Structural Properties of Multi-layer Graphene (MLG) Films Prepared by Flame Technique in Open Environment

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ABSTRACT

Two multi-layer graphene (MLG) films were prepared on copper foils by flame synthesis technique with propane gas as carbon source at different temperatures (600^0 C and 700^0C). The structural, morphological and chemical properties, of the synthesized MLG were studied. X-ray diffraction shows that the structure of MLG films is polycrystalline with preferential orientation in the [101] direction. Morphological properties were observed by AFM images, the grain size and average surface roughness of the obtained MLG films are found to increasing with temperature increases and decreasing with the distance. The Fourier transform infrared spectroscopy (FTIR) spectrum showed the stretching vibration of C=C aromatic ring and the stretching vibration from C-C bond. Also the oxygen-containing functional groups have been appeared like C=O, C-O and C-OH.

الخصائص التركيبية لاغشية الكرافين متعدد الطبقة المحضر بواسطة اللهب في بيئة مفتوحة

الخلاصة:

تم تحضير اغشية الكرافين متعدد الطبقات على رقاقة النحاس باستخدام تقنية الترسيب باللهب مع استخدام غاز البروبان كمصدر للكربون عند درجات حرارة مختلفة(600^0C و 700^0C). حيث ان هذه الطريقة تسمح لتحضير انواع متنوعة من مواد الكاربون النانوية. كما تمت دراسة الخصائص التركيبية والمورفولوجي والكيميائية للأغشية المحضرة. أظهرت دراسة تحليل حيود الأشعة السينية (XRD) لأغشية الكرافين متعدد الطبقات بانه ذو تركيب سداسي متعدد البلورات بالاتجاه [101] . من خلال دراسة خصائص المورفولوجي عن طريق مجهر القوة الـذري (AFM) وجد ان الحجم الحبيبي ومعدل خشونة السطح للكرافين تزداد بزيادة درجة الحرارة ونقصان المسافة. أظهرت تحويلات فورير الطيفية للأشعة تحت الحمراء (FTIR) وجود اصرة C=C والتي تشير الى اهتزازات الحلقة السداسية (عطرية) بالإضافة الى وجود اهتزازات ناتجة عن الاصرة C-C مع وجود اواصر اوكسيد مختلفة مثل C=O و C-O و C-OH.

INTRODUCTION

Graphene is the name refer to a flat monolayer of carbon atoms tightly bounded into a two-dimensional 2D honeycomb lattice, which is a basic building of all other graphitic materials. It can be wrapped up into 0D fullerenes, rolled into 1D nanotubes or stacked into 3D graphite [1]. This purely two-dimensional form of carbon existed only within three-dimensional graphite or tightly packed to another solid surface[2]. Two-dimensional graphene has especially attracted a lot of attention due to of its unique electrical properties such as very high carrier mobility, and the quantum Hall effect at room temperature, In addition, some other

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properties of graphene that are equally interesting include its unexpectedly high absorption of white light (2.3%), high elasticity, high surface area, [3], and conciliate such conflicting qualities as brittleness and ductility[4]. The preparation of graphene sheets of both large area and high quality has become an important challenge. There are several ways to produce single or few-layer graphene (FLG), such as micromechanical cleavage, epitaxy growth in ultrahigh vacuum, atmospheric pressure graphitization of SiC, chemical oxidation of graphite and chemical vapor deposition (CVD) using transition metals as catalysts[5]. A promising method of producing graphene layers is the method of synthesis of graphene in flames. The studies confirm that the process of achieving a flame graphene cannot compete with other existing methods. The process of formation of graphene in a flame is continuous, rapid, and cheap technique [6]. Flame synthesis is a high-temperature synthesis technique, which includes only a single-step process, resulting in a large-scale approach for fabricating diverse materials involving low-dimension carbon structures such as CNTs, fullerenes, and amorphous carbon thin films[7].

Experimental work

Preparation Method

Multi-layer graphene (MLG) films are grown on copper foils with thickness 80 μm by diffusion flame, where the mixing of fuel and oxidizer (air) occurred after ignition. The substrates were cut into small pieces with dimensions of 2×2 cm^2 and cleaned by distilled water to remove any dust that may be attached to the surface and then cleaned by alcohol solution in order to remove the impurities and some oxides. After preparation of the foil, it is placed in the substrate holder and then the propane burner switched on and pointed on the substrate in parallel direction for heating the foil before deposition process. Afterwards, the substrate rotated toward the propane burner in perpendicular direction to diffuse carbon atoms into foil from one side and then the propane burner switched off and the foil cooled down to room temperature. Finally the MLG films annealed in oven vacuum for two hours at 200^o C and low pressure about 0.08 Mpa. In order to explain the structural properties of MLG films at different preparation conditions, X-ray diffraction measurement has been done according to the JCPDS card (Joint Committee on Powder Diffraction Standards), using SHIMADZU 6000 X-Ray diffractometer system (with λ = 1.54 Å). The grain size distributions of the MLG films prepared under various conditions were analyzed using atomic force microscope (AFM) from (CSPM-AA3000). Chemical composition of MLG films have been measurement by Fourier Transform Infrared (FTIR) spectroscopy (8400S, Shimadzu with wavenumber over the range 500 to 3500 cm^{-1}.

Results and Discussion

XRD Results

XRD pattern of MLG film deposited at 600^0 C is shown in Figure 1. The strong and sharp peak at 2θ = 43.57 corresponds to an interlayer distance of 2.075 Å for (101) orientation, which is consistent with the layer spacing of JCPDS standard card (230064) of graphite, which has interlayer distance equal to 2.027 Å. This difference due to the interlayer distance of graphene is slightly larger than that of bulk graphite. Because graphene oxide (GO) has many defects or nanoholes, it is reasonable that thermally reduced graphene would also have many defects and nanoholes. Therefore, GO and MLG can have oxide groups of C−Ox with an sp3 bond in their defects and nanoholes[8]. Moreover, there are two broad peaks at 2θ = 14.28 and 2θ = 17.1, corresponding to the *d*-spacing of 6.19˚A and 5.17˚A respectively along the (002) orientation for graphene oxide has the largest interlayer distance because of its intercalated H_2O molecules and various oxide groups such as hydroxyl, epoxy and carboxyl[9]. In the XRD pattern of MLG deposited at 700^0C, the strong and sharp peak at 2θ = 43.52 corresponds to an interlayer distance of 2.077 Å for (101) orientation. In addition , there is weak and broad peak at 2θ = 29.53 corresponds to an interlayer distance of 3.022 Å along the (002) orientation, which is not consistent with the layer spacing of normal graphite (~3.4 Å) this shift is indicative of a lower degree of crystallization and the presence of some defects that were possibly caused by the presence of CO_2., This suggests the existence of regions of expanded stacking of more corrugated or disordered graphene sheets, probably existing at the edge areas[10].

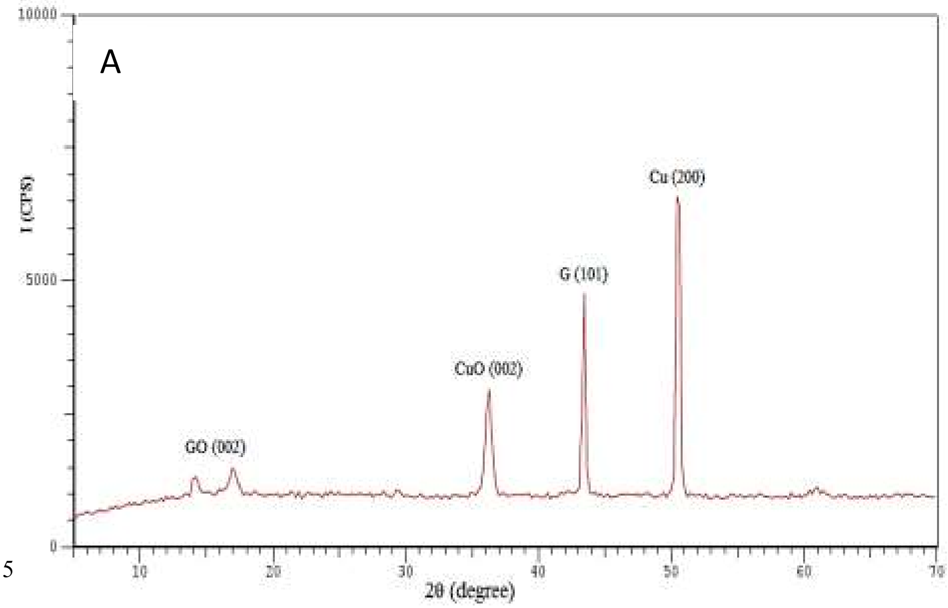


Figure (1): XRD spectrum of multi-layer graphene synthesized at 600^0 C.

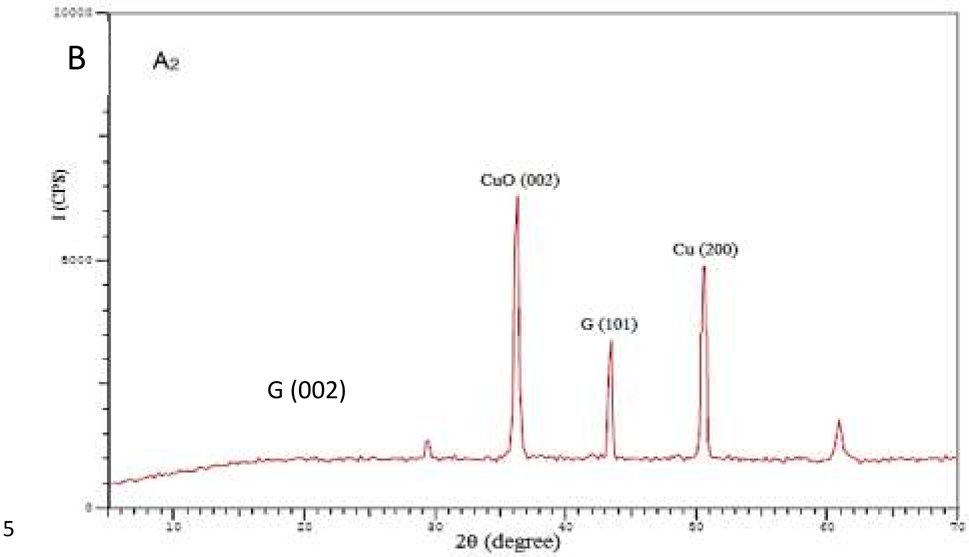


Figure (2): XRD spectrum of multi-layer graphene synthesized at 700^0 C.

FTIR Results

FTIR spectroscopy is presented as a non-destructive analytical tool to determine the chemical bonds between atoms in materials. Figure 3 shows the FTIR spectrum of multi-layer graphene deposited on Cu at temperature (600^{0}C). As shown in Figure 3 the presence of different types of oxygen functionalities in graphene film, the band at 1614.4 cm^{-1} can be attributed to the stretching vibration of C=C aromatic groups, the bands at 1729.6 cm^{-1} and 1064.7 cm^{-1}, which correspond to the stretching vibrations from C=O carbonyl/carboxyl present at the edges of graphene film due to the partial reduction of the surface of MLG during heat treatment[11] and the stretching vibrations from C-O in the epoxide group referring to little contribution of CO_2

dissolution from air content. Some peaks are seen around 1510.3 cm^{-1} can be attributed to the stretching vibration from single bounded C-C and the emergence of the vibrational band at 2917.1 cm^{-1} can be attributed to C-H group due to replacement of unstable hydrogen atoms with oxygen atoms. Figure 4 shows the FTIR spectrum of multi-layer graphene deposited on Cu at temperature 700^0C. Also the same vibration bonded of C=O, C=C, C-O, C-C and C-H stretching vibration are formed, centered at (1725.6 cm^{-1}, 1616.4 cm^{-1}, 1062.8 cm^{-1}, 1520.2 cm^{-1} and 3016.1 cm^{-1}) respectively. We see the spectral consist many other bands these bands come from low purity of MLG film due to the high temperature of substrate which lead to contamination of the film with ions of other materials. According to the results of Figure 3 and Figure 4 the relative intensity of FTIR transmittance peak changes with the change of temperature and also the positions and width of observed peak are also change for the most part in each spectrum. The shift of the C=C bond (aromatic functional group, skeletal vibrations from unoxidized graphitic domains) from 1614.4 cm^{-1} to 1616.4cm^{-1} due to the change of particles size, this is due to increased carbon concentration and peaks became broad on increasing graphene content

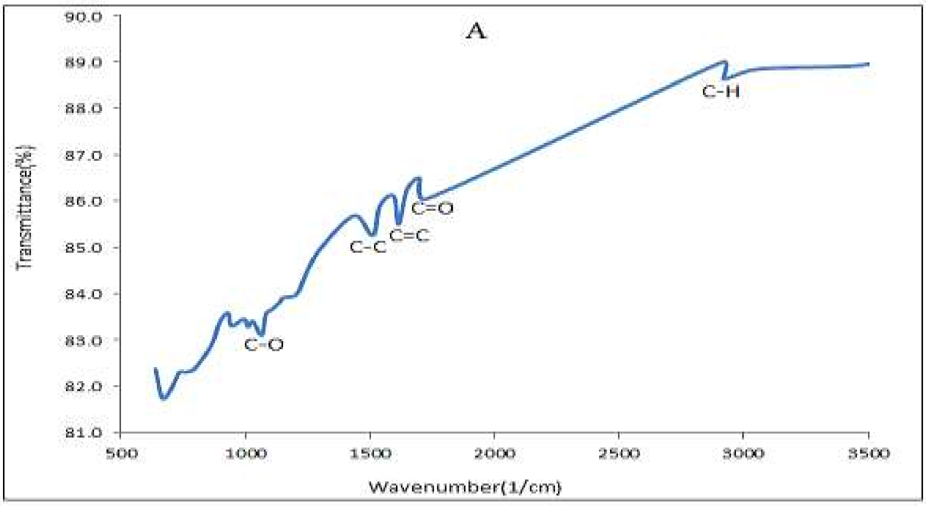


Figure (3): FTIR spectrum of MLG synthesized on Cu at 600^0 C.

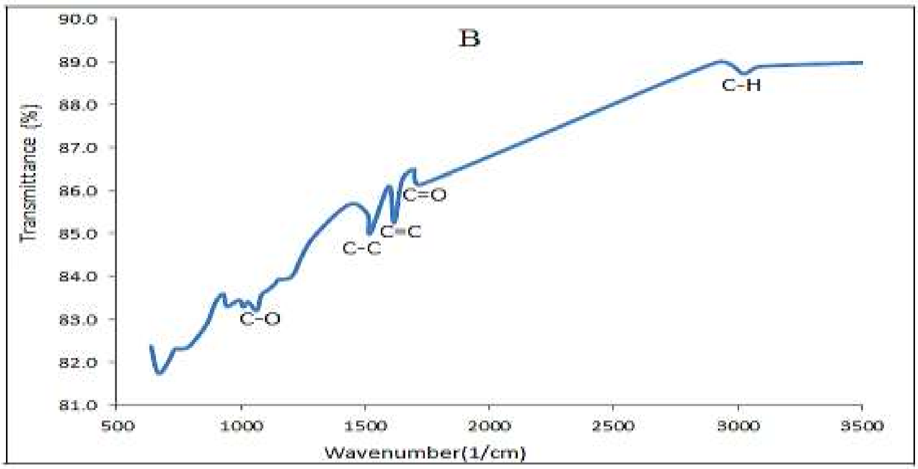
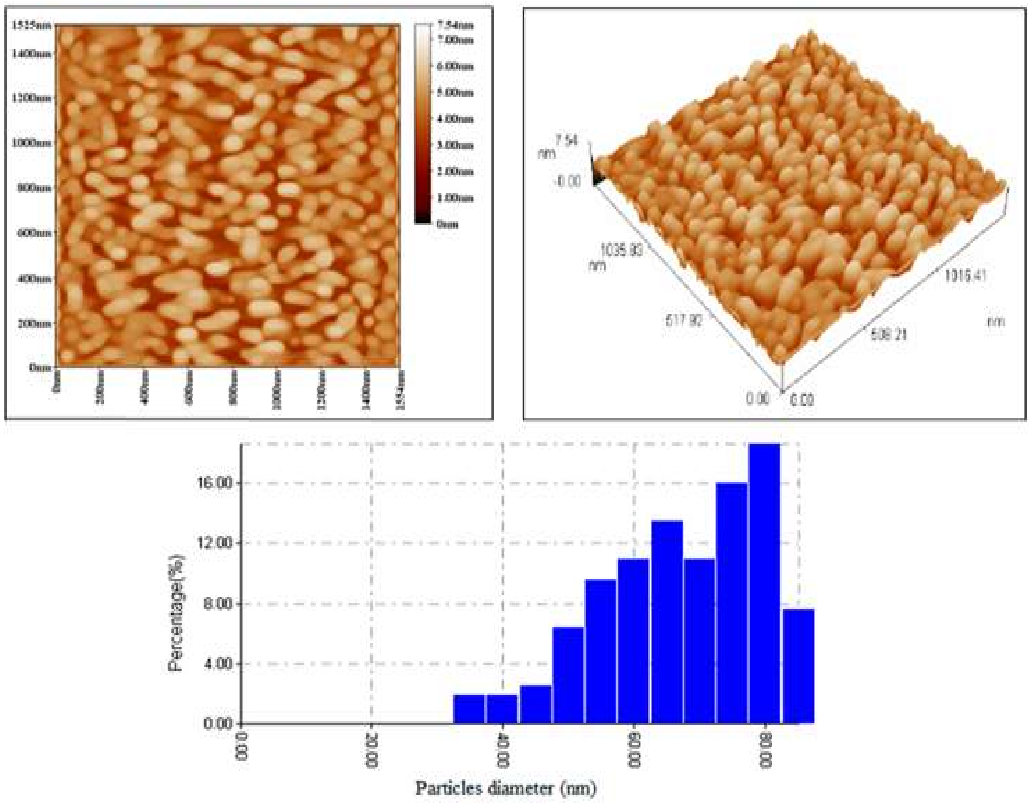


Figure (4): FTIR spectrum of MLG synthesized on Cu at 700^0 C.

AFM Results

AFM images of MLG films have been studied to examine the effect of the substrate temperature and a distance between burner-substrate on particles size and roughness. Figure 5 and Figure 6 shows the morphology of MLG deposited on copper foils at 600^0 C and 700^0 C respectively. The images show that MLG films have semi-spherical shapes and from graphical (2D and 3D) we see that the number and particles distribution decreases with increasing in temperature. Also it is found from Table 1 the particles size increased with increasing the substrate temperature of MLG. The decrease in the particles number and increase in the particles size is probably related to the increase in temperature due to the particles become much closer to each other. The particle density becomes greater, where the particles begin to agglomerate with different sizes creating thin MLG film. Figures 5 and Figure 6 show the effect of varying distance between the burner and the substrate on the particles density and size. These figures reveal that very small size particles could be recognized when we increase the distance between burner and substrate. The samples prepared at small burner-substrate distance (6 cm), shows that the film contains almost large particles randomly distributed over the substrate. The presence of different particle sizes in small burner-substrate distance is related to the fact that almost all the carbon particles will reach the substrate. When the burner -substrate distance is increased to (10 cm), a limited number of particles are distributed over the substrate surface. The sizes of these particles are varied from small sizes and large sizes spreading homogeneously on a wide area of the substrate. The increase in the distance reveals that no large particles reach the substrate. Another information that we can extract from the AFM topography, is the roughness of both the substrate and the sample. It should be noted that the roughness values are an average value taken from a small area of the sample (the scanned part or an even smaller part selected after scanning) compared with the entire substrate, so those numbers don't refer to the whole films in absolute way, and the roughness may slightly change depending on the region under study. Table 1 illustrates the effect of the temperature on the average surface roughness. The surface roughness increases when increasing temperature due to increasing the particles size make the film has higher roughness. The average roughness at different burner -to-substrate distances as given in table 1, where the average size results show the average film roughness for the films produced at 10 cm as compared to this produced at 6 cm. This implies that 10 cm distance produces a MLG film, which has a large amount of smaller sizes leading to a reduction in the surface roughness because of only smaller particles have of higher kinetic energy can reach the substrate surface at long distance.



Figure(5): 3D, 2D AFM images and the average size of MLG deposited at 600^0 C.

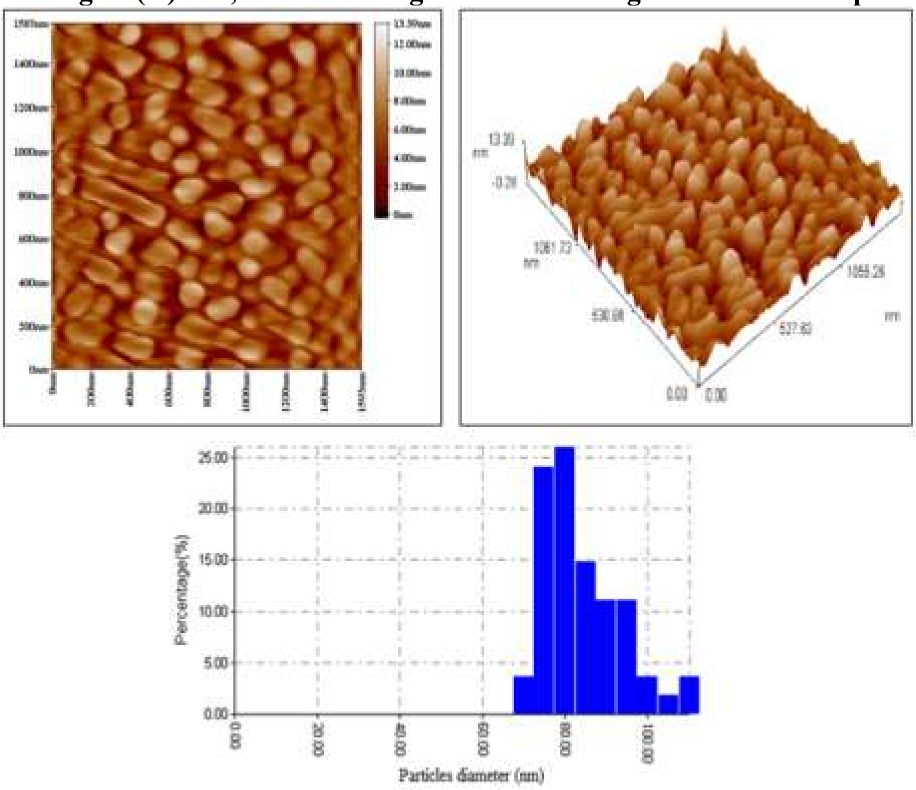


Figure (6): 3D, 2D AFM images and the average size of MLG deposited at 700 ^{0}C.

Table (1) The results of morphology characteristics of MLG films.

Distance (cm)	Temperature (C)	Avg. Diameter (nm)	Avg. Roughness (nm)
10	600	64.85	0.67
6	700	81.80	1.57

CONCLUSIONS

In this article, MLG films were prepared by the flame method. the substrate temperature play important role to growth graphene film, at a temperature of 600°C, graphene films on Cu are still observed, Further reduction of the temperature to 500ºC results in the formation of an amorphous carbon film, FTIR spectra exhibit the presence of C=C and C-C bonds which indicates the formation of MLG at different temperatures. AFM results show the grain size and average roughness increasing with increasing substrate temperature and decreasing in the distance.

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