

Growth and Structural Properties of Graphene Oxide Thin Film with Spray Pyrolysis Technique

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Abstract. The spray pyrolysis technique (SPT) is one of the most useful and simple methods to grow graphene oxide (GO) thin film. Good-quality GO thin films were fabricated by spray coating with GO powder (prepared by the modified Hummers method) on glass substrates. Raman spectroscopy, Field Emission Scanning Electron Microscope (FESEM), X-ray diffraction (XRD) analysis, and UV–visible spectroscopy were done to observe the presence of functional groups in the growth thin films and to determine the structure of GO. From the result of XRD test, the GO demonstrates peak at $10.58^\circ(2\theta)$, while the Raman spectroscopy reveals the presence of two prominent peaks, known as D and G bands, as well as 2D band. The I_D/I_G ratio for spray-deposited GO film was calculated with the value of 0.84. FESEM images showed that the glass substrates were completely covered by GO at different magnifications with a sheet-like structure. The optical absorption of graphene oxide was also observed at a wavelength rang of 275-350 nm.

1. Introduction

Graphene-based materials exhibit remarkable electronic, optical, and mechanical properties, which has resulted in both high scientific interest and huge potential for a variety of applications. Graphene is recognized as an allotrope of carbon in the shape of 2D, atomic-scale, and honey-comb pattern according to which every vertex is formed by a single atom [1]. Graphene oxide (GO) is an intermediate in the chemical synthesis of graphene before the oxygen functional groups are removed thermally or chemically to obtain graphene. Hence, both graphene oxide (GO) and reduced graphene oxide (RGO) properties are interesting from a research perspective and have potential for the development of new applications [2]. The transition between the insulating GO and conducting graphene state is accompanied by a change in the optical properties of the material. The covalent oxygen functional groups in GO give rise to remarkable mechanical strength along with molecular-level chemical sensing capability. The presence of functional groups also implies modification of the graphene electronic structure. Therefore, the chemical composition of GO, which can be chemically, thermally, or electrochemically engineered, allows tunability of its optoelectronic properties [3, 4]. Recently, GO has been potentially used in many modern applications such as sensors and solar cell [5,6]. Spray pyrolysis technique (SPT) is well known techniques to grow nanoparticles [7]. With this technique, thin film material could be grown on glass substrate homogeneously. The advantage of this method is being simple, low operating cost as well as effectiveness [8]. In this study, SPT was used to



grow graphene oxide (GO) thin films on glass substrates. The prepared thin films were characterized using different analytical techniques to study the properties of GO growth by SPT.

2. Experiment

2.1. Synthesis of GO

GO was synthesized according to the modified Hummers method. The steps of the experiment are as follows:

(1) A mixture of 120 ml sulphuric acid (H_2SO_4 , 96%) and 13.3 ml phosphoric acid (H_3PO_4 , 75%) was put in an ice bath.

(2) Next, 1 g of graphite was added with proper stirring, followed by the addition of 6 g of potassium permanganate (KMnO_4) in a very slow manner, keeping the temperature less than 20 °C. Then the solution was heated up to 50 °C and stirred for 8 h.

(3) The solution was cooled to room temperature and poured onto ice water (133.3 mL) with 1 mL of 30–35% hydrogen peroxide (H_2O_2).

(4) A filtration process was performed and followed by the centrifuge process (4,000 rpm for 1 h). Subsequently, the supernatant was decanted away.

(5) The remaining solid materials were washed twice in succession with 66.6 mL of water, 66.6 mL of 30% HCL, and 66.6 mL of ethanol. The obtained solid was dried under vacuum overnight at room temperature [7,8].

2.2. Cleaning of substrates

For the cleaning process, the glass substrates were put in a methanol bath, and the ultrasonication process was run for 15 to 20 min. The substrates were rinsed well with deionized water and finally dried using nitrogen gas [9].

2.3. Film preparation

For the spray deposition method, the instrument comprised an airbrush nozzle (0.3 mm aperture size), timer, beaker solution, thermocouple probe, hot plate heater, and air pump compressor (about 4 bars of pressure). Figure 1 shows a typical spraying system. The thin films were prepared by spray coating GO dispersion in deionized water (0.9 M) onto a glass substrate at 170 °C [10]. Figure 2 shows the prepared GO thin film sample on glass. The diameter of the nozzle was 0.3 mm, and the distance between the nozzle and substrate was 40 cm.

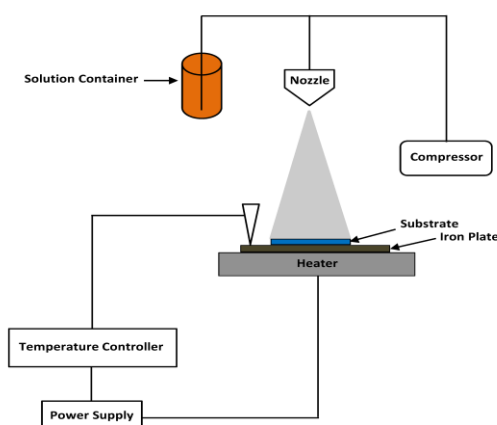


Figure 1. Schematic of spray pyrolysis system



Figure 2. The GO thin film on glass substrate prepared by SPT

2.4. Film structure

X-ray diffraction (XRD) patterns were recorded using Philips X-ray diffractometer model X'Pert with $\text{CuK}\alpha$ (1.5406\AA) radiation operated at 40 kV and 25mA. The patterns were recorded automatically with scanning speed of 2 deg/min.

Field emission Scanning Electron Microscope (FESEM) was recorded using SEM Model Quanta 250 FEG (Field Emission Gun) attached with EDX Unit (Energy Dispersive X-ray Analyses), with accelerating voltage up to 30 KV, FEI Company, Netherlands. The average film thickness of GO thin film (113 nm) was determined accurately after deposition by using FSEM as shown in Figure 3.

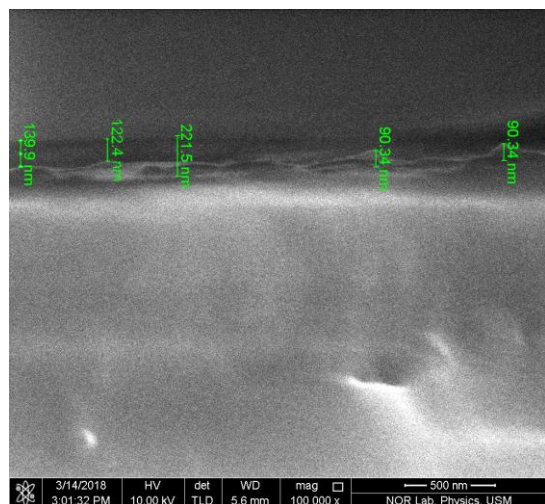


Figure 3. A FESEM image shows thickness of GO thin film

Raman Spectroscopy analysis was done using Nicolet 6700 Spectrophotometer (Thermo Scientific) at room temperature in the spectral range of $1000\text{--}3500\text{ cm}^{-1}$.

UV-visible absorbance (λ), was measured at normal incidence in the wavelength $200\text{--}800\text{ nm}$ by means of a double beam spectrophotometer (JASCO model V-670 UV-Vis-NIR).

3. Results And Discussion

After preparing the thin films of GO by using SPT, several thin films samples have been made. The best results were obtained for the following growth parameter; the temperature was $170\text{ }^{\circ}\text{C}$, diameter of the nozzle was 0.3 mm with distance of 40 cm from the surface of substrate. The samples then were analyzed further to examine the quality of the prepared films.

3.1. Raman Spectroscopy

Raman spectroscopy analysis determined the structural and chemical bonding of molecules. As shown in Figure 4, there are two prominent peaks, D and G bands [11]. The D band is located at $1,343\text{ cm}^{-1}$, which is attributed to the graphitic domain (carbon, sp^2). The G band is at $1,583\text{ cm}^{-1}$, which is associated with disordered edges (sp^3). It is noted that the additional graphene peak on the 2D band is located at around $2,718\text{ cm}^{-1}$. The 2D band is highly sensitive to the number of graphene layers when a few layers of graphene are compared to GO. In this sample, the 2D band's intensity is attenuated, and its bandwidth is broader. The intensity ratio of the D band over the G band (ID/IG) was used to investigate the amount of structural defects and disorders [12,13]. For this sample, the ID/IG ratio has a value of 0.84, a result that confirms the fabrication of GO.

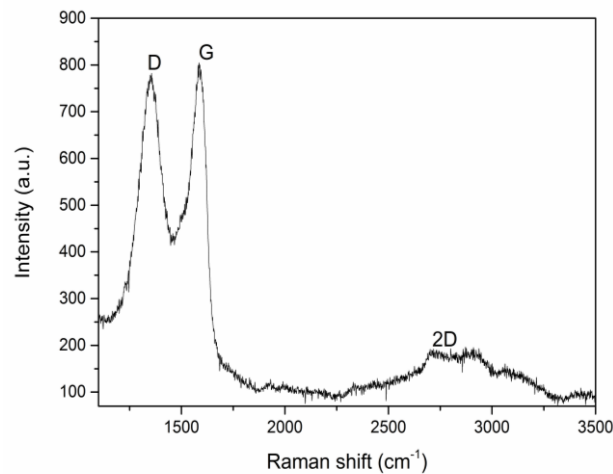


Figure4. Raman spectrum of graphene oxide thin film

3.2. X-ray Diffraction (XRD)

XRD technique is used to determine the presence of functional groups on the sample surface. After the chemical modification of graphite by the improved method to obtain the GO, it was shown that the peak (002) is at around 10.58° (2θ). As shown in Figure (5). Further analysis reveals that $D_{(002)}=0.4$ nm. It is clear that the measured values are due to the presence of graphene oxide on the surface of the substrate [14,15], and the intensity values indicate that few layers of graphene oxide are formed on the substrate. This result corresponds to the result obtained from Raman spectrum measurements.

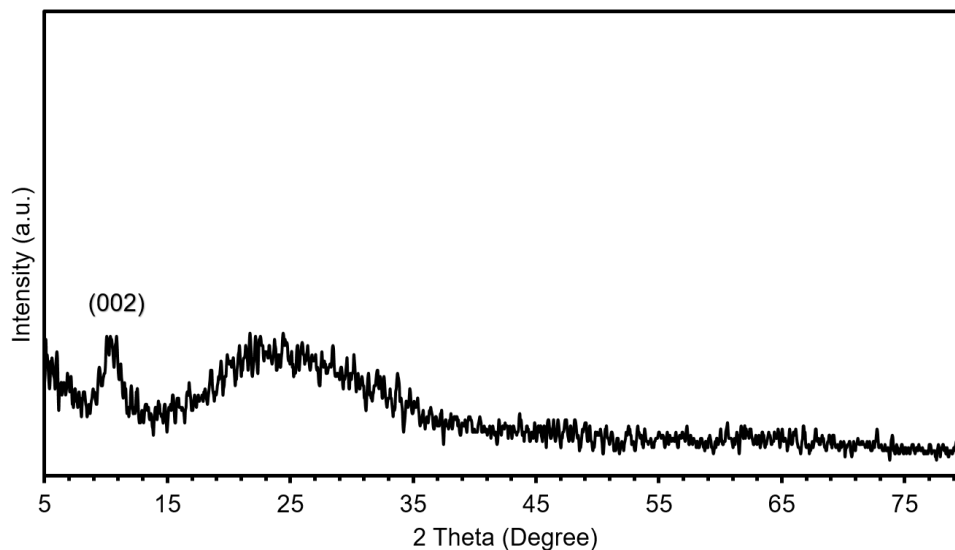


Figure 5. XRD patterns of graphene oxide

3.3. Scanning Electron Microscopy (SEM)

The SEM images of the prepared GO thin film with different magnifications are shown in Figure 5 (a) and (b). It is clear that we have a uniform GO coating with sheet-like structure. This sheet-like structure indicates that graphite has been exfoliated during the oxidation process. This homogeneous coating confirms the effectiveness of this technique to be used for large-scale applications.

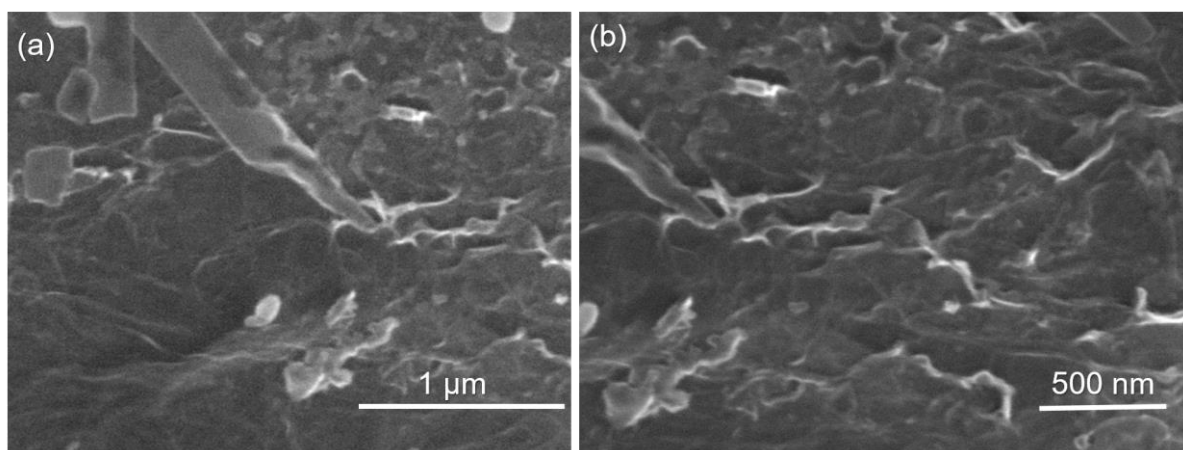


Figure 6. SEM images of GO-coated glass by SPT at different magnifications.

3.4. D. UV–visible spectroscopy

The optical absorbance spectrum of GO thin film with a thickness of 113 nm in UV-V is the spectral range shown in Figure 7. Graphene oxide exhibits a strong absorption edge in a wavelength range of 275–350 nm. Illakkiya et al. [16] reported a band at 230 nm, which is attributed to π - π^* the transition of the aromatic C=C bond. A shoulder peak at 270 nm corresponds to n - π^* the transition of the carbonyl group.

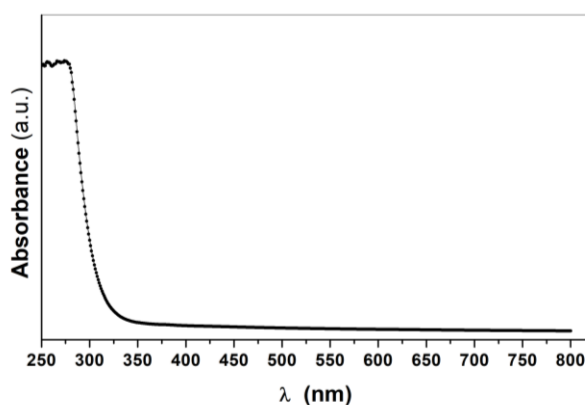


Figure 7. Optical absorbance spectra of GO thin film

4. Conclusion

The spray pyrolysis technique (SPT) is well known for growing nanomaterials. The prepared GO thin films can be used for varying applications such as gas sensors, solar cells, polymer-based composites, and photodetectors. The highlights of this method are that it is simple and effective, with a low operating cost. However, a thin film of GO was prepared on glass substrates by SPT in a controlled factor, including temperature at 170 °C, diameter of the nozzle at 0.3 mm, and substrate distance of 40 cm. The results of the Raman spectroscopy and XRD analysis reveal the structural properties and quality. The absorption spectrum of graphene exhibits a peak around 275–350 nm. This analysis suggests that the SPT can give good results and promising. These results may later be used in the wide range of advanced electronic, optic and material for the future.

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