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Development of High Purity, Few-Layer Graphene Synthesis by Electric Arc Discharge Technique

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In this study, high purity graphene nanoflakes (GNF) were synthesized by electric arc discharge technique. The arc discharge method is more advantageous than other graphene synthesis methods for producing cheap and good-quality graphene with minimum defects and not including dangerous chemicals. Because of this advantages, the arc discharge method is one step ahead of all graphene synthesis methods. In order to synthesize GNF, a DC electric arc discharge reactor was designed by our team. Electric arc discharge method based on a principle that provides a constant current between two high purity graphite electrodes to vaporize. After the arc discharge, nanoparticles accumulate on the inner surface of the reactor. The voltage stabilizer DC power source is used to create a current in the environment and the discharge usually occurs in a range 20–60 V. This current can be adjusted depending on the diameter of electrodes, the distance between electrodes and arc current varies between 100 and 150 A. Different characterization techniques such as the Raman spectroscopy, scanning electron microscope and transmission electron microscope were used to characterize the graphene layers synthesized by the arc discharge method. The L_D/L_G ratio was calculated as 0.66 while the L_G/L_{2D} was determined as 1.31. These values show that the purity of the synthesized graphene is compatible to that of commercially supplied graphene. Besides, the synthesized graphene has fewer layer than commercially supplied one. Transmission electron microscope observations confirmed the typical wrinkled feature of graphene.

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PACS/topics: graphite, graphene, electric arc-discharge, Raman spectroscopy

1. Introduction

Carbon has many allotropes such as graphite, diamond, nanotube C_{60} (fullerene), and also graphene. Graphene has a densely packed hexagonal honeycomb-shaped atomic structure with an sp^2 hybridization. Graphene has extraordinary electrical, thermal, mechanical, and optical properties [1, 2].

Graphene can be synthesized using two different approaches such as top-down and bottom-up methods. The general top-down methods are micromechanical cleavage [3], electrochemical exfoliation [4], exfoliation of graphite intercalation compounds (GICs) [5], solvent-based exfoliation [6], exfoliation of graphite oxide [7], evaporation with laser [8], and arc discharge [9]. On the other hand, epitaxial growth on silicon carbide [10], SiC degradation on high temperature [11], chemical vapor deposition (CVD) are commonly used bottom-up methods [12]. Among all these methods, arc discharge has many advantages such as low cost production, high efficiency and synthesis opportunity without any catalysis usage [13].

In this study, few layers of graphene were synthesized by utilizing a homemade arc discharge chamber designed by our team. Helium (He), nitrogen (N) and their mixtures were used to understand the effect of reactor atmosphere on the synthesis of graphene. The purity and the number of graphene layers were determined via the Raman spectroscopy. The purity of synthesized graphene also depends on the diameter of the electrodes and arc current. Therefore, optimum synthesis conditions were obtained at electrode diameter of 12 mm and arc current of 150 A in a He+N_2 atmosphere. The crumpled texture of graphene was observed by TEM examinations.

2. Materials and methods

Few layered graphene flakes were synthesized using DC arc discharge in a stainless steel reactor which was designed by our team. The graphene synthesis diagram and the image of designed arc discharge reactor were shown in Fig. 1a and b, respectively. High purity graphite rods (99.9%) with a diameter of 10 mm and 12 mm were used as electrodes. Reactor was kept under pressure for approximately 5 min. Helium, nitrogen and their mixtures were used as reactor atmosphere. Arc current varied between 100 and 150 A. The experimental conditions were summarized in Table I.

The synthesized GNF were collected from the inner surface of the reactor. Anode consumption, slag formation and the inner surface of reactor after the synthesis were shown in Fig. 2a and b, respectively. The results of synthesized graphene were compared to a commercially supplied graphene by OOO Holding Zolotaya Formula, Russia.

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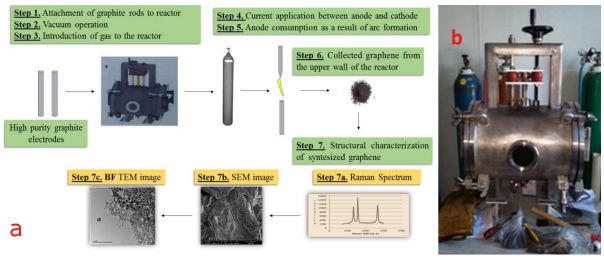

Fig. 1. (a) Graphene synthesis diagram, (b)graphene synthesis reactor.

TABLE I

Experimental conditions

gas connection on system	He, N_2, He + N
gas pressure	0.1 bar
electrode diameters	10 mm/12 mm
current interval/vacuum period	100–150 A/5 min

Fig. 2. (a) Anode consumption and slag formation, (b)reactor inner surface after experimental studies.

Morphology and structure analysis of the samples were carried out on a high-resolution transmission electron microscope (TEM) HRTEM JEOL JSM 6335F. The Raman spectra was recorded from 500 to 3000 cm^{-1} with a Renishaw in via spectrometer with an excitation wavelength of 532 nm.

3. Results and discussion

The graphene synthesis studies started with 8 mm graphite electrode in He atmosphere using 130 A arc current. The Raman spectroscopy result showed too weak 2D band in the spectrum. Experimental studies were performed by increasing the diameter of the electrode and arc current. The quality evaluation of the synthesized graphene was carried out using the Raman and TEM analysis techniques. The images of the synthesized graphene were shown in Fig. 3.

3.1. Raman spectroscopy

Figure 4a–c shows the Raman spectra of the synthesized graphene using 10 mm electrode in He atmosphere, 12 mm electrode in He+N_2 atmosphere and commercially supplied graphene, respectively.

L_D/L_G and L_G/L_{2D} ratios were calculated for both synthesized graphene and commercially supplied graphene. In the Raman spectra, D and G bands are in a range 1000–2000 cm^{-1}. Also, the specific 2D band for graphene, can be observed at 2000–3000 cm^{-1}. L_D/L_G ratio provides us information about graphene purity and this ratio should be between 0 and 1 [14]. L_G/L_{2D} ratio is related to the number of graphene layers [15]. Wu et al. [16] reported that L_G/L_{2D} value of 0.25 corresponds to a single layer.

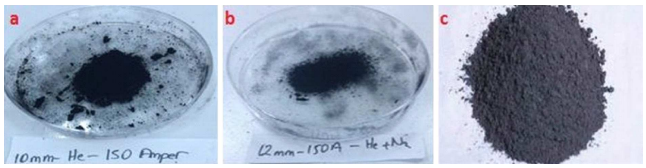

Fig. 3. Synthesized and commercial graphene samples: (a) 150 A, 10 mm, He, (b) 150 A, 12 mm, He + N_2, (c) commercial graphene.

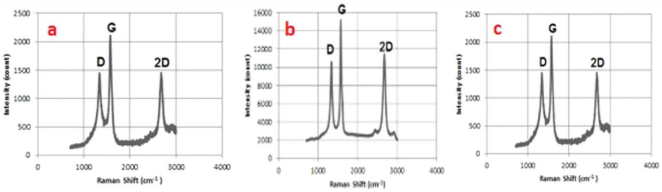

Fig. 4. Raman spectra of synthesized and commercial graphene samples: (a) 150 A, 10 mm, He, (b) 150 A, 12 mm, He + N_2, (c) commercial graphene.

In the arc discharge technique, it is believed that the inert gas acts as a "quencher" for the carbon vapour, which attains super saturation followed by nucleation and growth of carbon nanotubes [17]. In the light of this knowledge, different gas atmospheres were used as a buffer gas for synthesis of carbon nanoflakes in the arc discharge reactor.

Table II summarizes band ratios of graphene synthesized by electric arc discharge (EAD) using different electrode diameters, arc current reactor environments and commercially supplied graphene. The effect of electrode diameter on the purity of synthesized graphene was also studied. Best results were obtained in mixture of He + N_2 atmosphere and 150 A current value. In this atmosphere, purity increases and number of layers decreases when the electrode diameter increases. According to our studies, the purity of graphene and number of layers were found to be comparable with commercial graphene results.

TABLE II

Band ratios for experimental parameters

Experimental parameters	L_D/L_G ratio	L_G/L_2D ratio
commercially supplied graphene	0.55	1.4
10 mm – 150 A – He	1.02	1.32
12 mm – 150 A – N_2+ He	0.66	1.31

3.2. TEM results

Bright field (BF) TEM images of the synthesized graphene with 10–12 mm graphite rods in different buffer

gases (He, He+N_2) were shown in Fig. 5a and b. The TEM investigations show that graphene synthesis was successfully achieved in EAD and also was compatible with the literature [9–18]. Graphene flakes have wrinkle surfaces. For this reason, optical thickness of graphene is variable and graphene have transparent structure.

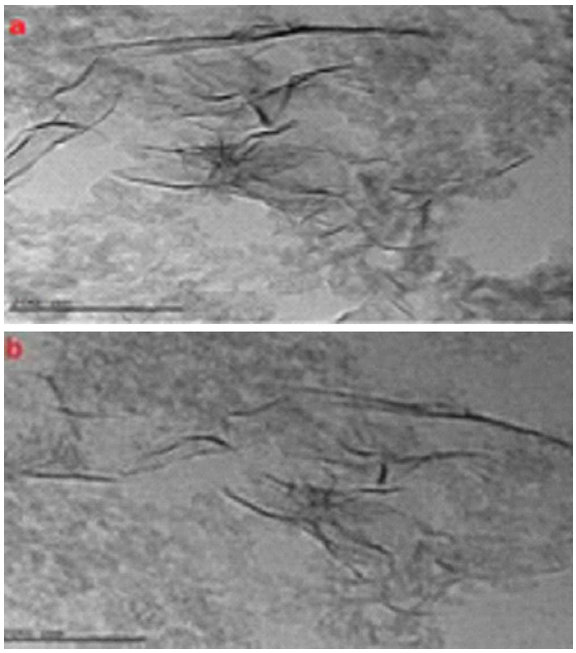

Fig. 5. BF TEM images of the synthesized graphene: (a) 150 A, 10 mm, He, (b) 150 A, 12 mm, He + N_2.

4. Conclusions

Experimental conditions and device parameters (current, electrode size, type of gas used in the reactor) affect the properties of graphene (purity, number of layers, crystallinity) synthesized in the EAD system. In our study, graphene synthesis was performed in different electrode diameters and gas environments in EAD system, designed and manufactured by our project team. The properties of the synthesized graphene were tried to be determined by the Raman spectroscopy, SEM and TEM techniques. According to Raman and TEM analyses, graphene synthesis was successfully achieved by EAD. The 2D peak, which is specific to graphene in the Raman spectrum, was seen at around 2700 cm^{-1}. The commercial graphene was also examined for comparison. The results show that the graphene synthesized by EAD was very similar with commercial graphene in terms of purity and number of layers. The degree of purity of the synthesized samples was increased by increasing both the current and the electrode diameter. The increase in current prevent cathode damage by increasing the electron density of the current in the EAD [19]. The gases introduced into the reactor also affected the purity and the number of layers of the graphene. In EAD, the presence of inert gases promotes the nucleation and growth of carbon nanomaterials by acting as quenchers [17]. The best results in terms of purity and layer number was obtained in He + N_2 environment at 12 mm electrode diameter and 150 A arc current. This result was comparable with the purity and layer number of commercially supplied graphene. High magnification BF TEM images confirmed the wrinkled feature of the synthesized graphene by EAD.

Acknowledgments

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