

Large area graphene sheets synthesized on a bi-metallic catalyst system

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ABSTRACT

Large area graphene sheets (several micro meters) were synthesized on a bimetallic catalyst system utilizing acetylene as the hydrocarbon source. After a simple purification, graphene sheets were thoroughly characterized by several microscopy techniques. It was observed that as the hydrocarbon rate increased from 4.5 to 8 ml/min, the diameter of the graphene sheets increased from a few hundred nanometers to a few micrometers. Therefore, by varying the hydrocarbon flow rate, we were able to control the size and the layer number of the CVD grown graphene sheets. This is a substrate free synthesis which makes it very attractive and flexible for a scaled up graphene production.

Keywords: large area, graphene, chemical vapor deposition, scale up production, catalyst system.

1 INTRODUCTION

Graphene, a monolayer of graphite, is one of the allotropes of pure carbon [1]. This 2D material has exceptional electrical and mechanical properties making it an excellent candidate for a wide range of applications [2,3,4,5]. Single-wall carbon nanotubes are formed by rolling a graphene sheet into a hollow seamless cylinder. Several groups around the world are utilizing graphene in various areas such as nanoelectronic, solar cell devices, sensor, batteries, and transparent electrodes, just to name a few [6,7,8,9]. Due to its extraordinary properties, graphene has also been incorporated into other materials to create nanocomposites with novel and enhanced properties [10]. Since most of the applications require large area graphene sheets, development of an efficient and large scale synthesis has been explored in the recent years. Current production methods of graphene films include mechanical or thermal exfoliation of graphite, chemical approaches such as chemical vapor deposition and epitaxial growth on various

substrates [11,12,13,14]. Furthermore, large area graphene sheets are synthesized on thin film substrates such as copper or nickel foils, which depending on their size limit the dimensions of the desired product [7,15,16]. Although a lot of research has been conducted, fabrication of large area graphene still remains a challenge [17]. Synthesizing graphene sheets on particular substrates makes it difficult to scale up and might not be very practical for many applications [18]. Another disadvantage of using different type of thin film substrates to synthesize graphene is the difficulty of transferring the as-produced product without any damage, onto other surfaces for characterization or other functions. Chemical vapor deposition (CVD) is a well known technique previously used for carbon nanotube synthesis [19,20]. This is a very attractive method because the reaction parameters can be adjusted in order to control the growth and morphological properties of carbon nanostructures. In addition, this method has the potential to scale up for a large production of carbon materials. Previously we have reported synthesis of graphene nanosheets by utilizing the radio-frequency CVD technique [21]. In this work, we optimized the growth parameters in order to synthesize large area graphene sheets on transition metal nano-particles. Since the graphene sheets are not synthesized on any particular films or substrates, they can be deposited virtually on any surface (with little to no damage) making our method flexible for a wide range of applications. The purified product can be solubilized and deposited on various surfaces by using several methods such as membrane filtration, spin coating, airbrushing etc. [22,23]. In this manuscript we present a practical and scalable substrate free method for production of large area graphene sheets.

2 EXPERIMENTAL DETAILS

The Fe-Co/MgO catalyst system with a stoichiometric composition of 2.5:2.5:95 wt.%, was prepared by the impregnation method [21]. Graphene sheets were

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synthesized via RF-cCVD on the MgO supported Fe-Co bimetallic catalyst system utilizing acetylene as a hydrocarbon source. Approximately 100 mg of the catalyst was uniformly spread into a thin layer on a graphite susceptor and placed in the center of a quartz tube with an inner diameter of 1 inch. The tube was purged with Argon (the carrier gas) for 10 minutes at 150 ml/min. Next, the RF generator was powered on and used for heating the graphite boat to the desired synthesis temperature. Once the temperature reached 1000 °C, acetylene was introduced for 30 minutes. The flow rate of the hydrocarbon was varied between at 4.5-8 ml/min. At the end of the synthesis, the system was cooled down under the presence of Argon for 10 minutes. The as-produced carbon nanostructures were purified in one step by washing with a diluted hydrochloric acid solution under sonication.

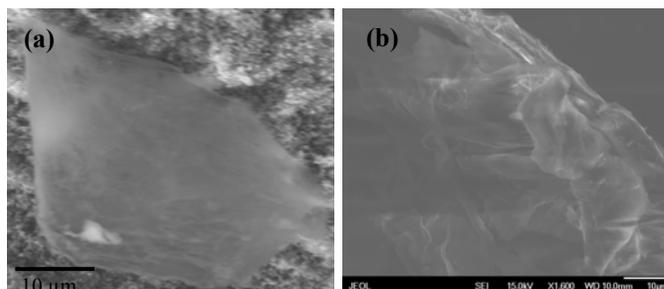
2.1 Characterization Techniques

Transmission Electron Microscopy (TEM) images were collected on a field emission JEM-2100F TEM (JEOL INC.), equipped with a CCD camera. The acceleration voltage was 100 kV for the graphene analysis. The carbon nanostructures were homogeneously dispersed in 2-propanol under ultra-sonication for 30 minutes. Next, a few drops of the suspension were deposited on the TEM grid, dried, and evacuated before analysis. Scanning Electron Microscopy (SEM) images were obtained using a JEOL 7000F high-resolution scanning electron microscope. The final products were mounted on aluminum pins with double-sided carbon tape and their corresponding SEM images were obtained. Scanning Tunneling Microscopy (STM) images were obtained from a homebuilt beetle-style STM with RHK technology SPM1000 controller and XMP software with Axon CV4 current amplifier. STM imaging was performed in dry N₂ at room temperature. A drop of graphene solution (flakes of graphene dispersed in isopropanol) was deposited on an Au/mica substrate and allowed to dry in air. Atomic Force Microscopy (AFM) measurements were performed using a Veeco Dimension 3100 instrument with a scan range of 90 μm for the “x/y” direction and 6 μm for the “z” direction. After the graphene sheets were individually dispersed into 2-propanol solution, a few drops of the final solution were pipetted onto Si substrates. Next, the substrates were air dried and placed directly under the AFM tip for morphology analysis.

3 RESULTS AND DISCUSSIONS

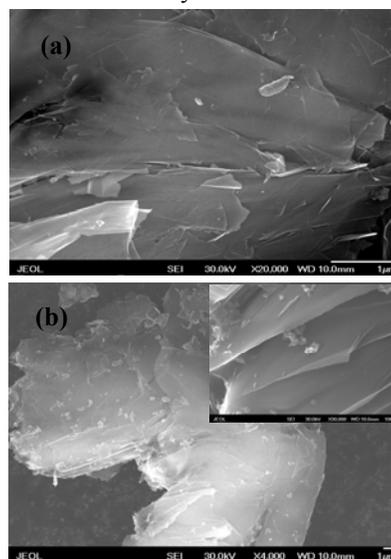
Large area graphene sheets were synthesized via RF-cCVD method, utilizing acetylene as a hydrocarbon source. As the flow rate of acetylene was varied from 4.5 to 6 and 8 ml/min, the size of the graphene sheets increased from a few hundred nm to a few μm. We have previously reported that when the flow rate of acetylene was set at 4.5 ml/min, graphene sheets with diameter of around 100 nm were synthesized [21]. For this work, the flow rate of acetylene

was increased to 6 and 8 ml/min and the as-produced graphene sheets were characterized by several microscopy techniques. Figs. 1(a) and (b) show the SEM images of graphene sheet synthesized on the Fe-Co metal nanoparticles utilizing acetylene at 6 ml/min. The diameter of the graphene sheets varies between 30-50 μm. These semi-transparent sheets demonstrate that few-layer graphene were synthesized at both hydrocarbon rates. EDAX analysis were also performed (not-shown here) to confirm the presence of carbon structures.



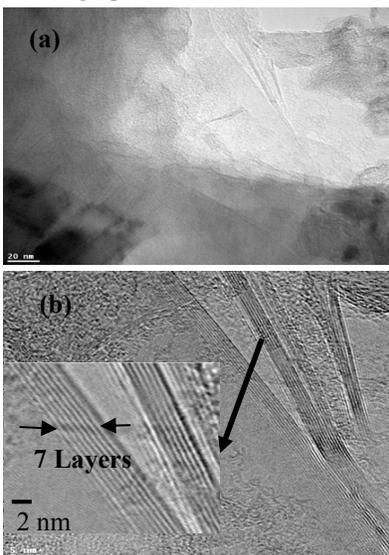
Figures 1(a) and (b): SEM images of graphene sheets synthesized on the bi-metallic catalyst system utilizing acetylene at 6 ml/min.

Similar results were also noticed as the flow rate of acetylene was increased to 8 ml/min. SEM images on Figs. 2 (a) and (b) show that graphene sheets with large diameters were synthesized. In this case there is no significant difference in size when compared to the results obtained from the lower hydrocarbon rate (6 ml/min). The SEM images also revealed that the large scale graphene sheets are very flaky. This could be due to the high rate of hydrocarbon which contributes to synthesis of graphene sheets with non-uniform layers.



Figures 2(a) and (b): SEM images of graphene sheets synthesized on the bi-metallic catalyst system utilizing acetylene at 8 ml/min. The scale for the inset image in (b) is 100 nm.

TEM analyses were performed on the RF-cCVD grown graphene sheets utilizing acetylene at various flow rates. Fig. 3(a) shows the TEM image of the graphene synthesized with acetylene at 6 ml/min. Fig 3 (b) shows a high magnification TEM image indicating the layers of the graphene sheets overlaid on the TEM grid. It was observed that most of the graphene sheets have between 6-8 layers. We are currently working on modifying the synthesis conditions to lower the number of layers and increase the diameter of the graphene sheets.



Figures 3 (a) and (b): TEM image of graphene sheets synthesized utilizing acetylene at 6 ml/min. The inset image in (b) shows a high magnification TEM image indicating the number of graphene layers.

Figs. 4 (a) and (b) present the low and high magnification TEM images of the graphene sheets synthesized with high hydrocarbon flow rate. As seen in Figure 4 (a), the simple acid treatment did not fully remove the metal catalyst particles entirely, which can be possibly explained by the entrapment of these metallic nano-clusters between the graphitic sheets. As a result a more sophisticated purification process needs to be used in order to fully remove the non-graphitic impurities from the samples.

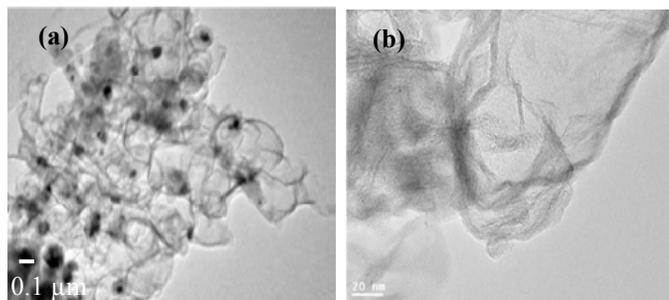


Figure 4 (a): Low magnification TEM image of graphene sheets synthesized utilizing acetylene at 8 ml/min. (b) High magnification TEM image of the CVD grown graphene sheets.

AFM measurements of the graphene sheets synthesized at two different hydrocarbon rates, were performed for thickness analysis (Figs (a)-(f)). It was noticed that as the flow rate of the hydrocarbon increased from 6 to 8 ml/min, so did the number of graphene layers. The graphene sheets synthesized with acetylene at 6 ml/min were found to have between 5 to 7 layers. This is in good agreements with the microscopy measurements shown in Fig. 3. On the other hand, the samples synthesized with the highest flow rate were seen to have a larger number of layers (between 12-21).

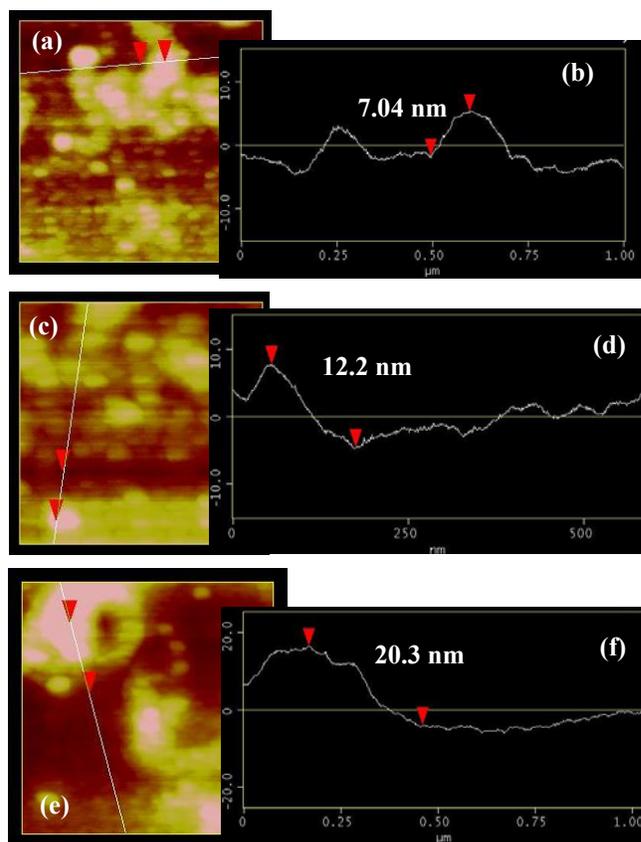
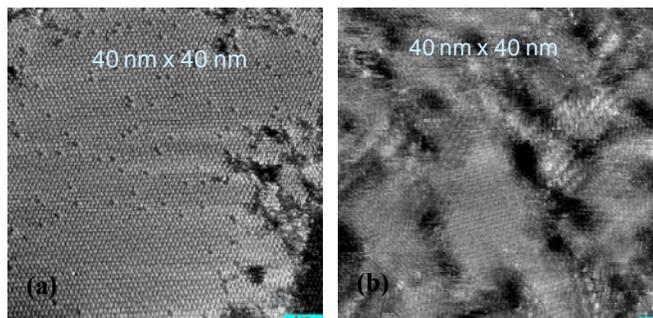


Figure 5(a): 5 $\mu\text{m} \times 5 \mu\text{m}$ AFM scan of graphene sheets overlaid onto a Si surface synthesized with acetylene at 6 ml/min. (b) The corresponding height image indicating the presence of graphene sheets with 5-7 layers. (c) and (e) AFM image scans of the graphene sheets synthesized utilizing acetylene at 8 ml/min. Their corresponding height images are shown in (d) and (f) respectively.

STM imaging was done on graphene flakes collected on atomically flat Au/mica substrates. Figs. 6 (a) and (b) show the STM topographic images of graphene sheets that were synthesized at different hydrocarbon flow rates. In bulk graphite, the carbon atoms on the surface are not equivalent. This results in an asymmetry of the surface atom electronic environment that produces a threefold symmetry pattern. Our FFT analysis is consistent with the threefold symmetry pattern (not shown here). The dark

regions in the image correspond to vacancy islands that are one atomic layer deep pits in the Au{111} surface; a characteristic due to growth conditions [24].



Figures 6 (a) and (b): STM image of the graphene flakes synthesized with acetylene at 6 ml/min and 8 ml/min respectively.

During the CVD process, hydrocarbon decomposes in the presence of a catalyst system and the carbon atoms start rearranging themselves into various carbon nanostructures. Graphene synthesis at high temperatures is not fully understood yet. It is believed that at high temperatures (1000 °C or higher) the catalyst nano-particles start melting, generating a better wetting property which is more suitable for the formation of the graphene structure [25]. Another theory is that magnetic metal atoms aid to the so called “cutting” process of graphene and unzipping CNTs [26]. It was noticed that as the flow rate of the hydrocarbon increased, the diameter as well as the layer number of the graphene sheets increased. This can be explained by the concentration of acetylene on the catalyst nano-particles. Similar phenomenon was also observed by others [16]. A low hydrocarbon flow rate leads to a low carbon accumulation onto the metal nano-particles, synthesizing graphene sheets with small diameters and very few layers.

In conclusions, this is an economical and attractive method which can be scaled up to synthesize large area graphene sheets. By increasing the flow rate of acetylene from 4.5-8 ml/min, the size of the graphene sheets increased from nm to μm range.

4 ACKNOWLEDGMENT

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