Modified Unzipping Technique to Prepare Graphene Nano-Sheets

B H Al-Tamimi1, S B H Farid1 and F A Chyad
Department of Materials Engineering, University of Technology, Baghdad, Iraq

Abstract. Graphene nano-sheets have been prepared via unzipping approach of multiwall carbon nanotubes (MWCNTs). The method includes two chemical-steps, in which a multi-parameter oxidation step is performed to achieve unzipping the carbon nanotubes. Then, a reduction step is carried out to achieve the final graphene nano-sheets. In the oxidation step, the oxidant material was minimized and balanced with longer curing time. This modification is made in order to reduce the oxygen-functional groups at the ends of graphene basal planes, which reduce its electrical conductivity. In addition, a similar adjustment is achieved in the reduction step, i.e. the consumed chemicals is reduced which make the overall process more economic and eco-friendly. The prepared nano-sheets were characterized by atomic force microscopy, scanning electron microscopy, and Raman spectroscopy. The average thickness of the prepared graphene was about 5.23 nm.

1. Introduction
Nanotechnology regarded as a new branch of science which involves study and manipulation the properties of materials at nanoscale. In fact the behavior of a specific material will be changed completely when it becomes at nanoscale. This change in the behavior of materials at nanoscale is rejoiced for the revolutionary changing in the crystal structure and the quantum confinement effects [1,2].

Carbon is an important element in the periodic table which can be exist in many fields, it can found for writing as a graphite and can be use like jewelry as a diamond. In nanoscale, carbon element can be exist in many different forms such as fulluerene, carbon nanotubes (CNTs), nanodiamond (ND), carbon nanoscrolls (CNS), diamond like carbon (DLC) and graphene sheets (GS). All these forms of carbon consisting only carbon element, but they are differ due to the different in the way at which these carbon atoms arrange them self [1,2].

Graphene nano-sheet is a one-atom thick planar sheet of sp2-bonded carbon atoms, which is packed densely in a honeycomb crystal lattice. The graphene lattice posses many fascinating properties including high electron mobility, extraordinary high thermal conductivity, stiffness, and strength. The graphene as a material of high mechanical stress and low density (2.2 gm/cm3), it may be suggested for application in nano-robots, nano-composites and nano-electronics and others [3,4].

Actually it has been understood that the mechanical, thermal, and electronic properties of the graphene are mainly dependent on some factors which are the morphology (shape and size of the planar sheet) and the atomic structure of it as well as the presence or absence of structural defects [5], which in turn depend on the preparation methodology [6,7]. For example the edge of a graphene sheet can be either zigzag-shaped or armchair shaped, or a mixture of both [7]. A zigzag morphology of the graphene is expected to give metallic electrical properties, where a semiconducting or metallic transport is expected with armchair configuration [8].
Essentially, there are two distinctive methodologies that can be employed to produce the graphene. They are bottom-up and the top-down strategies. The first relies on the generation of graphene from suitably designed molecular building blocks undergoing chemical reaction to form covalently linked (2D) networks. The second strategy relies on exfoliation of graphite into graphene [9]. Also it is noticed that the graphene can exist in many forms, it can exist as a sort of sheet, membranes with some noticed ripples, ribbons and scrolls due to the interactions of Van der Waals between adjacent sheets [5,10].

As a result of that the carbon nanotubes (CNTs) is now produced in large scale, its reasonably to start with the carbon nanotubes to produce the graphene. In fact, carbon nanotubes can be regarded as layers of graphene sheets that rolled up into tubes form. Thus, graphene nanoribbons (GNRs) can be produced by unzipping these carbon nanotubes. In fact, longitudinal unzipping or cutting and unraveling of multi-wall carbon nanotubes (MWCNTs) can be achieved via exposing it to a strong oxidizing solutions. After that, the oxidized nano-sheets (graphene oxide) can be reduced directly to obtain graphene nano-sheets [11]. The unzipping process of the carbon nanotubes seems to be similar to that occurs to graphite. Where, a linear or spiral cut takes place throughout the oxidation stage that depends upon the initial site of attack and it was noticed that the presence of inherent defects at the surface of nanotubes regarded as a site for cutting or unzipping initiation [12]. On the other side the aggressive effect of the oxidant materials in the oxidation stage had been reported and studied the harmful effect of the oxygen-functional groups which can take place at the edges of the graphene sheets on the properties of the prepared material [13].

In this work, the graphene is prepared from multiwall carbon nanotubes (MWCNTs) through optimized process parameters that reduced the cost via minimizing the amount of the used chemicals and reduce the effect of the oxidants on the final properties of the produced graphene.

2. Materials and Methods
The starting materials were multiwall carbon nanotubes (95%, Nanoshel LLC. USA.), Sulphuric acid (98%, Himedia, India), Potassium Permanganate (99.5%, BDH, UK), Hydrogen Peroxide (30%, Sigma Aldrich, Germany), Ammonium Hydroxide (33%, Sigma Aldrich, Germany), Hydrazine Monohydrate (80%, Schar Lab, Spain), and Hydrochloric acid (35.4%, Gainland Chemical, UK).

An oxidation stage of the carbon nanotubes was first performed to perform the unzipping process and obtain graphene oxide. 150 mg of multiwall carbon nanotubes was suspended in 150 ml of the concentrated sulphuric acid. The solution was stirred via magnetic stirrer for 15 hr. at room temperature. Then, a 450 mg of the potassium permanganate is added and the stirring was continued for additional 3 hr.

After that, the obtained solution was heated at 60°C for 1 hr by means of a water bath. The stirring is continued in order to encourage the reaction. The temperature of water bath was then raised to 75°C and then the solution was let for 1 hr to stabilize. A dark solution is formed, which was allowed to cool to room temperature.

The prepared solution was mixed with 400 ml of iced water and 5 ml of the hydrogen peroxide. Afterward, the solution was filtered via vacuum filtration through cellulous nitrate paper. The final step of the oxidation stage is washing out the obtained graphene oxide. The obtained solid material was dissolved in 150 ml of deionized water and stirred for 1hr. The solution was again filtered and was dissolved once more in 150 ml of ethanol. A final vacuum filtration was performed.

Next to the oxidation stage, the reduction stage is performed to convert the graphene oxide to graphene. The material was suspended in 150 ml of water. A 100 μl of the concentrated ammonium hydroxide and a 100μml of the hydrazine monohydrate were then added. The solution was heated at 90°C for 2hr in a water bath. The resultant solution was vacuum filtered and let to dry in air.

The prepared graphene was characterized by Atomic force microscopy, Scanning electron microscopy, and Raman spectroscopy.

3. Results and Discussions
‘Figure (1)’ shows 2D and 3D AFM image of the produced graphene nano-sheets. The nano-sheets have ribbons-like appearance due to that they were originated from unzipping of the carbon nanotubes.
Moreover, the morphology reflects the hexagonal character of the graphene lattice. The AFM analysis attached with the figure shows that the minimum thickness was around 1.23 nm, which should correspond to few-graphene sheet. In addition, the maximum thickness of the stacked sheets was 5.23 nm. Figure (1) also reflects regular and uniform microstructure with high surface area at the nanoscale. These characters make this graphene meets the requirement in electronic field and that for the nanocomposites [13].

Figure 1. 2D and 3D AFM image of the prepared graphene nano-sheets.

The result of Raman spectroscopy illustrated in 'figure (2)'. The characteristic graphene Raman peaks are obvious. The intensity ratio (ID/IG) of the two main peaks (G at 1605 cm⁻¹ and D 1360 cm⁻¹) is equal to (1.1). This value of the intensity ration indicates that the carbon atoms is nearly all sp² hybridization and is graphitic with some non-crystalline feature [13], which supports the low thickness observed with the AFM. The figure shows high intensity of the G band, which is another indication of the small thickness of the prepared graphene.

SEM images of the prepared graphene in two different scales are shown in 'figure (3)'. The figure shows that the prepared graphene sheets assemble thin wrinkled paper-like structure. The SEM images are thus conforms the AFM and Raman results. Besides, the SEM images show a dominant character of the microstructure that reflects the stacking of graphene sheets is substantially disordered and the graphene sheets are agglomerated and overlapped.
Figure 2. Raman spectrum of the prepared graphene nanoribbons.

Figure 3. SEM image of the prepared graphene.

4. Conclusions
A modified unzipping technique is used to obtain graphene nano-sheets from MWCNTs. In this work, the used materials for the both the oxidation stage and the reduction stage were reduced. Consequently, the harmful effect of the aggressive chemical is minimized and the overall cost of the process is reduced. The
produced graphene characterized by its high quality and small thickness that make it is suitable for several applications.

6. Acknowledgements
The authors thank the stuff of laboratories in Department of Materials Engineering and the Center of Nanotechnology and Advanced Materials in the University of Technology for the help in the experimental activity.

References
[1] Arshad H W and Imran W K, 2016, Synthesis of Graphene Nano Sheets by the Rapid Reduction of Electrochemically Exfoliated Graphene Oxide Induced by Microwaves, J. Chem. Soc. Pak, 38, No. 01, pp. (11-16).

[2] Balamurugan T, Chellakannu R, Shen-Ming C, Selvakumar P, 2017, One-Pot Green Synthesis Of Graphene Nanosheets Encapsulated Gold Nanoparticles for Sensitive and Selective Detection of Dopamine, Scientific Reports, 7.

[3] Stephen W, Ricardo M, John K.G and Claudia C, 2010, Production Of Graphene From Graphite Oxide Using Urea As Expansion-Reduction Agent, Elsevier, Carbon, 48, pp. (3463-3470).

[4] M. Gautami, A. H. Jayatissa, and G. U. Sumanasekera, 2010, Synthesis And Characterization Of Transferable Graphene by CVD Method, IEEE Nanotechnology Materials and Devices Conference, USA.

[5] Sergey M, 2011, Physics And Application Of Graphene – Experiments, Published by Intech, India.

[6] Long Z., Jiajie L, Yi H, Yanfeng M, Yan W and Yongsheng C, 2009, Size-Controlled Synthesis Of Graphene Oxide Sheets On a Large Scale Using Chemical Exfoliation, Elsevier, Carbon, 47, pp. (3365-3380).

[7] Van N D and Thanh H P, 2010, Graphene and Its One-Dimensional Patterns: From Basic Properties Towards Applications, Advances In Natural Science: Nanoscience And Nanotechnology, 1, pp. (1-14).

[8] Jessica C D, Jose M R H, Xiaoting J and David A C, 2008, Bulk Production Of a New Form Of sp2 Carbon: Crystalline Graphene Nanoribbons, Nano Letters, 8, No. 9, pp. (2773-2778).

[9] Raghu M, 2012, Graphene Nanoelectronics- From Materials to Circutes, Published by Springer.

[10] Fang L and Yong Z, 2010, Substrate-Free Synthesis of Large Area, Continuous Multi-Layer Graphene Film, Elsevier, Carbon, 48, pp. (2394-2400).

[11] Biwei X, Xifei L, Xia L, Biqiong W, Craig L, Ruying L and Xueliang S, 2014, Graphene Nanoribbons Derived From the Unzipping Of Carbon Nanotubes: Controlled Synthesis and Superior Lithium Storage Performance, The Journal of Physical Chemistry, 118, No. 2, pp. (881-890).

[12] Dmitry V K, Amanda L H, Alexander S, Jay R. L, Ayrat D. B. Katherine P and James M T, 2009, Longitudinal Unzipping Of Carbon Nanotubes to Form Graphene Nanoribbons, Nature Letters, 458, pp. (872-876).

[13] Dhanraj B. S, Joyashish D, Ajay K, Mohammed A and Vijayaamohanan K P, 2011, Electrochemical Unzipping Of Multi-Walled Carbon Nanotubes for Facial Synthesis of High-Quality Graphene Nanoribbons, J. A. C. S. Journal of American Chemical Society, 133, pp. (4168-4171).