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Physical and chemical mechanisms affecting electrical conductivity in reduced graphene oxide films

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ABSTRACT

This article focuses on the influence of surface topography (roughness), surface chemistry (carbon and oxygen functional groups) and physical (film thickness) parameters on the electrical conductivity of graphene oxide (GO) and reduced graphene oxide (rGO) films. This study was carried out to understand how changes in chemistry, roughness and film thickness, arising from the reduction process, alter the electrical properties of the films. Improved understanding is needed to control and optimise these parameters in graphene/rGO films for future applications where targeted property performance is needed. Films with smooth surfaces, measured using confocal imaging, and lower thicknesses have been shown to possess higher electrical conductivity. X-ray diffraction patterns shows minor changes in d-spacing, though improvements in crystal perfection, orientation and crystallinity could be concluded. X-ray photoelectron spectroscopy shows a significant decrease in the oxygen present at the surface as the films are exfoliated to reduce their thickness. Conductivity improves as the materials become increasingly defect-free, achieved by careful control of reduction and post-processing techniques. Ideal practical conductivity is achieved for films of 4 μm thickness: beyond this point, no practical gains are made (about 25 exfoliation trials from the bulk cast film).

1. Introduction

Graphene is an exciting material being widely investigated today [1,2] not only out of academic curiosity but also for its potential applications in a wide range of areas such as flexible electronic devises, catalysis, sensors and energy conversion and storage [3]. A major reason that graphene research has progressed so fast, as compared to other areas, is that the laboratory procedures enabling us to obtain high-quality graphene are relatively simple and cheap [3].

Though the material has excellent intrinsic properties, such as electron mobility of 2.5×10^5 cm^2 V^{-1} s^{-1} and Young's modulus of 1 TPa [3], corresponding bulk properties are difficult to achieve with typical preparation methods. This has hindered the transfer of research into large-scale practical uses.

Understanding the surface topography of films of graphene oxide (GO) and its analogues helps to identify their influence on electrical and physio-chemical properties. In particular, film thickness, roughness and functionality (such as OH and COOH groups) influence electrical conductivity, one of the most interesting properties for use in practical applications. This work focuses on the relationship and interpretation of how electrical conductivity (σ, S cm^{-1}) changes due to the various combinations of surface roughness and thickness of graphene oxide (GO) and reduced graphene oxide (rGO) films.

Wang et al. have concluded that electrical conductivity of graphene films increases as their thickness decreases and similar behaviour has been observed in a variety of other materials [4,5], with correlations observed between thickness, roughness and electrical conductivity. This has encouraged us to carry out further work in this area.

Films of GO/rGO were made using Hummer's method [6] and then reduced using a variety of techniques. Finally, they were mechanically exfoliated using an adhesive tape. X-ray photoelectron spectroscopy was carried out to quantify the elemental composition, providing further information on how electrical conductivity was affected by this property.

2. Materials and methods

2.1. Materials

Graphite flakes and hydroiodic acid (HI) were purchased from Sigma-Aldrich, New Zealand with hydrochloric acid (HCl) and sulphuric acid (H_2SO_4) being supplied by Macron Chemicals, USA. Potassium permanganate ($KMnO_4$) and hydrogen peroxide (H_2O_2) were obtained from J.T. Baker, Netherlands and ECP Chemicals, New Zealand, respectively. Hydrobromic acid (HBr) was bought from Scharlau, Spain. All these chemicals are of analytical reagents grade.

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2.2. Methods

2.2.1. Synthesis and reduction of graphene oxide

GO was synthesised via a modified Hummers and Offerman's method [6] using H_2SO_4, $NaNO_3$ and $KMnO_4$. Typically the oxidation process took 2 h for adding all the chemical components, and the final mixture was left overnight for overall completion. Adding water and subsequent addition of hydrogen peroxide (H_2O_2) made the manganese salts soluble and the yellowish intermediate graphite oxide formed was purified by washing. The suspension from the synthesis was then ultrasonicated and dried to form films on a petri-dish in an oven, maintained at 50 °C for reduction. The films need to be removed carefully to avoid cracks and physical hole. The GO suspension and flexible films are shown in Fig. 1.

It is assumed that the oxidation of graphene to graphene oxide involves the initial formation of epoxides, and then alcohols and eventually ketones/aldehydes/carboxylic acids (along edges and defects). The molar populations of these and the level of the desired reduction determine the amount of reductant that needs to be used. It has been suggested in the literature that 150 mmol is needed to reduce the groups present in 420 mmol (0.42 mol) of GO to a large extend [7].

This chemical synthesis gave GO, which was further treated with reducing agents to remove oxygen functional groups. These groups lower the conductivity of GO as they disrupt the delocalisation of the π-system with their electron withdrawing properties since they break the extended aromaticity of the graphite/graphene sheet and the removal of these functional groups was necessary. The GO films obtained by drying out the suspension in a petridish were reduced by hydrohalic acids (HBr and HI). Fig. 2 illustrates structures of graphene oxide and reduced graphene oxide.

This reduction process leaves with varying population of oxygen functional groups, different surface roughness and increased thickness in GO films which depends on nature of reducing agents. With HI and HBr-rGO, a distinct effect on thickness after reduction process has been noticed. Hence, a series of testing methods have been used to understand their effect on the electrical conductivity of GO and rGO films.

- For roughness measurements, same GO films were used to reduce with HBr and HI for comparison.
- For X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) analyses, GO, HBr-rGO and HI-rGO samples of approximately 5, 40 and 100 μm were used.

The main focus of experiments was to determine the surface topography, elemental and physical characteristics of graphene oxide and reduced graphene oxide films, in order to understand their influence on electrical properties of the films.

2.2.2. Chromatic confocal microscopy

The chromatic confocal imaging was carried out with MicroGlider® 600 instrument (FRT, Germany) with a measuring range of 600 × 600 mm in the "xy" directions and 600 μm on the "z" direction.

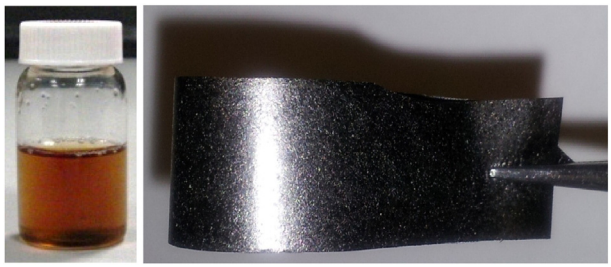

Fig. 1. GO suspension (left) and rGO film (right).

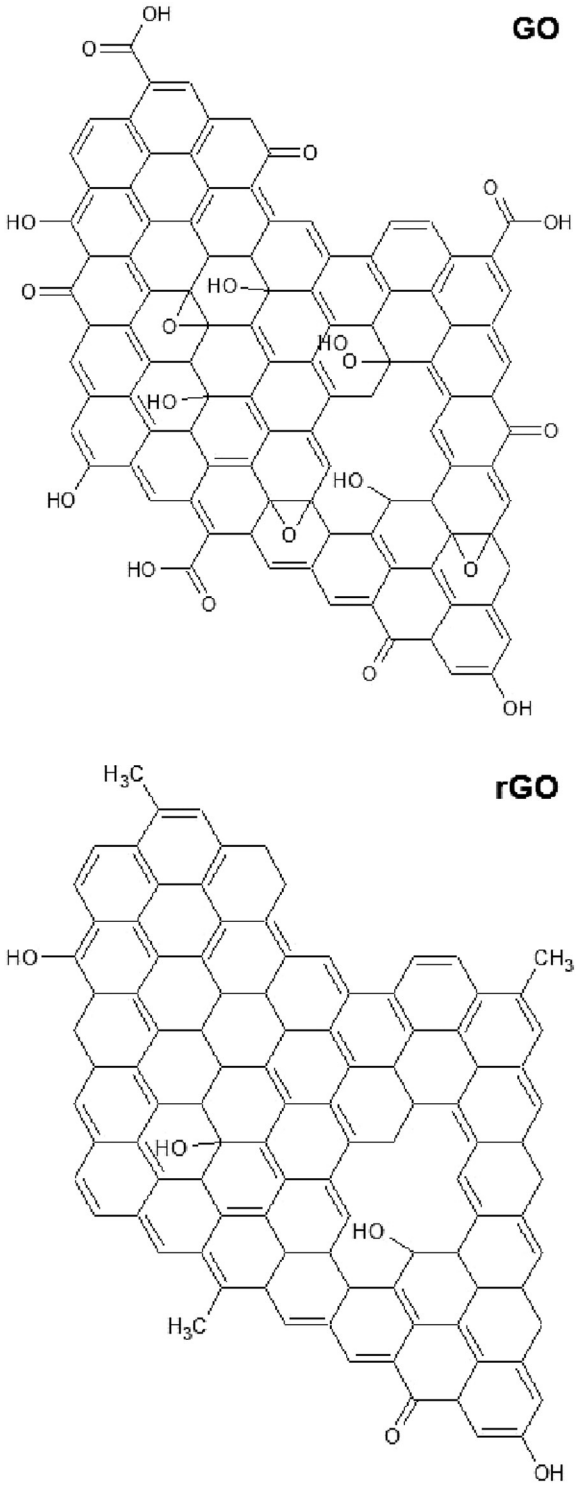

Fig. 2. Chemical structure of GO and rGO.

The roughness/flatness (average deep roughness, R_z) can be measured with a resolution of 2 μm in the lateral and 6 nm on the vertical directions. The maximum speed of the measuring head was 300 mm·s^{-1} with a load capacity of 40 kg.

Average deep roughness (R_z) is the average of max peak-valley distances in 5 succeeding sections. One single rough deep is the distance between the highest peak and the deepest groove within the single measuring line (Fig. 3).