



Reduction of Graphene Oxide by New Chemical and Green Methods

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ABSTRACT

This research deals with the preparation of Graphene Oxide (GO) from Graphite using Hummers method and then reduction of GO by three different methods (local olive leaf extract method, pure oleic acid method and sodium hypochlorite - urea in an alkaline medium method). The reduced Graphene Oxide (rGO) was analysed by infrared FTIR in the range of 400-4000 cm^{-1} , and it was found that there are functional groups of oxygen such as epoxy group, and carbonyl group. Then rGO was analysed by UV-VIS spectroscopy in the range of 200-800 nm. Also, the structure and particle size of these sheets were studied by FESEM and EDX. It was revealed that the dimensions of the formed rGO by local olive leaf were within 500 nm-20 μm , while the reduction by chemical method in the presence of sodium hypochlorite and urea in an alkaline medium led in to a particle size in the range of 200 nm-2 μm . Based on the EDX result, the GO composition is 53.22% carbon and 29.67% oxygen. The best method for synthesise of rGO was pure oleic acid method at temperature of 440 $^{\circ}\text{C}$ with a heating rate of 2.3 $^{\circ}\text{C}/\text{min}$. In this method, the particles were in the range of 200 nm-2 μm and based on EDX results, they were composed of 72.04% carbon and 24.32% oxygen.

Keywords: Graphene Oxide GO, reduced Graphene Oxide rGO, Green and Chemistry method, New method.

1. Introduction

Nanoscience and nanotechnology preparation and manufacturing are accelerating due to the interim requirements and the global technical explosion in all sectors. In this regard, researchers and those who interested in this field are competing to obtain new and high quality product to meet the needs and requirements of modern development.

Graphene and its oxide (GO) have attracted a great attention due to their interesting electronic properties [1]. Graphene (Gr) is known as an allotropic form of carbon consisting of 100% carbon, discovered experimentally in 2004 [2]. It is a material composed of a single layer of atoms arranged in hexagonal rings resembling

a honeycomb [3]. It is known by high electronic conductivity, superior mechanical strength and flexibility, thermal conductivity, high electronic mobility and visible light penetration [4-5]. Graphene is a two-dimensional material on two levels (2D) [6]. It has a pattern of hybridization SP^2 in one layer, with unique characteristics as it is the only material that is on one layer, while the rest of the bodies are three-dimensional (3D) [7-10]. Graphene also has special electrical properties with a high transferability of an electron at normal temperature (250,000 $\text{cm}^2 \text{V}^{-1}$) [4,8]. Electrons can only move between carbon atoms in the two-dimensional lattice. [11] It has exceptional thermal conductivity and remarkable mechanical properties

[12], i.e., young's modulus of 1 TPa and internal strength of 130 GPa [13]. Pure graphene appears in the form of a sheets, which gives it a porous character in addition to the presence of gamma electrons [14] Theoretically it has a very high specific surface area of 2600 m²/g. [15-17] The preparation of graphene depends on the reduced of graphene oxide [18-21] as represented in Figure (1) [18].

Graphene oxide (GO) is of great interest due to its low cost, accessibility, and wide convertibility compared to graphene. Graphene oxide contains a c=c ring and oxygen. It also contains other functional groups such as hydroxyl -OH, alkoxy C-O-C, carbonyl group C = O, carboxyl group -COOH, and other groups that contain oxygen [22], and the presence of polar groups on the surface of graphene GO reduces thermal conductivity and electrophoresis [23]. GO is highly hydrophobic [24], and graphene oxide is prepared by using a modified Hummers method [25-28]. The calculated specific surface area of GO and rGO by BET through absorbing N₂ were 170m²/g and 530m²/g, respectively. [29] The graphene oxide is reduced by removing as much oxygen as possible to reach the

graphene, as illustrated in the figure (2) [8].

The graphene oxide is reduced to graphene using wet and chemical reducing agent such as NaBH₄ [28], hydrazine [30-32], and dimethyl hydrazine [4-5], by thermal method [2,33] or using environmentally friendly products [34]. Although the traditional methods of preparing graphene and its oxide are highly cost-effective, they are not environmentally friendly. Therefore, some researchers resort to find a green alternative way to recover graphene oxide by using natural products instead of toxic reducing agents [4-5]. For example, vitamin C [35] lemon peel extract [36] palm leaf oil extract [37], aloe vera extract [38], lycium barbarum extract [39] and others. The preparation of nanostructures usually occurs through two methods, bottom-up and top-down [40]. The size of the intended nanoparticles is indicated by the quality of their production technology and the kind of the used constitutes, especially in the field of optical technologies and medical. Characterization of graphene and its oxide is carried out through the dispersion of graphene oxide (GO) using atomic force microscopy (AFM), Raman spectroscopy,

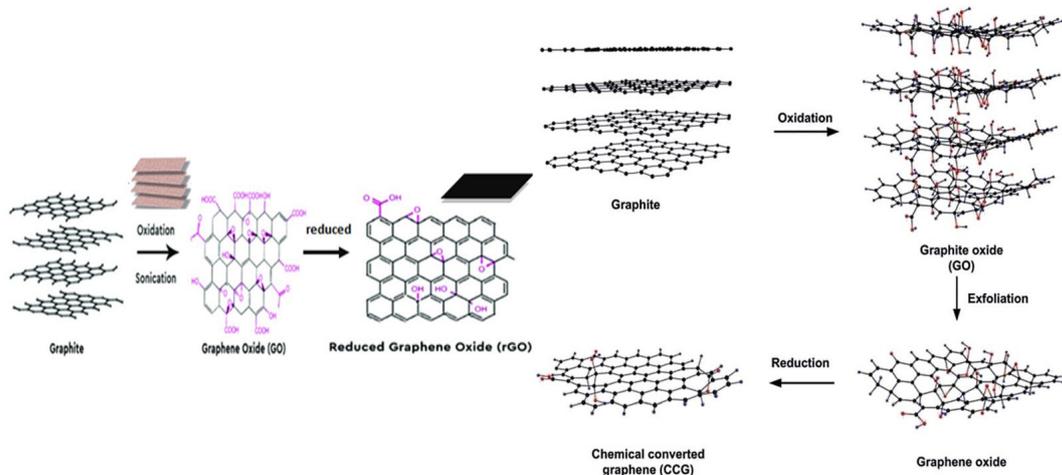


Fig. 1- The stages of formation of graphene from graphite[18].

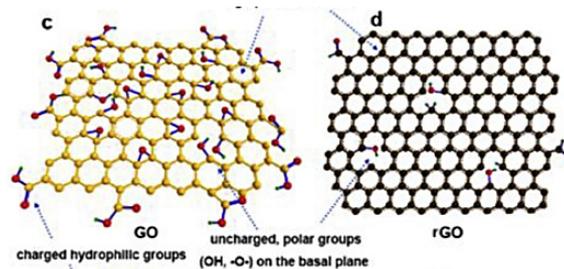


Fig. 2- Forms of graphene and its derivatives: (C) GO, (D) rGO[8].

transmission electron analysis (TEM), UV-VIS spectroscopy, field emission scanning electron microscopy FESEM and energy-dispersion by X-ray (EDX). In order to distinguish between the number of its layers, it is few-layers if it ranges between (1-3 layers), multi-layers (4-10 layers) and a thick-layer (> 10 layers), [1]. In spectral scanning transmission, electronic energy is responsible for luminescence. The GO functional group comes from specific electronic devices transitions between antibonding and molecular bond evidence for containing different oxygen-containing functional groups such as hydroxyl groups (C-OH), carboxyl groups (COOH), carbonyls (C=O), epoxy (C-O-C) and aromatic (C=C) [42]

Graphene oxide (GO) and reduced graphene oxide (rGO) are used in a wide variety of applications, such as water purification, fuel cells [7], and biological applications, among its applications in cancer patients [43] and early detection of Alzheimer's disease using a biosensor based on electrochemical oxidation and reduction made of graphene oxide and gold nanowires, quantitative determination of serum microRNA-137 in the blood [44]. In the pharmaceutical field as a drug [45] and in many physical and chemical applications as an electrode [46]. In the environmental field [47] as the analysis of each of the ions of lead Pb^{2+} , copper Cu^{2+} , and cadmium Cd^{2+} , mercury Hg^{2+} and other ions [48], desulfurization H_2S from the air stream [49] gas sensor [50], in the preparation of carbon quantum dots [51], in the manufacturing of ultra-fast conductors and transistors [43] and high-capacity energy storage [52].

Research objective

This research aims to synthesize reduced graphene oxide by several methods, starting with the preparation of graphene oxide by Hummers method and then reduced it by three methods, and finally the comparison between these methods.

2. Experimental details

2.1. Material and Methods

The materials used in this research are high-purity materials, which are: 325 mesh graphite powder (QuallKems), olic acid made by MERK - hydrochloric acid 37% (Shamlab) NaOCl 12% - sodium nitrate 96% (HIMEDIA) - potassium permanganate 99% (SiscoResearchLab)- urea, ammonium - pure Sodium hydroxy sodium (SDFCL)- sulfur acid 98% (SHAM CHEMI)-

fertilizer - diluted double water - local olive leaves. Spectrophotometric (SHEMADZU), and infrared FTIR were used for characterization.

2.2. Preparation of graphene oxide from the Hummers method

150 ml of concentrated sulphuric acid H_2SO_4 is gradually and carefully added to 2gr of pure graphite and 2 gr of $NaNO_3$, the colour of mixture is black at the beginning. The mixture is stirred for 10 min in a water bath, then by adding 10 gr of solid potassium permanganate $KMnO_4$ the colour of the mixture gently turns into an oily green colour. The mixture is stirred for 10 h at a temperature of 20 °C, then the mixture is stirred for 3h at a temperature of 50 °C. While observing the colour change from oily green to clear green, the mixture is cooled and then it is diluted with double water. Drip to 250ml turns brown. As shown in Figure (3), to complete the oxidation stage of graphite to graphene oxide (GO), 20ml of hydrogen peroxide (20% H_2O_2) is added gradually and gently in a water bath avoiding fizzing, and the colour turns light brown, then it is stirred for an hour and washed by 0.1M chloride acid [53-54]. After that, centrifuged several times to remove traces of sulphuric acid and potassium permanganate. Then, a little distilled water was added and ultrasound for 5h. Figure (4) shows the steps for preparing graphene oxide from graphite [56].

2.3. Reduction of graphene oxide (GO) to graphene by several methods

- A- A green method based on Olive Leaf Extract.
- B- A green method based on pure Oleic Acid
- C- Chemical reduced method in the presence of hypochlorite and urea in an alkaline (Figure 5).

A- A green method based on Olive Leaf Extract

Reduction of GO in a green method with aqueous extract of olive leaf [2], where 2gr of graphene oxide was reduced to rGO by adding 50ml of olive leaf extract which was prepared by taking local olive leaves from the city of Lattakia. It was washed, dried and milled, till the extraction is made by 50gr of dry olive leaves with 200ml aqueous distillation for six hours and at a temperature of 80 with stirring in a loosely covered container, then the mixture is filtered using filter cones with micro-pores of 0.4 μ m and centrifuged at pH = 10 (adding 4ml of concentrated ammonium water to the reaction mixture). Then the mixture

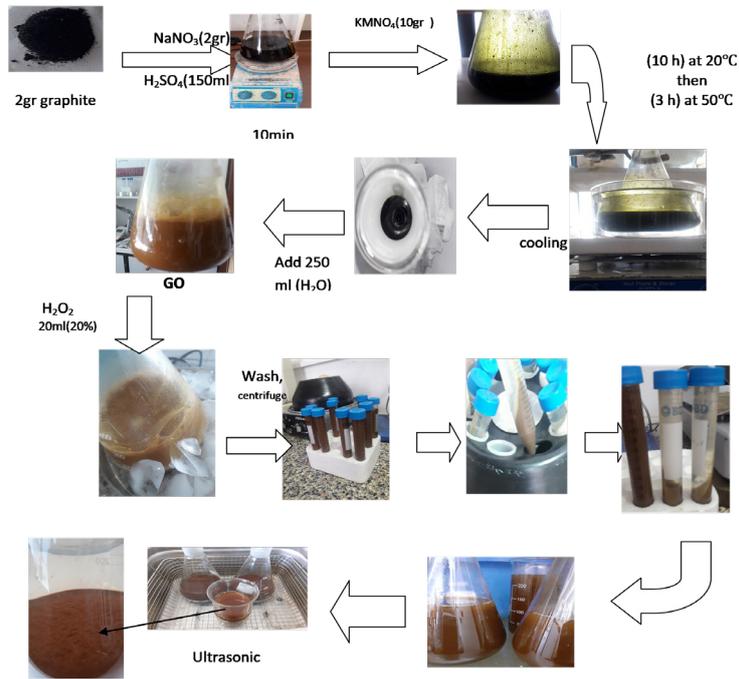


Fig. 3- diagram of the Hummer method preparation to graphene oxide.

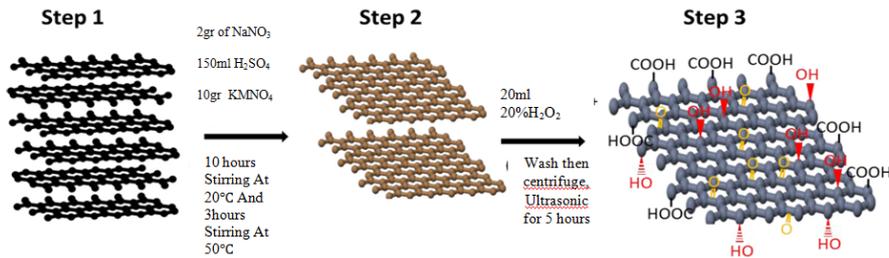


Fig. 4- Steps to prepare graphene oxide from graphite through graphene oxide.

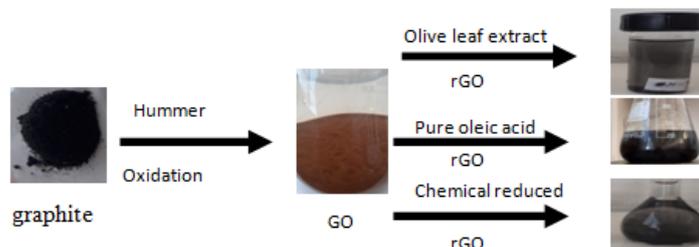


Fig. 5- diagram of the methods used to reduce graphene oxide.

is heated to boiling temperature for 10h and the suspension colour turns from a yellowish brown to a dark black colour. The mixture is left until it cools for 24h and then exposed to the ultrasound for of 1h, then the mixture is filtered and washed with double distillation water several times to remove the remnants of the olive leaf extract. Final

substance is dried and the study is conducted on it.

B- A green method based on pure Oleic Acid

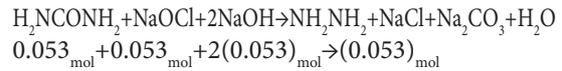
This method is used for the first time to reduce graphene oxide, where 25ml of oleic was mixed with 1.5gr of GO. The volume is supplemented with 200ml dual distillation water and heated for 10h at

a temperature of 80-100 °C. This temperature was chosen to ensure the oxidation of oleic to azelaic. At this stage, the color is gradually changed from brown to black and the solution is left to cool for 10h. The resulting mixture is washed several times with hot water, it is separated using a separating, and 2 -3 ml hexane is added to ensure disposal of the remnants. Then it is washed several times with hot water and ultrasound for an hour, filtered and dried until analysis. Figure 6 shows the scheme for reduction of rGO to graphene using oleic acid.

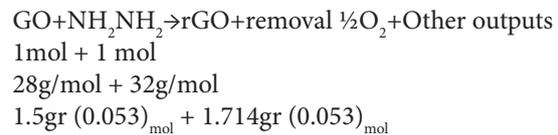
Approximately 1 gr of rGO was placed in this method in the incinerator at a temperature of 440 °C with a heating rate of 2.3 °C /min.

C- Chemical reduced method in the presence of Hypochlorite and Urea in an Alkaline

Where 1.5gr of graphene oxide is added to 3.58ml of 12% hypochlorite, and it was stirred and washed to raising bubbles are observed in the mixture. After adding 4.24 gr of solid sodium hydroxide NaOH, the color of the solution remains light brown color without changes. By adding 3.18 gr urea CH₄N₂O, the color of the mixture turns black (the reaction diffuses into heat). Leave the solution for an hour, and notice an increase in the appearance of bubbles. Maybe The oxygen is expected to be expelled from graphene oxide to rGO, then the reaction mixture is stirred for half an hour using a stirrer and then left for an hour to lie down and be sediment and washed with distilled water to get rid of sodium carbonate and then exposed to ultrasound, the scattering of the rGO resulting from this stage is high, and it forms a stable film that does not disappear in a mechanical method (scraping) when placed in a Petri dish. It is also believed that the formed hydrazine reduced from the reaction as in the following equation:



The theoretical quantity required in order to reduced 1.5gr of graphene oxide GO to convert it into rGO is:



Analyses were performed at

FESEM scanner in Arya electro optic- Iran, Damascus - Syria SEM- EDX, FTIR spectrum in the Department of Chemistry - Faculty of Science - Tishreen University. UV-VIS Spectroscopy at the Higher Institute for Environmental Research, Tishreen University

3. Results and discussion

In this paper, reduced graphene oxide (rGO) was formed by three methods (extract of olive leaves method - a green chemistry reducing it with pure oleic acid method - a chemical reduced method in the presence of hypochlorite and urea in an alkaline.). Also, a spectral scan was performed based on infrared within the range of (400-4000) cm⁻¹ after drying the sample, and mixed with KBr, for the product of reduce graphene oxide (rGO) by the used methods. For comparing the synthesized (rGO) and pure graphite, a spectral scan and an electronic scan o of graphite is illustrated in Figure (7).

Graphite has an aromatic ring containing C=C In addition to the presence of a peak at 650 cm⁻¹ evidence of the presence of a C-C bond in the structure [55] existence of two peaks at 2400 cm⁻¹ showed C-H bonding [56] there is also an

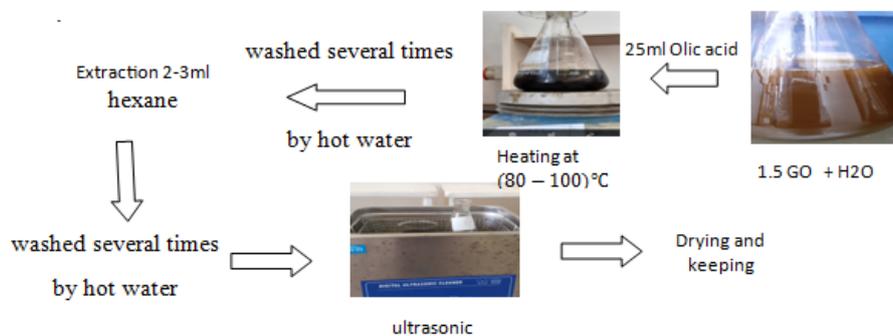


Fig. 6- Scheme for rGO to graphene based on oleic acid.

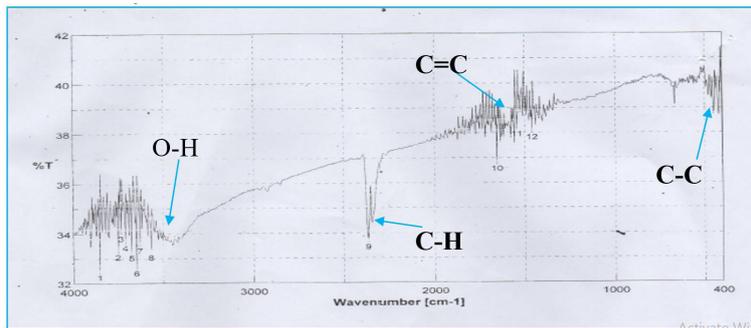


Fig. 7- FTIR spectrum of graphite in its pure form.

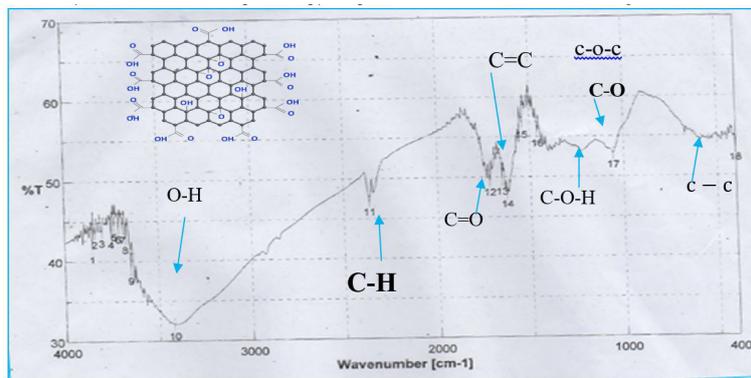


Fig. 8- FTIR infrared spectrum for graphene oxide.

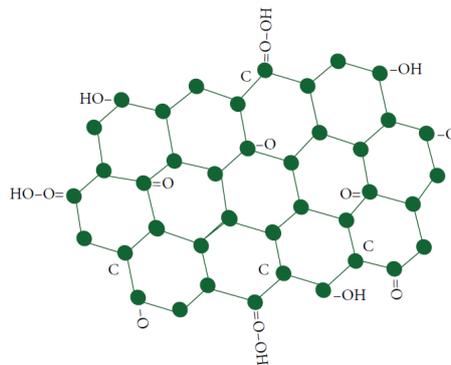


Fig. 9- The schematic structure of graphite oxide (GO)[22].

absorption peak at 3400 cm⁻¹ possibly due to moisture in the water during the analysis [22]. Then infrared spectroscopy was performed and the result is shown in Figures 8 and 9.

Existence of a peak at 650 cm⁻¹ is the evidence of the presence of a C-C bond in the structure [55] and existence of two peaks at approximately 2400 cm⁻¹ showed C-H bonding which proved the presence of carboxylic acid in structure [56]. Absorption peak at 1188 cm⁻¹, 1290 cm⁻¹ and 1387 cm⁻¹ are related to oxy groups C-O, C-O-C and hydroxyl COH groups, respectively. The absorption

within the range of 1648 and 1409 cm⁻¹ belongs to carboxylate vibration COO⁻ and the absorption peak of 1720 cm⁻¹ returns to the presence of carbonyl groups C=O, the absorption peak of 1621 cm⁻¹ returns to the presence of aromatic C=C groups absorption peak of 3400cm⁻¹ indicates the presence of hydroxyl resulting from the vibration of OH vibration in the feedstock, and the wide absorption of about 767 cm⁻¹ is due to the vibration and extension of C=O. While the absorption bands are toothed in the region from 1000-1500 cm⁻¹ is due to the symmetric and asymmetric vibration

and expansion of =O-C and -C=O. [22 , 57-65]. The oxygen (O) molecules are distributed on edges of the graphene oxide GO, which indicates the successful manufacturing of graphene oxide GO [66]. EDX of GO prepared in this method showed that the weight percentage of carbon and oxygen are 51.32% and 44.27%, respectively, and some other impurities such as K, Mn, Na, N, S in very small percentages are present [67]

A- A green method based on Olive Leaf Extract

The substances in the Olive Leaf Extract contribute to the reduce of graphene oxide rGO, as the olive leaf extract contains many compounds,

and a comparison was made between graphite and rGO from graphene oxide, and it was shown in Table (1).

It becomes evident that there is a difference in the grain size between graphite and rGO. studied the optical spectrum for both graphene and rGO to clarify this issue, figures (10-11-12) are illustrated in the following:

The previous figures are the best solution to differentiate between graphene and graphite using a solvent (50% water - 50% ethanol) volume to volume ratio. There is also a maximum absorption peak at ~ 237 nm, which is due to the presence of the π - π^* bond. As for the presence of an absorption

Table 1-comparison between graphite and graphene prepared in a green method

solvent	weight	Graphite	Comparison	rGO
Water	0.1 gr/10ml	precipitation scatter	> <	precipitation scatter
Ethanol	0.1 gr/10ml	precipitation scatter	< >	precipitation scatter
(50%-50%)v/v water- ethanol	0.1 gr/10ml	precipitation scatter	> <	precipitation scatter
The color is in the dry state		black	-	very black

Scattering a solution	Graphite	rGO
Water	good	good
Ethanol	medium	good
50% water – 50% ethanol	medium	good

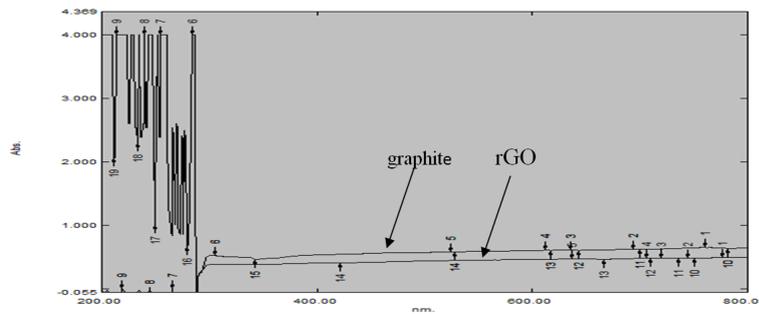


Fig. 10- Spectral scanning of graphite and rGO using a solvent (100% water).

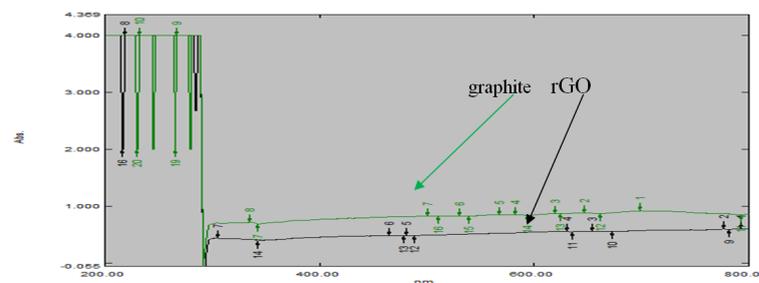


Fig. 11- Spectral scanning of graphite and rGO using solvent (100% ethanol).

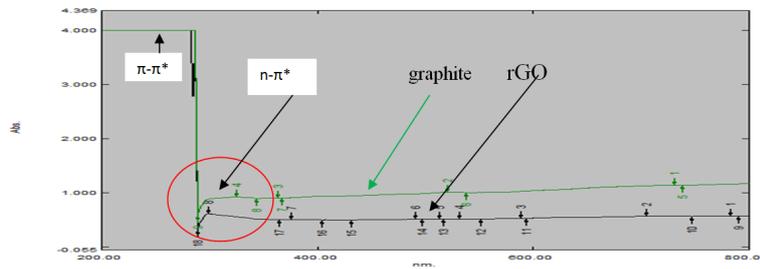


Fig. 12- Spectral scanning of graphite and rG using a solvent (50% water - 50% ethanol).

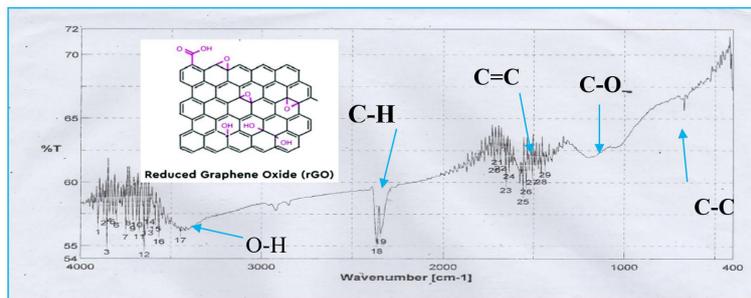


Fig. 13- FTIR spectrum of rGO based on olive leaf extract.

peak at ~ 300 nm, it is due to the $n-\pi^*$ transition [26].

The reduction of graphene oxide actually depends on the decrease of the oxygen group from the graphene oxide and the duration of this process. The wide peak at the 3400 cm^{-1} belongs to the O-H groups wavelength and is due to the presence of olivine. Existence of two peaks at 2400 cm^{-1} showed C-H bonding which proved the presence of carboxylic acid in structure[56] which is responsible for reduced process. [22,57-65] Also, olive leaf extract contains many organic compounds that contribute to the reduced process. Then the laminar structure of the product was traced back to graphene oxide based on FESEM image shown in Figure (14).

B- A green method based on pure Oleic Acid

Reduced graphene oxide by this method was analyzed by FTIR as shown in Figure (15), this image showed the presence of powder scattered of the prepared material and the clarity of the clumped rGO slices increased with clarity when increasing the magnification up to 500 nm.

Besides the presence of OH groups at the wavelength of 3400 cm^{-1} , existence of two peaks at 2400 cm^{-1} showed C-H bonding which proved the presence of carboxylic acid in structure [56]. It is believed that oleic acid helps to return graphene

oxide, and it is converted to azelaic, where azelaic contains two carboxylate groups [68-70]. The lamellar structure of rGO was also traced by relying on FESEM as shown in the figure (16). Based on these figures, by increasing the magnification starting from $200\text{ }\mu\text{m}$, the images showed the presence of scattered powder of the prepared material and the clarity of the stacked graphene slices increases clearly when the magnification is increased to 500 nm.

The size and radii of the reduced graphene oxide were examined after grinding it in a mortar and returning product with oleic acid and exposing it to heat in the incinerator at a temperature of $440\text{ }^\circ\text{C}$. The results of scanning electron microscopy is represented in the figure (17)

The image was investigated, and it was found that there are stacked sheets on top of each other, and their radii ranged from ($2\mu-200\text{nm}$). The EDX spectrum was studied as shown in the Figure (18).

It can be concluded from the EDX spectrum of this method that an energy band appears at an energy value of 0.277 Kev , a characteristic peak of carbon, and that the weight percentage of carbon is 72.04%, and the atomic percentage of carbon is 77.44%. The atomic percentage of oxygen is 18.92%, in addition to the presence of a small trace of other elements in very small percentages, such as K, Mn, Ca, N, S, Cl, and its percentage is 3.64%.

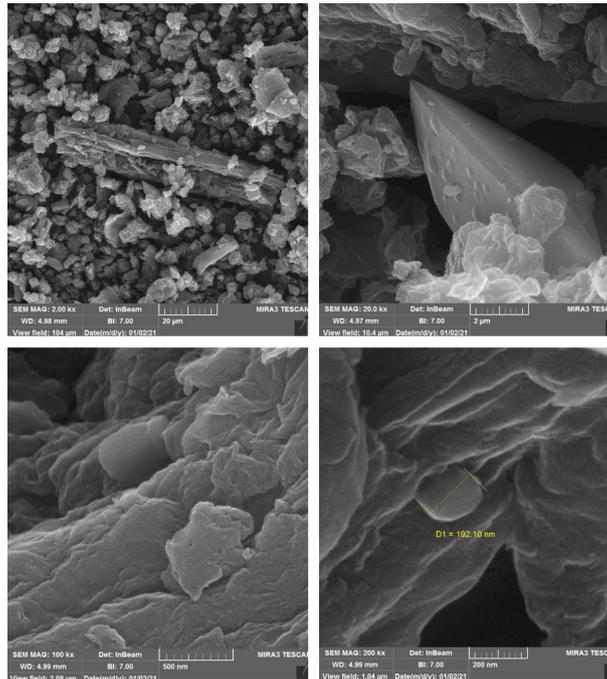


Fig. 14- FESEM for rGO using olive leaf extract.

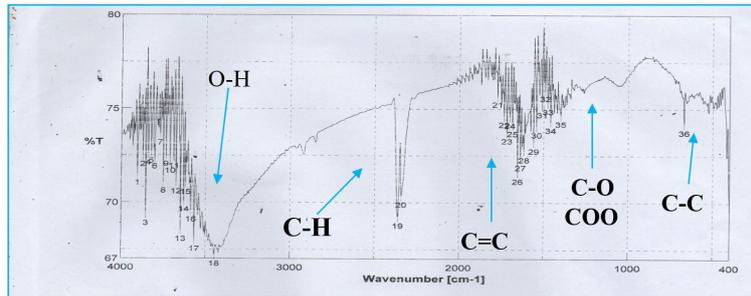


Fig. 15- FTIR spectrum of rGO based on oleic acid.

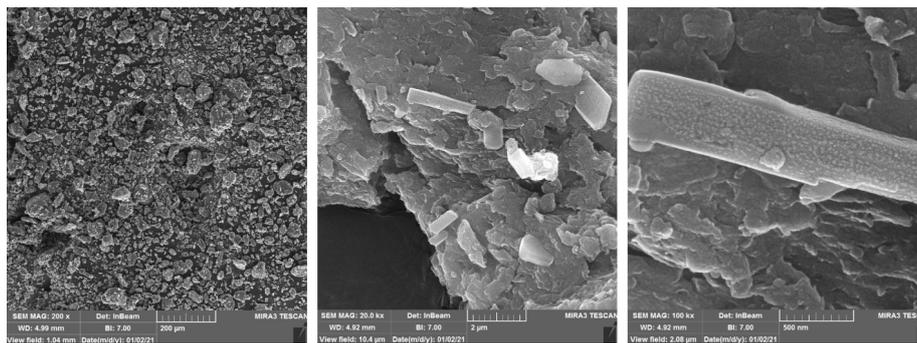


Fig. 16- FESEM of rGO based on pure oleic.

C- Chemical reduced method in the presence of hypochlorite and urea in an alkaline

Reduced graphene oxide for this method analyzed by FTIR as shown in Figure (19).

It is noticed from the previous figure that

the number of peaks in the studied spectrum has decreased, which indicates the purity of the product of graphene oxide reduced depending on the chemical reduced, as well as the decrease in the width of the peak indicating the presence of

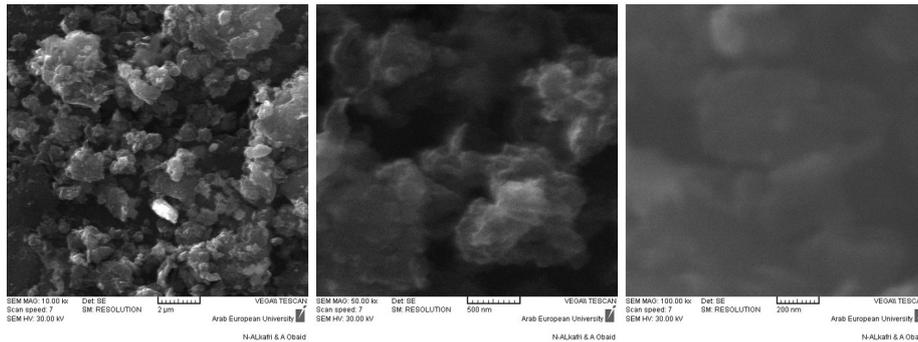


Fig. 17- FESEM of rGO based on pure oleic after a temperature of 440 °C at a rate of 2.3 °C /min.

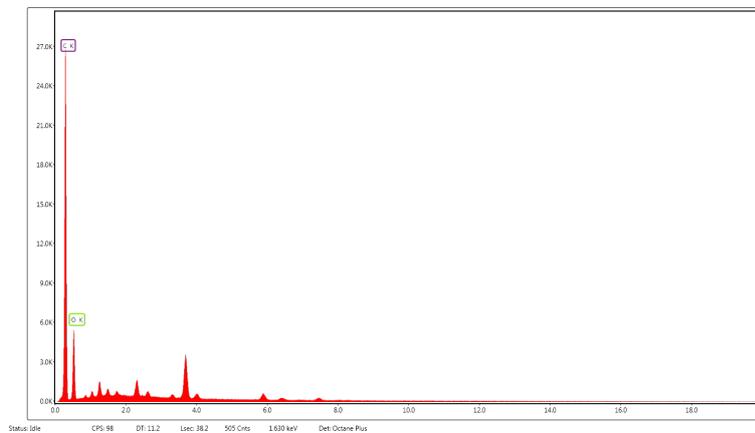


Fig. 18- EDX spectrum of rGO based on pure oleic after a temperature of 440 °C at a rate of 2.3 °C /min.

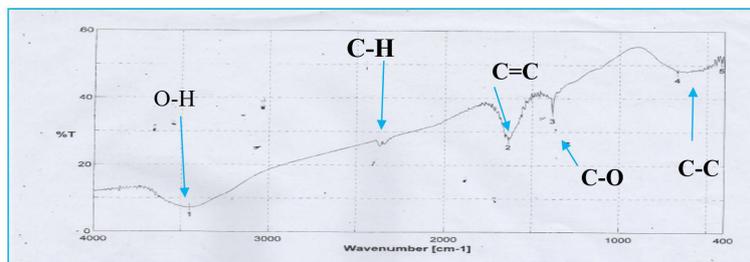


Fig. 19- FTIR spectrum of rGO based on chemical method.

OH groups at a wavelength of 3400cm^{-1} , which indicates the reduced of graphene oxide, as well as the lamellar structure has been traced. Of rGO by relying on FESEM with increasing magnification starting from $50\mu\text{m}$, where the images showed the presence of powder scattered of the prepared material, and the clarity of the stacked rGO slices increases with clarity when increasing the magnification to reach 500nm , as in Figure (20).

After that, rGO was milled in this way in order to improve its small particle size and measured on the scanner. Then, the size and radii of the

graphene oxide return product were traced back to the grinding, and the results were electronic scanning images as in the figure (21)

Radii was ranged from ($2\mu\text{-}300\text{nm}$) for sheets in this method, and the EDX –ray was studied as shown in the figure (22).

It can be concluded from the EDX spectrum of the synthesized rGO produced by this method that an energy band appears at an energy value of 0.277Kev , which is a characteristic peak of carbon. The weight percentage of carbon is 53.22% , and the atomic percentage of carbon is 62.7% . Also, an

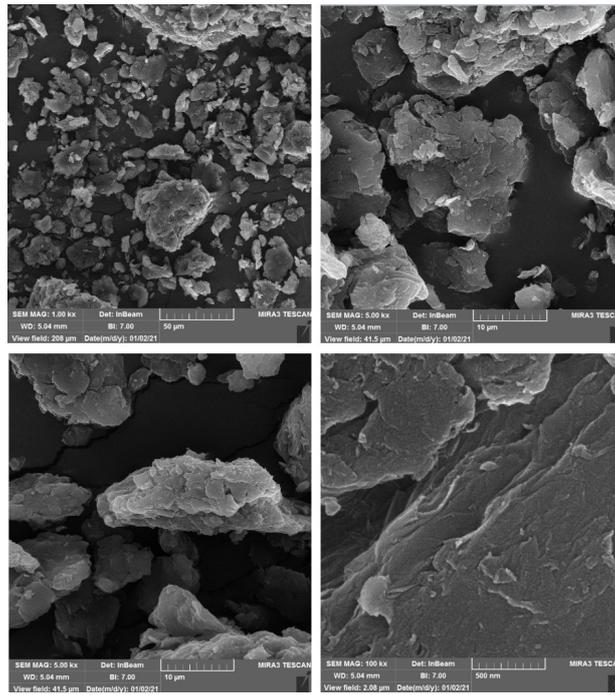


Fig. 20- FESEM of graphene oxide reduced based on chemical.

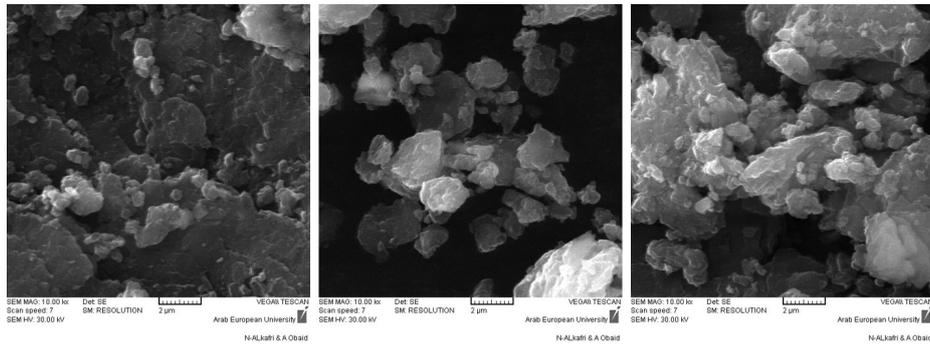


Fig. 21- FESEM of rGO based on chemical and then milled.

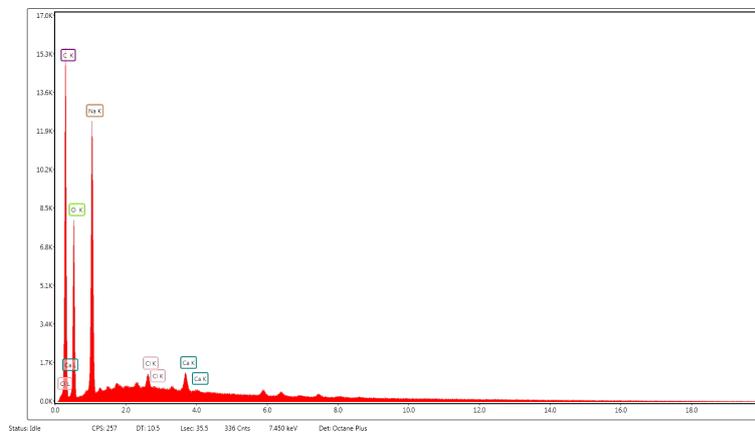


Fig. 22- EDX spectrum of reduced graphene oxide based on chemical.

Table 2- Comparison between the present research and literature

Name	Method	Weight %		Particle size	References
		C K	O K		
GO	Hummer	51.32%	44.27%	-	[66]
rGO	local olive leaf extract	-	-	(20 μm - 500 nm)	this work
	pure oleic acid, 440 °C and milled	72.04%	24.32%	(2 μm - 200 nm)	this work
	chemical method and milled	53.22%	29.67%	(2 μ -200nm)	this work
	furnace at 200 °C for 1hour	-	-	10 μ	[2]
	sodium hydroxide	38.52%	42.01%	(100 – 500)nm	[3]
Autoclave at ~170 °C for about 10 hours	68.28%	20.33%	-	[12]	

energy band appears at an energy value of 0.525 Kev, a characteristic peak of oxygen. The weight percentage of the oxygen spectrum is 29.67%, and the atomic percentage of oxygen is 27.1%. An energy band appears at an energy value of 1.105 Kev, a characteristic peak for sodium. The weight percentage of sodium is 15.11%, and the atomic percentage of sodium is 9.3%. The presence of sodium in this sample is due to the usage of sodium hypochlorite and sodium hydroxide. In addition, elements such as K, Mn, Ca, N, S, Cl are present in very small percentages, and their percentage does not exceed 1%. The comparison was made between the different methods used in this work and the methods reported in the literature. The results of the research were compared with the reference studies as shown in the table (2).

In this work, the best method for synthesizing reduced Graphene Oxide rGO was pure oleic acid treatment at a temperature of 440 °C and a heating rate of 2.3°C / min. The size of the formed particles was in the range of 200 nm-2 μm , and the EDX result revealed that the composition is 72.04% carbon and 24.32% oxygen.

4. Conclusions

In this research, Graphene Oxide (GO) was prepared from Graphite by Hummers method. GO was then reduced by three different methods, i.e. local olive leaf extract method, pure oleic acid method, and sodium hypochlorite and urea in an alkaline medium method. Pure oleic acid method at the temperature of 440 °C with a heating rate of 2.3 °C/min was the best method for preparation of reduced Graphene Oxide (rGO). rGO particle size was in the range of 200 nm-2 μm . EDX revealed that the chemical composition is 72.04% carbon and 24.32% oxygen. After that, rGO was synthesized by a chemical method in the presence of sodium hypochlorite and urea in an alkaline medium with a particle size of 200 nm-2 μm , and based on the

EDX result the composition is 53.22% carbon and 29.67% oxygen.

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