Structural and the Optical Properties of Graphene Prepared by Electrochemical Exfoliation Technique

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Abstract

In this research, graphene suspension was prepared by electrochemical exfoliation of graphite electrodes immersed in aqueous solution which contains sulfuric acid, nitric acid and distilled water ($H_2SO_4/HNO_3/H_2O$). DC biases of 10 V have been applied and the graphene foam was deposited on glass slide. The structural and optical properties of graphene was characterized via X-ray diffraction (XRD), scanning electron microscope (SEM), energy dispersive spectroscopy (EDS), optical microscopy (OP) and Uv-Vis spectroscopy respectively. The XRD pattern shows crystalline structure of graphene with sharp peak at 26.59^o corresponds to an interlayer distance of 0.334 nm of (002) orientation which matching with the interlayer distance of normal graphite. The SEM of graphene was showed that thin layered graphene structures with wrinkled shapes. The compositions of graphene consist of carbon and oxygen with atomic percentages 82.75% and 12.01%, respectively. The absorbance spectra using UV-VIS was exibited the graphene suspension and graphene film have two transitions included π-π^* and n- π^* respectively.

Keywords: Graphene, electrochemical exfoliation, aqueous solution, graphite electrode.

1. Introduction

Graphene is a single atom-thick plane of carbon atoms arranged in a honeycomb lattice, is the conceptual building block for many carbon allotropes, from three dimensional graphite (a stack of graphene sheets), to one-dimensional carbon nanotubes (seamless graphene cylinders), to zero-dimensional buckyballs (closed graphitic cages)[1]. Graphene is a wonder material with many superlatives to its name. It is the thinnest material in the universe and the strongest ever measured. Its charge carriers exhibit giant intrinsic mobility, have the smallest effective mass (it is zero) and can travel micrometer-long distances without scattering at room temperature. Graphene can sustain current densities 6 orders higher than copper, shows record thermal conductivity and stiffness [2]. In recent years, graphene has been produced by many kinds of physical and chemical methods. Among them, graphene derived from chemical oxidation-reduction method exhibits extensive defects, while graphene prepared by CVD, liquid phase production, and mechanical cleavage of graphite presents no defects [3]. The electrochemical method has the advantages of being single-step, easy to operate, environmentally friendly (if using ionic liquid electrolytes or aqueous surfactants) and operates at ambient conditions. Highly controllable flakes can be formed without the need for volatile solvents or reducing agents. Recently, electrochemical methods have been used by a number of research groups to produce graphene in milligram and gram quantities[4] such as ***Prashant Tripathi et al***. prepared high-quality graphene by exfoliation of graphite electrode in alkaline solution as electrolyte[5], ***Ching-Yuan Su et al***. synthesized high-quality thin graphene films by exfoliation of graphite in many different electrolytes including (HBr, HCl, HNO_3, and H_2SO_4)[6] also ***Khaled Parvez et al.*** prepared of graphene via exfoliation of graphite flakes in aqueous solutions ($(NH_4)_2SO_4$, H_2O)[7]. The aims of this research are preparing of graphene suspension and depositing on glass slide to study optical and structural properties.

2. Experimental work

In this work, graphite rods were used as electrodes (i.e. anode and cathode) with dimensions (3 cm x 3.16 mm) and weight of 0.47 gm before exfoliation as shown in Fig.(2a). In addition, the separation distance between graphite electrodes was fixed to be

4 cm, these electrodes were immersed in aqueous electrolyte consist of sulfuric acid H_2SO_4 (0.69 gm) and nitric acid HNO_3 (0.19 gm) of 1:3 volume ratio added to 1000 ml of de-ionized water to make pH solution value around 3, at room temperature. The process of electrochemical exfoliation was conducted by applying constant current (DC) bias on the graphite electrode, 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. When applying the high bias to the graphite, it will quickly separate into small pieces and spread in solution surface as shown in Fig.(2c). During the exfoliation there are two types of graphitic flakes formed; one gets sediment 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). After preparation of graphene, the glass slide was washed with distilled water to remove any oil or dust that might be on the substrate surface and then placed in a clean beaker containing HCL acid for 5 min; finally it is put in ultrasonic bath with distilled water for 10 min then dry. A pipette was used to deposit the graphene foam Fig.(2d) on the glass surface. Afterwards, sonication of the glass slide by ultrasonic cleaner with power 50 watt to insure that the film homogenous and smooth. Finally, the graphene film was heated at 200°C for 120 minutes under vacuum.

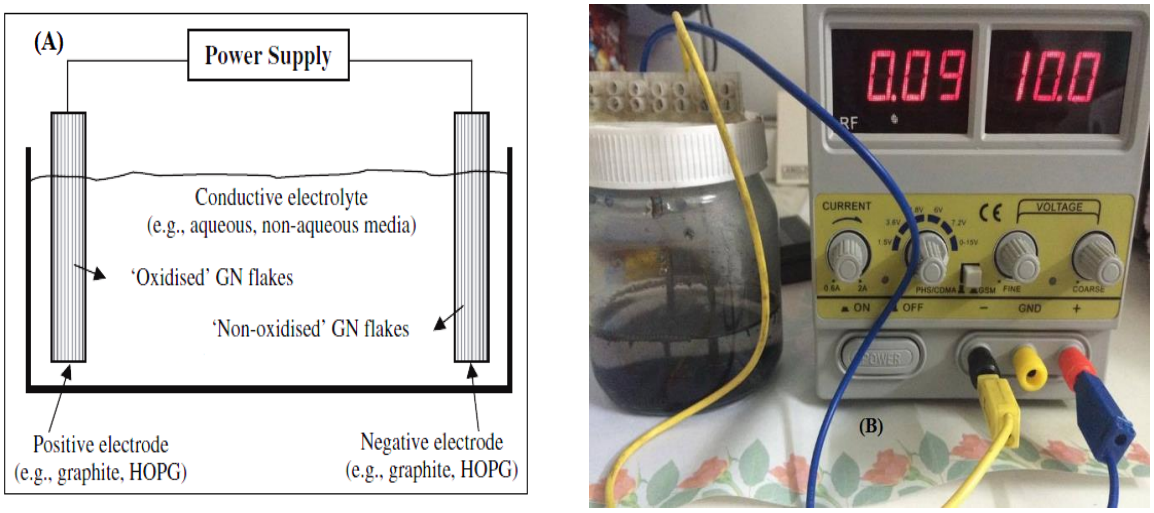

Fig.(1): a) Schematic illustration of electrochemical exfoliation process. b) expermiental setup of this work.

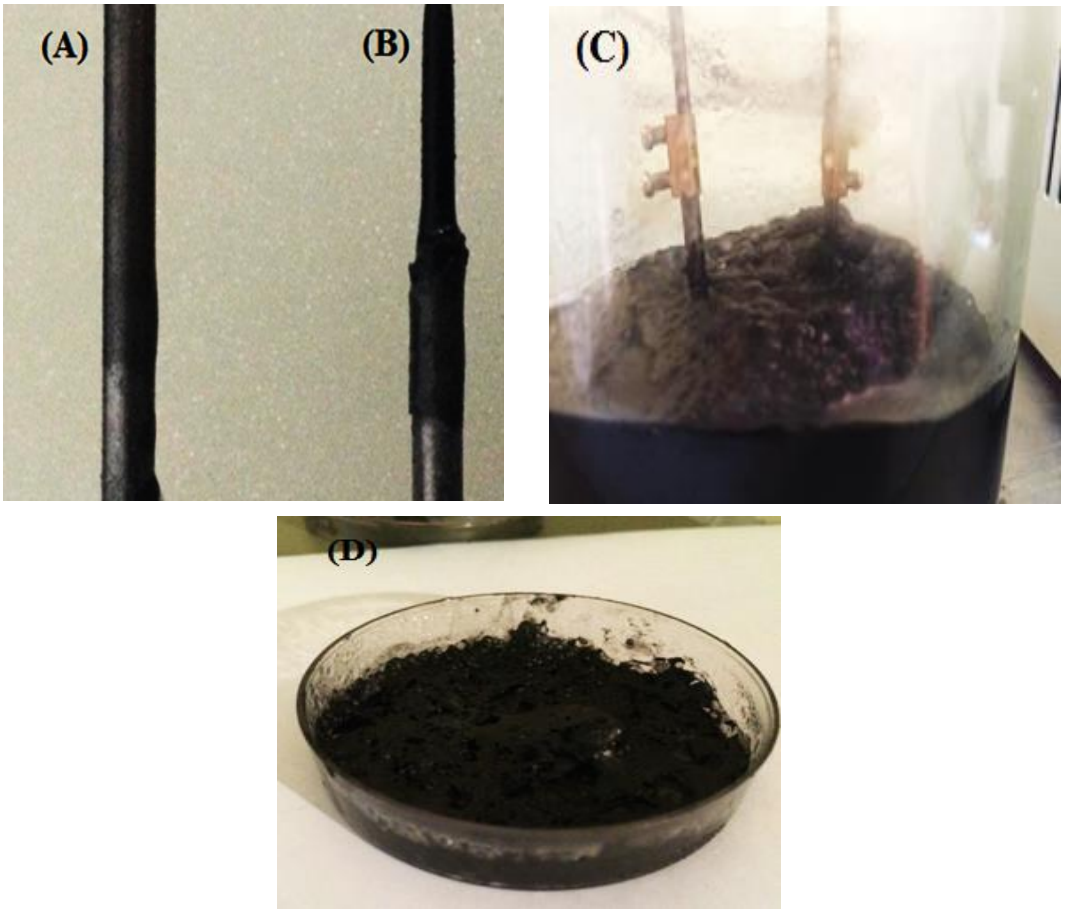

Fig.(2): Graphite electrodes a) before exfoliation and b) after exfoliation. c) the dispersed graphene sheets in aqueous solution after applying +10 V for 50 min. d) foam of graphene.

3. Material characterization

Structural properties were measured by X-ray Diffraction (XRD) according to the Joint Committee on Powder Diffraction Standards (JCPDS) card, using Shimadzu XRD-7000 X-ray diffractometer using CuKα (λ =1.54050A^o) irradiation operated at 40 kV and 30 mA. In addition, scanning electron microscopy (SEM) (model the VEGA Easy Probe) and Energy-dispersive x-ray spectroscopy (EDS) was used for the quantitative elemental analysis of the chemical characterization of graphene (Inspect S; produced by FEI Company, Eindhoven, The Netherlands). The transmittance optical microcopy (model olympus bx 60) was used to known the topography and structural information at 1000x. Optical properties measured by UV-V is single beam spectrophotometer (model Lambda 750, Perkin Elmer) was used to record the optical spectrum of the graphene film within the wavelength ranging from 200 nm to 400 nm.

4. Results and Discussion

4.1 X-ray Diffraction

Fig.(3) shows the natural graphite (graphite electrodes) before exfoliation process, which is polycrystalline in nature and has a intense and sharp peak at 2θ equal to 26.6^o corresponding to an interlayer distance of 0.334 nm along the (002) orientation calculated using Bragg's law as in :

$$2d\ sin\theta = n\ \lambda \quad \text{.....(1)(Bragg's law)}$$

here λ is the wavelength of X-ray is beam (0.154606 nm), θ is the scattering angle, n is order of diffraction peak, d is interplane distance.

This is consistent with the layer spacing of normal graphite according to JCPDS standard card (230064), which has interlayer distance equal to 0.335 nm. Also has diffraction peak at 2θ of 54.6^o corresponding to the interlayer distance of 0.16 nm along the (004) orientation.

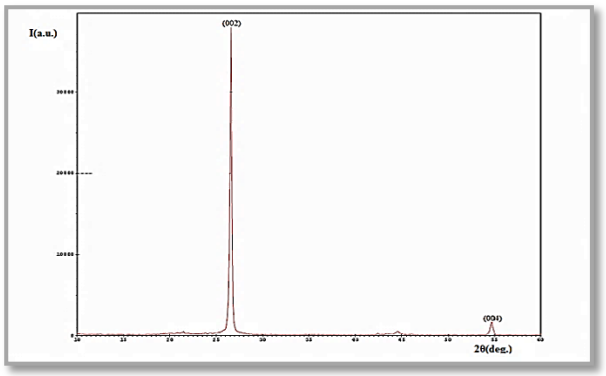

Fig.(3) : XRD pattern of the graphite electrode.

Fig.(4) show the XRD results of graphene film deposited on glass slide, the XRD pattern exhibited a sharp diffraction peak at 2θ=26.59 degree, corresponds to an interlayer distance of 0.334 nm for (002) orientation estimated by Eq1. which is consistent with the layer spacing of JCPDS card (230064), which has interlayer distance equal to 0.335 nm. While the orientation of (004) was vanished due to annealing process make the structure of graphene more crystalinity toward single crystalline. The crystallite size of graphene film has been measured by applying Scherrer's eq. as shown below [8]:

$$L = \frac{k\lambda}{B\cos\theta} \quad \text{.....(2) (Scherrer Eq.)}$$

where L is crystallite size (nm) equal to 15.34 nm, B is FWHM and k is a constant (k=0.89). Also from XRD pattern there are two small peaks at 2θ=19.6 and 2θ = 21.95 corresponding to the d-spacing of 0.45 nm and 0.4 nm respectively along the (002) orientation. The slightly lower 2θ angle of graphene with large d-spacing compared to graphite suggests that, graphene contains only a small amount of functional groups.

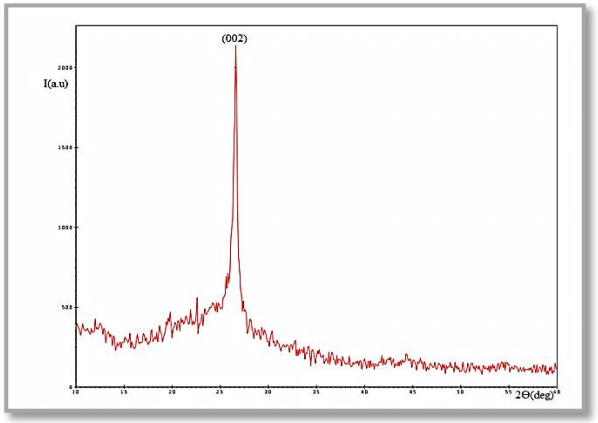

Fig.(4): XRD pattern of the graphene film.

4.2 Scanning Electron Microscopy (SEM)

The surface of the graphene film was analyzed with SEM, and the image is represented in Fig.(5) at scale bars =5µm. The SEM image of graphene shows a typical worm-like shape with thin layered graphene structures. The stacked graphene laminates appear wrinkled, which is something typical of graphene sheets as confirmed in the literature [4]. Revealing a crumpled and rippled structure which was the result of deformation upon the exfoliation and restacking processes. Corrugation and scrolling suggested the intrinsic nature of graphene, because the 2D membrane structure would be thermodynamically stable via blending [9].

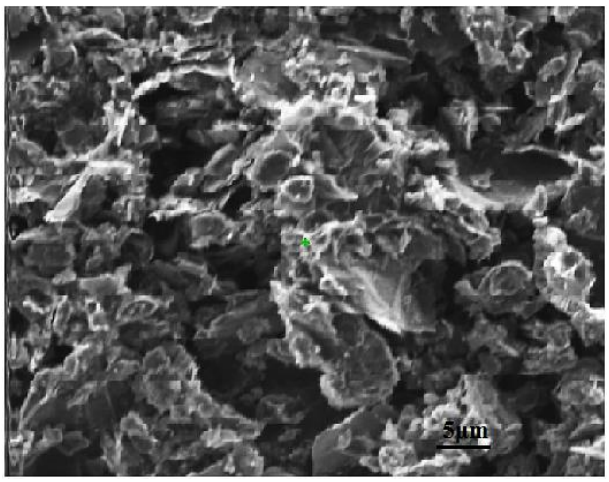

Fig.(5): SEM images of graphene film prepared by electrochemical method at Scale bars =5µm.

4.3 Energy Dispersion Spectroscopy (EDS)

Fig.(6) shows the elemental composition of graphene in terms of atomic percentages are as following: C: 82.75 % and O: 12.01 %, upon applied of DC potential (E = +10 V), at the anodic graphite rod, water molecules easily undergo oxidation to yield free radicals which, in turn lead to the formation of oxygen containing functional groups, on the graphene sheets, These sheets are exfoliated from the anodic rod, upon action of water and potential, which act cumulatively to remove layers of graphene that collapse into the solution. Thus the graphene generated in the ionic liquid medium also has an oxidized graphene component.

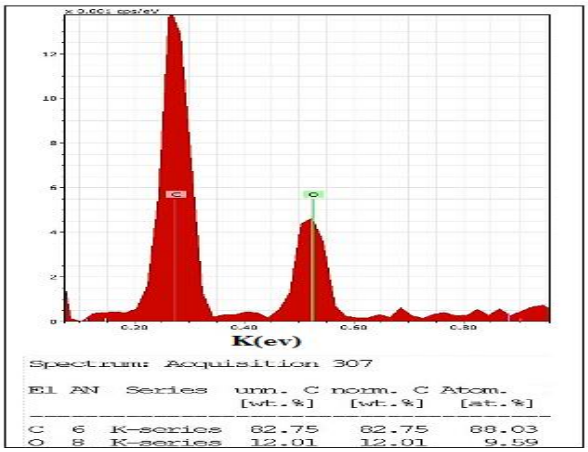

Fig.(6): Energy dispersive spectroscopy plot of graphene film.

4.4- Optical Microscopy (OM)

Fig.(7a and b) shows optical microscope images of graphene film prepared by electrochemical method at 500 X and 1000 X magnification. The color of the graphene film changes depending on its thickness. From these figures we can see there are impurities with the graphene film due to present residual ions from aqueous solution and the graphene film not uniform above the glass slide.

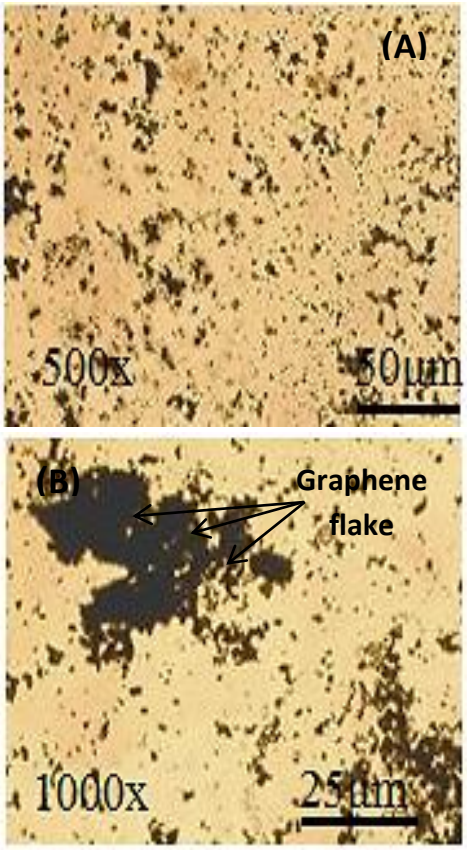

Fig.(7): Optical microscope images of graphene film magnified at a) 500x and b) 1000x.

4.5 UV-Vis Spectroscopy

Uv-visible absorption spectra of prepared graphene suspensions have been shown in Fig.(8a and b), In Fig.(8a), maximum absorbance was obtained at about 230 nm, corresponding to π-π^* transition of aromatic C=C bonds, and shoulder peak at ~295 nm represented n-π* transitions of C-C bonds. The spectrum obtained is in agreement with the previously reported results[10-11]. Fig.(8b) shows the Uv-Vis absorption spectrum of graphene film deposited on glass slide, the maximum absorbance peak was obtained at about 225 nm, corresponding to π-π^* transition of aromatic C=C bonds, and another peak at 290 nm of n-π* transitions of C-C bonds. The Uv-Vis spectra of graphene suspension showed a blue shift due to of the presence of water content in the ionic liquid which makes the viscosity of the electrolyte reduced.

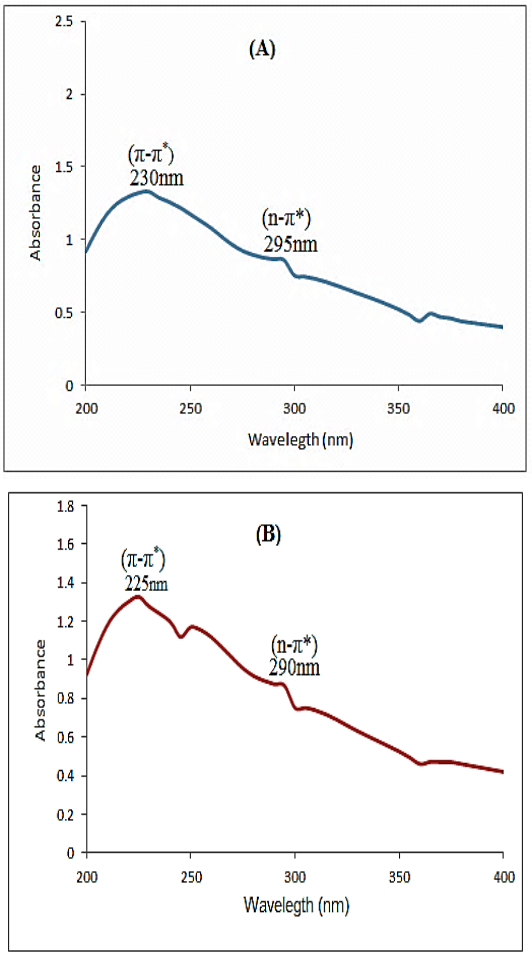

Fig.(8): Plot of absorbance vs. wavelength for a) graphene suspension and b) graphene film.

5. Conclusions

In conclusion, we have successfully prepared good quality graphene suspension by electrochemical exfoliation of graphite employing aqueous electrolyte. This technique is a one-step simple procedure to attain the objective and has the potential to be scaled up easily at relatively low costs. The exfoliated graphene sheets exhibit crumpled morphology has been characterized by optical microscopy and scanning electron microscopy, while the energy dispersive spectroscopy and X-ray diffraction showed that the structure of graphene film has small amount of defect and a few oxygen concentration. The characterization of optical properties of graphene has been shown two main transitions for graphene which agreement with the previously reported.

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الخلاصة

في هذا البحث، تم تحضير عالق الكرافين بواسطة التقشير الكهروكيمياوية لأقطاب الجرافيت المغمورة في محلول مائي لحامض الكبريتيك وحامض النتريك وماء مقطر ($H_2SO_4/HNO_3/H_2O$). تم تسليط فرق جهد من نوع انحياز DC بقيمة 10 V و تم ترسيب رغوة الكرافين على لوح الزجاج. الخصائص التركيبية والبصرية للكرافين شخصت عن طريق حيود الاشعة السينية(XRD) والمجهر الالكتروني الماسح (SEM) ومطياف المشتت للطاقة (EDS) والمجهر الضوئي(OP) ومطياف الضوئي بالمنطقة الفوق البنفسجية والمرئية(Uv−Vis) على التوالي. اظهر نموذج حيود الاشعة

السينية للتركيب البلوري للكرافين قمة حادة عند 26.59^{o} والتي تقابل مسافة بين المستويات تساوي 0.334 nm بتجاه (002) تتوافق مع المسافة بين المستويات للجرافيت الطبيعي. اظهر فحص SEM لتراكيب الكرافين بانه متكون من طبقات قليلة مع وجود اشكال متجعدة. البنية التركيبية للكرافين تتكون من كاربون واكسجين بنسب ذرية % 82.75 و% 12.01 على التوالي. اظهرت اطياف الامتصاص بواسطة Uv-Vis لعالق الكرافين وغشاء الكرافين يمتلك انتقالين تضمنت $\pi-\pi^*$ و $\pi-n^*$ على التوالي.

كلمات مفتاحية: كرافين، تقشير كهروكيميائية، محلول مائي، اقطاب جرافيت.