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Consequence of oxidation method on graphene oxide produced with different size graphite precursors

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ABSTRACT

Exfoliation method is a most cost effective method for producing chemically derived-graphene (CDG) yet electronic performance of CDG strongly depends on the lateral and vertical dimensions of graphene especially in regards to the development of macroscopic scale films. This work demonstrates the variation in functionality of Graphene oxide (GO) prepared via Marcano-Tour's and modified Hummer's method using two different sized graphite precursors. Reduced GO papers were fabricated using vacuum filtration and examined by Hall probe and Raman spectroscopy to ensure their quality. A correlation between oxidation-controlled GO size with their overall electrical conductivity is explored by Fourier Transform Infrared spectroscopy (FTIR), Thermo Gravimetric Analysis (TGA) and X-ray Diffraction (XRD) techniques. This study reveals that the modified Hummer's method suitably preserves basal planes of GO produced from larger GO flakes with less inter-sheet resistance and illustrates the importance of comparing synthetic methods for producing large area high quality graphene related nanostructures.

1. Introduction

Graphene is a promising material because of its extraordinary mechanical, electronic, magnetic and optical properties [1–3] which are anticipated to impact semiconductor and composite industries for a variety of applications in the area of energy [4–7]. A grand challenge identified by the graphene community is standardization of graphene products due to the variations in performance and the diverse methods for production [8,9]. The projected cost of nanographene is about US $ 11/kg [10] which is an important factor that makes nanographene completive with other nanocarbons (i.e. fullerenes, nanotubes) in commercial applications. Exfoliation methods represent a substantial number of published and granted patents [11] and have the most immediate potential for low-cost and large scale production.

Chemically-derived-graphene (CDG) is most often prepared into graphene oxide (GO) from graphite oxide and reduced either chemically, thermally or both [12]. Graphite oxide is converted into single layer GO in polar solutions due to the presence of oxygen functional groups creating an electronegative repulsion. Consequently, it is desirable to improve the oxidation of graphite but without doing so at the expense of the sp^2 hybridized structure of carbon atoms on their basal surfaces. Chemical and thermal reduction imparts further damage to the graphene basal planes and disrupts the carbon sp^2 hybridized structure depending on the reactivity of GO [13]. Ultimately the electronic performance of CDG depends on the lateral and vertical dimensions of graphene especially in regards to the development of macroscopic scale films [14].

Carbon-based sheet-like nanomaterials like graphene oxide can be assembled into papers or membrane like macroscopic arrangements under a specific directional flow. Papers fabricated from reduced graphene oxide have attracted significant attention for their use in electrode energy devices [15], ultrathin flexible electrode materials [16–18], protective layers [19] and filters for chemical separation [20–22], where nanoscale properties of GO influence the performance at a macroscopic level.

Reduced GO papers prepared via vacuum filtration have been studied previously using hydrazine, thermal annealing under a mixture of Hydrogen and Argon, and the combination of the two methods by Zhao

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Table 1
Summary of synthetic methods referenced and used in this work for comparison. Reagents were added to 3 grams of graphite.

Method	Systems	$NaNO_3$ (g)	H_2SO_4 (ml)	$KMnO_4$ (g)	H_3PO_4 (ml)	Reaction conditions
Hummer's [62]	HGO	1.5	69	9	/	Reacted for > 1 h at 35 °C, quenched in water
Hummer's [62]	HGO+	1.5	69	18	/	Reacted for ~20 h at 35 °C, quenched over ice
Improved [62]	IGO	/	360	18	40	12 h at 50 °C, quenched over ice
Hummer's [46]	HGO	/	69	9	/	Reacted for 2 h at 35 °C, quenched over ice

et al. [23]. They found the combination of hydrazine and thermal annealing to be the most effective at restoring conductivity. However, one of the disadvantages to hydrazine aside from its toxicity [24] is also that it renders reduced GO insoluble [25] and difficult to spread on to substrates. In addition, Su et al. found that during thermal annealing, ultra large GO sheets break into small domains [26]. Zhang et al. measured the conductivity of reduced GO (rGO) papers prepared using L-ascorbic acid (L-AA) and found them to be comparable to papers reduced by hydrazine. The results demonstrate an inexpensive and effective method for restoring conjugation effectively without using high temperature thermal annealing [27] that is an environmentally friendly alternative without the need for surfactants to stabilize the resulting rGO dispersion.

Identifying and quantifying the various functional groups present in GO is a complex task and to date there is still much debate about the structure of GO [28]. Owing to the number of variables such as parent graphite, oxidation paths, chemical exfoliation and reduction methods, many are seeking to understand the impacts on the resulting reduced GO devices previously. In order to realize properties desired for composites, thin films or adhesives, various factors that affect the size of GO sheets, such as post-treatment of parent graphite [29], oxidation conditions [30–32], pH value [33] and controlled centrifugation [34] must first be addressed. The number of studies related to graphene oxide has sharply increased since 2010 [35,36] and factors that are currently complicating the speed at which GO and rGO can be commercialized are cost, time of production and volume of production [37].

The influence of parent graphite source on subsequently prepared GOs has been studied previously using five different types of commercially sourced graphite [38]. Researchers concluded that the properties of the parent graphite significantly influenced the properties of corresponding thermally reduced GO but they did not yet explore the oxidation methods. Qi et al. prepared GO from a 200 µm graphite precursor, controlled GO flake size through various ultrasonication times and studied the electrical resistance [39]. There is unavoidable fracturing of GO sheets during the oxidation and exfoliation processes which result in GO sheets with smaller area than the parent graphite and an increase in inter-sheet contact resistance in conductive thin films due to a larger amount of inter-sheet junctions [40].

Synthesis of ultra large GO sheets can be controlled by modifying the oxidation/exfoliation. However, researchers only studied GOs after various reaction times using the same oxidation method (Hummer's) throughout each of these experiments [41,42]. Researchers also synthesizing graphene nanoribbons from carbon nanotubes found that the combination of $KMnO_4/H_2SO_4$ very effectively cuts the basal planes leaving formed edges with carbonyl groups [43]. Rodriguez-Pastor et al. determined that this cutting mechanism optimizes the exfoliation into single sheets and found Hummer's method to be more successful than $KClO_3/HNO_3$ mixture as used in Brodie's method for producing single layers [44]. However they found that GO synthesized by Hummer's method has significant amounts of oxidative debris compared to GO synthesized with Brodies method and results in either large-single sheets, or small (humic) and very small (fulvic) entities oxidized at the edges. Shi et al. prepared GO using Marcano–Tour's improved and Hummer's methods to determine how the procedures and reagents influenced the structure of GO and rGO nanosheets [45]. The study concluded that rGO prepared via Marcano–Tour's improved method was successful in producing rGO with less defects but this considered only one size or source of parent graphite.

Recently, Chowdhury et al. systematically studied the role of graphite precursor and $NaNO_3$ in the synthesis of GO by Hummer's method utilizing various graphite sources and sizes namely, 20, 40, 150 µm and found that $NaNO_3$ reduced crystallite sizes of GO sheets by cleaving the basal plane [46]. The results suggested a potential way to use Hummer's method and preserve the lateral dimensions of the parent graphite within GOs as synthesized and preserve the sp^2 hybridized structure of the carbon basal planes.

In this work, we revisit Mercado-Tour's method in comparison with Hummer's method without $NaNO_3$ and use large and small sized commercially available graphites to investigate the influence of each oxidation method on the basal planes of graphite while preparing GO. We use these small and large graphite sources to explore the range of resulting structures and functionality of GO for better understanding of the subsequent reactivity to L-Ascorbic Acid and suitability for further thermal reduction.

2. Experimental

2.1. Materials

Bulk graphite was purchased from Sigma Chemical Company, USA (Cat# 332461, Lot: MKBK4082V) and sieved graphite flakes (size of 420 µm, U.S. Standard Sieve Series No. 4,) was procured from Humboldt, Chicago, USA. For the remainder of the text we designate this Graphite precursor as G4 and SP-1 graphite powder (size < 100 µm lot # 060706) was purchased from Bay Carbon Inc., USA and used without further purification. We will refer to this precursor as G3 in this paper. Table 1 outlines the differentiators in oxidation protocols used herein and relates them to previously reported works. Sulfuric acid and phosphoric acid used in this work was (85% w/w aqueous solution, ACS grade) purchased from Alfa Aesar chemical company, USA, (Cat #33260). H_2SO_4 and H_2O_2 were procured from Fischer Chemical Company, USA (Cat# A300-212, CAS# 7664–93-9 Lot: 135111) and Sigma-Aldrich Chemical Company, USA (CAS# 7722–84-1), respectively. L-ascorbic acid (L-AA) was also purchased from Sigma-Aldrich Chemical Company, USA.

2.2. Synthesis of graphene oxides

Graphene oxide by Marcano-Tour's improved method is abbreviated here as I-GO was prepared from both graphite sources (i.e. G3 and G4 as mentioned in the "Materials" section) by adding 3 g of graphite to a mixture (360 ml/40 ml) of sulfuric acid and phosphoric acid (85% w/w aqueous solution, ACS grade) and then gradually adding 18 g of KMnO4. The mixture was allowed to stir for 12 h at 45 °C temperature and subsequently it was neutralized by pouring over 400 ml ice. Then the mixture was cooled to room temperature and further was neutralized using hydrogen peroxide to it.

Graphene oxide produced by modified Hummer's method is abbreviated as H-GO. In a typical procedure GO was produced from both the sources of graphite as mentioned earlier by adding 3 g of graphite to 69 ml of H_2SO_4 and then adding 9 g of $KMnO_4$ gradually while the mixture cooled on ice. The mixture was stirred for 2 h at 35 °C following