Structural and optical properties of spin coated graphene oxide films

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Abstract. Graphene oxide (GO) is a derivative of graphene, consisting of an atomic layer of carbon bonded to oxygen functional groups such as hydroxyl and epoxide, which make it insulating and hydrophilic. This novel material has attracted much research recently, although there is varying information in the literature, because the properties may depend on the synthesis technique and form (powder, film, solution). An investigation of the structural and optical properties of spin coated GO films was made. GO powder was purchased from Sigma Aldrich (15-20 sheets, 4-10% edge-oxidized) and used to prepare a GO suspension in distilled water (1 mg/ml), which was ultrasonicated and centrifuged. The supernatant black solution was spin coated on silicon substrates to produce films. The solution was characterized using photoluminescence (PL) and UV-vis absorption measurements, while the GO powder and films were assessed using X-ray diffraction (XRD). A broad absorption band was observed at 273 nm, although subsequent PL measurements showed that this was not an efficient excitation wavelength. Instead, the weak blue luminescence observed at 444 nm could be excited at 325 nm. Blue luminescence has been attributed to thoroughly exfoliated GO suspensions, while red emission (not observed here) to poorly dispersed suspensions. The Raman peak of water was observed on the short wavelength side of this emission. The XRD pattern for the commercial GO powder had a peak near $2\theta = 13.3°$. This low angle, compared to the corresponding peak of graphite (26°), indicated much wider spaced interplanar layers as a result of oxidation, but showed that the GO was stacked in multiple layers. A weak band near 30° suggested that the powder probably also contained a small amount of graphite. This was absent for the film since it was likely removed by centrifuging. The XRD peak of the film was shifted to $2\theta = 13.8°$, indicating a small reduction in the interplanar spacing. Although the XRD data corresponded to stacked GO, the optical properties suggest that significant reduction was present in the commercial powder.

1. Introduction

Nanoscience and technology are at the forefront of modern research which deals with the exploration and exploitation of nanomaterials. Since its discovery in 2004, graphene – one of the most promising nanomaterials, has increased research interest in graphene-based nanomaterials [1-2]. Graphene oxide (GO) is of great interest due to its low cost, easily scalable and widespread ability to convert to graphene i.e. chemically modified graphene. GO is a derivative of graphene which consists of an atomic layer of carbon bonded to oxygen functional groups such as hydroxyls and epoxides on the top and bottom surfaces and edges of each sheet. GO is produced from the oxidation of graphite using principle methods developed by Hummers [2]. GO has unique properties which depend on the method of synthesis, the material form as well as the level of oxidization in the compound [3]. GO can be reduced using chemical and physical treatments. The reduction of GO partly restores the structure and properties of pristine graphene. Different reduction processes results in different properties of reduced GO (rGO). These properties of GO and rGO makes them potential candidates for the coatings as transparent electrodes for light-emitting diodes (LEDs) [4] and solar cell devices [5]. For this work we investigated the structural and optical properties of spin coated GO films. These GO films will be used to form coatings over phosphors thin films i.e. ZnO:Zn and $La_2O_2S:Eu^{3+}$, which can provide protection from environmental degradation and its effect on the optical properties.

2. Experimental

GO powder (15-20 sheets, 4-10% edge oxidized) was purchased from Sigma Aldrich and used as received. 100 mg of GO powder was suspended in 100 ml of de-ionized water under ultrasonication for 30 min. Then the black solution was centrifuged at 4000 rpm for 30 min to separate large particles from the exfoliated GO sheets. 40 µL of the supernatant solution was dropped onto a cleaned silicon (100) wafer and spin coated at 3000, 4000, 6000, or 8000 rpm for 30 s. The coated samples were dried on a hot-plate at 100 °C in air for 10 min to evaporate the solvent. The coating process was repeated 5 times Structural and optical properties of the films were then assessed. X-ray diffraction (XRD) using a Bruker D8 Advance instrument was used to analyze the crystal structure of the powder and films. The scans were measured in the conventional theta-2theta configurations in the range 5-80° in a step of 0.01° while the X-ray generator was set at 40 kV and 40 mA. Scanning electron microscopy (SEM) performed with a JEOL JSM-7800F instrument was used to assess the surface morphology and uniformity of the films. Atomic force microscopy (AFM) was performed using a Shimadzu SPM-9600 system to analyze the surface topography. The optical properties were analyzed using UV-vis spectroscopy (PerkinElmer Lambda 950) to measure the absorbance of the solution, while photoluminescence (PL) of the solution was recorded using an Edinburgh Instruments FLS980 system with xenon lamp (325 nm excitation wavelength) and PL of the film was excited using a Kimmon IK series He-Cd 325 nm laser and recorded with a Hamamatsu R942 photomultiplier tube attached to an Horiba iHR320 spectrometer.

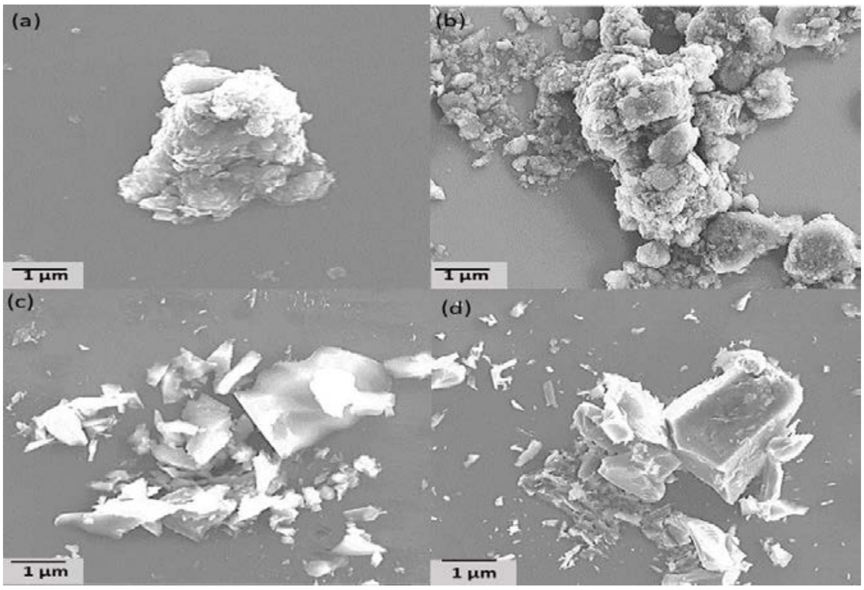

Figure 1. SEM images of GO films spun at (a) 3000, (b) 4000, (c) 6000 and (d) 8000

3. Results and discussion

3.1. Surface morphology

The morphology and uniformity of all films were observed using SEM images recorded at an accelerating voltage of 10 kV and higher magnification and are shown in Figure 1. The GO films are not uniform all over the substrate. Instead, the GO sheets look clustered, heavily wrinkled and scattered on the surface of the wafer, which results in less coverage of the silicon surface. This could have resulted due to minimum adhesion of the solution onto the surface of the wafer during spin coating and the Van der Waals attraction between the sheets. The film spun at 4000 rpm has greater coverage of the GO sheets on the substrate surface compared to others and therefore was used for further evaluation. The surface topography of this film was examined using AFM as shown in Figure 2, where the height of GO clusters was estimated to be about 100 nm.

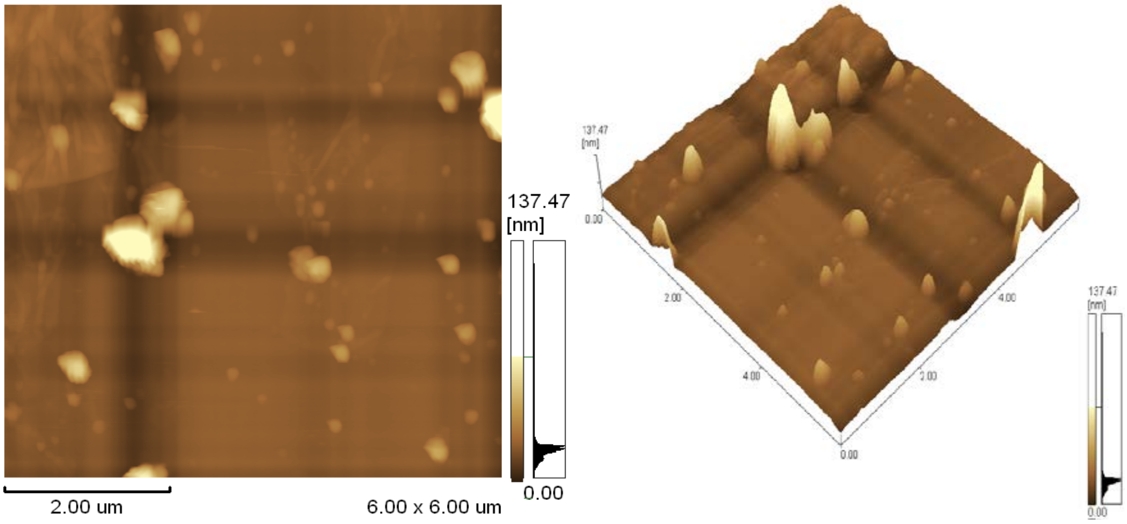

Figure 2. 2D and 3D AFM images of 4000 rpm spun sample. The dark bands intersecting at the particles are image processing artifacts due to the line-by-line background leveling algorithm.

3.2 X-ray diffraction analysis

XRD patterns of the GO powder and film are presented in Figure 2. The (001) XRD peak of the GO commercial powder was found at $2\theta = 13.3°$, corresponding to an interplanar spacing of 0.665 nm (i.e. significantly expanded compared to 0.335 nm between the sheets of graphite). Diffraction corresponding to the *c*-axis interplanar spacing is only possible for multiple layers, which indicated that the GO was not thoroughly exfoliated into single sheets and may thus be visualized as multilayered graphite oxide. A weak peak near $2\theta = 30°$ corresponding to the (002) plane is due to incomplete oxidation as the commercial powder is only 4-10% edge oxidized. The XRD pattern of the film only shows the characteristic peak at $2\theta = 13.8°$ with interplanar spacing of 0.641 nm. Peaks from the silicon substrate were avoided by not rotating the sample, which was placed at a slight mis-orientation perpendicular to the diffractometer rotation axis. Most of the unoxidized graphite layers were probably removed during centrifugation. Based on literature, the XRD peak of graphite occurs near $2\theta = 26°$ and when it has been oxidized the intensity of this peak sharply decreases and forms a new peak at around $2\theta = 15°$ [6]. When graphite oxide is thoroughly exfoliated to form single or few layers of GO, the XRD peak shifts to lower angles at $2\theta \sim 10°$ due to further expansion of the interlayer distance [7]. The XRD results of the GO samples are therefore in good agreement with published reports available in the literature.

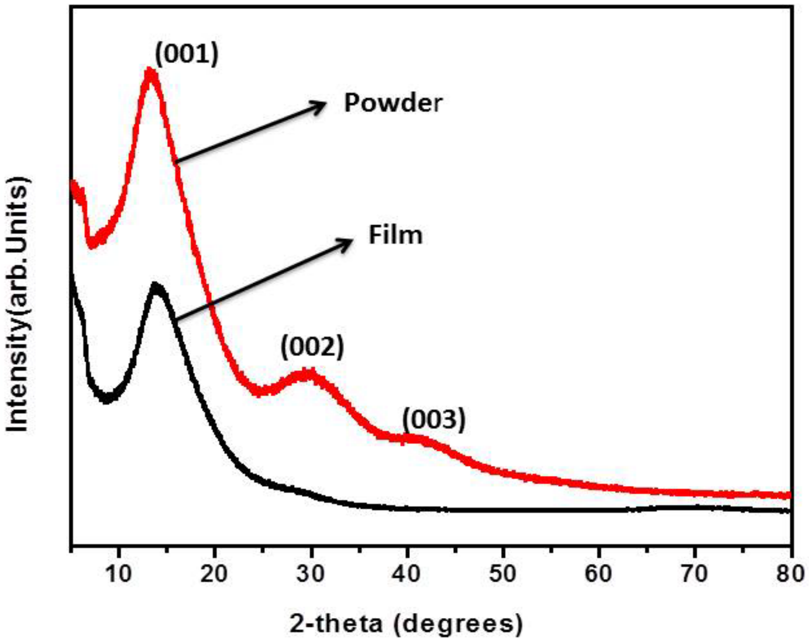

Figure 3. XRD patterns of GO powder and film.

3.3 Optical and photoluminescence studies

The absorption spectrum of the GO suspension in the range 200-800 nm is shown in Figure 4. The maximum absorbance of the commercial powder was found at 273 nm. The same peak was observed by Uran et al. [8] for different graphite materials (powder and rod) and assigned to graphene. In support that it could be the graphene peak, Thema et al. [9] and Eda et al. [10] have reported a red shift from 230 nm to ~270 nm for rGO which is most likely due to a decrease in the concentration of the carbonyl groups because GO sheets with less oxygen functional groups bonded to the carbon atoms have more sp2 hybridized C-C bond similar to pristine graphene which its referred to as rGO. The optical absorbance of GO is reported to have two characteristics peaks i.e. the main peak at 230 nm due to π-π^* transitions of the C=C bonds and a shoulder peak at ~320 nm is attributed to the n-π^* transitions of the C=O bonds, which were not observed.

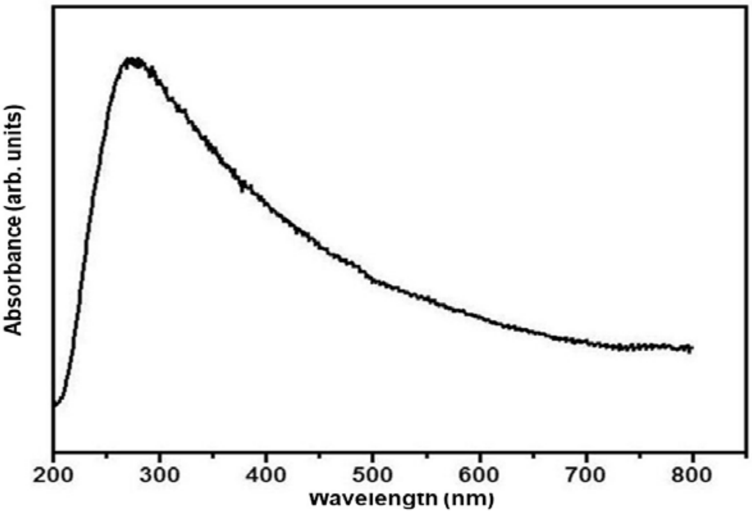

Figure 4. The absorbance spectrum of the GO suspension.

The PL spectra of the GO suspension and film are shown in Figure 5. Since the commercial powder is partially oxidized, a weak luminescence in the blue region at 444 nm was observed when excited at 325 nm for the suspensions and at 420 nm for the film. Due to the non-uniformity of the film, the luminescence of the film was very weak compared to the suspension. In agreement with the present results, Du *et al.* [11] reported a blue PL band of GO when excited at 320 nm and Eda *et al.* [10] reported similar results for highly exfoliated GO suspensions when excited at 320 nm. In contrast to our results, Chien *et al.* [12] reported a long wavelength (red) band when excited at 325 nm which Eda *et al.* [10] identified as emission from poorly exfoliated suspensions. Based on literature, GO is reported to have two main PL bands i.e. one in the blue band and another in the long wavelength band due to the opening of the band gaps caused by oxygen functionalities from oxidation. Only the blue emission was observed from our samples.

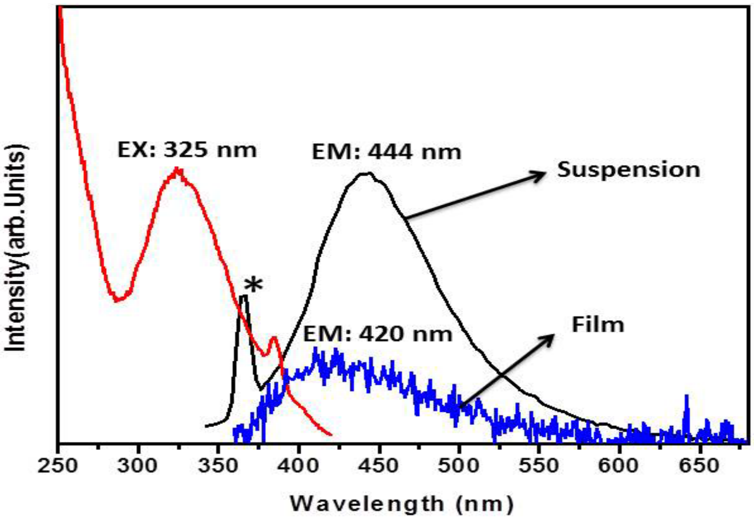

Figure 5. PL spectra of GO suspension and film. The peak labelled * is the Raman peak of water.

4. Conclusion

The commercial GO powder was partially oxidized (4-10%) and thus behaved as reduced, which was observed by the black colour compared to a yellow brown colour reported for well oxidized GO. The GO films were deposited on silicon substrates using spin coating technique. The SEM images revealed that the film spun at 4000 rpm had better surface coverage of the GO sheets. The XRD and UV-vis revealed that the powder still contained unoxidized graphite layers at $2\theta = 26°$ which was supported by the shift in UV absorbance from 230 nm to 273 nm assigned to reduced GO. XRD of the film showed that the deposited GO was better exfoliated than in the original commercial powder, which is attributed to removal of the larger particles by centrifuging. PL measurements of the suspension and film showed a blue luminescence, which has been reported for highly exfoliated GO. Due to the poor uniformity of the GO films spin-coated over the substrate, alternate ways of producing such films will also be investigated in future work.

5. Acknowledgements

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