Synthesis, Structure Parameters and Optical Properties of Graphite and Graphene Oxide Sheet

MOH.G.Al-khattib\textsuperscript{1,2}, Ahmed Samir\textsuperscript{2}, Nasser N. Morgan\textsuperscript{1,2}, Safwat Hassaballa\textsuperscript{1,2}, Mamdouh Abdel aal Ahmed\textsuperscript{1}, Abdou A. Garamoon\textsuperscript{1,2}

\textsuperscript{1}Physics Department, Faculty of Science, Al-Azhar University, Cairo, Egypt
\textsuperscript{2}Center of Plasma Technology, Al-Azhar University, Cairo, Egypt

Abstract

GR (graphite) and GO (graphene oxide) nanosheets were synthesized on Cu substrate (transition metal catalyst) by direct current plasma enhanced chemical vapor deposition (DC PE–CVD). The plasma parameters have been optimized to produce high quality of Gr and GO nanosheets. The influence of mixture gas ratio (\(\text{C}_2\text{H}_2 / \text{H}_2\)) has been studied, which has main function for conversion of Gr sheet to GO sheet. The crystal structure and identification sheets were determined by X – ray diffraction. The structural and optical properties of the Gr and GO nanosheets were characterized by Raman, FTIR and UV-VIS spectroscopy. The FTIR results investigate of oxygen-containing groups on the GO nanosheets and Raman spectra evolves ordering and disordering sheets.

Keywords: Graphite, Graphene Oxide, Raman spectroscopy and optical properties.

I. INTRODUCTION

Carbon based nanomaterials such as carbon nanotube (CNT), fullerene and graphene have gained considerable interest scientific and engineering, because of their potential application which suggested use as multifunctional materials and wide range of technology [1]. Among these materials, graphene offers a unique monolayer or few layers of sp\(^2\) hybridized carbon atoms arranged in a two-dimensional honeycomb lattice which has attracted much attention since its discovery in 2004 [2]. Due to its excellent physical and mechanical properties [3–5], it is a good candidate for various applications such as nano electronic, sensor, catalysis and photovoltaic [4–6].

Recently, GO an oxidized form of graphene, has gained more attention due to it is easy to functionalize, unique physical chemical properties and its application [7]. GO contains a large amount of reactive oxygen atoms on the surface, resulting from the presence of epoxy, carboxyl and hydroxyl groups. These unique properties of GO make it a promising nanomaterial for solar cells application, nano-electronics, polymer composites, \(\text{H}_2\) production, intercalation materials, drug delivery, sensor, catalysis, photovoltaic flexible electronics, chemical sensors and liquid crystal technology [8-11].

As experimental process, GO has been prepared by modified Hummer’s and chemical exfoliation method methods [12]. In this article, GO prepared by direct current plasma enhanced chemical vapor (DCPE–CVD) deposition on catalytic transition metal substrates. The chemical vapor deposition (CVD) method has been widely used to synthesis carbon nanosheets [13]. However, due to the high growth temperature (~1000 °C) required for thermal decomposition of hydrocarbons, plasma enhanced chemical vapor deposition (PECVD) has been utilized to achieve low-temperature growth of GO by using reactive species generated in the plasma. This method has already been used for the low-temperature growth of carbon nanotubes (CNTs) with vertically aligned CNTs [14-16].

II. EXPERIMENTAL PROCEDURE

Carbon-based nanostructure materials have been prepared by plasma-enhanced CVD (PE-CVD) in which gaseous carbon sources are reacted under specific condition and deposited on to metal substrate. The different metal substrate such as Ni [17,18], Cu [18,19], Pt [20] and NiFe [21] have been studied. In this work, a Cu substrate was chosen for use as the metal catalyst due to its grain size, etchability, and preferred of industry [18]. Cu substrate is used cathode in PE-CVD chamber (see Fig. 1) in circular shape with radius 30 mm and thickness 50 μm. The copper substrates were cleaned to remove chemical and particulate contaminations such as oil, wax, grease, rust, oxide and dirt in ultrasonic cleaning machine. The prepared cleaning solution was mixture of de-ionization water and addition of %5 HCl. The cleaning process was completed at 40 °C for 25 min. The cleaned substrates were rinsed with de-ionization water, and dried in air. The Cu substrate was later placed in the PE-CVD chamber (see Fig. 1(a)). At that point, the rotary pump (RP) was run for 45 to 60 min to bring the pressure to under ~10^{-3} Torr.

Specific properties were investigated for the growth, synthesis, characterization and evaluation different kinds of Carbon-based nanostructure films.
Heating was allowed to progress linearly from room temperature to 500 °C [22–24]. A high amount of hydrogen was found to significantly enhance carbon nanostructure film uniformity at elevated temperatures [25]. Also, the presence of H₂ prevented the rolling of sheets into nanotubes and other graphitic polyhedral particles [26]. Thus, H₂ gas was fed in at 100 standard cubic centimeters per min (sccm) under 5 Torr. At that time, the applied plasma voltage (~ 600 V) was set, and the Cu surface was exposed to different mixture gas ratio (acetylene (C₂H₂) / hydrogen (H₂)) as: G1 (C₂H₂ / H₂ : 100 / 0 sccm), G2(C₂H₂ / H₂ : 50 / 100 sccm) and G3 (C₂H₂ /H₂ : 10 / 100 sccm) at reaction time 20 min, after which the voltage was turned off and the gas flow lines were shut off. At that moment, thermal quenching (cooling) was allowed to take place. Subsequently, the samples were taken for characterization.

**III. CHARACTERIZATION**

The instruments used for identification and characterization of sheets were (i) Phillips X-ray diffractometer for the X-ray diffraction (XRD) analysis was used to analyze crystal phase of the material. Cu-Kα irradiation was used at a 2θ scan rate of 2.0°/min under 40 kV accelerating voltage and 20 mA of applied current. (ii) attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectrometer (Perkin Elmer Spectrum 100) for the spectra in KBr medium at room temperature in the region of 4000–400 cm⁻¹ wave number range. (iii) The Raman spectra were obtained using Raman spectroscopy NRS-2100 (Jasco, Japan) with a 514 nm Ar ion laser as an excitation source. (IV) UV–VISABLE diffuse reflectance spectra (Jasco, Japan) of prepared sheets were detected to analyze light absorption ability.

**IV. RESULTS AND DISCUSSION**

**A. X-ray diffraction**

X-ray diffraction patterns of synthesized G1, G2 and G3 films are shown in fig. 2. For G1 film (100 sccm C₂H₂: 0 sccm H₂ at 500 °C), the sharp and intense diffraction peak appears at 26.69° corresponds to (002) plane with interlayer distance 0.342 nm, was attributed to prefect stacked GR film [27]. For G2 film (50 sccm C₂H₂: 100 sccm H₂ at 500 °C), exhibit two weak diffraction peaks at 9.86° corresponds to (002) plane with interlayer distance 0.899 nm and 25.7° corresponds to (001) plane with interlayer distance 0.355 nm which attributed to disorder GO and GR films respectively. For G3 film (10 sccm C₂H₂: 100 sccm H₂ at 500 °C), the broad diffraction peak appears at 10.67° corresponds to (001) plane with interlayer distance 0.831 nm, which indicated GO nanosheet is formed. Similar results have reported by other authors [27 – 30].

**Fig. 1 Schematic diagram of the DC PE-CVD chamber.**

**Fig. 2 X-ray Diffraction of G1, G2 and G3 sheets.**

These results suggested that, absence of hydrogen gas H₂ (in G1 sheet) was allowed to nucleation process can be occur, which carbon – carbon molecule layers are expanded in very fine regular stack sheet with small interlayer distance 0.342 nm due to strong interlayer van der waals interaction, which attributed to long – range order of stacked GR sheet [28]. The hydrogen gas (H₂) in G2 and G3 samples acts a catalyst, which in G2 sheet (H₂ / C₂H₂ : 2 / 1) reduced nucleation process that
allowed to oxygen intercalated into interlayer spacing of GR to formed disordered GR sheet. The G3 sheet is rich of H₂ gas (H₂ / C₂H₂ : 10 / 1) that accelerate growth process more than nucleation process to formed very fine sheet with interlayer distance 0.831 nm which indicates that the interlayer van der Waals interaction have been weakened effectively compared with that of GR, indicating that oxygen intercalated into the interlayer spacing of GR is largely and broad peak in X-ray diffraction associated to expanded and oxidized few-layered graphene nanosheets [28-30].

**B. Attenuated Total Reflectance - Fourier Transform Infrared (ATR-FTIR)**

The formation of GR and GO sheets were further confirmed by FTIR measurements which provide semi-quantitative information about functional groups of sheets. The ATR-FTIR spectra of GR, disordered GR and GO are shown in Fig. 3. For GO sheet, the ATR-FTIR spectra contains several functional group and shows obvious and strong oxidation peaks, including the characteristic peaks of O-H stretching vibrations at about 3200 cm⁻¹, C=O stretching vibrations from carboxyl and carboxylic groups at about 1850 cm⁻¹, C-OH stretching vibrations at about 1290 cm⁻¹ and C=O stretching vibrations at about 1178 cm⁻¹ [29-32]. The FTIR thus confirmed the presence of hydroxyl, carboxyl and epoxide groups in the basal plans of GOs. These peaks illuminate that the GO sheet contains abundant oxygen functional groups at the edges and basal plane of the nanosheets [32]. On the contrary, the FTIR spectra of GR show a strong decrease in the signal intensity with respect to the oxidized sheet (GO). The broad peak at 3250 cm⁻¹ for GR sheet might be attributed to the O–H stretching vibration of absorbed water molecules and the characteristic band at 1300 cm⁻¹ is corresponding to vibration absorption of CH₂ group in various hydrocarbons. Meanwhile, the peaks of carboxyl group decrease significantly and a new peak at 1653 cm⁻¹ is ascribed to the skeletal vibration of aromatic ring. The stretching vibrations of carboxyl groups or conjugated carboxyl groups cannot be observed in the FTIR spectra of GR, which formation of regular stacked GR sheet without oxygen functional groups [33]. The disordered GR is intermediate region between GR and GO sheet, which its spectra exhibit some of functional groups of GR and GO sheets.

**C. Raman spectroscopy**

The crystalline ordering and domain structure of GO and GR sheets were investigated by Raman spectroscopy at an excitation wavelength of 514 nm under ambient condition in the spectral range 1000 – 3000 cm⁻¹. As shown in Fig. 4, the Raman spectra of GR exhibit a strong band at 1584 cm⁻¹ G – band (first order scattering of E₂₉g phonon from sp² carbon atoms) and a relatively weak band at 1355 cm⁻¹ D – band (breathing mode of k-point photons of A₁g symmetry), corresponding to the vibration of sp² hybridized graphitic domains and sp³ hybridized carbon or structural defects, respectively [34]. The low intensity I_D/I_G value (0.46) for natural GR implies that the graphitic domains are essentially intact. In the Raman spectra of GO, the D band shifts downward to 1349 cm⁻¹ and becomes prominent, and the G band is broadened and shifted up to 1588 cm⁻¹ because of the presence of isolated double bonds [35]. The intensity ratio I_D/I_G of GO (0.65) is higher compared to that GR sheet (0.46). The typical G and D bands corresponded to the GR sp² carbon atoms in the horizontal hexagonal lattice and the sp³ carbon band, respectively. The D band was associated with the crystal defects, such as amorphous carbon or edges that can break the symmetry and selection rule [34,35]. The high ratio of I_D/I_G indicated the high degree of disorder of the resulting GO sheet, which may be ascribed to the structural defects, demonstration effective oxidation intercalation. The relative Raman D/G intensity ratio (I_D/I_G) is inversely proportional to the average size of the sp² domains (Saito et al.,2011). This result suggests a decrease in the average size of the sp² carbon domains to formation GO nanosheet, in compression of stacked GR sheet.
D. UV–Vis spectrum

Fig. 5 shows the UV–Vis spectrum for GR and GO in reflectance mode. The UV–Vis reflection spectrum of GO exhibits two characteristic features that can be used as a mean of identification: a maximum at 234 nm, corresponding to π → π* transitions of aromatic C–C bond, and a shoulder at ~295 nm, which can be attributed to n → π* transitions of C–O bonds [36]. For GR sheet, the UV–Vis reflection spectrum exhibits one characteristic feature at 232 nm, corresponding to π → π* transitions of aromatic C–C bond to confirmed regular carbon – carbon sheet structure [36].

![UV-Vis spectrum](image)

Fig. 5 UV-Vis reflection spectra for GO and GR sheet reflectance mode.

V. CONCLUSION

From previous results, DC PE–CVD method was successfully grown of carbon nanosheets (GR and GO). Plasma parameters predominate of type, morphology structure and feature of sheet, C<sub>H</sub>/H<sub>2</sub> ratio (10 / 100 sccm) is a tuning point of GR to GO sheet. DC PE–CVD method successfully achieved low temperature growth of GR and GO sheet at reduced substrate temperature 500 °C. Based on the Raman spectra of sheets, ordering stacked GR sheet was produced with I<sub>D</sub> / I<sub>G</sub> (0.46) ratio and this order is destroyed to form disordered GO nanosheet with I<sub>D</sub> / I<sub>G</sub> (0.65) ratio. The ATR-FTIR results confirmed the existence of oxygen- containing groups of the prepared GO nanosheets and UV – Vis illustrate reflection mode, which sustained to powerful using in optoelectronics technology. Further study must be achieved to transfer of GO sheet to monolayer graphene sheet.

ACKNOWLEDGEMENTS

This work has been supported by Center of Plasma Technology, Al-Azhar University, Cairo, Egypt.

REFERENCES

[16] Denysenko IB, Xu S, Long JD, Rutkevych PP, Azarenkov NA, Ostrikov K. Inductively coupled Ar/CH<sub>4</sub>/H<sub>2</sub> plasmas for low-


