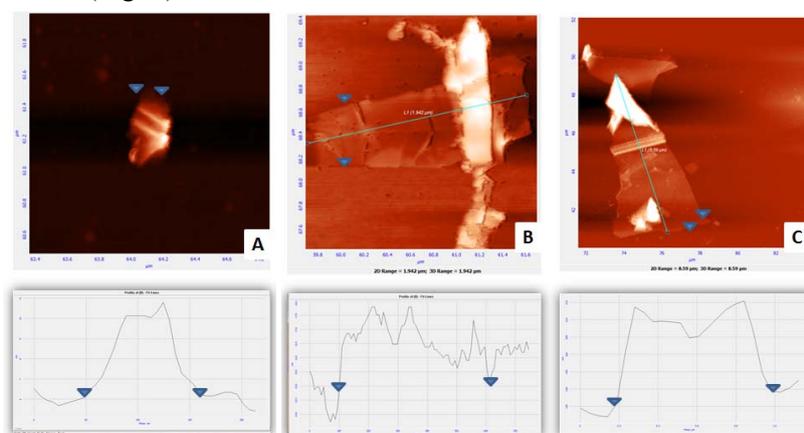

Fig. 4: (A) AFM image of a FLG flake synthesized from graphite with a starting flake size of 1-2 μm (B) AFM image of a FLG flake synthesized from graphite with a starting flake size of 45 μm (C) AFM image of a FLG flake synthesized from graphite with a starting flake size of 350 μm

Table 1 summarizes the effect of different starting flake sizes on the average lengths and thicknesses obtained in the as produced graphene. The largest graphene flakes were obtained with a starting flake size of 350 μm. However, the thickness of these larger flakes are much thicker, which points toward incomplete exfoliation. Further sonication is able to reduce this thickness, but at the expense of size due to fragmentation of the graphene sheets. The ability to tailor the final graphene length and average thickness by varying the starting flake size offers additional control over the synthesis parameters as different graphene products can be produced for various applications.

Table 1: Table of comparison between average lengths and thickness of exfoliated FLG derived from graphite of different flake sizes

Starting Flake Size [μm]	Average length [μm]	Average thickness [nm]
1-2	< 0.50	4 – 6
45	< 2.00	4 – 8
350	< 10.00	15 – 30

4. Summary

Thermal exfoliation followed by facile exfoliation is an effective method to achieve unfunctionalised thin stacks of graphene sheets. The current process can be optimized by tuning the crucial parameters such as the intercalant to oxidizer ratio, the thermal expansion time as well as the starting graphite size. Fine-tuning of these parameters would yield sheets that are thinner, larger in dimensions and an understanding on how

these parameters affect the final product would be essential to synthesizing graphene sheets that can be implemented into many applications.

5. Acknowledgements

6. References

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