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Preparation of Graphene via Electrochemical Exfoliation Method for Environment Applications

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ABSTRACT

In this research, electrochemical exfoliation process of the graphite as electrode immersed in a sulfuric acid, nitric acid and water ($H_2SO_4/HNO_3/H_2O$) was used to produce high-quality graphene. The structural and chemical properties, of the prepared graphene were studied. XRD shows that the structure of graphene is polycrystalline with preferential orientation in the (002) and (004) direction. Raman spectra showed two intensive peaks I_G and I_{2D} corresponding to 730.01 and 628.04. Fourier transform infrared spectroscopy(FT-IR) spectrum showed the stretching vibration of C=C aromatic ring 1649.19 cm^{-1} and the stretching vibration from C-H 1456.30 cm^{-1} bend. Also the oxygen-containing functional groups have been appeared like O-H, C=O and C-O. After preparation of graphene and characterization, environmental testing was conducted to purify the mixture consisting of water and oil. Naked eye noted that the water has been purified from oils, and also water samples have been tested using optical microscopy.

INTRODUCTION

Graphene is a two-dimensional substance made out of hexagonal structure like honeycomb,has attracted great interest.This material has different new properties of interest such as superior electrical conductivity (10^6 Ω^{-1} cm^{-1}), almost transparent in visible light [1],high intrinsic carrier mobility ($2.5\times10^5 cm^2$ V^{-1} s^{-1}) [2],specific surface areahigh (2630 m^2g^{-1})[3], strength of mechanical excellent (Young's modulus > 1 TPa) [4], and thermal conductivity high (up 3000 W m^{-1} K^{-1})[5]. These characteristics make graphene as one of the most promising future materials that have the potential possibility of applications in photonics, electronics and many other areas [6].In the field of organic electronics, the greatest challenge is to develop an electrode that should be very flexible and transparent besides being very strong[7].Graphene research has expanded quickly since this material was isolated for the first time in the year 2004.The research was informed by theoretical descriptions of graphene's composition structure and characteristics [8]. Proven high-quality graphene can also be surprisingly easy to isolate, making more research possible. Andre Geim and Konstantin Novoselov won at University of Manchester Nobel Prize in Physics in 2010 to conduct pioneering experiments in respect of graphene two-dimensional material [9].Electrochemical synthesis is also cheaper and greener method is likely to be able to produce large amounts of the few layer graphene (FLG). Using electrochemical method of Liu *et al.* few layer graphene peeled from graphite in the anode in ionic liquids [10]. Lately, it has developed a new process one-step for the synthesis of high-quality few layer graphene. This method is reported for the first time by Ching-Yuan Su.*et al.* in 2011 [11]. The allotropes of carbon known are Graphite,

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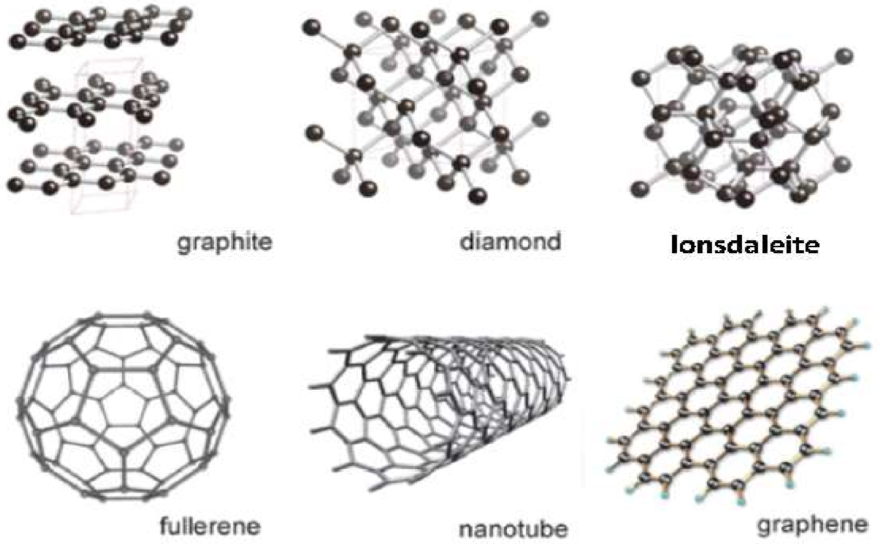
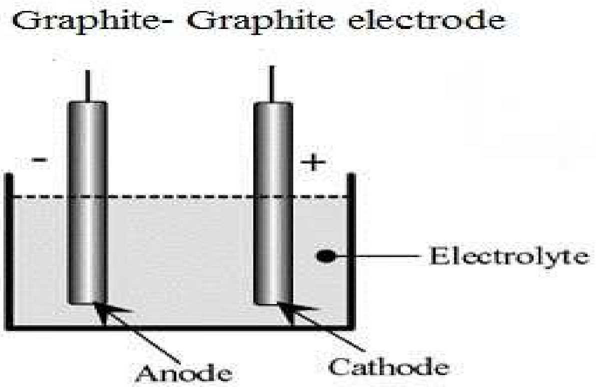
Diamond, Lonsdaleite, Fullerenes, Nanotubes and Graphene. Fig. 1 shows crystallographic structures of these allotropes.



Figure(1)the common naturally-occurring sp^2 and sp^3 allotropes of carbon occur indifferent crystallographic forms. Graphite: Hexagonal; stacked flat layers of 3-coordinated sp^2 C. Diamond: Cubic; framework of 4-coordinated sp^3 C. Lonsdaleite: Hexagonal; framework of 4-coordinated sp^3 C. Fullerenes: Closed cage molecules sp^2 C: C_{60}, C_{70}, C_{76}, *etc.* Nanotubes cylindrical fibers of sp^2 C, single tubes or nested. Graphene: one-atom-thick graphitic layers with sp^2 bonding[12].

Experimental work

The Electrochemical cells consisting of two electrodes: an anode (the electrode occurs oxidation reaction) and a cathode (the electrode occurs reduction reaction). The concentrated HNO_3 /H_2SO_4 in 1:3 volume ratio was used to prepare graphene , so solution (0.69 gm of H_2SO_4 and 0.19 gm of HNO_3) to make its pH value around 3 using graphite as anode and cathode. We performed electrochemical exfoliation of the graphite in the H_2SO_4 and HNO_3 to obtain high quality of the graphene, as shownin fig. 2 the experimental setup.The bias of 1 Volt was first applied of the graphite electrode for 5 minute, then by increasing the bias to 10 Volt for other 5 minute. The elementary low bias helps to moistening the sample, before implementation a high bias of 10 Volt, graphite still yet as a one piece. Once has been applied the high bias to the graphite, was quickly separated into small pieces and spread in the solution surface. The graphite works as the electrode and source of the graphene for exfoliation electrochemical. The process of electrochemical exfoliation was conducted by applying constant current (DC) bias on the graphite electrode. Noted that 10 volt activated to the exfoliation and oxidized graphene. Remove undesirable of large graphite particles produced in the process, the solution is left for 3 or 4h to take it enough time to drop down to bottom, and it can then be used for more characterization and film preparation. Occur of all these experiments electrochemical exfoliation at room temperature. The application of high voltages on the anode resulted in the slow exfoliation of graphite through edges. During the exfoliation there are two types of graphitic flakes formed; one gets regimented at the bottom which consists of thick graphitic pieces. The second type of graphitic sample floats on the surface of electrolyte. These flakes are nearly transparent and have been found to consist of few layer graphene (FLG).



Figure(2): the experimental setup.

In the environment test, the system consists of two filters. The filter is a capsule was filled with powder: The first consist of graphene powder and the second consist of carbon powder. The mixture was prepared by added 100 ml of distilled water and 50 ml of oil, with mixing for the homogeneity of the mixture at room temperature. The mixture passed through the two filters, the first filter consists of graphene powder and the second filter consist carbon powder. Containers have been placed at the end of the two filters, the two containers containing of water samples refinery.

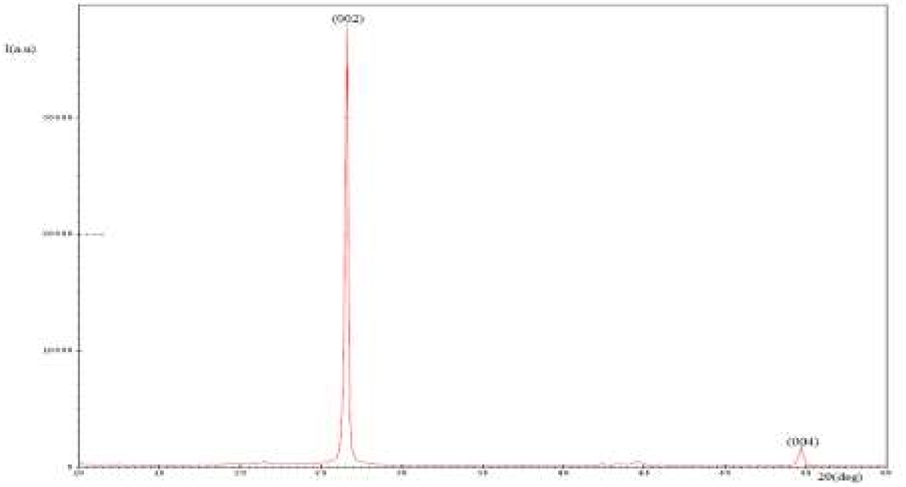
Material characterization

Structural properties of graphene, XRD measurement has been done according to the Joint Committee on Powder Diffraction Standards (JCPDS) card, using Shimadzu XRD-7000 X-ray diffractometer using CuKα (λ =1.54050 A^o) irradiation operated at 40 kV and 30 mA. The Raman spectra of the graphene with Sentera Raman microscope Bruker co., Germany with a green laser at an excitation wavelength of 532 nm.FT-IR spectral analysis was performed to confirm the chemical structure of graphene (8400S, Shimadzu),FT-IR spectrum software was used to generate a plot of transmission (%) vs. wave number (cm^{-1}) in the range of about 400 to 4000 cm^{-1} for graphene.

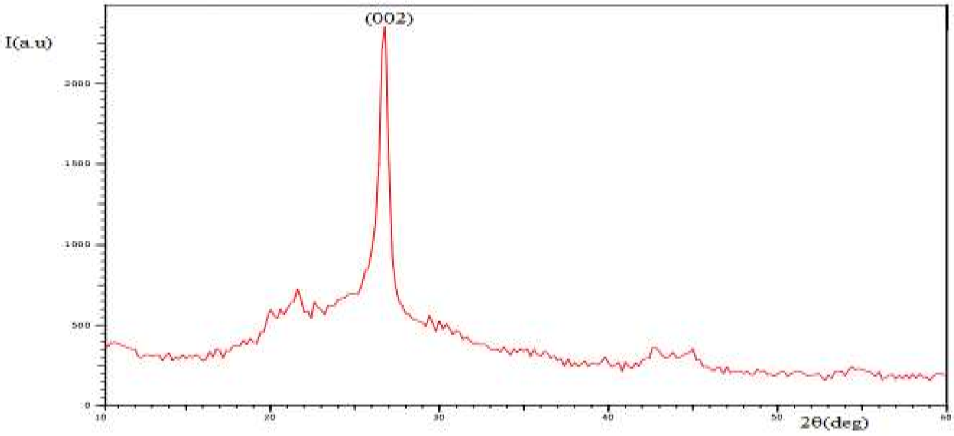
Results and Discussion

The X-Ray diffraction (XRD) is employed for the identification and understanding the crystalline growth nature of grapheme prepared by the electrochemical exfoliation method. In Fig. 3, shows the natural graphite (graphite electrodes), the graphite has a powerful and sharp peak at 26.6^o of 2θ corresponding to the highly organized layer structure with an interlayer distance of 0.33 nm along the (002) orientation, also has diffraction peak at 54.6^o of 2θ corresponding to the structure of layer with interlayer distance of 0.16 nm along the (004) orientation. The diffraction pattern of graphite electrode shows two different located peaks (002) and (004) at (2Ө= 26.6066^o and 54.6870^o), respectively. Using data from X-ray diffraction (XRD), and fig. 3 and fig. 4 of the X-ray shows the patterns of XRD for grapheneand was seen clearly (002) peaks, which have been mapped also to the distance layer to layer (d-spacing = λ / 2 sin θ).

The diffraction pattern of graphene as prepared shows different located peaks (002) at (2Ө= 26.7192^o), see fig. 4. The X-ray diffraction patterns of graphene show high diffraction peaks showing good crystallinity. The diffraction peaks agree with those given in JCPDS data card of graphite (002) and (004) plane. X-Ray diffraction (XRD) was used to verify these steps during the reaction and also to investigate if any other defects would be introduced to the lattice during this process.

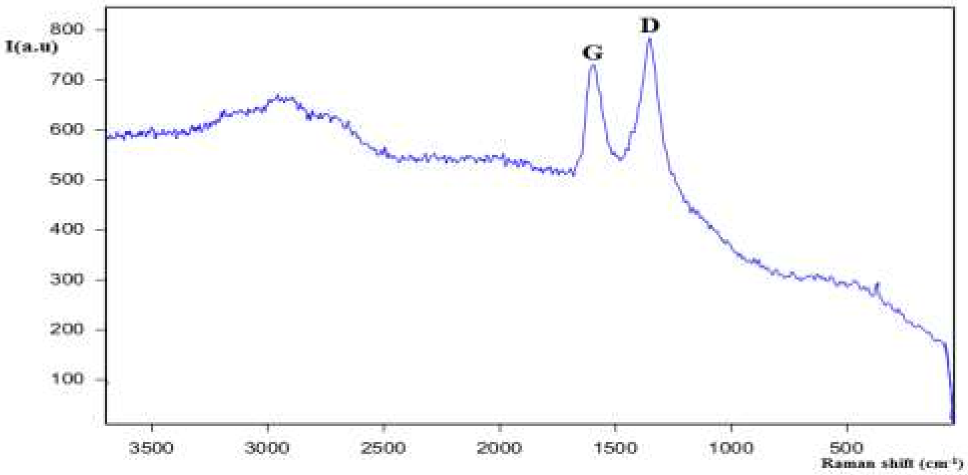


Figure(3): XRD pattern of the electrode graphite.



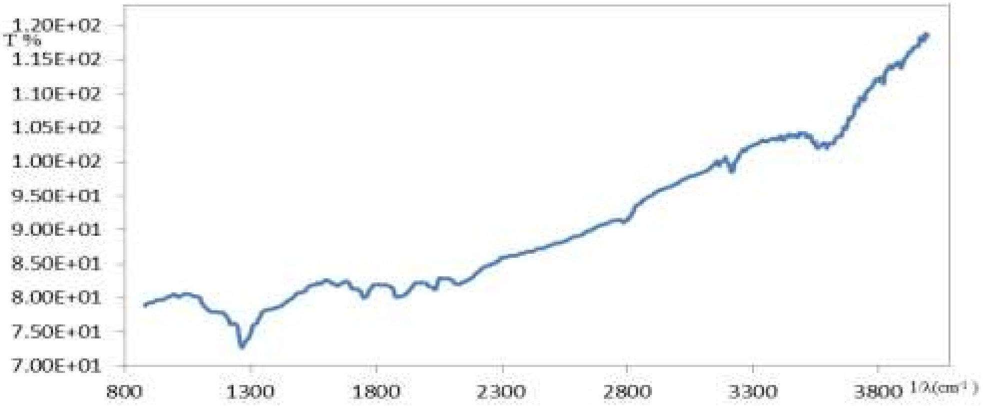
Figure(4): XRD pattern of the graphene.

Raman Spectroscopy an excellent instrument for the detection of the monolayers, it also provides some useful information about the change in the structure of graphene flake due tothe change in defect density. In Raman spectroscopy, D band indicated the extent of defects while G band refers to the nature of the graphitic. The characteristic peaks of graphene, as shown in fig. 5 are identified for graphene namely D-band at 1350 cm^{-1} and G-band at 1593 cm^{-1}. In fig. 5 show, band D at approximately 1350 cm^{-1}, caused by, attributable to structural defects. Band G, at approximately 1593 cm^{-1}, and is usually observed for all graphitic structures can be attributed to the development of vibrational E_{2g} exist in SP^2 bonded graphitic carbon. Showed I_D/I_G peak height ratio of ~1% confirming high crystallinity. In graphene see the ratio of I_{2D}/I_G is 0.860, so they graphene product is the Multi-layer graphene.



Figure(5): Raman spectrum of graphene.

Fourier transform infrared spectroscopy (FT-IR) a powerful instrument to determine molecular mechanism associated with the formation of oxide. FT-IR spectral analysis was performed to confirm the chemical structure of graphene.In fig. 6 the peak of the graphene shows that O-H stretching vibrations spotted at 3475.84 cm^{-1} was dramatically lowered because deoxygenation. Stretching vibrations from C=O at 1714.77 cm^{-1} were still showed because the mechanism of exfoliation fundamentally due to the expansibility of CO_2 evolved into gaps between graphene sheets during fast heating, and C-O stretching vibrations at 1093.67 cm^{1} due to clearer and which were caused by remaining carboxyl groups .



Figure(6): FT-IR transmittance spectrum of graphene as a function to wave number.

Environmental testing was conducted, using material produced "graphene" as filters to purify the contaminated water, "oils" and this test showed the contaminated water was purified.When considering the naked eye note that the water has been purified, purification of oils, and also has been testing purified water samples with optical microscopy. When examining samples under the microscope, we note that the water samples free of oil.

CONCLUSIONS

In this article, electrochemical methods produce high-quality graphene by process of exfoliation electrochemical of the graphite. X-Ray Diffraction was used to determine the structural properties of the graphene, for graphene the sharp peak at 2θ =26.7192° indicates a highly organized crystal structure with an interlayer spacing of 0.333374 nm , which is consistent with the layer spacing of normal graphite. Raman spectroscopy, noted that the intensity ratio of I_D to I_G band can be used as an indication of defects quantity. The intensity ratio, I_D/I_G and I_{2D}/I_G values for the graphene were calculated as 1.0739and 0.860respectively. The I_{2D}/I_G ratio of graphene sample demonstrated is the multi-layer graphene. FT-IR spectra exhibit the presence of the graphene were calculated as O-H (hydrogen functional group,C=O (carbonyl functional group), C-O (alkoxy functional group).

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