

RESEARCH PAPER

Preparation and characterization of chemically converted graphene from natural graphite

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Abstract

Recently, reduced graphene oxide has attracted enormous attention as a nanomaterial for its exceptional electric, thermal, and mechanical properties. One of the most promising applications is to blend it into polymer matrices for the preparation of electrically conductive nanocomposite. In this work, graphene oxide (GO) was reduced using hydrazine hydrate via a modified Hummer process to produce reduced graphene oxide nanomaterial (RGO). RGO was characterized by several techniques, including Raman spectroscopy, energy dispersive radiographic diffraction, transmission electron microscopy, elemental analysis by radiography spectroscopy, thermogravimetric analysis, electrical conductivity, and surface area measurements. The characterization processes indicate the formation of material on the nanoscale consisting of high-specific surface area thin graphene sheets, which in turn impart good thermal stability and electrical conductivity. As such, RGO may find use as an electrically conductive filler for polyurethane composites which is the aim of a second part to be published of this work.

Keywords: Graphene oxide, Raman spectroscopy, Reduced graphene oxide, Transmission electron microscopy, Thermogravimetric analysis, Radiography diffraction

1. Introduction

In recent years, nanocomposites have attracted enormous attention owing to their rheological, mechanical, electrical, and thermal properties.¹ The unique properties of these composites are not only restricted to the type of polymer used, but they also depend on the type of filler used. Graphene and reduced graphene oxide (RGO) are the most effective fillers in nanocomposites due to their structures as a single layer of two-dimensional (2D) sp^2 hybridized carbon atoms. When these fillers are blended into the polymer matrices, additional nanosized adhesion spots are present on the flakes surface and edges, which leads to modification of the composite matrix and the microcellular system. These changes in the nanocomposites lead to them becoming electrically conductive and harder.^{2,3} Graphene oxide has been prepared by adding

potassium chloride to graphite after mixing with fuming nitric acid as reported by Brodie.⁴ Then an improvement has been made by replacing 60% of fuming nitric acid with concentrated sulphuric acid and slowly adding the chlorate.⁵ Modification of this method was done by dissolving $NaNO_3$ and $KMnO_4$ in concentrated H_2SO_4 .⁶ In this method, oxidation was done in few hours; however low yield was obtained, and toxic gases were released. Other modifications were also reported by Yu *et al.*^{7,8} including oxidation using K_2FeO_4 instead of $KMnO_4$ at room temperature. Partial replacement of $KMnO_4$ with K_2FeO_4 while using less amount of H_2SO_4 led to shorter oxidation time.

RGO has different names, such as modified graphene, chemically converted graphene, simply graphene and functionalized graphene. The most widely adopted and cost-effective approach to graphene production commences with the oxidation of

Received 26 February 2024; revised 3 May 2024; accepted 13 May 2024.
Available online 17 July 2024

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<https://doi.org/10.62593/2090-2468.1030>

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natural graphite, comprised of a series of flat graphene sheets bound by weak Van der Waals forces.^{9,10} Through the use of highly oxidising agents, these graphite sheets are separated into graphene oxide (GO).¹¹ In GO, the carbon atoms' plane is loaded by oxygen-encompassing groups, expanding the interlayer distance, and rendering the atomic-thick layer hydrophilic. These oxidised layers can be further separated, and through the application of reducing agents, the oxygen-containing groups can be eliminated, resulting in graphene-like sheets known as RGO.

The goal of this work is to prepare graphene oxide by oxidation of natural graphite followed by reduction of GO to RGO via the use of modified Hummer's technique.⁹ This is followed by the use of different methods for characterisation of the prepared samples of both GO and RGO as shown in the results of this paper. Since graphene has many applications one of which is the preparation of electric conductive graphene-based polymer nanocomposite and based on the promising results obtained from this current work, the authors identified the future goal is to prepare samples of a polyurethane nanocomposite using the prepared samples of RGO as a filler. These samples will also be characterized using different methods to determine their properties.

2. Experimental procedure

2.1. Preparation of graphene oxide (GO)

Typically, GO is synthesized using a modified version of the Hummers technique,⁹ starting from graphite powder (95–99%, Sigma Aldrich Merck). Initially, 27 ml of sulfuric acid (H_2SO_4) (98%, Sigma Aldrich Merck) is added to 0.225 and 0.12 g of graphite powder and sodium nitrate (NaNO_3), respectively, and the mixture is thoroughly mixed and then stirred at 66 °C, after which it is cooled to 0 °C. Gradually, 1.32 g of potassium permanganate (KMnO_4) (90%, Sigma Aldrich Merck) is added slowly to the previous mixture, and stirred for 6 h, till the solution turns dark green. To remove excess KMnO_4 , 0.675 ml of hydrogen peroxide (H_2O_2) (30%, Sigma Aldrich Merck) is added slowly with stirring for 10 min, prompting an exothermic reaction, and then the mixture is left to cool. Subsequently, 10 ml of hydrochloric acid (HCl) (37%, Sigma Aldrich Merck) and 30 ml of deionized water (DIW) are added. Finally, the mixture is centrifuged by an Eppendorf centrifuge for 7 min at 5000 rpm. After decanting the supernatant, the residual material is collected and washed multiple times with HCl and

DIW. After that, the GO solution is dried in an oven at 90 °C for 24 h to produce GO powder.¹²

2.2. Reduction of exfoliated GO with hydrazine hydrate

A 250 ml round-bottom flask is filled with 100 mg of GO and then 100 ml of water is added producing a heterogeneous yellow brown colored solution. After that, the previous mixture is agitated with a 150 W ultrasonic bath cleaner until reaching total clear dispersion. After adding 1 ml of 65% hydrazine hydrate (Sigma Aldrich Merck), the mixture is then heated for 24 h at 100 °C in an oil bath with a water-cooled condenser. The reduced GO progressively precipitates as a black solid during this process. A medium fritted glass funnel is used to filter the final product, which is then separated by washing it completely with methanol (5×100 ml) and water (5×100 ml). The product is then dried on the funnel under constant airflow until a solid product cake forms.¹³

2.3. Characterisation of RGO nanosheets

2.3.1. Radiographic diffraction (XRD)

Using a Malvern PANalytical Model X'Pert Pro rotating anode radiographic diffraction (XRD) fitted with a Cu $\text{K}\alpha$ tube and Ni filter ($d = 0.1542$ nm), the produced sample is subjected to XRD analysis. At a scanning rate of 20 min^{-1} , data is collected over scattering angles (2θ) ranging from 10° to 70° .

2.3.2. Transmission electron microscopy (TEM)

The microstructure of both GO and RGO samples is examined using transmission electron microscopy (TEM) with a JEOL-2100 F instrument. TEM specimens are prepared by depositing the as-prepared sample dispersions onto carbon-coated TEM grids via drop casting, followed by air drying.

2.3.3. Raman spectroscopy (RAM)

RAM was carried out using a lab RAM-HR France Confocal Raman microscopy system with argon ion laser wavelength of 532 nm and a spot size of $2 \mu\text{m}$ and its power is 2 mW. The Raman spectra are recorded from 500 to 2000 cm^{-1} . The wave number is calibrated using the Si peak, located at 520 cm^{-1} , as a reference.

2.3.4. Thermogravimetric analysis (TGA)

Thermogravimetric analysis 250001 R (TA instruments, USA), is used to determine thermal stability of samples. A sample of around 0.3 mg is heated

linearly at a rate of 20 °C while being measured over 30–700 °C in a nitrogen environment.

2.3.5. Elemental analysis

Further confirmation of GO and RGO formation is conducted through elemental analysis using energy dispersive radiography spectroscopy (EDX) with a HITACHI S-3400N instrument, Japan. This analysis aids in identifying the elemental composition of the particles.

2.3.6. Surface area measurements and electrical conductivity determination

Surface area is measured using the nitrogen adsorption Brunauer-Emmet-Taller (BET) in a Quantachrome Nova2200e surface area analysis. The conductivity is determined by the leakage current of the sample under the electrical field of 0.1 mv/m. For leakage current measurements, a small sample is inserted into a hollow cylinder with an inner diameter of 0.7 cm and compressed between two brass pistons. A Kelithley DC current model 6220 with a four-point probe is used to detect conductivity. To calculate ohmic conductivity, the following formula is used:

$$\sigma = L/RA$$

Where σ is the electrical conductivity. L is the sample distance, A is the piston surface area and R is the resistivity.

3. Results and discussion

3.1. X-ray diffraction (XRD)

The XRD patterns of GO and RGO are depicted in Fig. 1. Graphite shows an intense peak at $2\theta = 26.69^\circ$ with interlayer intense distance of 0.34 nm corresponding to 002 plane of well graphite.

After the oxidation of graphite to GO, the basal inter spacing between the 002 planes of graphite peak increases and shifts to 0.81 nm, a new broad peak emerges at angle $2\theta = 10.98^\circ$, replacing the peak at $2\theta = 26.29^\circ$ which is found to be consistent with literature.¹⁴ This expansion is attributed to the introduction of oxygen and water molecules between the oxidised graphene layers due to oxidation. The XRD pattern after subsequent reduction of GO to RGO with hydrazine hydrate is slightly higher than graphite, indicating the reduction of numerous oxygen groups and the formation of disordered, aggregated, and randomly packed graphene sheets characterized by a broader and lower intensity peak.¹⁵

3.2. Raman spectroscopy (RAM)

Fig. 2 clearly illustrates that GO and RGO exhibit higher amorphous characteristics compared with natural graphite. Graphite exhibits a pronounced G band appearing at wave number 1581 cm^{-1} , which is ascribed to E_{2g} modes named as first order scattering.

Due to the disruption of the conjugated system in graphite, the Raman spectra of GO (Fig. 2a) shows an intensification of the D band at 1353 cm^{-1} and a shift in the wider end of the G band to 1597 cm^{-1} . After GO is reduced (Fig. 2b), the G band shifts from 1597 cm^{-1} to 1594 cm^{-1} because more sp^3 carbon atoms are converted to sp^2 carbon atoms, and the D band narrows and becomes more noticeable.¹⁶ Furthermore, the degree of disorder in the graphitic structure affects the relative strength of the D band in relation to the G band.

The lowered graphene oxide D/G intensity ratio is 1.15, which is somewhat less than the graphene oxide D/G intensity ratio of 1.37. As a result, it can be deduced that reduction causes reduced graphene

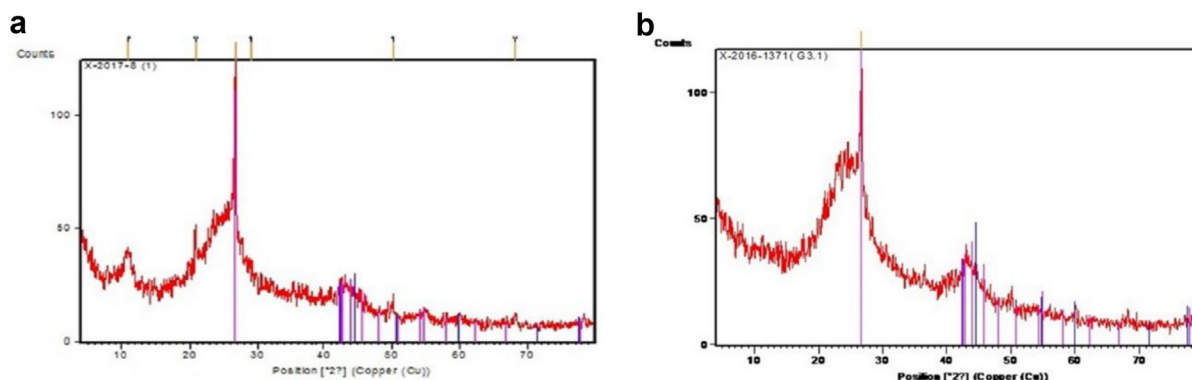


Fig. 1. Radiographic diffraction of a) Graphene oxide and b) Reduced graphene oxide nanocrystals.

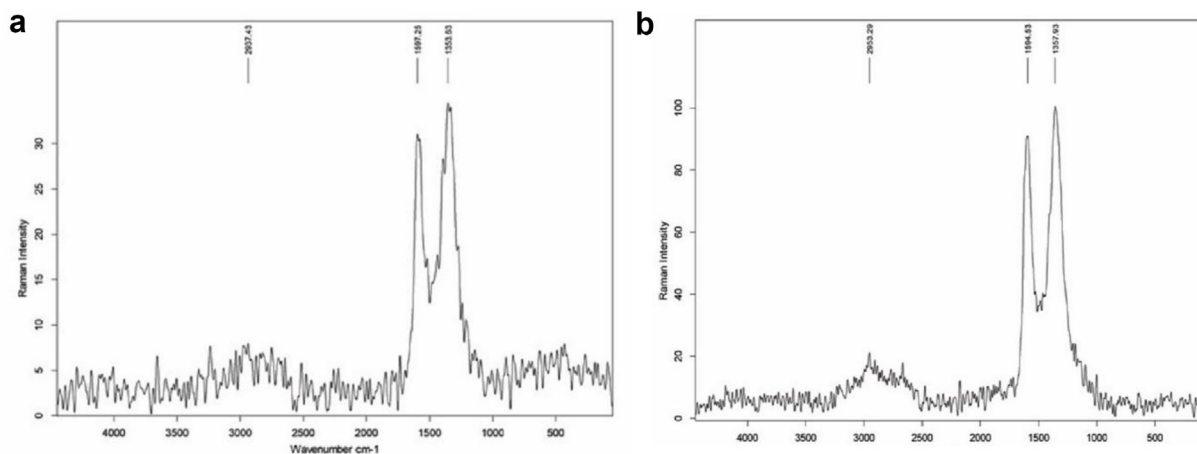


Fig. 2. (a) Raman spectrum of graphene oxide nanocrystals. (b). Raman spectrum of reduced graphene oxide nanocrystals.

to expand, edge planes to increase, and in-plane sp^2 domains to shrink to some extent.

3.3. Morphology examination by TEM

The morphology of crystallinity of GO sheets in layer structure is observed through TEM images after its crystallinity is determined by XRD. TEM images are depicted in Fig. 3a. Where some parts are shown in grey and black colour pointing to oxygen and carbon. The grey parts reflect that the structure of the sample is very thin or in an atomic state. While the black parts are due to the stacking of some (GO) structure exfoliated nanolayers produced by oxidation of graphite which is found to be consistent with the literature.¹⁷ The Black parts of the image also indicate that upon graphite oxidation, oxygen attaches to graphene sites randomly converting sp^2 carbon bonds to sp^3 bonds. This process leads to the formation of many wrinkles somewhere across the GO platelets and may also cause the GO sheet to bend which is suggested by

Schniepp *et al.*¹⁸ The TEM analysis of RGO is presented in Fig. 3b. The data obtained indicates that the structure of RGO is in the form of an amorphous carbon structure and composed of a few random layers stacked along each other with fewer wrinkles and folds. This suggests the restoration of sp^2 carbon and the transition from a polycrystalline to a two-dimensional monocrystalline graphene-like structure following the reduction of GO.¹⁹ The TEM image also reveals small clusters separated by an amorphous bonded matrix, forming a barrier between clusters.

3.4. Thermogravimetric analysis

Thermal analysis of GO reveals its thermal instability, as illustrated in Fig. 4, wherein it undergoes decomposition in three distinct steps. The initial weight loss, occurring between 50 °C and 120 °C, is ascribed to intercalated water molecules evaporating. The subsequent step, observed from 120 to 440 °C, results from the loss of oxygen-containing

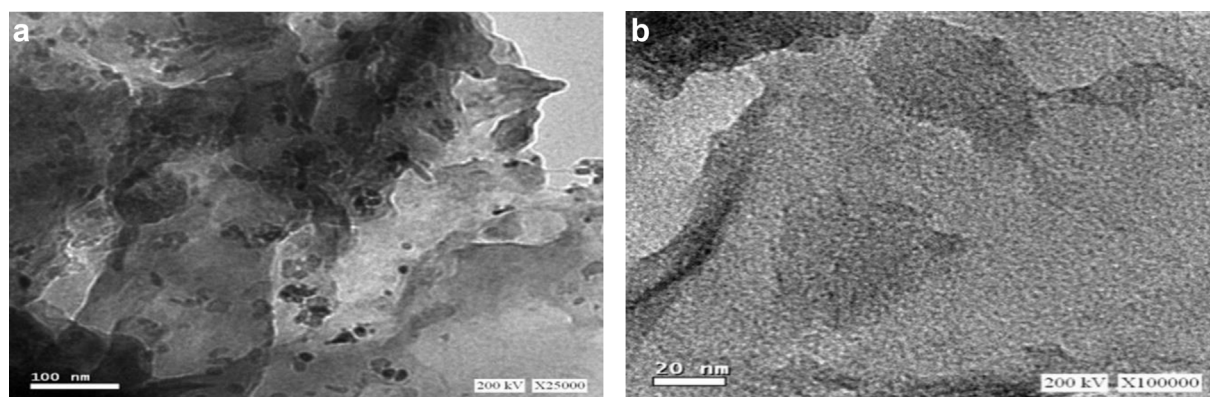


Fig. 3. Transmission electron microscopy of (a) graphene oxide and (b) reduced graphene oxide nanocrystals.

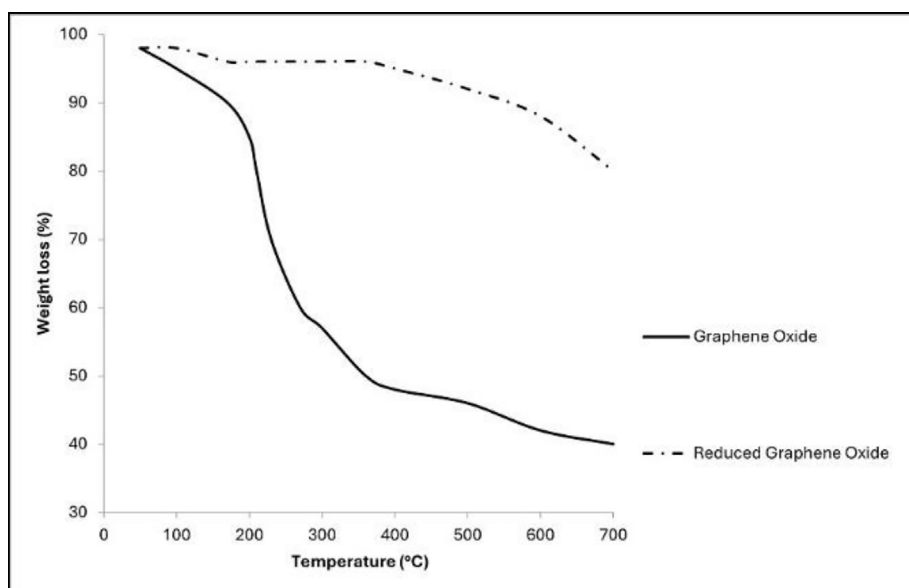


Fig. 4. Thermogravimetric analysis of graphene oxide and reduced graphene oxide.

groups. Finally, above 440 °C, further decomposition occurs due to the presence of unstable carbon remnants within the structure and the pyrolysis of oxygen functional groups such as C–O, C=O, and OH leading to the generation of CO and CO₂ vapors.^{20,21} RGO exhibits similar characteristics but with a lower degree of weight loss compared with GO (Fig. 4). This suggests that a significant portion of the oxygen-containing functional groups in GO has been reduced, consequently enhancing the stability of RGO.

3.5. Electrical conductivity, surface area, and elemental analysis

The outcomes obtained from matching the experimental data for the three parameters of are summarized in Table 1. These findings indicate that the conductivity of RGO is notably more reliable compared with that of GO, with a conductivity approximately five orders of magnitude superior to that of GO but still lower than graphene, possibly due to the presence of oxygen within its network since the existence of oxygen-containing groups is known to diminish electrical conductivity.²¹ However, GO can be utilized in various applications due to its strong hydrophilicity which ensures its good

dispersibility in many solvents and facilitating the synthesis of composite materials.²²

Surface area analysis of RGO by nitrogen gas adsorption reveals a specific surface area value of (364 m²/g). This high value is notably lower than that of graphene (2620 m²/g).²³ This discrepancy may be attributed to the agglomeration of GO (70.5 m²/g) during the reduction process, which can cause partial overlap and coalescence of the reduced layers, consequently reducing the surface area of the material.

In Elemental analysis (EDX) experiments the grid used as a carrier for the samples is composed of copper (Cu) and is excluded from the calculations. EDX demonstrates sharp optical absorption signals from the carbon and oxygen atoms within the range of 0–1 keV, indicating the presence of GO and RGO nanocrystals, as depicted in Fig. 5. Table 1 illustrates an increase in the atomic ratio of carbon to oxygen in RGO compared with GO. This can be attributed to the hygroscopic nature of GO where any trapped water between its layers contributes to a higher oxygen content. On the other hand, the water repelling nature of RGO makes it exhibit reduced water content. Also, RGO can result from incomplete reduction of graphene oxide so having oxygen remaining even in its reduced state

Table 1. The results of measurements of electrical conductivity, surface area, and elemental analysis.

Data	Atomic C (%)	Atomic O (%)	Conductivity (sm ⁻¹)	Surface area (m ² /g)
Graphene oxide	61.09	38.91	0.031	70.5
Reduced graphene oxide	88.49	11.51	2400	364

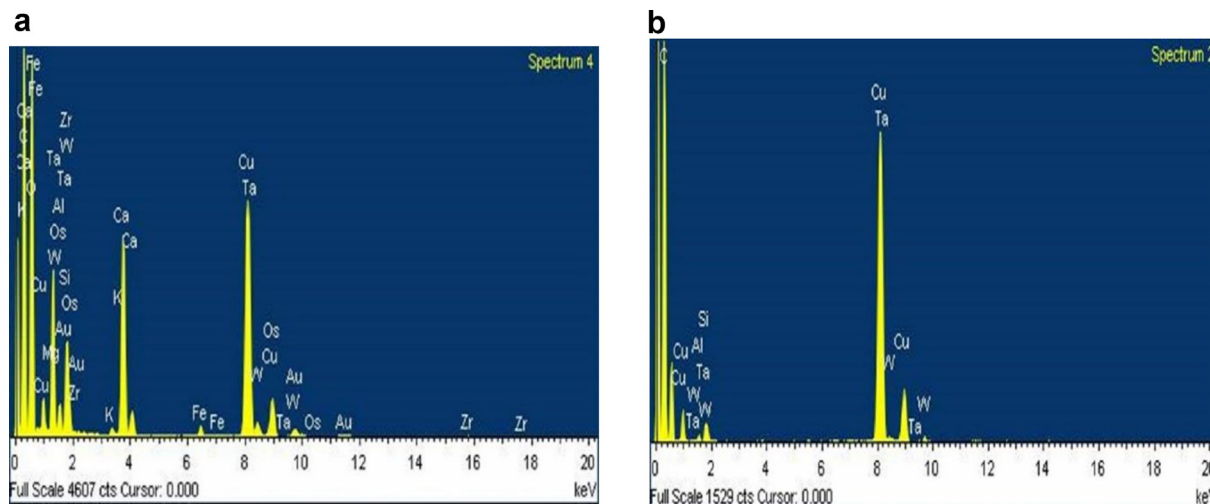


Fig. 5. Energy dispersive radiography spectrum of a) Graphene oxide and b) Reduced graphene oxide.

therefore having less oxygen content compared with GO.

3.6. Conclusions

In the current work, graphite was reduced using hydrazine hydrate after being oxidised using a modified version of Hummer's approach.⁹ XRD, TEM, and Raman analysis are used for the characterisation of the prepared GO and RGO. With the aid of these techniques, the structure of these materials was confirmed (by RAM and EDX) and it was shown that RGO had more crystallinity than GO (by XRD), a better-quality flat surface, and less folding (by TEM). TGA further validated the high thermal stability of RGO caused by the elimination of oxygen containing functional groups from GO by reduction.^{20,21} The presence of oxygen-containing functional groups was also confirmed by EDX which indicated that the oxygen content decreased after reduction of GO to RGO where the carbon-to-oxygen ratio measured by EDX for RGO exhibited a higher value than that of GO. Additionally, the measured bulk conductivity of RGO was found to be as high as 2400 sm^{-1} relative to 0.031 sm^{-1} for that of GO. Therefore, the electrical conductivity measurements proved that GO is a poor electrically conductive material which can be improved by reduction.²² In summary, the process of reducing GO yielded a carbon-based material having superior electrical conductivity due to the creation of thin layers of graphene with a high specific surface area.²³ Finally, the authors were able to prepare and characterize RGO from graphite through this work based on the fact that graphene has many applications among which is the preparation of electrically

conductive graphene-based polymer with nanocomposite. The authors identified the goal of the second part of this paper to be the use of the prepared RGO in this work as a filler material in polyurethane nanocomposites.²⁴

Author contribution

Dr Elmorsi provided the analytical measurements carried out in this manuscript. She wrote, submitted and revised the manuscript. Dr Shokry supervised the practical work and contributed to writing and revising the manuscript. H. Elsgogy carried out the preparations of the work.

Conflicts of interest

There are no conflicts of interest.

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