

One-step reduction, characterization and magnetic behaviour of exfoliated graphene oxide

E.D. DIKIO*, F.T. THEMA, A.M. FARAH, N.D. SHOOTO

Applied Chemistry and Nanoscience Laboratory, Department of Chemistry, Vaal University of Technology,
P.O. Box X021 Vanderbijlpark, 1900, South Africa

The functionalized graphene (GO) was fabricated by a simple method of chemical reduction in a polar aprotic solvent. This paper therefore, describes a versatile and synthetic route for the preparation of reduced graphene oxide (RGO) and its behavior when exposed to magnetic field environment. The characterization results of transmission electron microscopy (TEM), scanning electron microscopy (SEM), Raman spectroscopy and the attenuated total reflectance-Fourier transform infra-red (ATR-FTIR) analysis indicate that graphite was exfoliated and reduced to graphene layers.

Keywords: *chemical reduction; hydrazine hydrate; graphite oxide; reduced graphene oxide; exfoliate*

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1. Introduction

Graphene – a single layer of carbon atoms arranged in a hexagonal lattice is the newest member in the family of carbon allotropes [1]. Although isolated graphene was reported for the first time in 2004, the progress it made over these years is enormous [1].

Graphene is a rapidly rising star on the horizon of materials science and condensed-matter physics [2]. This strictly two-dimensional material exhibits exceptionally high crystal and electronic quality. Despite its short history, it has already revealed a cornucopia of new physics and potential applications [2].

Many properties of graphene are superior to those in all other materials, so it is very tempting to use it in a variety of applications, ranging from electronics to composites materials [3]. Historically, the electronic properties of graphene attracted most attention [3]. Electrons in graphene behave like massless relativistic particles which govern most of its electronic properties [3]. Probably, one of the most spectacular consequences of such unusual dispersion relation is the observation of half-integer quantum Hall effect and the absence of localization [2].

The latter might be very important for graphene-based field effect transistors.

For this reason, extensive efforts have been made to obtain graphene, including chemical vapor deposition (CVD) [4], micromechanical exfoliation of graphite [1] and the reduction of graphite oxide [5]. Among these methods, the reduction of graphite oxide is a promising path toward high yield production of graphene. It is generally known that the defective graphene structure obtained by this method hinders its application in the field requiring excellent conductivity, such as transparent conductive film [6]. On the contrary, as a sensing material, the defective area in graphene layers plays a positive role, exhibiting good capability of the intercalation with target molecules and ions [7].

Generation of mechanical stresses conferred to graphite in exfoliation is a problem that can be approached by putting to use its ability to form intercalation compounds [8]. Through penetration of some metals or oxidizers between graphene sheets making up the crystalline structure of graphite it is possible to achieve an increase in the separation and further weakening of the interplanar coupling [8].

A remarkable place among the graphite intercalation compound is occupied by the graphite oxide (GO) to be more exact, graphite hydroxide which is produced in the reaction of natural crystalline

*E-mail: ezekiield@vut.ac.za

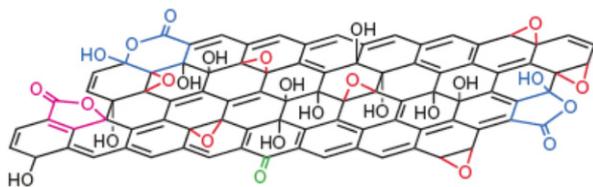


Fig. 1. The structure model of the graphite oxide species [10].

graphite with strong oxidizers in water medium [9]. Graphite oxide obtained with the maximum possible degree of oxidation represents an array of uncoupled graphene sheets, with oxygen atoms and hydroxyl groups grafted on both sides [10]. They form covalent bonds with carbon atoms in these sheets [10], Fig. 1.

In this study, we have adopted an approach for the production of graphene nanosheets by chemical reduction of graphene oxide using hydrazine hydrate as a reducing agent in aqueous solution. We synthesized and characterized graphene oxide (GO) and reduced graphene oxide (RGO) by transmission electron microscope (TEM), scanning electron microscope (SEM), Raman Microscope and Fourier Transform infrared attenuated total reflectance spectroscopy (FTIR-ATR). Powdered and dispersed GO and RGO in water were exposed to a magnetic field to determine their magnetic property.

2. Experimental

2.1. Materials

Sulphuric acid, hydrochloric acid, hydrogen peroxide and potassium permanganate were purchased from Sigma-Aldrich in South Africa while flake graphite powder and hydrazine hydrate were imported from Germany. Filter paper qualitative Advantec 90 mm was bought from Tokyo Roshi Kaisha Ltd in Japan.

2.2. Synthesis of graphene oxide and graphene

Natural flake graphite powder (2.0 g) was weighed and placed into a round bottom flask, 46 ml of concentrated sulphuric acid was added and the mixture was cooled in an ice bath, 6.0 g of potas-

sium permanganate (KMnO_4) was gradually added over a period of 30 min with continuous stirring. The mixture was stirred at 35 °C for 2 hours, then 92 ml of distilled water was slowly added to the mixture and the temperature was maintained below 100 °C for 15 min. Finally, 280 ml of 30 % hydrogen peroxide (H_2O_2) solution was added to the mixture. The product was finally filtered with 500 ml of 10 % hydrochloric acid (HCl) solution to remove metal ions and then thoroughly washed with distilled water. Brown pasty material of GO was obtained. GO (3.0 g) was weighed to make colloidal dispersion in distilled water with continuous stirring at a temperature of 35 °C. A solution of hydrazine hydrate (H_2O_4) that weighed 10 % of the GO dispersed in water was added as a reducing agent and left for 3 hours to stir. After this, the filtrate turned from brown to black and was filtered to obtain a black pasty material of graphene.

2.3. Sample preparation

Sonicated small amounts of colloidal dispersions of GO and RGO were dropped on a silica oxide and thin glass substrates and left to dry overnight at room temperature.

2.4. Characterization

Transmission electron microscope (TEM) images were obtained on Fei Tecnai G2-20 operated at 200 kV using an energy filter of 20 eV. The surface measurements were recorded with a JEOL 7500F field emission scanning electron microscope (FE-SEM). Raman spectra were obtained using Horiba Jobin Yvon HR 800 model DU 420A-OE with a power of 20 mW at a wavelength of 514.5 nm with an argon ion laser from 100 to 4000 cm^{-1} . Attenuated total reflectance (ATR) FT-IR spectra were recorded on a Perkin Elmer Spectrum 100 spectrometer in the 4000–500 cm^{-1} region.

3. Results and discussion

Flake graphite powder reacting with sulphuric acid and potassium permanganate in the presence of hydrogen peroxide produced brownish graphene oxide (GO) Fig. 2(a). The GO readily forms sta-

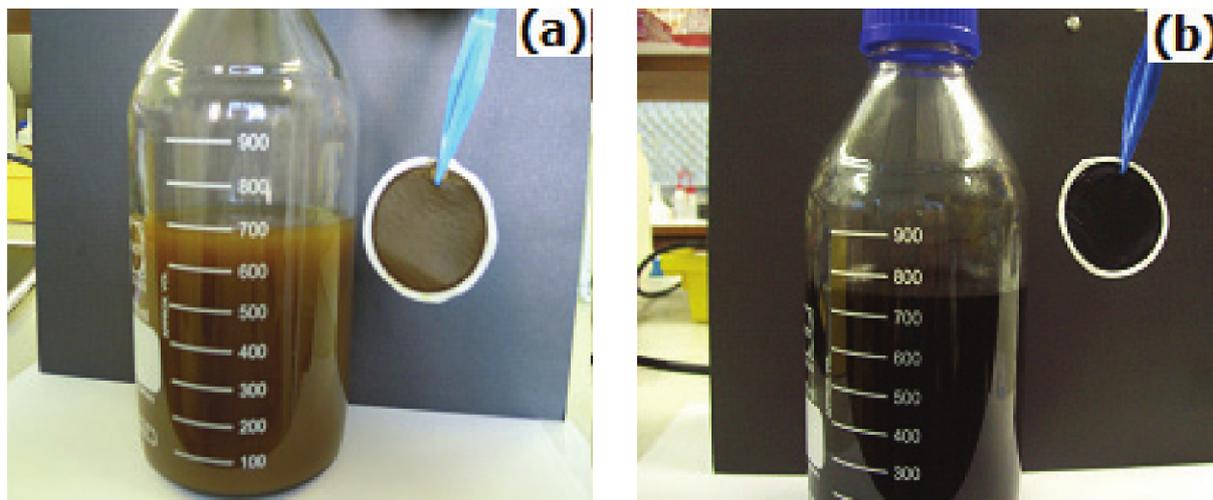


Fig. 2. A picture of synthesized (a) brownish graphene oxide (b) blackish reduced graphene oxide.

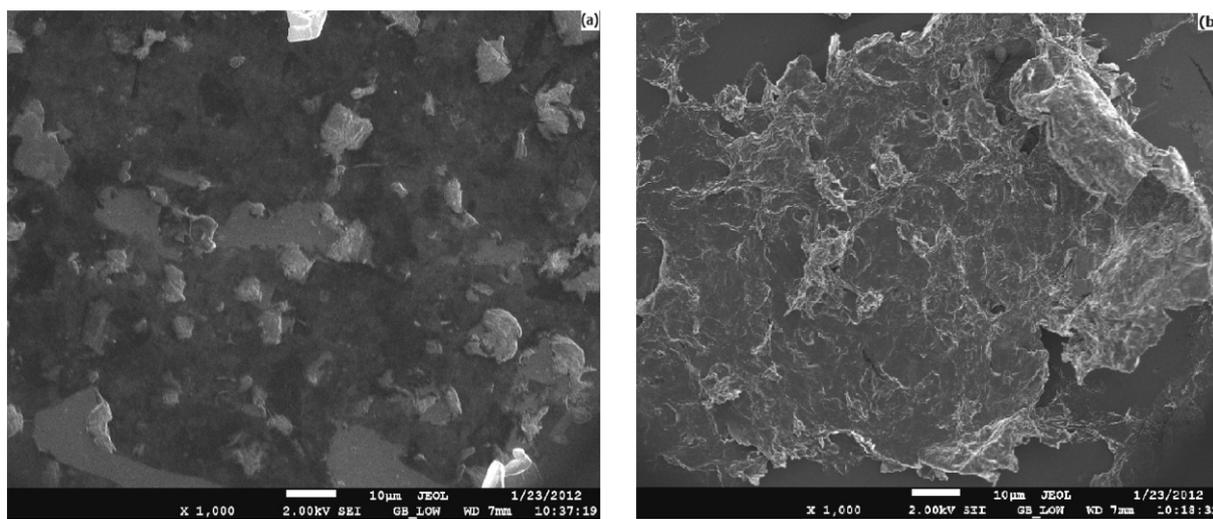


Fig. 3. Scanning electron micrographs of (a) graphene oxide and (b) reduced graphene oxide.

ble colloidal suspensions in water [11, 12]. After ultrasonic treatment, the exfoliation process brings about stable dispersions of graphene oxide [13, 14]. Addition of hydrazine hydrate as a reducing agent, produced the graphene oxide which was homogeneously dispersed in water to turn from brownish to black, Fig. 2(b), causing the reduction of graphene oxide to graphene aggregates, which formed a blackish precipitate [13].

Fig. 3(a,b), shows the scanning electron micrograph images of the morphology of graphene oxide and reduced graphene oxide. According to some reports [15–18], when the chemical conversion of

graphite oxide to graphene takes place, holes and defects are easily produced on the carbon grid. It is possible that these holes are a result of removal of oxygen functional group species during the reduction process. It is also possible that the nanocomposites can grow around these holes and defects and are inclined to insert into graphene sheets [19]. In addition, the rigid particles may also easily sink into the supported materials [20]. By visual inspection, it can be seen that the GO image looks lighter while the RGO image looks darker. This could be attributed to the fact that as the oxygen functional species are removed during the reduction process,

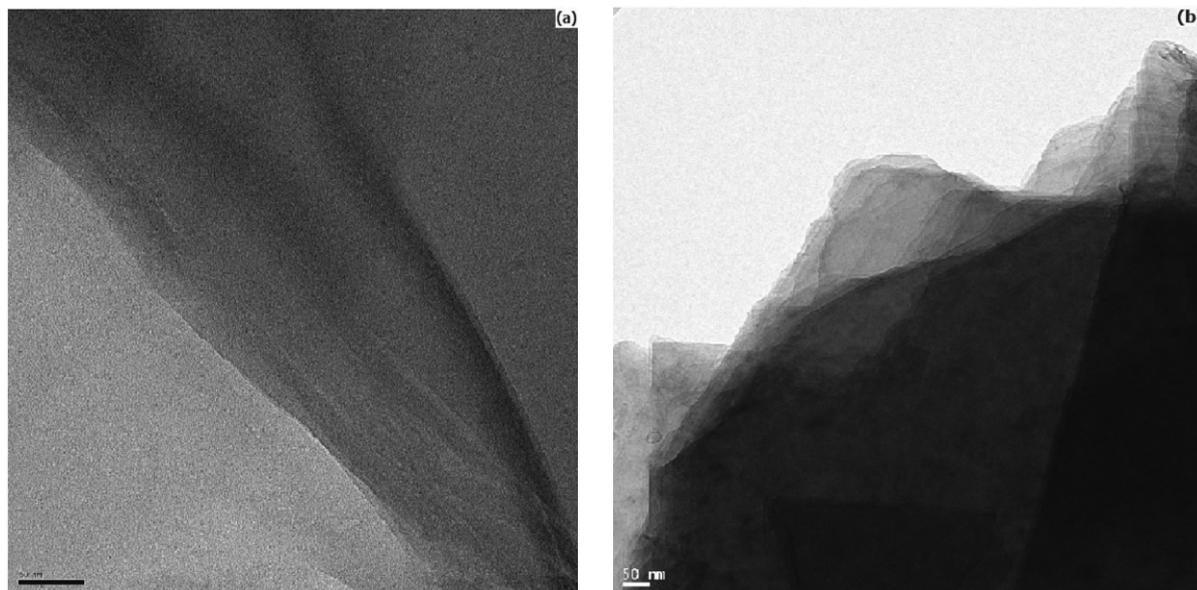


Fig. 4. Transmission electron micrograph of (a) graphene oxide and (b) reduced graphene oxide.

the GO sheets separated during intercalation stick now together, which results in more compact arrangement and decrease in interlayer spacing of the single sheets. This further confirms the reduction of GO into RGO.

The morphology and structure of the graphene oxide and reduced graphene oxide were studied by transmission electron microscope (TEM) analysis. The transmission electron microscope spectra of graphene oxide and reduced graphene oxide are presented in Fig. 4(a,b). Fig. 4(a) shows large GO sheets which can be observed on the top of the copper grid. The most transparent and featureless regions are likely to be a monolayer of GO. Different from bulk GO sheets, the reduced graphene oxide, RGO sheets, are no longer totally flat and smooth but always exhibit some corrugation, where they resemble crumpled silk veil waves. Especially, any particular area of the particle shows considerable folding Fig. 4(b). As reported previously [16], this phenomenon is because the thermodynamic stability of the 2D membrane results from microscopic crumpling via bending or buckling. This phenomenon also supports the fact that the coarse aggregates have been exfoliated completely. When the modification process is completed, a very spectacular change in morphology can be observed.

The Raman spectra of GO and RGO are presented by Fig. 5(a,b). It is well known that Raman scattering is very sensitive to the microstructure of nanocrystalline materials. Fig. 5(a) shows the Raman spectra of graphene oxide while Fig. 5(b), shows the Raman spectra of reduced graphene oxide. A comparison of the spectra of graphene oxide with that of reduced graphene oxide shows that the D- and G-bands of graphene, which are observed at 1355 and 1605 cm^{-1} , are shifted to 1340 and 1586 cm^{-1} , respectively. Simultaneously, the relative intensity of D/G has increased after hydrothermal reaction, which is confirmed by Lambert [21] and Stankovic [22]. This further confirms that graphene oxide was reduced to graphene. The absence of the 2D band around 2726 cm^{-1} after oxidation indicates that all graphite layers have been oxidized. Two peaks around 1500 cm^{-1} (D and G band) are essentially identical to the characteristic peaks of graphene oxide. Therefore, oxidized expandable graphite (EG) is the same material as graphene oxide (GO) made from graphite.

Fourier transform infrared and attenuated total reflectance spectroscopy (FTIR-ATR), spectra of graphene oxide and reduced graphene oxide are presented in Fig. 6. The spectra show a peak of reduced graphene oxide, representing O–H stretching

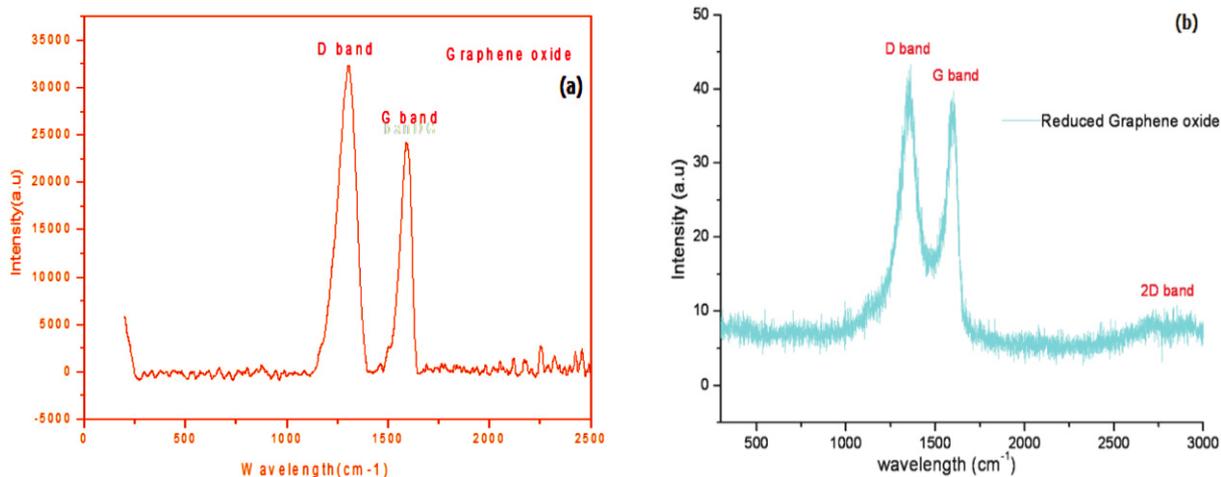


Fig. 5. Raman spectra of (a) graphene oxide and (b) reduced graphene oxide.

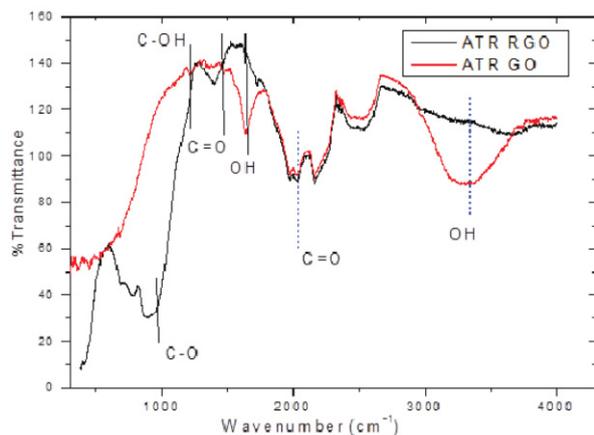


Fig. 6. Fourier transform infrared (FTIR) and attenuated total reflectance (ATR) spectra of graphene oxide and reduced graphene oxide.

vibrations observed at 3400 cm^{-1} , which was significantly reduced due to deoxygenation. The carbonyl stretching vibration, $\text{C}=\text{O}$ at 1720 cm^{-1} in this spectrum is due to the mechanism of exfoliation, mainly as a result of the expansion of CO_2 evolved into the interstices between the graphene sheets during the rapid heating. The $\text{C}-\text{O}$ stretching vibration observed at 1060 cm^{-1} is due to the carbonyl groups remaining after the reduction process. The mechanism of exfoliation is mainly caused by the peeling of graphitic structure to pave way for the entering of oxygen during the oxidation process. The stretching vibrations at 1220 cm^{-1} and 1060 cm^{-1} on the

graphene oxide spectra indicate skeletal vibrations from unoxidized graphite flakes. The ATR spectra suggest that the bulk of the oxygen-containing functional groups have been removed from graphene oxide. This again confirms the reduction of graphene oxide by chemical reduction method.

The magnetic behavior of both GO and RGO in aqueous and solid states is presented in Fig. 7(a–c). Graphene oxide and reduced graphene oxide, Fig. 7(a), were dispersed in deionized water and placed in 150 ml sample bottles which were placed in contact with semicircular magnets in a high magnetic field. Solid samples of graphene oxide and reduced graphene oxide, Fig. 7(b–c), were also placed in the same magnetic field at room temperature. Both experiments showed the absence of any magnetic interaction in the presence of an external magnetic field with the graphene oxide and reduced graphene oxide.

4. Conclusion

In conclusion, we have demonstrated that commercial flake graphite powder can be oxidized into graphene oxide and reduced into graphene through one-step reduction of exfoliated graphene oxide in polar aprotic solvents. The chemical reduction method by hydrazine hydrate treatment, produced graphene and reduced graphene oxide. The characterization of GO and RGO resulted in the products



Fig. 7. Exposure to magnetic field from a semicircular magnet, (a) solution of graphene oxide and reduced graphene oxide (b) powdered graphene oxide and (c) powdered reduced graphene oxide.

that were completely exfoliated. Magnetic analysis of RGO and GO in deionized water showed the absence of magnetic properties both in the solution and in the solid state, which is an indication that neither RGO nor GO are paramagnetic.

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