Modified hummers method synthesis and structural characterisation of graphene oxide

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Abstract. Graphene oxide (GO) was synthesised using modified hummers method. X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Fourier Transform Infrared Spectroscopy (FTIR), Raman Spectroscopy (RM) and Atomic Force Microscopy (AFM) were utilised to acquire the structural properties of GO. Each spectroscopic technique reveals unique features about the surface morphology of graphene oxide. XRD confirmed the crystalline nanosheets stacking of a carbon honeycomb. SEM and TEM revealed wrinkles and folding of planar honeycomb layers. FTIR and RM indicated the presence of carbonyl, alkoxy, epoxy, and hydroxyl functional groups. AFM further confirmed the surface roughness and the thickness of the GO nanosheets.

1. Introduction

Graphene oxide (GO) is a new interesting material which is derived from graphene and the oxygen functional group(s) [1]. GO is known to possess some interesting properties such as high surface area, high mechanical stiffness, high Young's modulus and exceptional thermal conductivity [2-3]. Due to these properties GO has attracted enormous great research interest. Nowadays, the synthesis and modification of GO has been one of the major focus and interesting part of graphene related research. The structure of graphene oxide can be defined as a layer of graphene with a number of oxygen functional group(s), such as hydroxyl (OH), epoxy (C-O), carbonyl (C=O) and alkoxy (C–O–C) distributed on the graphene surface [4]. GO is a promising material for future technologies due to the oxygen functional group(s) as well as their minute size and shape [5]. This material has been identified as a potential candidate for advanced semiconducting applications such as water treatment as well as gas sensing [1].

The presence of the oxygen containing functional groups in GO influence this material's hydrophilic behaviour and its polar nature, as a result, GO can be easily dispersed in several solvents such as water [6], in the process gaining advantage in terms of other peculiar properties over its precursor graphene. These functional groups highlight the opportunities for surface modification in GO which is very much suitable for nanocomposite materials.

This paper is focused on the synthesis and structural characterisation of graphene oxide. Accordingly, the synthesis of graphene oxide is more favourable over other graphene materials due to its low cost, easy access and its ability to be easily converted to graphene [7]. Graphite which is defined as a packed layers of graphene is the main source of graphene oxide [8]. GO has been synthesised using modified hummers method and was further characterised using various spectroscopic instruments including X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Fourier Transform Infrared Spectroscopy (FTIR), Raman Spectroscopy (RM), and Atomic Force Microscopy (AFM).

2. Materials and Methods

2.1 *Reagents used for the synthesis of graphene oxide*

The materials used in this study were purchased from Sigma Aldrich. The materials are: graphite (99% purity), sodium nitrate (99% $NaNO_3$), potassium permanganate (99% $KMnO_4$) and sulphuric acid (98% H_2SO_4), hydrogen peroxide (50% H_2O_2), hydrochloric acid (35% HCl).

2.2 *Synthesis of graphene oxide*

The modified hummers method was used to synthesise the graphene oxide (GO) [9]. This method involves the treatment of graphite flakes with a mixture of sodium nitrate ($NaNO_3$), potassium permanganate ($KMnO_4$) and sulphuric acid (H_2SO_4). During the synthesis of GO, 120 ml of concentrated H_2SO_4 was measured and cooled to the temperature below 5°C in an ice bath. In the process 2.5 g of $NaNO_3$ and 2 g of graphite were slowly added to the H_2SO_4. The mixture was then allowed to stir for a maximum of 30 min under an ice bath at 300 rpm (revolution per minutes). 15 g of $KMnO_4$ was then added slowly to the mixture after 30 min with continuous stirring at 300 rpm. The temperature of the mixture was always kept below 5 °C. After $KMnO_4$ was successfully stirred into the mixture, the ice bath was replaced with an oil bath. The temperature of the mixture was increased and maintained in the range of 60 - 70 °C in the oil bath. The mixture was further allowed to stir for extra 30 min at 300 rpm. Furthermore, after 30 min of stirring, the mixture was then allowed to react whilst stirring for 24 h under room temperature in the oil bath still at 300 rpm.

After the full complete 24 h reaction, the mixture was cooled to a temperature below 5 °C in an ice bath, followed by gradual addition of 220 ml of de-ionized water drop by drop wise in the mixture to increase the temperature to 55 °C maximum while stirring at 300 rpm. Subsequent to the gradual addition of 220 ml of de-ionized water, the mixture was further heated in an oil bath and refluxed for 24 h at a temperature below 60 °C. The mixture was then cooled to room temperature and 50 ml of hydrogen peroxide (H_2O_2) was slowly added to eliminate excess of $KMnO_4$. The exothermic reaction occurred during the addition of H_2O_2 and the mixture changed to bright yellow. The mixture was then filtered and the obtained product (graphite oxide) was washed continuously with 0.1 M of hydrochloric acid (200 ml) to remove the metal ions. The graphite oxide was further washed with the de-ionized water for several times using centrifuge, until the pH value of the supernatant was approximately close to the pH of the water. Then, the graphite oxide was dried up in a vacuum oven at a temperature of 60 °C for 24 h. Finally, 5 mg of graphite oxide was exfoliated by sonication in a 100 ml of de-ionized water to yield several graphene oxide nanosheets.

2.3 *Characterization of graphene oxide*

X-ray diffraction characterisation of GO was conducted using Bruker D2 Phaser Diffractometer (λ = 0.15418 nm) which uses secondary graphite monochromated with CuKα radiation. The surface morphology of GO was investigated using ZEISS SEM and Perkin Elmer TEM. The presence of the oxygen functional groups on the hexagonal honeycomb sheets was confirmed by Perkin Elmer FTIR TWO spectrometer at the spectral wavenumber range of 400 to 4000 cm^{-1}. Perkin Elmer Raman Spectrometer was used to analyse the structural characteristics of GO at a laser voltage of 50% with a beam exposure of 10 s. Images of GO layers were further explored and obtained using Veeco-nano scope AFM in a contact mode.

3. Results and Discussion

3.1 *X-ray diffraction analysis*

The x-ray diffraction spectrum confirms that GO crystallises into nanosheets form with a sharp peak observed at $2\theta = 11.1^0$, which corresponds to the interlayer spacing of 0.791 nm as depicted in figure 1. In addition, this diffraction peak corresponds with the (001) plane of GO. However, the x-ray diffraction of the well-ordered graphene usually depicts a sharp peak at $2\theta = 26.7^0$ [10]. This simply suggests that the sudden changes in the GO peaks is due to the presence of the oxygen containing functional groups lying on the graphene surface. Experiments say the interlayer spacing of GO is ranging from 0.6 to 1.0 nm depending on the oxidation process involved during the synthesis procedure [11]. Since the measured interlayer spacing of GO (0.791nm) lies between 0.6 and 1.0 nm, it shows that the synthesised GO is highly oxidized. The Bragg law [12] has been used in the determination of the interlayer spacing. The oxygen functional groups lying on the graphene sheets are also responsible for the increase in the interlayer spacing of GO [13]. The observed value for the sharp peak of GO approximately corresponds with the values reported in the literature [14]. The crystal size of this material was calculated to be 4.7 nm (47 Å). The Debye-Scherrer [15] equation was used to calculate the crystal size.

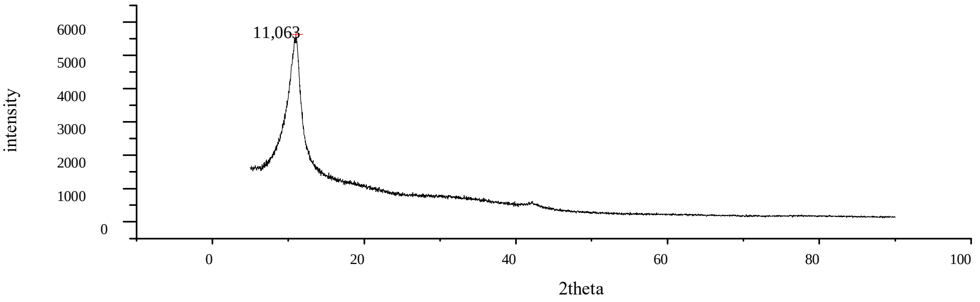

Figure 1. X-ray diffraction of GO.

3.2 *Scanning and Transmission Electron Microscopy*

The SEM micrograph suggests, the folding or piling of the layers with the surface morphology which is wrinkled, as shown in figure 2. This could be due to oxygen functional groups and other structural defects [16]. Based on the synthesis of GO by improved method, the wrinkles in GO are also caused by the folding of the GO sheets [17].

The TEM micrograph in figure 3 further complements the evidence of the wrinkles in the middle of the GO nanosheets. The wrinkles further extend towards the edges. The same observations were noted and reported by Singh et al. [18]. It must be noted that the TEM image was taken in the bright field mode of the microscope where only transmitted electrons are allowed to pass through the aperture. The dark region at the middle and the edges of the GO nanosheets may be caused by the presence of the wrinkles.

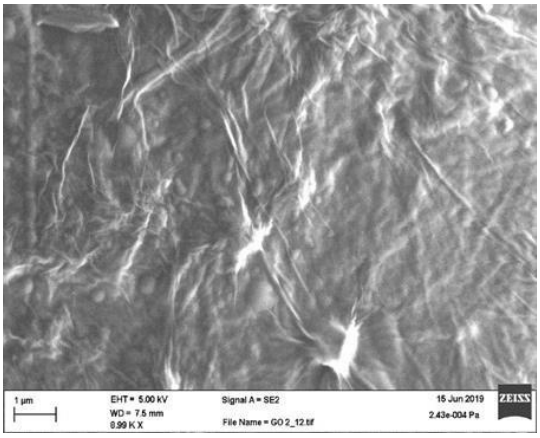

Figure 2: SEM micrograph of GO.

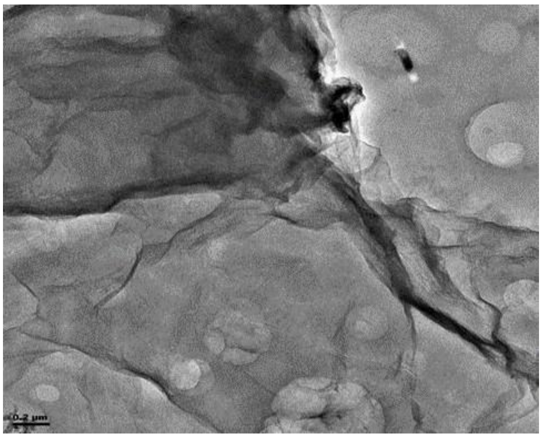

Figure 3: TEM micrograph of GO.

3.3 *Fourier Transform Infrared Spectroscopy*

In figure 4, the FTIR spectra of GO is shown. The spectra indicate the existence of various functional groups: hydroxyl (OH), carbonyl (C=O), epoxy (C-O), and alkoxy (O-C-O). The hydroxyl (OH) and carbonyl (C=O) groups stretching vibrations can be identified by the bands appearing at 3358 and 1728 cm^{-1} respectively. Furthermore, the bands appearing at wavenumbers 1224 and 1050 cm^{-1} correspond to epoxy (C-O) and alkoxy (O-C-O) stretching vibrations respectively. The obtained FTIR results are in good agreement with literature reports as outlined by Zhang et al. [19] and confirms the oxidation of graphite during the synthesis of GO via modified hummers method.

3.4 *Raman Spectroscopy*

According to many studies, the Raman spectra of graphene oxide usually exhibits two strong peaks, the D and the G peaks at approximately 1343 and 1598 cm^{-1} respectively [20]. In this study, the D and the G peaks are observed at 1308 and 1596 cm^{-1} respectively as illustrated in figure 5. The G peak is usually assigned to the carbon-carbon bond stretching and the D-peak is associated with the presents of the oxygen functional groups on the graphene sheets [20]. If the intensity of the D peaks is (ID) and that of the G peak is (IG), the increase in the intensities ratio of the D and the G, which is (ID/IG) usually indicates the decrease in the average size of carbon-carbon bonds [21]. The ratio of the intensities in GO is 0.82 as compared to the theoretical value of 0.84, which suggests an increase in the average size of the carbon-carbon bonds stretching on the graphene sheets. Consequently, an increased aromaticity in the GO structure which is related with enlarged surface area and improved stability. As a result, Raman spectroscopy was successfully conducted to confirm the chemical changes in the graphitic structure.

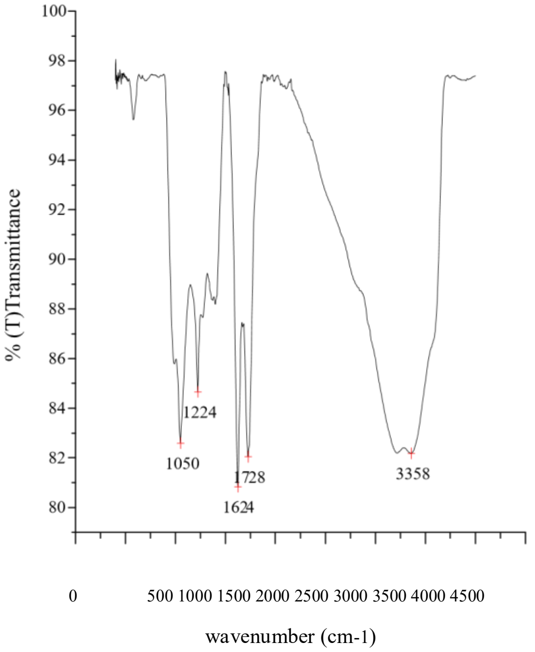

Figure 4. FTIR spectra of GO.

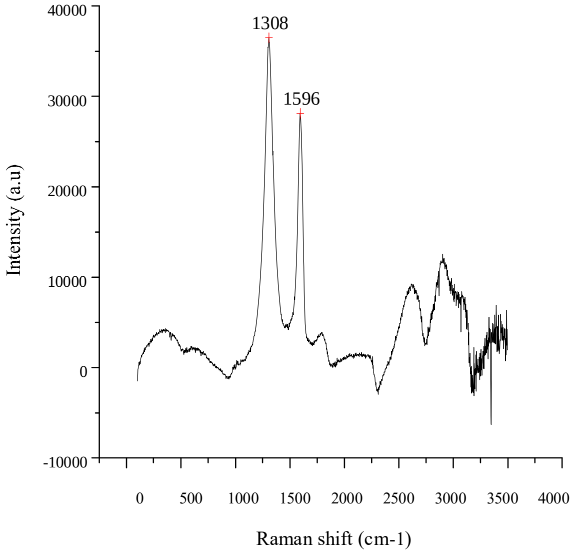

Figure 5. Raman Spectroscopy of GO.

3.5 *Atomic Force Microscopy*

Figures 6 and 7 shows that the AFM GO layers have different lateral sizes as well as different layer thickness. The folding or piling of the layers can also be observed which could have resulted when drying GO on the glass substrate as observed in figure 7. A typical height profile in figures 6 and 8 reveals the thickness of 2.993 nm of a single GO layer with the root mean square (RMS) value of the surface roughness of 1.134 nm due to the oxygen functional groups as reported in the literature. The thickness of graphene is approximated to range from 0.340 to 1.270 nm [22]. Therefore, since the obtained thickness of GO (2.993 nm) is out of the approximated range of graphene, this could be attributed to the presence of the oxygen atoms implanted on the graphene sheets causing the folding of GO nanosheets. As a result, GO is expected to be thicker than graphene because of the surface oxygen functional groups. However, this spectroscopic technique has difficulties in determining the exact number of layers in graphene and graphene oxide [23], which in turn implies difficulties in obtaining the exact thickness of GO.

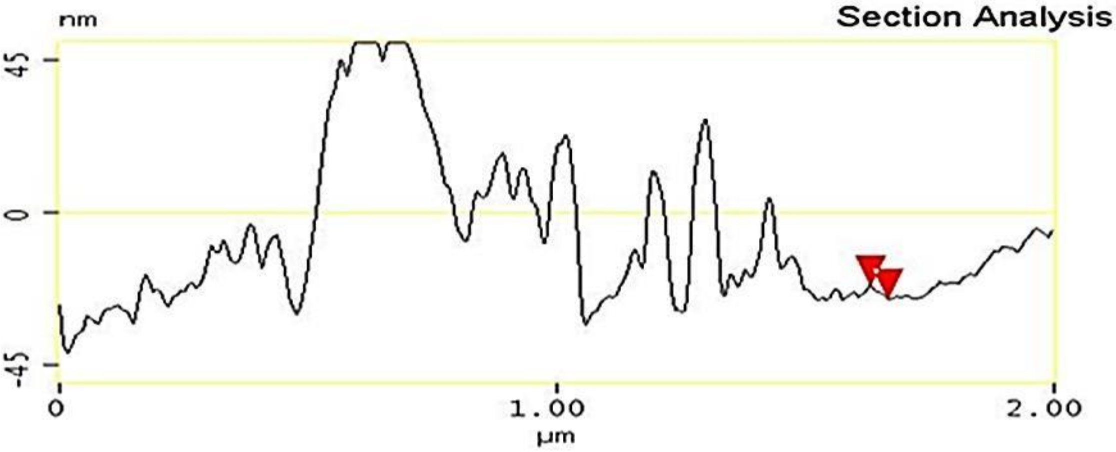

Figure 6: The sectional analysis of the GO nanosheets.

Figure 7: The AFM micrograph of GO nanosheets.

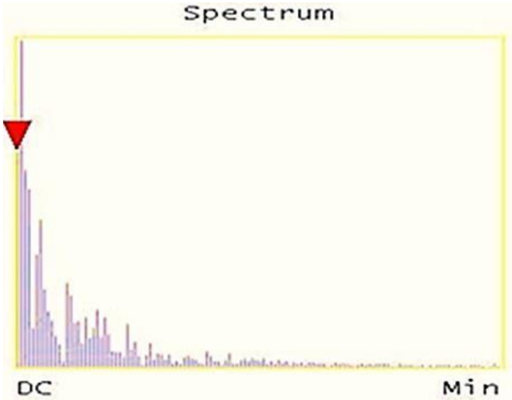

Figure 8: The spectral analysis of GO height profile.

4. Conclusion

Graphene oxide was successfully synthesised via modified hummers method. An acceptable interpretation of the surface morphology of graphene oxide using the different spectroscopic instruments was successfully achieved. Correspondingly, SEM and TEM complement each other on the explanation of the wrinkles and folding of the GO layers. The FTIR and RM results suggest the presence of the oxygen functional groups in the honeycomb sheets and AFM confirms that the synthesised GO are nanosheets with a rough surface due to the oxygen functional groups.

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