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Synthesis and characterization of Graphene produced from Iraqi date syrup

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Abstract— Graphene is a mono layer of hexagonal honey structure of carbon atoms. Iraqi date syrup was used as a carbon source for synthesis Graphene by expanded dehydration method, in which using of concentrated sulfuric acid as dehydration agent. The method name refers to expanded dehydration because of the increasing in volume with dehydration reaction. Characterization the prepared Graphene was done by FT-IR, XRD, SEM, AFM and UV-Visible techniques and compared with previous work. The final product was obtained by annealing at 600 °C or in other word thermal reduction to reduce all oxide groups combined with structure. Graphene XRD pattern shows wide peak at 002 plane centered at 2θ =23.758°, and d-spacing = 3.37 Å. AFM image shows that prepared Graphene in Nano sheets form. The method exhibit production yield about 9% and this is relatively high in comparison with other Graphene preparation methods.

Keywords— Graphene, Graphene oxide, Carbon, Dehydration, Nano sheets.

1. Introduction

Graphene is one of allotropes of carbon, is a two-dimensional, mono layer with honey comp atoms arrangement for carbon atoms in sheet form has one atom thickness. Graphene recognized by strong carbon –carbon bonding with sp2 hybridized [7], in which carbons atoms form a hexagonal packed and showed a structure analogous to benzene so it is thought that Graphene chemistry be same for that for benzene[29].

Geim and Noviselov produce Graphene by micromechanical exfoliation of highly oriented pyrolytic graphite HOPG [18]. Graphene received huge attention due to its extreme mechanical, electrical and optical properties, with high chemical and thermal stability [23] and, [6]; also, it has greatest essential carrier mobility at normal temperature [17].

Graphene oxide is an oxide form for Graphene in which Graphene oxide surface contains many functional groups; carboxylic acid group at edge while the basal plane contains epoxy / hydroxyl groups [27]. Graphene oxide may be reduced to get Graphene (chemically or thermally reduction) but it can not be reduced completely during reduction treatment; the product for this process contains residual oxygenated function groups so refer to this kind of Graphene as a reduced Graphene oxide to distinguish between it and pristine Graphene.

There are many methods and techniques used for Graphene synthesis in addition to micromechanical exfoliation method like liquid –phase exfoliation [15], Epitaxial growth for silicon carbide [4], Chemical Vapor Deposition CVD [24], chemical reduction of Graphene oxide by many reducing agents including Hydrazine [21], hydroquinone [5], and sodium borohydride [10] etc.

Many techniques used to characterize Graphene and its derivatives; XRD is one of the most important techniques used for Graphene characterization as well as it can be used to distinguish between Graphene and its Graphene derivatives, figure-1 shows the XRD pattern for Graphene, Graphene oxide and graphite; a wide peak at range between 10-25º is Graphene, while a sharp peak at 10º refer to Graphene oxide while graphite show only one peak appear sharply at 25º [11].

Visual or optical observations help to distinguish between Graphene and Graphene oxide, Graphene has a high charge carrier concentration and mobility and these lead to improve incident light reflection so Graphene show a metallic shining. The reduction of functional groups leads to improve electrical conductivity and increase in charge

carrier as well as electron mobility; all these will cause improving for reflection to incident light and finally made Graphene with metallic luster [19]. Absorption for Graphene with mono layer is flat in range 300-2500 nm and peak at about 250 nm in ultra violet range is assigned to electron band on $\pi -\pi$ bond [13].
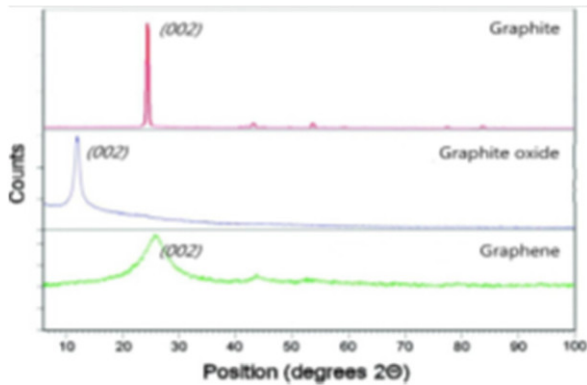

Figure 1: XRD patterns of graphite, graphite oxide and Graphene [11].

In the present work Graphene was prepared by expanded dehydration from Iraqi date syrup as carbon resource, with concentrated sulfuric acid as dehydration agent. The method was called as expanded dehydration because of increasing in volume during dehydration step. AFM images shows that the produced Graphene was found in Nano sheet form with curvature. All techniques used to characterize the produced Graphene were agreed with previous literatures, the significant point here is new way to prepare Graphene and the relative high yield for this method comparing with other Graphene preparation methods.

2.   Experimental work

2.1   *Materials*

- Iraqi date syrup (70 %) from Food & Beverage Company in Karbala contains (Glucose 35.5% and Fructose 27.9%) and the rest are proteins and mineral salt.
- H_2SO_4 (98%) CHD Company.
- HCl (37.5%) CHD Company.
- Deionized water (DI water).

2.2   *Preparation of Graphene*

The preparation of Graphene from Iraqi date syrup was done by expanded dehydration dates syrup (15.2 ml) with (5.5 ml) of concentrated sulfuric acid (98%) according to the following reaction.

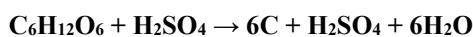$$C_6H_{12}O_6 + H_2SO_4 \rightarrow 6C + H_2SO_4 + 6H_2O$$

Figure 2 shows the step of Graphene preparation and as below:

- Heat (15.2 ml) of Iraqi date syrup in 2000 ml beaker with mixing, and after temperature reach to 40 °C, (5.5 ml) of concentrated sulfuric acid (98%) was added.
- In about 30 second after adding acid to dates syrup, along column of black carbon grows up inside the beaker.
- Add HCl (5 M) solution to Graphene with mixing for 5 hours to remove impurities by filtration.
- Wash Graphene with DI water several time until solution pH reached about 7.
- Using high speed centrifuge to separate water from Graphene.
- Drying the product at 110 °C under vacuum for 12 hours.
- Finally, the produced Graphene was annealed at 600 °C for 5 hours .
- As Victor mentioned [26] and in comparison, with other method for Graphene synthesis the production yield for this process is relatively high; the yield is about 9% as.
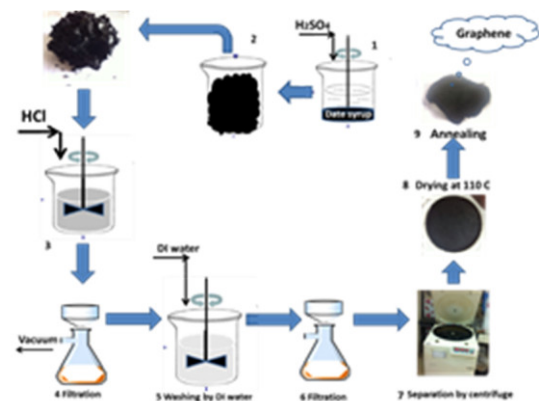

Figure 2: Graphene production steps by expanded dehydration

2.3   *Characterization*

To identify the Graphene produced it was examined by X-Ray diffraction system (SHIMADZU XRD-6000), while the functional groups of sample was studied by Fourier transformation infrared spectroscopy (BRUKER ALPHA model).Scanning electronic spectroscopy SEM was used to study morphology of Graphene while AFM (model AA3000) used to identify Graphene topography. The optical properties were investigated by using UV test (JENWAY model 6800UV/Vis. spectrophotometer).

3.   Results and Discussion

3.1   *X-ray diffraction*

XRD pattern for prepared Graphene by expanded dehydration method can be seen in figure 3, it shows wide peak centered at $2\theta = 23.758°$ at plane (002) with d-

spacing d_{002} =3.37 Å, which corresponded with data card (JCPDS no.75-1621), and this is agree with many literature for Graphene preparation in which XRD pattern exhibited same result i.e. Paredes [18], Stobinski [22], and Thema [25].
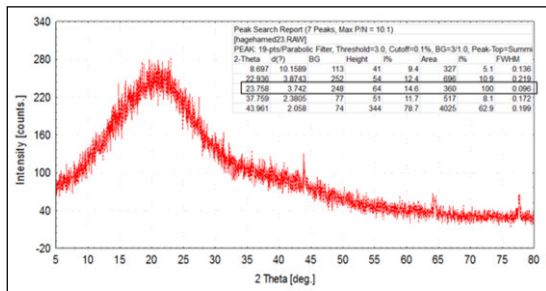

Figure 3: XRD pattern for final Graphene prepare by expanded dehydration.

3.2 *Fourier transformation infrared spectroscopy FT-IR*

Figure 4 shows FTIR spectra for Graphene produced by expanded dehydration method before annealing at 600 °C ,it is clear that Graphene has a many functional groups ; wide peak due to intercalated water molecules (≈ 3301.83 cm $^{-1}$) and bonded water molecules (≈ 1621.75 cm $^{-1}$) ,as well as peaks for COOH (1698.34 cm $^{-1}$) , OH (1200.79 cm $^{-1}$) and epoxide (1025.16 cm $^{-1}$) in C =C bond plan (1510.07 cm $^{-1}$). The effect of annealing process can be noted clear by comparing between FT-IR spectra for Graphene before and after annealing (as shown in figures 4 and 5), in which figure 5 shows that Graphene has a residual of organic functional groups number; these observations mean most of oxides groups were removed during annealing step in thermal reduction process and these agree with Xiu-Zhi Tang observation [28].The intercalated water molecules were vaporized at temperature reached 200 ºC while most of carboxyl groups started to remove above 200 ºC , and in temperature close 600 ºC the residual carboxyl groups and partially removing hydroxyl groups and this is agree with Mikhailov approval [23].
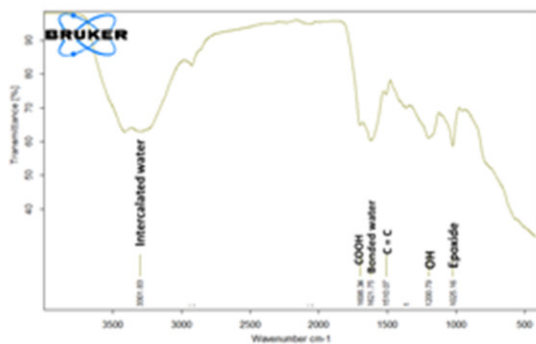

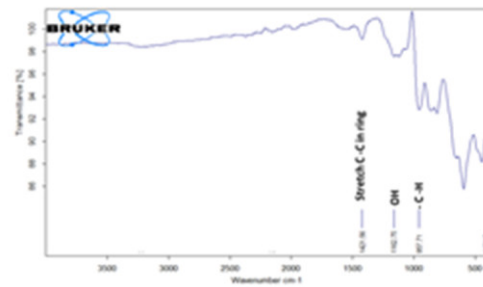**Figure 4:** FT-IR spectra for Graphene before annealing process.

Figure 5: FT-IR spectra for Graphene after annealing process.

3.3 *Optical properties*

Figure 6 shows the UV/visible spectra for Graphene before and after annealing the, the absorption at about 235 nm for Graphene before annealing to transfer $\pi - \pi$ of aromatic C $-$ C bonds and it was shifted gradually to about 257 nm for Graphene after annealing, this change refers to the gradual restoration of the π network within the Graphene layers, and that mean the reduction of functional groups which happens during annealing step (thermal reduction) as D. Li and co-workers proved [2].
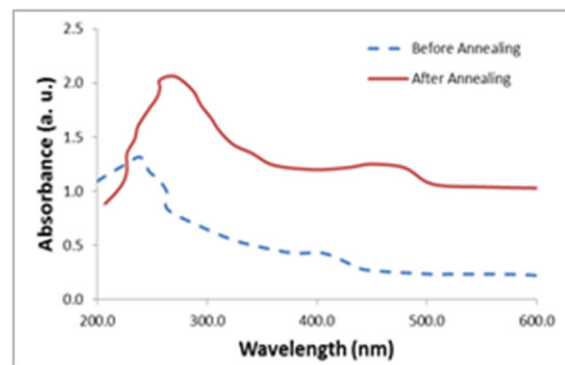

Figure 6: UV-vis absorption spectra showing change of Graphene before (dash line) and after (solid line) annealing process

3.4 *Scanning Electronic Microscopy SEM*

Scanning electron microscopy SEM   used in case of Graphene to identify single layer versus multilayers as well as is distinguish the defects in the crystals. Figure 7 for SEM image for prepared Graphene shows the sample has many layers of Graphene and it seem that Graphene layers have curvature with distortions as well as there as many defects at the surface due to the escaping of intercalated and bonded water molecules and other functional groups reduction during annealing step or thermal reduction and this is agree with McAllister [16].
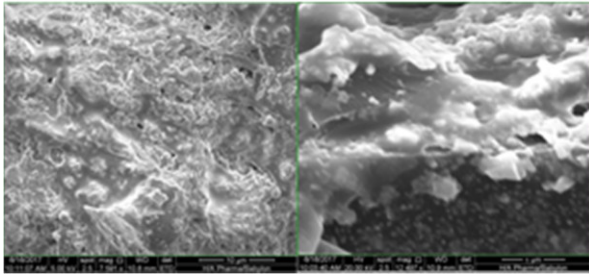
Figure 7: SEM image for as prepared Graphene.

3.5 *Atomic Force Microscopy AFM*

AFM imaging technique can be used to determine thickness at Nano scale successfully and show topographic of Graphene sheets; figure 8 (A and B) shows the 2D and 3D view for as prepared Graphene.
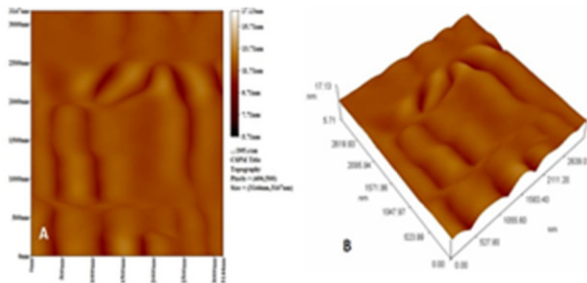

Figure 8: (A) 2D view of AFM topographic mode of Graphene sheets, and (B) 3D view

 On Nano scale Graphene sheets display a bumpy morphology with height range about 11.13-11.84 nm with roughness 0.144 nm (figure 9 -A) and height range about 12.15-12.29 nm with roughness 0.495 nm (figure 9-B) and that mean the prepared Graphene can be represented as a Nano sheets as Chengshou [1] and Paredes [18].

3.6 *Mechanism of functional groups reduction (Temperature-dependent)*

For studying the functional groups reduction during annealing step its proposed to study FT-IR spectra and XRD pattern together as seen in figure 3 for product Graphene (multi layer Graphene) after drying at 110 °C, it can be noted that product contain many functional groups ;peak for intercalating water molecules (≈ 3301.83 cm -1) and bonded water molecules (≈ 1621.75 cm -1) as well as other oxide groups peaks corresponding to OH, epoxides , and COOH groups (1200.79,1025.16 and 1698.34 cm -1) respectively in C = C bond sheet (peak 1510.07 cm -1) , it can be conclude that produced Graphene consists from many layers with d-spacing due to defects or Nano holes , oxide groups (hydroxyl , epoxide and carboxyl) and intercalated water in between layers and this is responsible for Nano curvature deformation. To reduce oxide groups and water from the product thermal reduction was used in which it was done by annealing treatment step , figure 10 through figure 14 show XRD pattern at different value of annealing

temperature (200, 300, 350, 400 and , 500) °C respectively, show that pattern at temperature 200°C exhibit peaks 2θ =22.37 ° and 2θ= 10.259°, and these peaks shifted toward right side while they are eliminated to be one peak after treated at 600°C (2θ =26.418 °) as shown in figure 1 for XRD pattern for final product. Jeong [10] proposed that thermal reduction effects can be explained as vaporization of intercalated water molecules at temperature reached to 200°C with lowering in crystals size du to crystals exfoliation by water vapor escaping and thermal treatment (annealing) here effect on the stacked layers to be fully exfoliation because of escape of large number of intercalated water molecules starting at temperature reached to about 200 °C , these exfoliated layers may be called Graphene (or chemical derived Graphene) .

Sangfeng suggest that annealing process lead to reduce functional groups in between stacked Graphene layers [19], and caused to produce wrinkled and small size of Graphene layers and this agree [20] at the same time the decomposition of oxygen-containing group as well as removing carbon atoms from plane which cause deformation of the carbon atoms plane. The exfoliation effect leads to structural damage of Graphene layers because of releasing of carbon dioxides a Kudin proposed [14]. McAllister [16] suggested that increasing in calcination temperature cause oxygen function groups decomposing into gases that create a huge pressure between stacked layers and according to state of equation the pressure exerted about 40 MPa at 300 °C while the exerted pressure reached to about 130 MPa at 1000 °C.
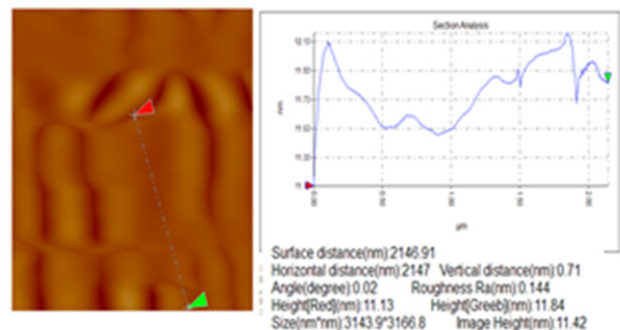

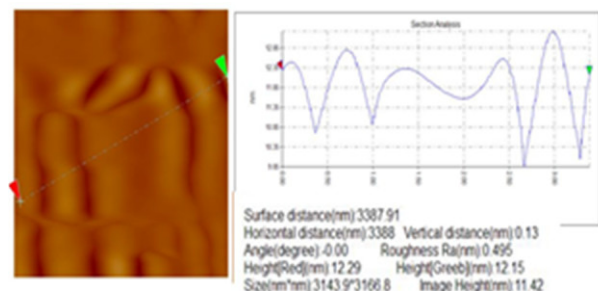**Figure 9-A:** View section line analysis with height range 11.13-11.48 nm.

Figure 9-B: View section line analysis with height range 12.15-12.29 nm.
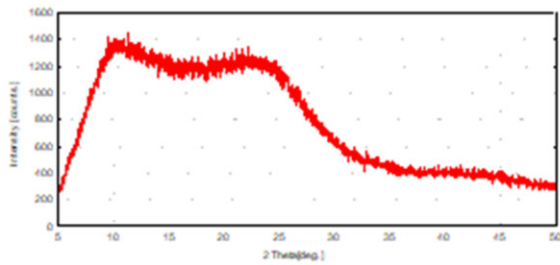
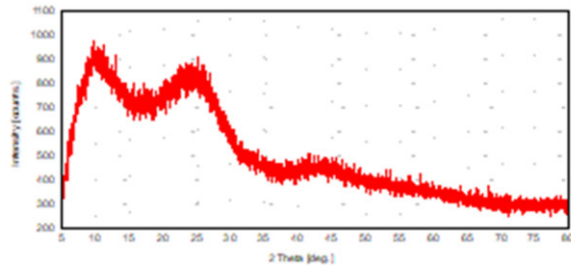**Figure 10:** XRD pattern for Graphene after calcination at 200 °C for 5 hours.

Figure 11: XRD pattern for Graphene after calcination at 300 °C for 5 hours.
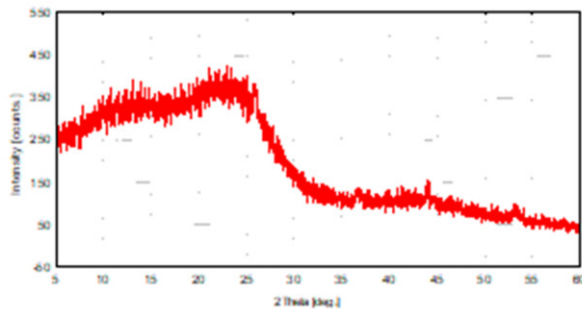

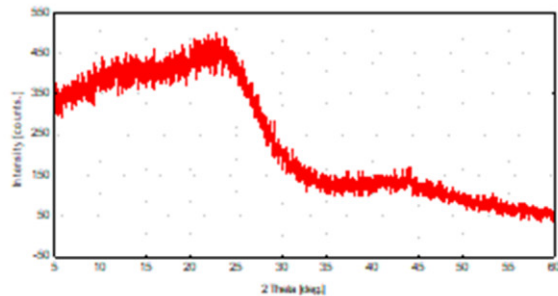**Figure 12:** XRD pattern for Graphene after calcination at 350 °C for 5 hours.

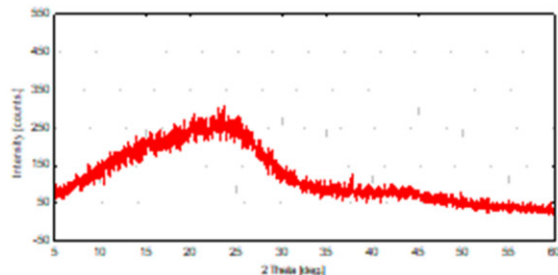**Figure 13:** XRD pattern for Graphene after calcination at 400 °C for 5 hours.

Figure 14: XRD pattern for Graphene after calcination at 500 °C for 5 hours.

4. Conclusions

Preparation of Graphene by expanded dehydration for Iraqi date syrup by effect of using concentrated sulfuric acid; lead to conclude the following:

- Because of expansion in volume associated with date syrup dehydration reaction, the method can be called expanded dehydration.

- The lagged carbon atoms take a large volume structure consist many randomly stacked layers.

- It can be concluded that produced Graphene with many stacked layers occupied by many functional groups (oxide groups) with water molecules (intercalated and bonded water) in between stacked layers as shown in FT-IR spectra so it can be said it was behaved like a Graphene oxide and this also noted clearly in XRD pattern, and UV-vis spectra.

- As shown in SEM image it can be conclude that annealing step work as thermal reduction process for oxide groups and associated water molecules which cause some defects on the surface due to escaping of water molecules and oxide groups.

- In addition it can be said that thermal reduction step can be considered as active for removing water molecules (intercalated and bonded) from Graphene structure while it is not able to remove totally oxide groups (hydroxyl , epoxide and carboxyl) as FTIR spectrum shown .

- AFM image show clearly that prepared Graphene in form of Nano sheets.

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تصنيع وتوصيف الكرافين المنتج من دبس التمر العراقي

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الخلاصة – الجرافين هو طبقة أحادية سداسية التركيب من ذرات الكربون. تم استخدام دبس التمر العراقي كمصدر للكاربون لتصنيع الكرافين عن طريق سحب الماء باستخدام حامض الكبريتيك المركز. وقد اطلق على هذه الطريقة بطريقة التوسع في الحجم المصاحب لعملية التجفيف نظرا للتوسع الحاصل في الحجم اثناء العملية , تمت معاملة المنتج بعد التفاعل بدرجة حرارة مقدارها 600 درجة مئوية لغرض اختزال المجاميع الاوكسيدية (الاوكسيد و الكاربوكسيل و الايبوكسي) من تركيب الكرافين . ولغرض تشخيص الكرافين المصنع تم استخدام مختلف التقنيات مثل UV, AFM,XRD, FT-IR, visible ,SEM . حيث تم فحص النموذج في جهاز الاشعة السينية XRD وقد اظهر النموذج θ=26.4182 مع مسافة تباعدية مقدارها 3.37 انكستغروم بينما اظهرت صورة المجهر الماسح الالكتروني SEM ان طبقات الكرافين المنتج ذات انحناءات وتشوهات و في نفس الوقت بينت صورة المجهر القوة الذرية AFM بشكل واضح ان الكرافين المنتج على هيئة صفائح نانوية .كانت النتاجية في هذه الطريقة عالية نسبية تقريبا 9% و بالمقارنة مع طرق تحضير الكرافين الاخرى يمكن اعتبار هذه النتاجية عالية نسبيا.

الكلمات المفتاحية – الكرافين، اوكسيد الكرافين، الكاربون، الصفائح النانوية .

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