

RESEARCH PAPER

# Synthesis and Characterization of Nano-Multilayer Graphene Grown by Ambient Pressure of Chemical Vapor Deposition from Naphthalene/Methanol

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## ABSTRACT

Multilayer graphene was synthesized by chemical vapor deposition from mixture of naphthalene/ methanol with ratios (1.5 g: 100 m L) respectively at ambient pressure and nitrogen as carrier gas with two different flow at 700 °C. The active sites for growth was Ferrocene with thickness reach to 125 µm. The product was characterized by Raman spectroscopy, scanning electron microscopy, and Energy Dispersive X-Ray Analysis. The analysis shows that high flow of carrier gas (250 cm<sup>3</sup>/min) was succeeded to produce graphene multilayers while the ether (100 cm<sup>3</sup>/min) witnessed many tubular structure in addition to graphene layers.

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## INTRODUCTION

Despite of appearance carbon nanotubes CNTs and fullerene after 1990s but graphite and graphene did not lost their shining so, they remained occupied huge attention on the world in many fields. Many literatures were [1] reported different techniques for synthesized graphene such physical and chemical exfoliation, oxidation of graphite by different oxidation reagents, physical vapor deposition, laser irradiation [2] and chemical vapor deposition (CVD) [3]. All the methods can produce few-sheets of graphene and graphite when choosing the specific condition

for preparation. Mostly the CVDs represent the best method for synthesized quantitative and qualitative planer and tubular of carbon which represent by carbon nanotubes CNTs and graphene respectively [4]. Ryuichi and Masataka were developed CVDs with plasma to synthesis [5] thin film of graphene at 1300 °C. Duygu et al. [6] was used a combined method of high-energy ball milling and ~0.57 Torr of pressure CVDs to synthesized Graphite-encapsulated Fe nanoparticles from CH<sub>4</sub>/H<sub>2</sub> at 1050 °C.

Aparna et al. [7] were prepared Few layer graphene by combining ball milling with exfoliants

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from low-cost graphite, in an aqueous medium containing a strong exfoliant (1-pyrenecarboxylic acid) and Methanol. Zoran and Silvio [8] design a very low-cost CVDs reactor for synthesized high quality single and multi-layer graphene at less than 1000°C from methanol with foil made of transition metals as catalyst for growth. Zhen et al. [9] succeeded to synthesized centimeter-scale single- to few-layer graphene films by CVD on Ni foils from mixture Methane/H<sub>2</sub>/Ar at 900°C. Cortes et al. [10] used acetylene as carbon source to synthesized Few-layer graphene by CVDs on a CuO deposited by sputtering over SiO<sub>2</sub>/Si substrates without post processing to transfer the CuO onto a dielectric substrate or the use of ultra-high vacuum during synthesis.

May et al. [11] used bi-metallic Co-Ni oxide/Al<sub>2</sub>O<sub>3</sub> substrate in CVDs method to synthesized multilayer graphene at a temperature range of 700-900 °C. Allaedini et al.[12] prepared few-layered graphene using (CVD) method with Ni-Ce-Fe as tri-metallic catalyst by using Carbon dioxide as the carbon source at 800°C. Hyosub et al. [13] synthesized Graphene with 2-3 layers was prepared on 100 μm-thick Fe foil as catalyst at low temperature by CVDs from acetylene as a hydrocarbon source. The studies shows that increase flow rate of acetylene from 5 cm<sup>3</sup> to 25-50 cm<sup>3</sup> and increase the exposure time from 5 min to 15-30 min , causing increase the thickness of graphene layer.

In this work multi-layers of graphene was

synthesized from Naphthalene/methanol mixture as source of carbon in CVDs method at 700 °C and Ferrocene as catalyst on SiO<sub>2</sub> support.

## MATERIALS AND METHODS

### Materials

Naphthalene from Sigma-Aldrich with 99% in purities, solvent Methanol (99.85%) from Hyman, England and Nitrogen gas N<sub>2</sub> as carrier gas with purities 99.999% was purchase from Emirates industrial gases. Ferrocene Fe (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> as catalyst sources was purchased from Sigma and Nitric acid (70%) from Fisher was used for purification.

### Synthesis process

Chemical vapor deposition was applied by mono-stage tube furnace (XIN YOO electronic components co. Ltd.) from Chania equipped with a quartz tube, 1.60 cm in length and 5 cm in diameter. The sources of carbon was solution of Naphthalene/Methanol (1.5g: 100 mL) which evaporated at 90°C. Fig. 1, shows the skim for CVDs system where two types of the graphene multi sheets was synthesized by CVD at ambient pressure. A ferrocene with ≈125 μm thick was used as catalyst over (3×7.2 cm<sup>2</sup>) SiO<sub>2</sub> support. Before the precipitation, the catalyst/substrate was baked on tube furnace at 700 °C in an atmosphere of N<sub>2</sub> (250 cm<sup>3</sup>/min) for 10 min to precipitation Fe on the support. The synthesis was done for 30 min. at 700°C, and 250 cm<sup>3</sup>/min consumption rates of realized N<sub>2</sub> for the first sample which a sign (G-

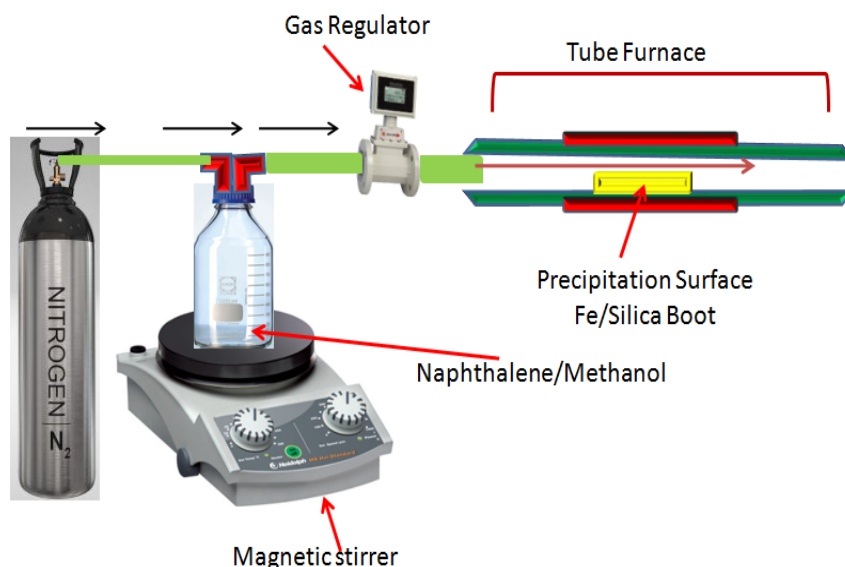


Fig. 1. The Skim of tube furnaces system used in the preparation Graphene by CVDs at 700 °C.

250). The second samples (G-100) was synthesis at the same conditions with reduce the flow rate of  $N_2$  gas to  $100 \text{ cm}^3/\text{min}$ . After deposition the furnace was switched off and allowed to cool at room temperature under a continuous  $N_2$  flow, then the product was purified by reflex with 1 M of HCl for 6 hours at  $80^\circ\text{C}$ .

## RESULTS AND DISCUSSION

The Raman spectroscopy was done by Sentara Infinity Bruker 1, for the range from  $100 \text{ cm}^{-1}$  –  $3500 \text{ cm}^{-1}$ . Scanning electron microscopy SEM, JEOL – JSM-6700F Japan with EDX system were used to shows the nature of surface and morphology with elements analysis for the synthesized materials.

The Graphene or graphite peak created from the first-order scattering process of the double vibration's degenerate phonon of center Brillouin zone which is due to  $sp^2$  bonded carbon, while, the disordered structure of the graphene edges sheets in graphene was represent by D band [14]. Mostly Measurement of  $I_G/I_D$  ratio is a well-known method for characterization the nature structure and disorder [15] for tubular graphene or graphite. The high intensity for 2D for graphite and graphene make it suitable to identify the nature of planer graphene and graphite by measurement the ratios of  $I_{2D}/I_G$  [16]. However the identification parameters between tubular structure and planer structure of  $sp^2$  carbon was the intensity ratios of 2D. The evaluation of the synthesized graphene structure G-250 and G-100 required Raman spectroscopy to probe structural and physical properties of graphitic materials, such disorder, defects, charges, and strain [17]. The Raman

spectroscopy shows the D, G, and 2D bands for G-250 at  $1360 \text{ cm}^{-1}$ ,  $1584 \text{ cm}^{-1}$ , and  $2740 \text{ cm}^{-1}$  respectively, the G-100 were  $1348 \text{ cm}^{-1}$ ,  $1548 \text{ cm}^{-1}$  while 2D band was very week (Fig. 2). Raise 2D for first sample G-250 refer to forming graphene with multi-sheets while reduce or weakness 2D for the second sample indicate to low ratios of graphene sheets [18].

May be the reason behind week intensity for 2D peaks due to interference with D+G peak due to forming tubular structure of graphene with the product as shown in SEMs images.

Fig. 3, and 4 include the SEM images for the two samples, the first, shows 3a and 4a bulk material for synthesized products. Fig. 3b, c and d shows different scale for G-250 which shows many planar fragments without any filaments structures. Fig. 4b, c and d shows many scales for the second sample include the many sheets of graphene with many agglomerate for filament of CNTs which mostly refer to MWCNTs.

The EDXs analysis of the prepared two samples are presented in Fig. 5, Which confirms that carbon is the dominant atomic composition when forming 68.36% and 45.06% for G-250 and G-100 respectively. The two samples contained oxygen with 5.34% and 8.13% respectively, in addition to present Fe, Si, Al, Au, Ca and Mo, which are the elements of the catalyst and support of catalyst. Carbon in the first sample has the highest weight percent compare the ether, and that may be refer to adequate ratios of the flow rate for carrier gas has played an active role in the CVDs system to producing graphene.

The phase diagrams of Fe necessary to predict

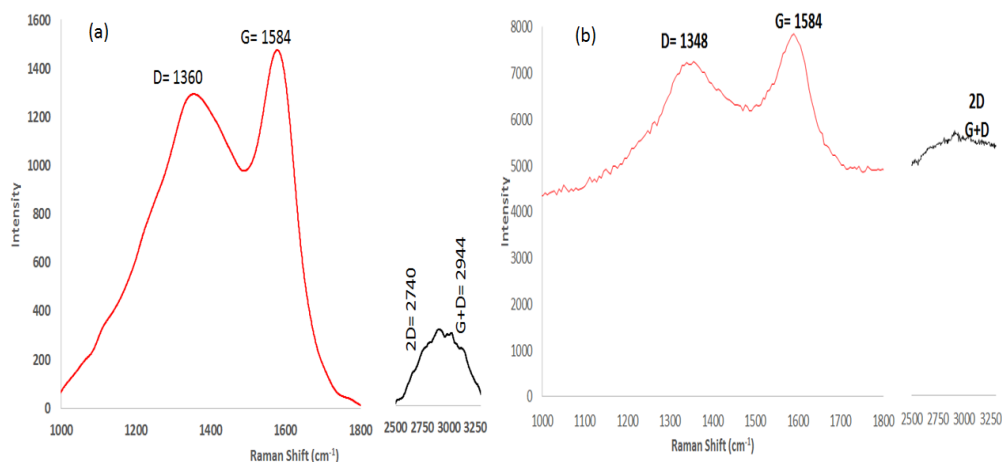


Fig. 2. Raman spectroscopy for (a) G-250, (b) G-100

the mechanism at the temperature of reaction in CVDs. The overall outcome of graphene synthesis, depend on Fe relatively high carbon solubility and that explained by phase diagram. Fig. 6, shows the phase diagram [19] it is notable that the

solubility of carbon can reach a maximum of Fe is estimated to have the carbon solubility of >25 %. The temperature of precipitation in this work, was 700 °C and the carbon solubility decreases to reach less than 1% causing spontaneous carbon

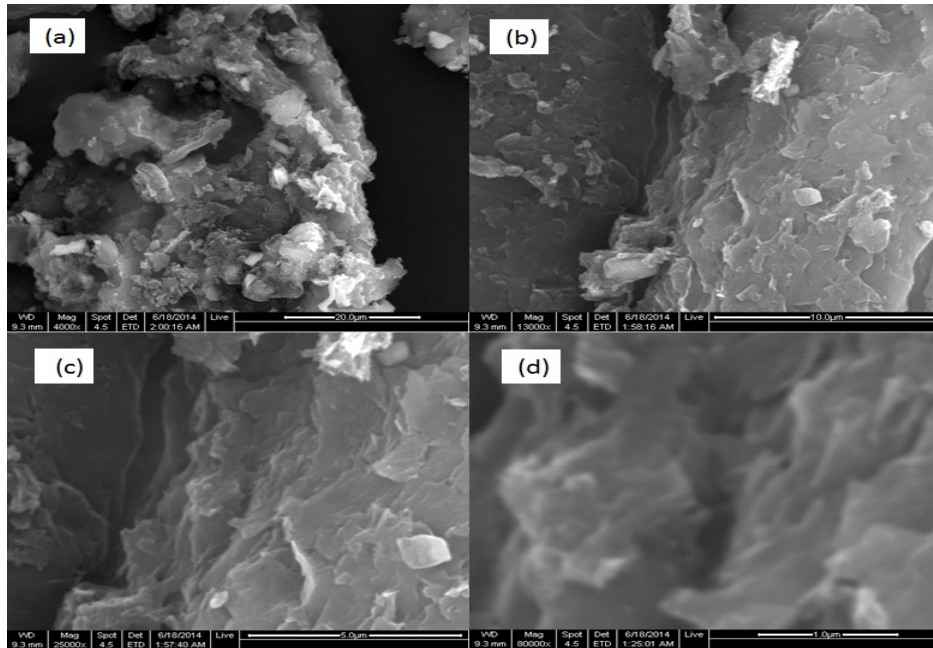


Fig. 3. SEM images for synthesized G-250 at 700 °C.

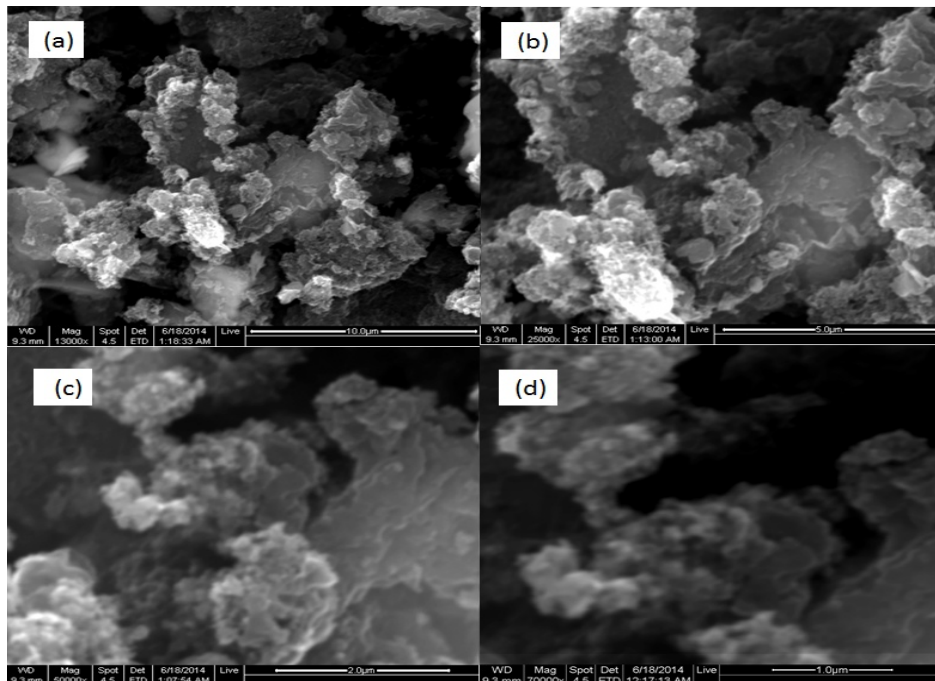


Fig. 4. SEM images for synthesized G-100 at 700 °C.

precipitation to gives graphene during the cooling stage, [20].

Chemical vapor deposition for the formation of graphene on Fe sites include a two-step [22]. The first step is the dilution or incorporation of carbon into the metal (dissolution), then followed by segregation when the graphene was formed after rapid cooling.

The suppose mechanism for graphene formation by the precipitation free radical/segregation process on the support with Fe catalyst was listed in equation 1 to equation 6. The mechanism have been agreement with Blakely's group [23] , when supposed the segregation compositional involves heterogeneity in thermal equilibrium under conditions that correspond to one phase field in the phase diagram [21] whereas precipitation indicates the inhomogeneity due to

the equilibrium phase separation [24]. The process required chemisorbs by the empty d-shell (1) for the hydrocarbon on the metal surface which followed by dissociates (2) through dehydrogenation, and the dissolute carbon (3) atoms will diffuse into the bulk metal. The last steps enhance the diffuse excess carbon to the surface (4), before the last step when (5) the segregation forming graphene which continues to produce graphite (6).

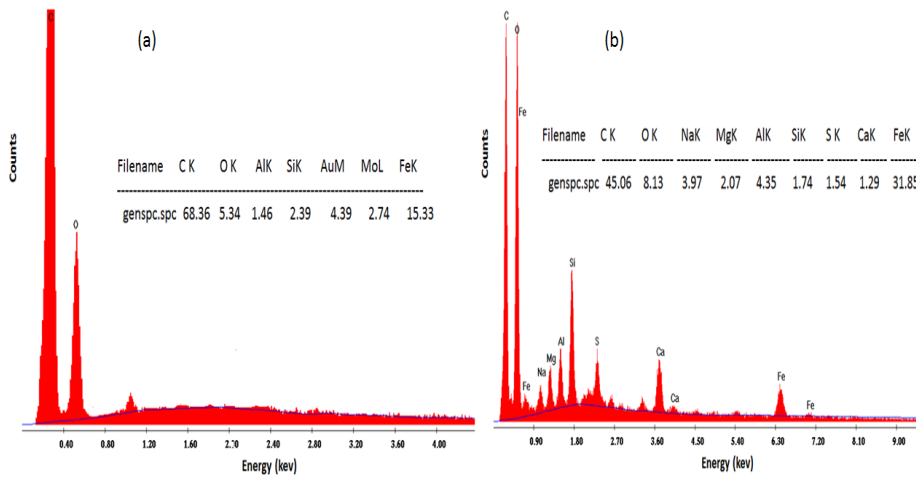
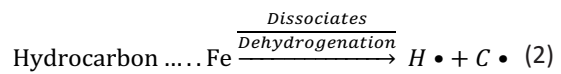
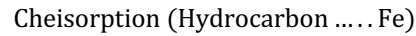
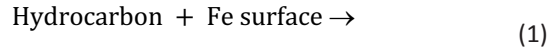


Fig. 5. EDX analysis for synthesized (a) G-250 and (b) G-100.

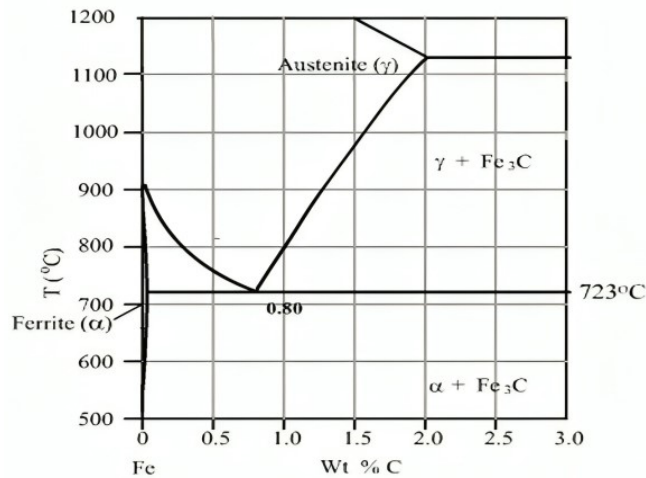
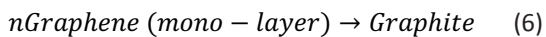
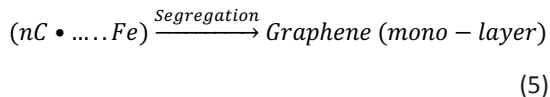
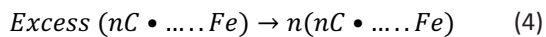


Fig. 6. Phase diagram for the binary system of Fe-C [21].



The chemisorption was active due to the empty d-shell/ an electron acceptor between Fe catalyst and free radicals respectively [25]. The segregation is responsible to make active site for growth by nucleation process which continues until the concentration of free radical in the bulk metal has reduce to reach equilibrium, [25] with nucleation.

The reason behind including G-250 graphene sheets only while G-100 shows a set of tubular structures in addition to graphene with high ratios of impurities can summarized to three reasons: i-From the phase diagram shows that the ability of Fe to saturation with carbon is low thus, the low flow velocity 100 cm<sup>3</sup>/min enabled carbon free radicals to react with Fe. The high flow at 250 cm<sup>3</sup>/min make the precipitation to accrue vastly without reactant with Fe. ii-the suppose mechanism by [26], mentions that graphene can be formed before reaching to Fe/SiO<sub>2</sub> and that kinetically favorite at high flow and that reduce the probabilities to react Fe with graphene. iii-Thermodynamically graphene more stable then CNTs[27] thus, high flow at 250 cm<sup>3</sup>/min make the probabilities for collision free radicals and forming graphene was easier than low rate which prefer to form CNTs.

## CONCLUSION

Graphene multi layers were synthesized at ambient pressure with two different flows of carrier's gas which shows critical parameters and important requirement to decided planer or tubular structure of carbon material. Thus, the functional analysis with spectroscopic images technique showed that catalyst at the conditions of preparation carbon sheets at 700°C unnecessary requirement for the synthesis of graphene. The results showed that flow of carrier gases can play important parameter for built carbon sheets or tubular structure when provided the ideal

condition for diffusion with rearrange the donor with acceptor electrons to forming uniform sheets or multi-form structures.

## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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