Carbonation and Preparation of Reduced Graphene Oxide Sheets from Cellulose

Reem Suhail Najm [1] and Ghazwan Hasan Al-Somaidaie[2]

[1,2]Department of chemistry, College of Education for Pure Science, Tikrit University, Tikrit, Iraq.

Abstract*: *The Preparation and characterization of Nano-cellulose graphene   without oxygen by reacting the active groups of pure cellulose with urea, and sodium hydroxide (R2), and Preparation of Nano cellulose graphene oxide (R3) NGO Using the modified Hummer method, by adding concentrated sulfuric acid H2SO4 with sodium nitrate, potassium permanganate and hydrogen peroxide H2O2 at a concentration of 30% , and Preparation of reduced Nano cellulose graphene (R4) by dispersing Nano- graphene oxide (R3), with concentrated hydrochloric acid (HCl) with an ultrasonic device, and adding hydrazine hydrate 80% (H2O. NH2 NH2), at a temperature of 100°C,

***Keywords:* *Cellulose, Nano cellulose graphene oxide, reduced Nano cellulose graphene , antibacterial*.**

1. Introduction

Nano carbons : Carbon is the chemical element symbolized by the symbol (C), the atomic number of which is six, it is found in the periodic table as a member of the fourteenth group, Where the shapes of carbon nanotubes were discovered with a very fixed nanometre size and hybridization is, sp2 [1], Carbon Nano is found in nature in two forms, diamond and graphite [2] , and materials related to carbon nanotubes such as graphene [3], fullerene [4], and nanotube [5], Nanotechnology in the future, where an important role in providing integration with Nano materials, (Nano carbon, Nano cellulose, etc. [6], Particles of carbon nanotubes include fullerenes (Cn, C60, C70, C84), sheet particles such as graphene (graphene oxide), as well as point particles such as activated carbon, carbon black, nanotubes single-walled, double-walled, few-walled or multi-walled, and diamond Nano and Nano Diamond [7-17], Nano Carbon Oxide, Nano carbon dioxide (CO) In some early studies on peeling, carbon was involved in oxidation and reduction by the German scientist (Schaghautt) in 1840 [18], and the Oxford chemist (Benjamin Brodie) was the first to prepare carbon dioxide (CO), Carbon by treating carbon with a mixture of nitric acid, potassium chlorate and sulfuric acid [19], The most common synthesis process for carbon dioxide is a modified Hummer that includes the use of sulfuric acid and potassium permanganate [20], The chemical composition of carbon oxides obtained from different methods of preparation, that their surface and the distances between their layers are similar to graphite, depending on the method of preparation, and that the distance between layers expands from (Ao3.4)(Ao13.2) CO is controversial and subject to intense competition, and the complexity of the structure and amorphous character of the material prevent accurate determination of the structure [21].

2. Research objective

3. Research methodology

3.1 Experimental: Materials and Chemicals.

Cellulose, Potassium permanganate, Sodium nitrate, Sulphuric acid, Hydrochloric acid, Potassium permanganate, Hydrogen peroxide, Hydrazine hydrate, Water, were obtain from Himedia & Scharlau &Poison as analytical grad.

3.2 Synthesis:

Synthesis of Nano cellulosic graphene without oxygen(R2).

Burning an appropriate amount of pure cellulose at a temperature of (100 ° C) with stirring until the color change is stable, then weights equal to the weight of cellulose from urea and sodium hydroxide were added to the ceramic jar and buried the jar with ground charcoal. (19-600) degrees Celsius / min for an hour, cool the product and wash it with distilled water (5 times x 15 ml) after ultrasonic atomization at a frequency of (50 Hz), and until the acidity function is stable at pH = 7 for the resulting black substance [22].
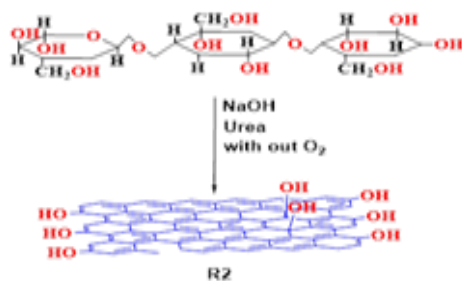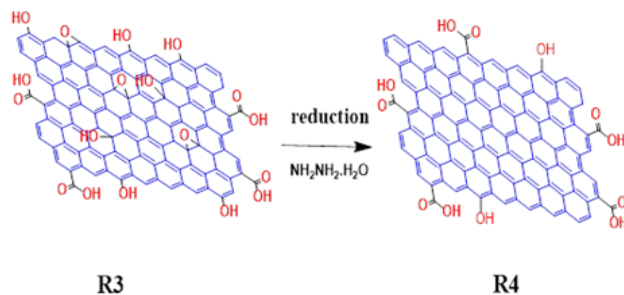

Equation 1. Synthetic of (R2).

3.3 Nano cellulosic graphene oxide synthesis by modified Hummer method(R3).

Put in a suitable flask 46 ml of concentrated sulfuric acid in an ice bath until the temperature homogeneity, then gradually add 1.5 g of sodium nitrate to it with stirring at 0 °C, add 1 g of the prepared graphene to the mixture gradually for 10 minutes, add 6 g to the mixture Gradually remove potassium permanganate over 15 minutes with caution and maintain the temperature below 20 °C, Leave the mixture in the ice bath for 5 minutes, raise the mixture from the ice bath and leave to stir magnetically for two hours, then add 46 ml of distilled water very slowly during 20 minutes, then raise the temperature to 98 °C for 20 minutes, then add 140 ml of Warm distilled water (50 °C) and left to stir for 10 minutes at room temperature, then 15 ml of hydrogen peroxide H2O2 at a concentration (30%), and left to stir for 30 minutes, then add 300 ml of distilled water and leave the mixture for 24 hours. Collect by centrifugation at 6000 revolutions/min (rpm), olive color, wash the precipitated product with 10% hydrochloric acid solution once, then with deionized water DIW five times (45 x 5 ml) until the pH is reached at pH = 7 and dry At a temperature of 60-70°C until the weight is stable [23].

## 3.4 Reduced Nano cellulosic graphene synthesis(R4).

Put in a suitable circular flask 0.1 g of the prepared graphene dioxide and add to it 1 ml of concentrated hydrochloric acid with a concentration of 37% with stirring until the solution becomes homogeneous (it became clear without plankton), 1 ml of aqueous hydrazine 80% was added to it, the mixture was raised at a temperature 100 °C for 2 h, the black precipitate was collected by centrifugation at 6000 revolutions per minute (rpm), washed with deionized water (DIW) (4 times x 20 ml) to remove unreacted hydrazine, and the product was dried in an oven at 70 °C [24].

Equation 2. Synthetic of (R4).

TABLE I: prepared compounds (R2-R4).

Comp No.	Structure and Name
R2	 GtC(without solvent)
R3	 GONC
R4	
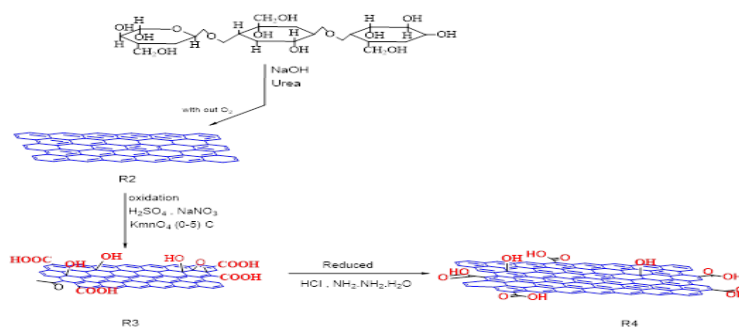
Scheme (1): Synthesis steps of prepared compounds (R2,R3,R4).

3.5. Measurement:

Melting point were determined using electro thermal melting point apparatus were(uncorrected) the FT-IR spectra were recorded in the University of Tikrit\ Department of chemistry, College of Education for Pure Science, Tikrit \Iraq, (FT-IR BURKER) in the range(400–4000/ cm -1),the Morphology determined using a Scanning Electron Microscopy,(FESEM- Belsorp\ TE SCAN Mini II / Czech Republic , Kashan University of Iran), X-Ray Powder Diffraction (XRD - Shimadzu 6000, Kashan University of Iran), Atomic Force Microscop(AFM (AFM Icon. Bruke Q600 US, Kashan University of Iran) , Thermal Gravimetric Analysis, (TGA, DTG, DSC , NETZCH SAT409PG\PC) , Biological activity(University of Tikrit\ Department of Biology, College of Science, Tikrit \Iraq.

4. Results and Discussion

Fig (1) ,The Compound(R2), Show that is spectra gave bands at (1558-1635) cm-1, due to the stretching of the double bond (C=C), and the emergence of distinct broad bands at the range (3419-3465) cm-1, , due to the stretching of the hydroxyl group and the appearance of a band at (2941) cm-1, due to the stretching of the aliphatic C-H bond.

Fig (2), for The Compound(R2), The X-ray spectrum (XRD), The value of the angle is(2 Θ)=24.271°, with a distance between layers (d = 3.66713), which is higher than graphite 27.92 nm, which indicates the presence of hydroxyl groups, and the increase in the distance between the layers indicates the occurrence of oxidation through the Debye-Shearer equation, then the granular size is calculated, which is equal to 84.62, the number of layers n equals 23.075, and it is clear from the spectrum that the sample retained good crystallinity in the composition of cellulose [25].

Fig (3), for The Compound(R2)The morphological images (FESEM) of, showed predominant micro-dimensions and this is consistent with its high granular size and indicates that the burning leads to the formation of graphite well under the conditions of the basic working method where the base works to deliver temperatures homogeneously and efficiently high chains of cellulose, thus ridding them of the oxygen atoms present in them by forming carboxyl groups and then releasing carbon dioxide[26]. From the images it is clear that the formed clusters with few interlayer distances, and the fact that the value of d is relatively high, this indicates the presence of cavities between the formed graphite clusters b with a homogeneous surface and clear edges of convergence c with the formation of Nano fibers d.

Fig (4), for The morphological (AFM) images by atomic force microscopy for the compound (R2) showed support for what appeared in the SEM images (a homogeneous spread a on the surface and edges b with the appearance of cavities and defects on them c with a similar phenomenon in The shape of the formed peaks d.

Fig (5)The thermal analysis as shown) for compound (R2) showed three stages of decomposition in TG and DSC, the first was at 102.23 degrees Celsius with a loss value of 63.10% TG and usually returns to thermal decomposition accompanied by the release of water molecules, and the second stage is at 600 degrees Celsius refers to the breaking of single and covalent bonds, The third stage represents the final dissolution of the layers after their formation, which is at 800 degrees Celsius [27].
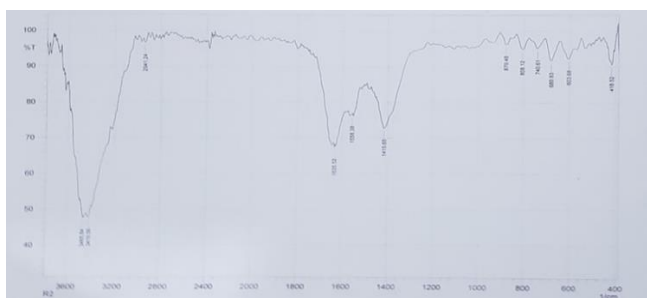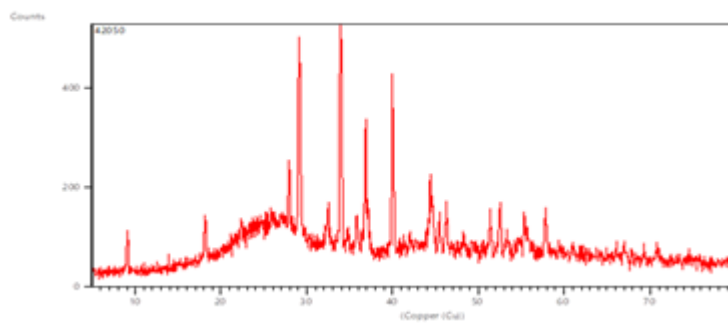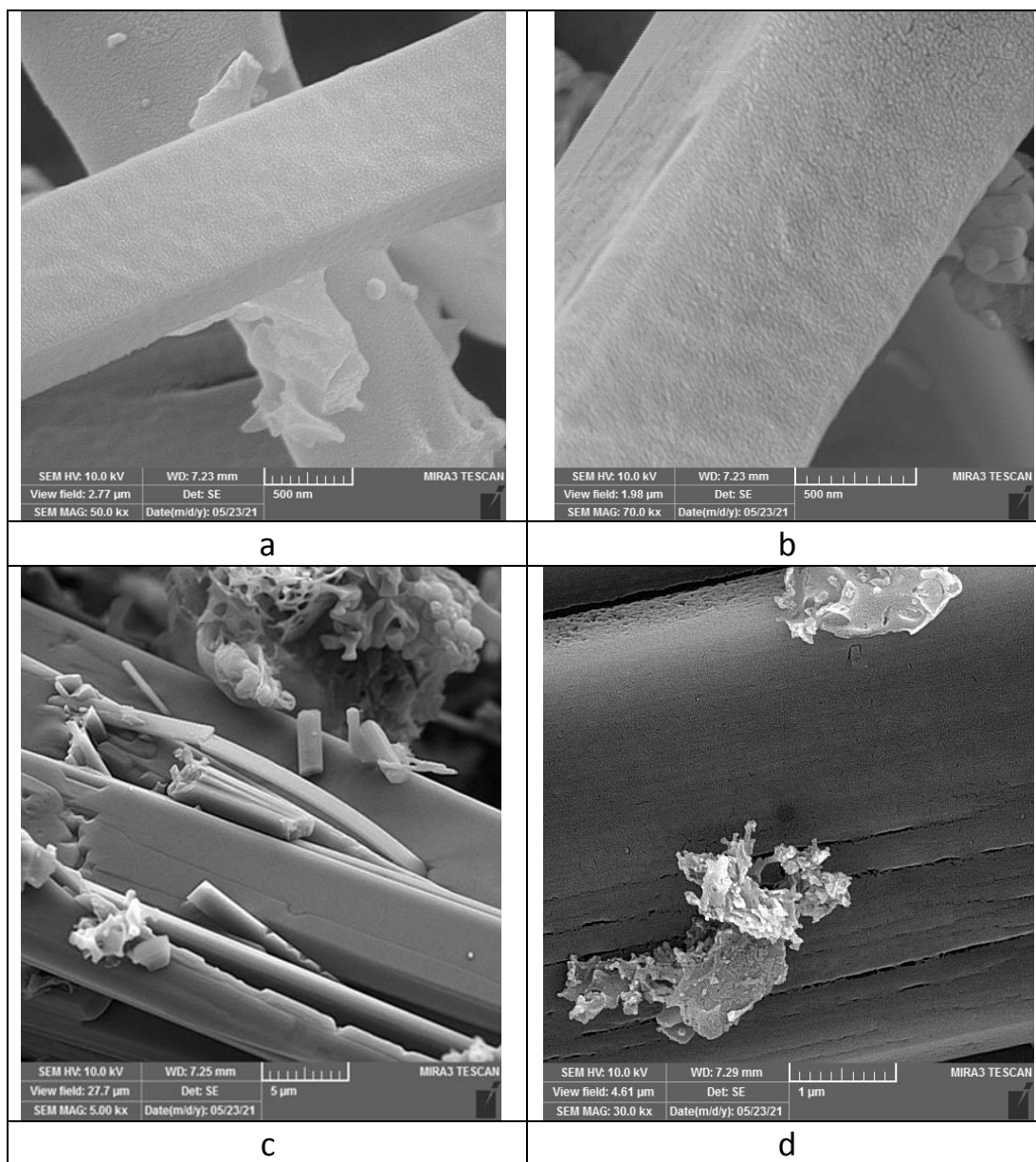
Fig. 1.FT-IR. for (R2).

Fig.2. XRD for (R2).

Fig.3. FESEM   for(R2).
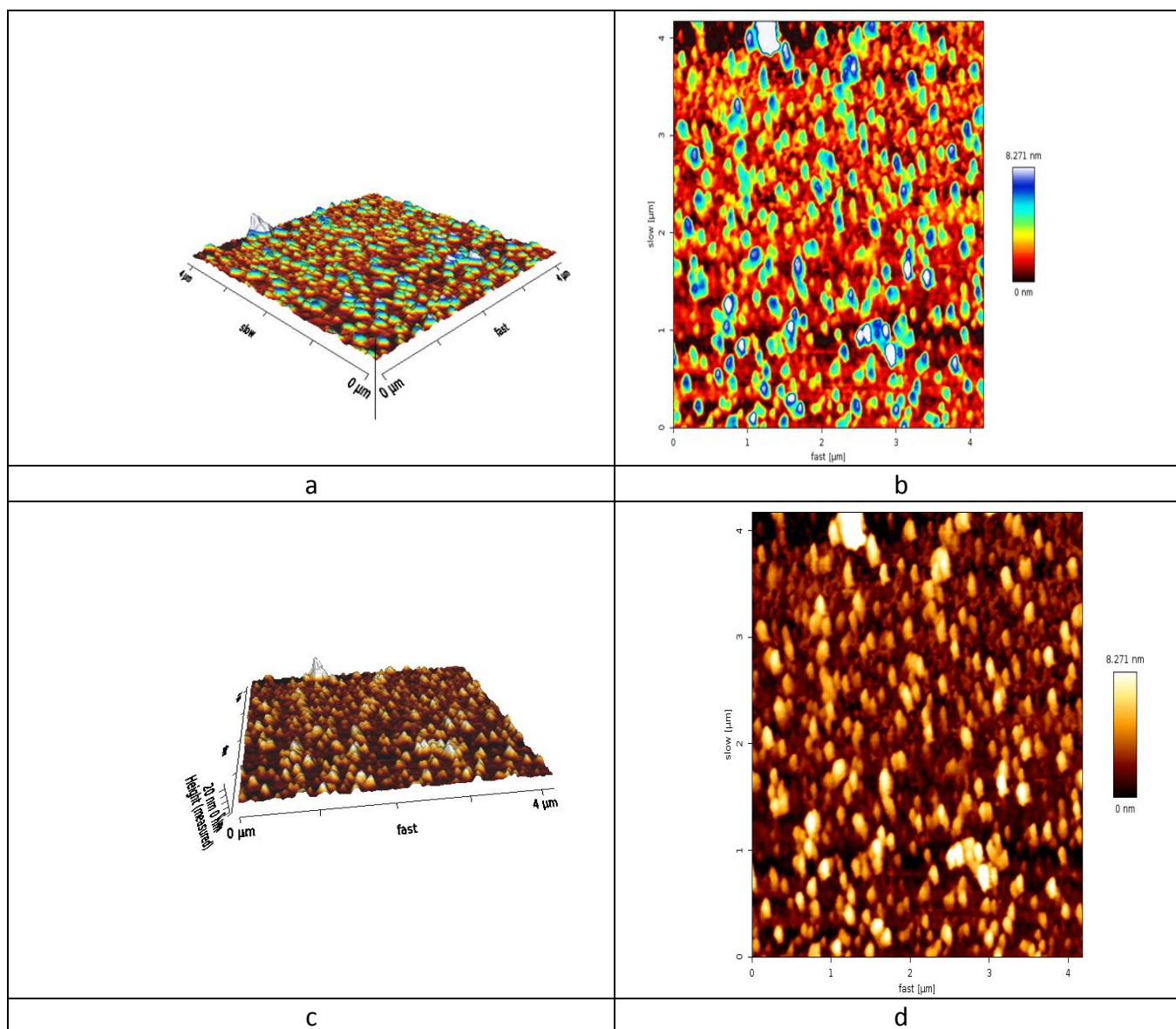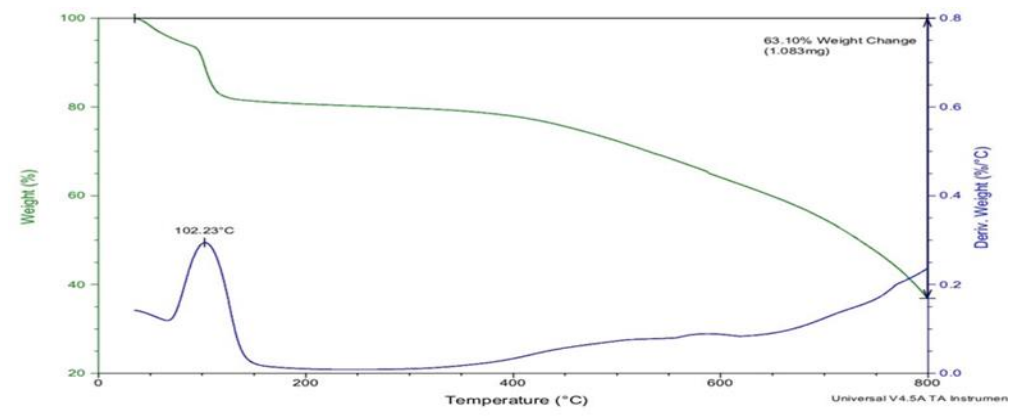
| a | b |
| c | d |

Fig. 4. AFM for(R2).

Fig.5. TG, DSC for(R2).

Fig (6),The infrared (IR-FT) spectrum of the compound (R3), showed distinct bands belonging to the

overlapping hydroxyl alcohol and carboxylic groups (OH), at (3415) cm-1, and two bands appeared at the range (1201, 1060). cm-1, belonging to the (C-O-C) group of the epoxy group, (165), and the appearance of the (v C = O) carboxylic band at the range (1635-1706 cm-1), The appearance of the bending and stretching bands at (2916) cm-1 belongs to the group (C-H), aliphatic, and the results were close as in the literature.

Fig (7), for The Compound(R3), XRD The X-ray spectrum of compound (R3) indicated an angle value indicated the angle value of(2Θ)= 32.371°, with a distance between layers (d)= 2.76340 , and with a grain size (D) equal to 17.73, and the number of layers (n) is 6.733 , These values are similar, as in the literature[28].

Fig (8), for The Compound(R3), Through scanning electron microscopy (FESEM), a clear change in the shapes of the plates a was observed compared to the parent sample R2 due to the efficiency of the oxidation and the appearance of the sample as having the lowest distance value between the layers according to the XRD calculations, this indicates that the sample is not homogeneous in surfaces, and the cavities appeared clearly between Sheets with a characteristic pattern no and graphene oxide in cracks on the b surface with semi-regular clusters spread cm and a structural pattern of different crystal shapes on the d surface.

Fig (9), for The Compound(R3), AFM images by atomic force microscopy The process of quasi-homogeneous diffusion of the assemblies which may be attributed to the survival of the bud carbonous outgrowths formed in the complex (R2) (a), which have sharp peaks b with better clarity compared to the SEM of plates c and their gaps d,.

Fig (10), for The Compound(R3), The first five stages appear at (78.62) due to the beginning of the decomposition of the hydroxyl, carbonyl and epoxy groups and the loss of CO_2. The second (274.59), the third (655.44), and the fourth at (228-327) are attributed to the breaking of the bonds of the carbon buds formed in their various forms, and then the stage was The fifth at 600 degrees Celsius is to break the carbon bonds (C-C)) and (C=C).
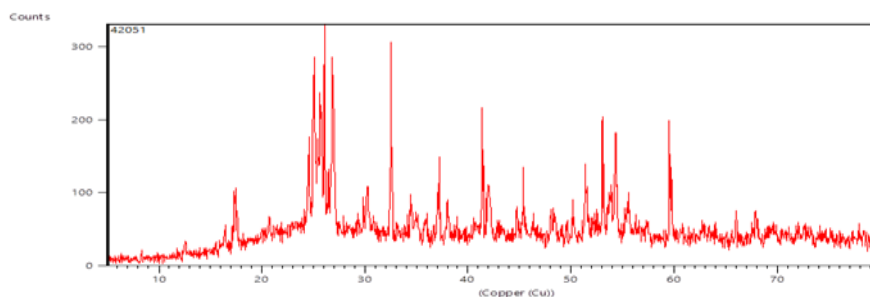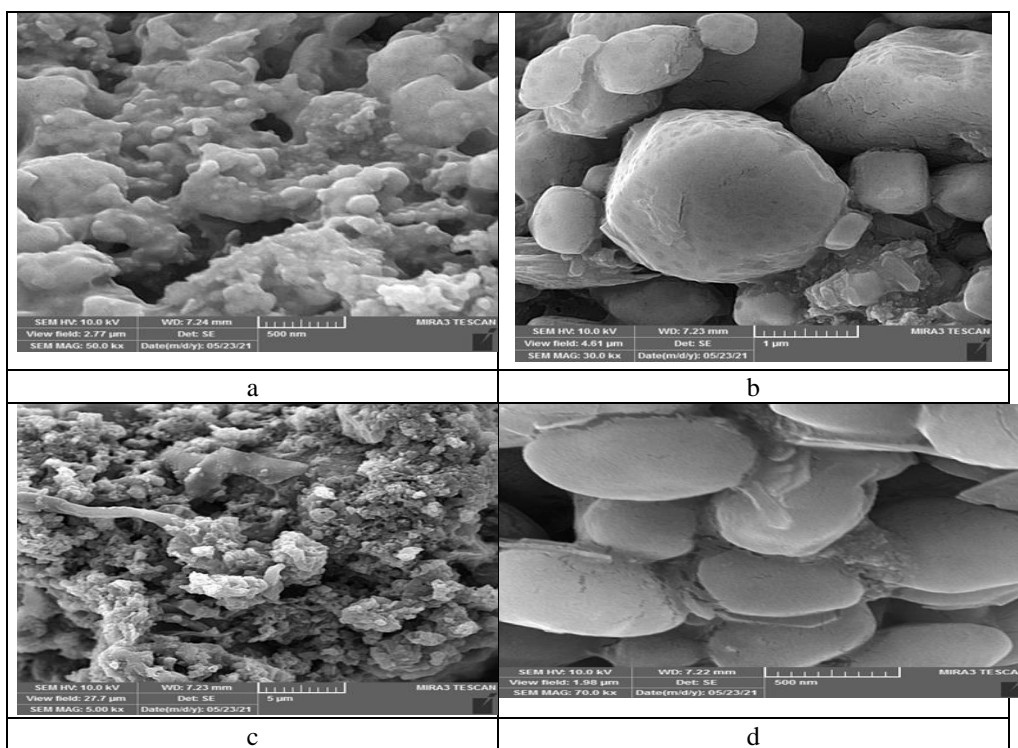

Fig.6. FT-IR. for (R3).
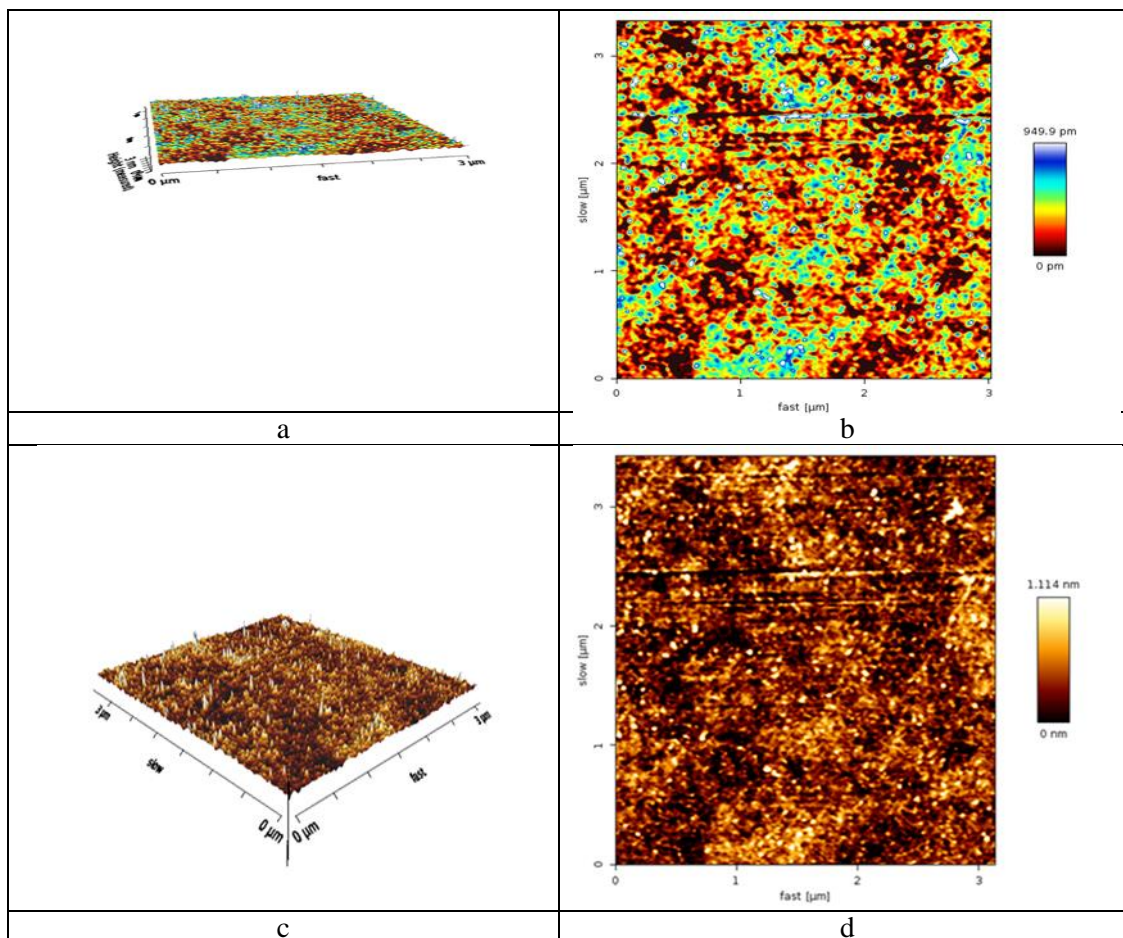

Fig.7 XRD. for (R3).

Fig.8. FESEM for (R3).

Fig.9.AFM for (R3)

Fig(10), for the Compound(R4) , FT-IR, The disappearance of the epoxy group due to the reduction process, however, the hydroxyl group peaks are still noticeable, although it is less intense compared to those of graphene oxide, The hydroxyl alcohols (ν OH), and the appearance of bands at the range (3307, 3062, 3097 cm -1) refer to the hydroxyl carboxylic groups, while the absorption peak at (1647) cm -1, indicates the hardening of the carbonyl carboxylate (ν C = O), and the absorption peak at (1577, 1596) cm -1, indicates the presence of the stretching of the double bond(νC = C),Indicates that graphene sheets were formed during the reduction process of graphene oxide.

Fig(11), for the Compound(R4) XRD , The X-ray spectrum of compound (R4) indicated an angle value indicated the angle value of(2 Θ)= 29.3733 °, with a distance between layers (d)= 3.04078 Å , and with a grain size (D) equal to = 21.67190n , and the number of layers (n) is 7.1270, These values are similar, as in the literature [29].

Fig(12), for the Compound(R4),FESEM, images of the compound (R4), by scanning electron microscope, The morphology of the sheets of reduced graphite oxide nanoparticles (R4) did not change much from that of graphene oxide sheets, but it is more pure due to the removal of water molecules trapped between the layers and oxidized assemblies on the plate and at varying distances. Nanoparticles with twisted edges indicative of a previous influx of moisture during removal.

Fig(13), for the Compound(R4),AFM: images by atomic force microscopy, The images give less widespread protrusions on plate a with a clear ripple b,c and clear cavities between plates d.

Fig(14), for the Compound(R4), The thermal analysis: Thermal decomposition was in one stage, which is (47.87.%) TG, indicating an increase in the stability of the sample, as the decomposition took place at (269.74) degrees Celsius, followed by thermal stability up to 800 degrees Celsius, and this indicates that the shapes are very close in their thermal energy, which is represented by the remaining structures on the surface and the edges of the lamina reduced.
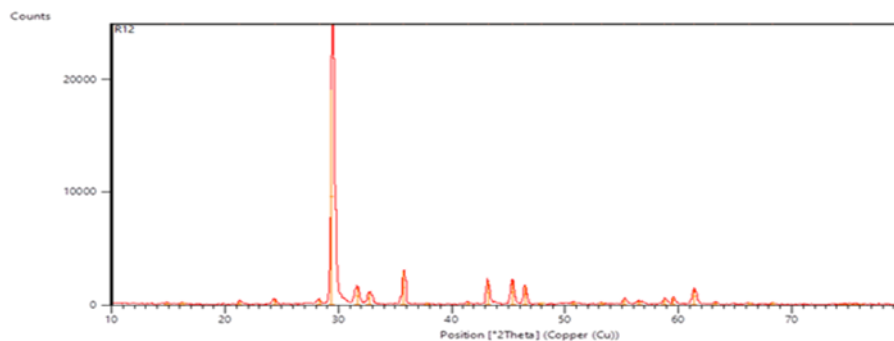

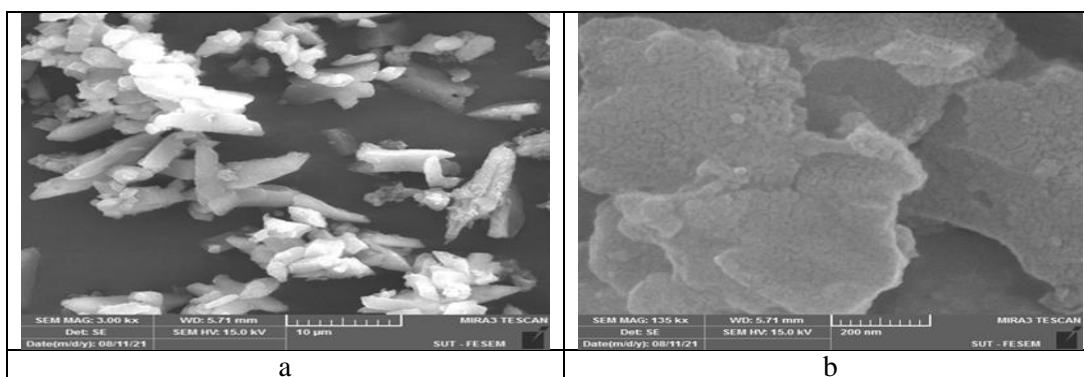Fig. 10. FT-IR. for(R4).

Fig. 11.XRD. for(R4).
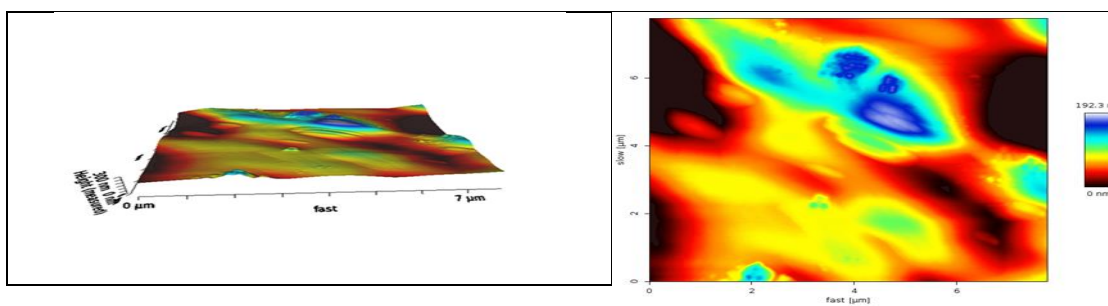
Fig. 12. FESEM. for(R4)
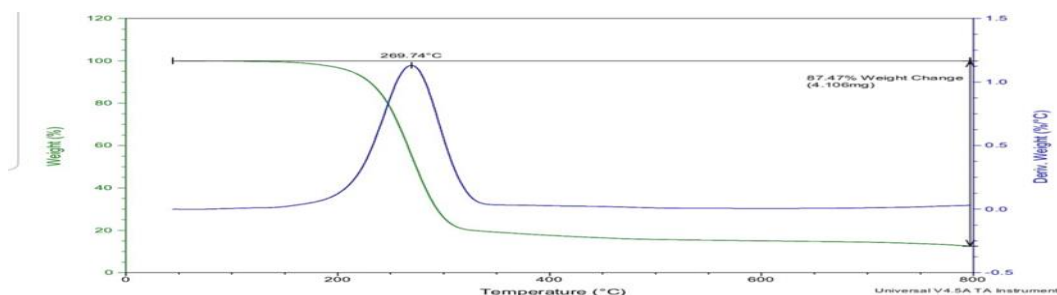

Fig. 13.AFM for(R4).

Fig14. TG, DSC. for(R4)

5. Biological activity

The results of the antibacterial screening. The some compound at a concentration of (50,100,150) mg/ml against all bacterial have been found, The inhibition zones were measured in mmandm , The compounds prepared in vitro effective inhibition towards our high Two types of bacteria namely: Staphylococcusaureus,E.coli, The compound (R4) showed high inhibitory values against both types of bacteria due to the fact that the compound (R4) which is reduced carbon dioxide contains an effective group, the hydroxyl group, which plays an important role towards bacteria.

TABLE II The inhibitory activity of the prepared compounds in the growth of a number of positive and negative bacteria (the diameter of the inhibitory circle measured in mm.)

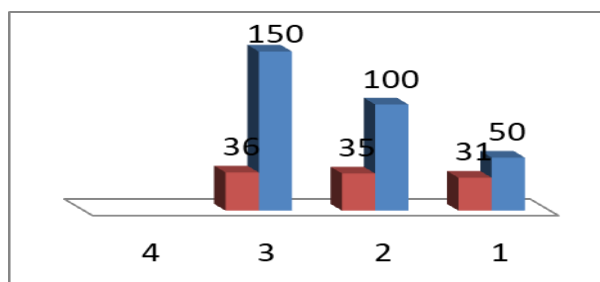| Comp. No.	Conc.	Staphylococcus aureus	E. coli
R3	50	-	-
	100	-	-
	150	-	-
R3	50	+++	++++
	100	+++	+++++
	150	+++	+++++

Fig. 15. Inhibitory activity of compound R4 against Staphylococcus Aureus.
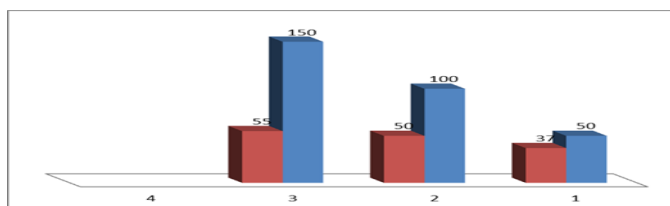
Fig. 16. Inhibitory activity of compound R4 against,E.Coli.

6. Acknowledgements

References

[1] H. Xu, S. M. Anlage, L. Hu, and G. Gruner, "Microwave shielding, of transparent and conducting single-walled carbon nanotube films Applied Physics Letters, vol. 90, no. 18, Article, ID 183119, (2007), doi:10.3390/nano9020164.(Journal Online Sources style) .

[2] G.M. Odegard ,S.J. V.Frankland ,and T.S. Gates, Effect of nanotube functionalization on the elastic properties polyethylene nanotube composites, AIAA Journal, vol.43, no. 8,pp.1828-1835.(2005), doi:10.7569/Jrm.2013.634115. (Journal Online Sources style).

[3] Yang, M. C. Gupta, and K. L. Dudley, "Towards cost, efficient EMI shielding materials using carbon nanostructure based Nano composites, Nanotechnology, vol.18,no.43, Article ID 345701,(2007), doi:10.1016/j.jconrel.2012.06.039. (Journal Online Sources style).

[4] Y.Zhou,F.Pervin,L.Lewis,andS.Jeelani,"Fabricationand characterization of carbon/epoxy composites mixed with multi-walled carbon nanotubes, Materials Science and Engineering A , vol. 475, no. 2, pp. 157–165,(2008), doi:10.1021/cr900339w.(Journal Online Sources style).

[5] R. Zhang, A. Dowden, H. Deng, M. Baxendale, and T. Peijs, Conductive network formation in the melt of carbon nanotube/thermoplastic polyurethane composite, Composites , Science and Technology, vol. 69, no. 10, pp. 1499–1504,(2009), doi:10.5772/61410. (Journal Online Sources style).

[6] D. Xu and Z. Wang, "Role of multi-wall carbon nanotube network in composites to crystallization of isotactic polypropylene matrix, Polymer, vol. 49, no. 1, pp. 330–338,(2008), doi:10.1002/adma.201300256. (Journal Online Sources style).

[7] Steiner SA, Baumann TF, Bayer BC, Blume R, Worsley MA, MoberlyChan WJ Shaw EL:, Nanoscale zirconia as a nonmetallic catalyst for graphitization of carbon and growth of single- and multiwall carbon nanotubes. Jam, chem, Soc, 131(34),12144-12154 ,(2009), doi:10.3390/nano9121758. (Journal Online Sources style).

[8] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, R. E. Smalley Nature,318,162,(1958), doi:10.1021/acsami.6b11034. (Journal Online Sources style).

[9] K. Tanigaki, T. W. Ebbesen, S. Saito, J. Mizuki, J. S. Tsai, Y. Kubo, S. Kuroshima, Nature,352,222,(1991), doi:10.1002/smll.201901724. (Journal Online Sources style).

[10] A. Y. Ganin, Y. Takabayashi, Y. Z. Khimyak, S. Margadonna, A. Tamai, M. J. Rosseinsky, K. Prassides, Nat. Mater.7,367,(2008), doi:10.1002/jbm.a.30073. (Journal Online Sources style).

[11] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I, V. Grigorieva, A. A. Firsov, science , 306, 6666, (2004), doi:10.1039/c8an00637g. (Journal Online Sources style).

[12] K. Yanagi, K. Iakoubovskii, H. Matsui, H. Matsuzaki, H. Okamoto, Y. Miyata, Y. Maniwa, S. Kazaoui, N. Minami, H. Kataura J. Am. Chem. Soc., 129, 4992,(2007), doi:10.1021/acsami.7b06598. (Journal Online Sources style).

[13] Kausar. A. Performance of polyaniline doped carbon nanotube composite. American Journal of Polymer Science & Engineering,5(1) 43-52,(2017), doi:10.1208/s12249-019-1466-0. (Journal Online Sources style).

[14] Kausar. A. Shielding Efficacy of Polymeric Nano- Structure. Res, J Nanosci Engineer, 2:9-14, (2018), doi:10.1021/acsami.9b03421. (Book style with paper title and editor).

[15] Kausar. A Thermal conductivity measurement of polyvinyl, pyrrolidone/polyethylene/graphem nanocomposite, NanosciNanotechnol ,6:34-36,(2016), doi:10.1021/acsami.5b11241. (Book style with paper title and editor).

[16] Review: V. K. A. Sreenivasan, A. V. Zvyagin, E. M. Goldys, J.phys. Condens Matter, 25, 194101,(2013), doi:10.3390/nano9040655. (Book style with paper title and editor).

[17] Y. Liu, V. N. Khabashesku, N. J. Halas,J.Am. chem. Soc. 127,2712,(2005), doi:10.1021/acs.nanolett.6b04405 . (Book style with paper title and editor).

[18] C. Schafhaeutl, "Ueber die Verbindungen des Kohlenstoffes mit Silicium Eisen und anderen Metallen, welche die verschiedenen Gallungen von Roheisen Stahl und Schmiedeeisen bilden," Journal für Praktische Chemic vol. 21, pp. 129 -157,(1840), (Book style with paper title and editor).

[19] B. C. Brodie, "XIII. On the atomic weight of graphite," Philosophical Transactions of the Royal Society of London ,vol.149,pp:249-259,(1859), doi:10.1038/nnano.2014.248. (Book style with paper title and editor).

[20] D. C. Marcano, D. V. Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, et al., "Improved synthesis of graphene oxide," ACS Nano vol. 4, pp:4806-4814. (2010), doi:10.1080/10408444.2017.1391746. (Book style with paper title and editor).

[21] H.Becker,G.O.Withaner, J.Sauder ,N.West and G. J, Prakt, Chemistry , 311,646, (1989), doi:10.3389/fimmu.2017.00763. (Book style with paper title and editor).

[22] M. Sevilla, A.B. Fuertes. Mater. Chem. Phys. 113, 208 (2009), doi:10.1002/smll.201102539. (Book style with paper title and editor).

[23] L. Shahriary and A. A. Athawale, "Graphene oxide synthesized by using modified hummers approach," Int J Renew Energy Environ Eng vol. 2, pp58-63(2014), doi:10.3109/17435391003628713. (Book style with paper title and editor).

[24] L. Tang, Z. Yang, F. Duan, M. Chen, Colleoids and Surfaces A physicochemical and Engineering Aspects, 520, pp.184-192,(2017), doi:10.1016/j.bbrep.2015.08.008, doi:10.3390/nano9030337. (Journal Online Sources style).

[25] M.L.Nelson and R.T.O'Connor, Journal of Applied Polymer Science, 8(3), pp: 1325-1341,(1964), doi:10.1021/acs.langmuir.6b01079.(Book style with paper title and editor).

[26] F.Carrillo, X. Colom, J.J. Suñol, and J.Saurin a. European, Polymer Journal, 40(9), pp: 229-2234,(2004), doi:10.1002/anie.201305137 .(Book style with paper title and editor).

[27] A. Alemdar, and M. Sain,. Bioresource Technology, pp. 99,1664-1671,(2008), doi:10.1016/j.carbon.2013.10.031(Journal Online Sources style).

[28] Aftan, M.M, Jabbar ,M.Q. Dalaf, A.H.,& Salih, H.K, application of biological activity of oxazepine and 2-azetidinone compound and study of their liquid crysallin behavior , Materials Today , Proceedings , 43, 2040 -2050, (2021), doi:10.1016/j.carbpol.2018.12.010. (Journal Online Sources style).

[29] Dalaf , A. H.Jumaa, F. H. &Jabbar , S. A.S. Synthesis and characterization of some 2,3-dihydroquinozoline and evaluation of their biological activity ,Tikrite journal of pure Science ,23,(8):66-67(2018), , doi:10.1098/rsos.172017. (Book style).