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Role of Ozone and UV Light on Oxygenated Groups Attached with Commercially Prepared Graphene Oxide.

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ABSTRACT

A low cost, simple and commercial method was studied to prepare graphene oxide (GO) Nano sheets for hydrogen storage. The technique was modified using ozone and UV-light treatment. The covalent functionalization between oxygenated groups and graphene oxide surface area increased successfully up to 31.5%. Fourier transform infrared spectroscopy (FTIR), Scan Electron Microscope (SEM) and energy dispersive X-ray analysis (EDX) shows different type of oxygen functionalities and fluffy surface morphology. The X-ray diffraction (XRD) gives more interplanar distance for graphene oxide (GO) and modified graphene oxide (MGO) prepared indicated by both broad and sharp peak.

Keywords: graphene, carbon nano-sheets, ozone, hydrogen storage, reducing KH_2PO_4

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INTRODUCTION

Graphene oxide and graphene nano-sheets have been focused as efficient and safe H₂ strong method. Exfoliated graphite oxide and graphene, besides low cost they have environmental friendliness [1] and convenient surface chemistry. The presence of oxygen groups such as RooH – RooR – oH –c=o and –cooH) enhance the adsorbate- adsorbent leading to more hydrogen strong capacity. Ozone is an easy way to modify carbon resulting carboxyl, hydroxyl groups, ethers and carboxyl groups. Adding ultraviolet conditions could enhance and improve ozone treatment [2-5].

The graphene oxide nano-sheets are water-dispersible due to carbonyl and carboxyl groups by modification with oxidation method [6]. Reduced graphene shows stability in water and many organic and inorganic solvents. Microwave treatment can improve the reaction efficiency and remove oxygen functional groups on graphene oxide surfaces. Reducing sugar can be used as environmental friendly reductant, thus graphene oxide stability can hold several days and stability can be measured using UV-Vis spectroscopy [7]. Herein, graphene oxide as Nano porous carbon sorbents has the ability to bind molecular hydrogen with excellent application [8]. Infra Red FTIR-analysis is studied for all experiments, the (SEM) scan electron microscope characterize micro pore surface area and wt.% oxygen distribution [9]. The X-ray diffraction (XRD) and TDA/TDA thermal analysis is studied for graphite, graphene oxide and graphene.

MATERIALS AND METHODS

Commercial graphite fine powder Extra Pure (Loba Chaemie Pr Ltd, 107). Other chemicals were from Sigma-Aldrich Inc., Japan.

Preparation of graphene oxide (GO) and reduced graphene oxide(RGO).

Graphene oxide (GO)

Modified Hummers method was used to prepare graphene oxide, where (15)gm KMnO₄ and (5)g graphene powder were put, in 500 ml. round bottom flask and stirred until homogeneous. A (9:1) mixture of sulfuric acid (H₂ SO₄) and phosphoric acid (H₃PO₄) were sulfuric acid was added to homogeneous mixture. All system was placed in ice-water bath the reaction was heated to 50° C with stirring 12h. Stirring continued until liquid paste was formed. The liquid paste was washed with distilled water until pH value was reduced down to 6. The filter cake was dried in vacuum oven at 80°C for 48h.

Preparation of reduced graphene (RGO) by Exfoliation process

The dried graphite oxide was chemically exfoliated at 80°C water bath for one hour. The suspension was subjected 15 min. to (540 rpm, 5 min. per cycle) yielding the final product.

Preparation of ozonated modified graphene

A continuous flow of ozone gas 2LO₃/ min flow rate in 200ml (KH₂ PO₄ 23.86 g/L solution) or double distilled water (DDW) was subjected to final (GO) product into ozone system shown in Fig(1).

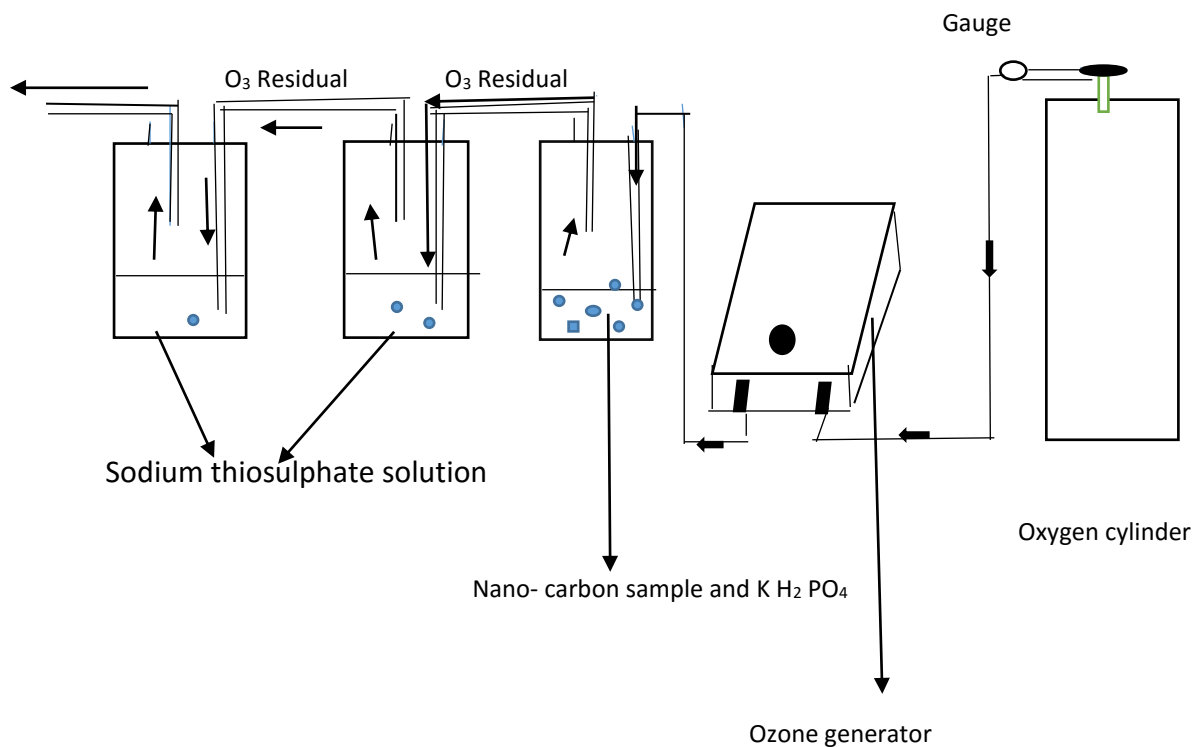


Fig.(1) System of ozone treatment for nano carbon material (Graphene)

Ozone treatment

The treatment temperature was varied from 25°C , 60°C , 70°C ,90°C till 115°C, in water bath and time of treatment was stabilized 20 min. for single experiment of (GO) in DDW and /or KH₂ PO₄. The treatment was repeated at ambient temperature (25°C) for 5,10,15 and 20 min. Then the treatment for (GO) was fixed at 25°C and 15 min but ozone dose was varied 2L /min, 4L/min, 6 L/min and 8L/min

One oxidation experiment was repeated at 15 min and 2L/min ozone dose at ambient temperature in presence of UV-40 WT/h.

Characterization:

Fourier transform infrared spectroscopy (FTIR) spectra of graphite, graphene oxide and modified graphene oxide was measured in 4000-400 cm⁻¹ wave number range. The functional groups introduced on modified graphene surface with ozone treatment were studied.

(SEM) Scan Electron Microscope and (EDX) –Energy dispersion X–ray Analysis

The selected samples of modified graphene oxide were studied by SEM graphene oxide surface. The (SEM) model Quanta 250 FEG (yield Emission Gun) attached with EDX Unit (Energy Dispersive &ray Analysis with accelerating voltage 30 K,V., modification 14X up to 100000 and resolution for Gun In).

X-Ray Diffraction

PA Analytical X-Ray Diffraction equipment mode X' pert PRO with Monochromatic Cu- radiation ($\lambda = 1.5406 \text{ \AA}$) at 50 K.V., 40 M.A. and scanning speed 0.02°/sec. were used. The reflection peak between $2\Theta=2^\circ$ and 60° ,

corresponding spacing (d, A^0) and relative intensities (I/I^0) were obtained. The different charts and relative intensities are obtained and compared with ICDD files.

RESULTS AND DISCUSSION

FTIR spectra for (GO) thermally reduced and its modification using ozone is studied.

Fig (2) shows the (GO) sample before modification with ozone showing a broad peak appears at (3222 cm^{-1} and 3429 cm^{-1}) generated from the stretching vibration of $-OH$, $COOH$, $C-OH$, and H_2O . The sharp peak in adjacent of (3747 cm^{-1}) indicated vibration at $C-OH$. The assigned peak at (998 cm^{-1}) is $C=O$ stretching.

Comparing oxygenated groups presents in Fig(2) with the following treated (GO), Fig. (3), samples with ozone treatment at different dose 2,4,6 and $8\text{ LO}_3/\text{min}$ for 15 min each singly at room temperature.

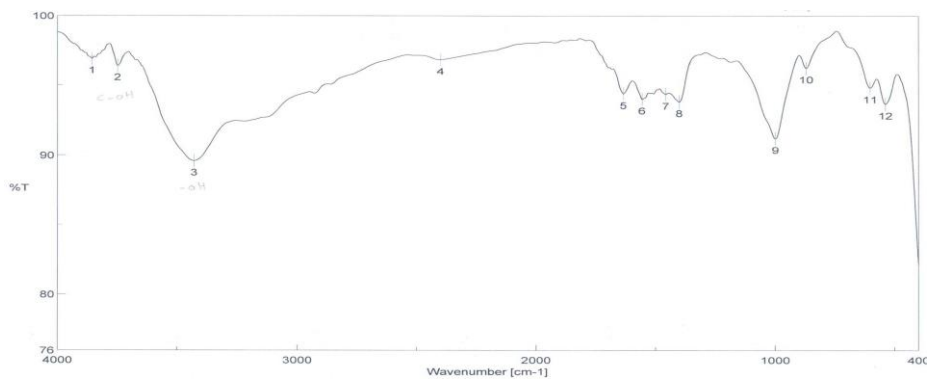


Fig (2): Original nano carbone grafite befor ozone treatment

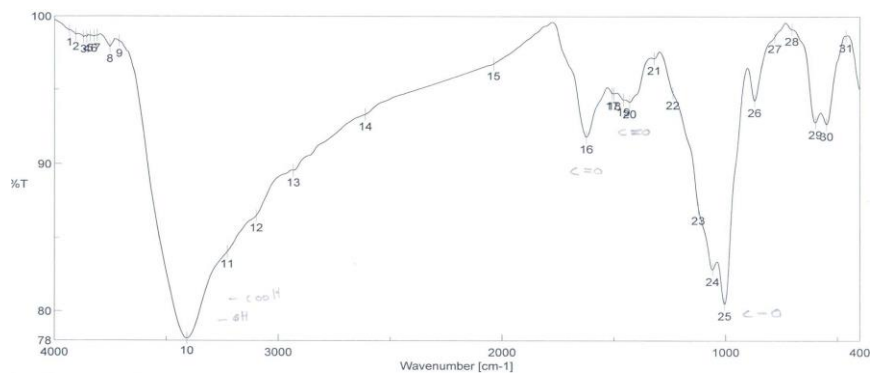


Fig (3): ozonated thermal treated Nano carbon graphene in presence of KH_2PO_4 15 min at room temperature.

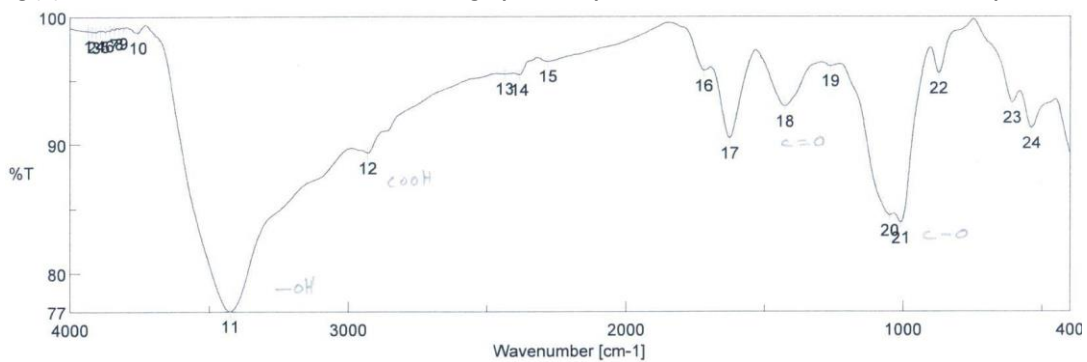


Fig (4):Effect of ozonation $4\text{ LO}_3/\text{min}$ 15min on introducing oxygenated groups to grapheme at room temperature

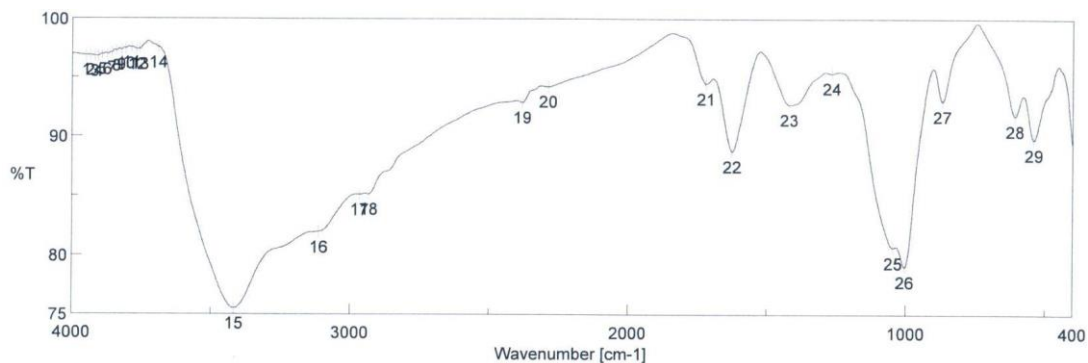


Fig (5): Effect of ozonation 6LO₃\min 15min on introducing oxygenated groups to graphene at rom temperature

Fig (3) showed the best introduced oxygen functional groups to (GO) in presence of K₂HPO₄ and 2LO₃/min. during 20 min. treatment time. The -OH and COOH broad peak appeared at (3408 cm⁻¹) while the C=O peaks were signed to (1429 cm⁻¹ – 1623 cm⁻¹). The sharp peaks at (1004 cm⁻¹ - 869 cm⁻¹) indicated the increase in C-O groups to graphene oxide treated sample. Fig (4), (5) and (6) shows the modification of (GO) with ozone flow rates 4, 6 and 8 LO₃/min., at room temperature and without reducing agent K₂HPO₄. Fig (5) with ozone oxidation of flow rate 6 LO₃/min illustrates the best broadness of -OH and -COOH groups at (3111 cm⁻¹ – 3416 cm⁻¹).

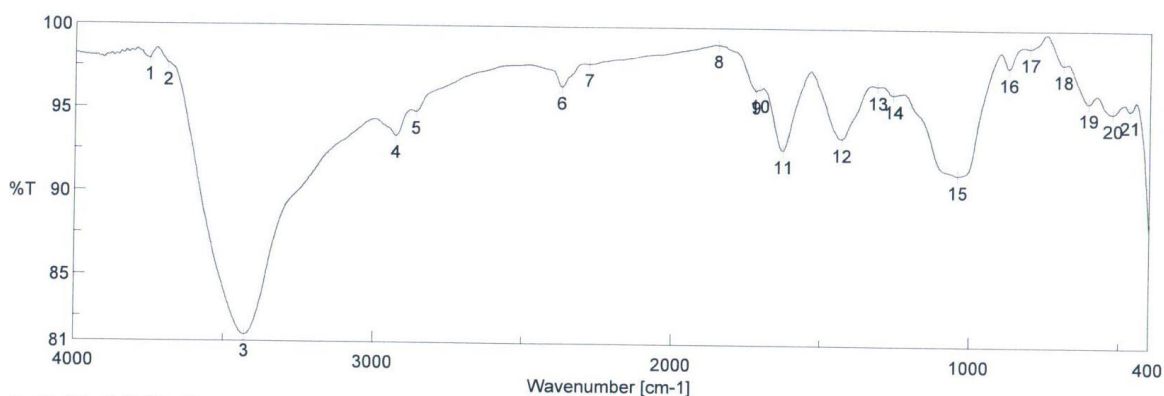


Fig (6): Effect of ozonation 8LO₃\min 15min on introducing oxygenated groups to graphene at room temperature

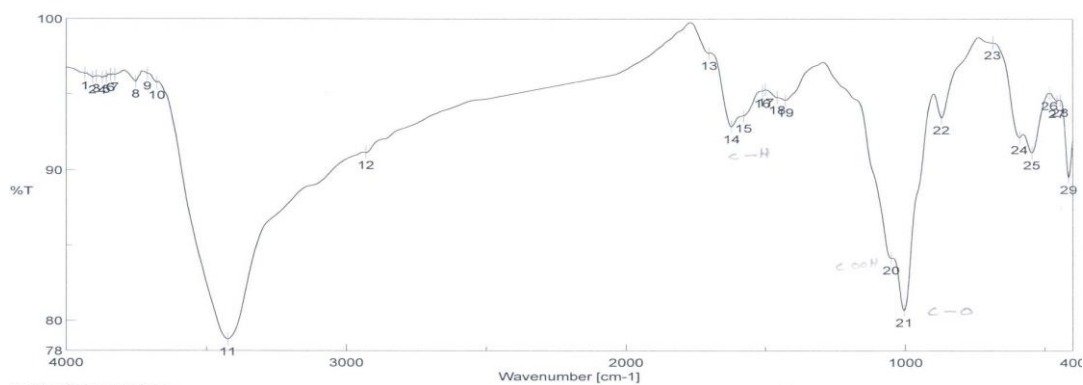


Fig (7): Effect of ozonation 2LO₃\min 15min on introducing oxygenated groups to graphene at 60 °C

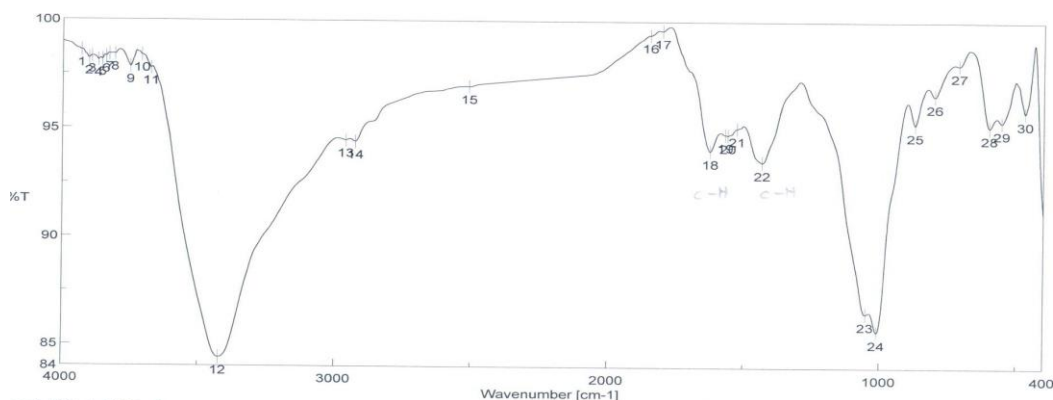


Fig (8) Effect of ozonation 2LO₃\min 15min on introducing oxygenated groups to graphene at 70 °C

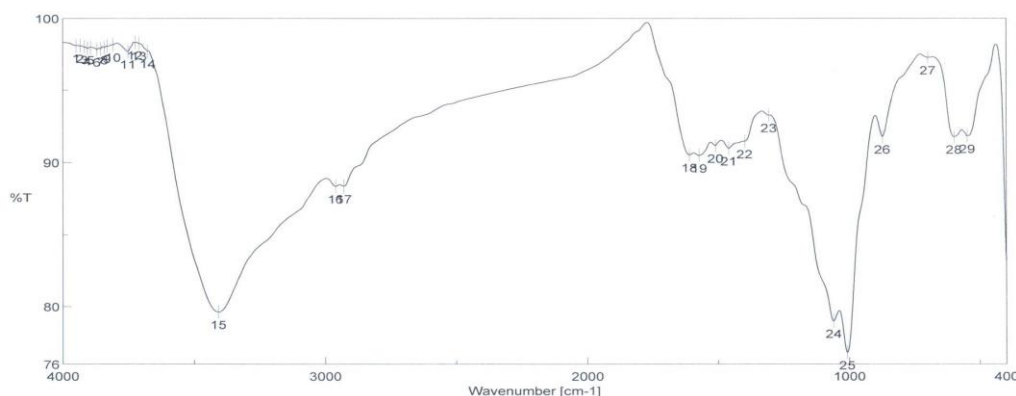


Fig (9): Effect of ozonation 2LO₃\min 15min on introducing oxygenated groups to graphene at 80 °C

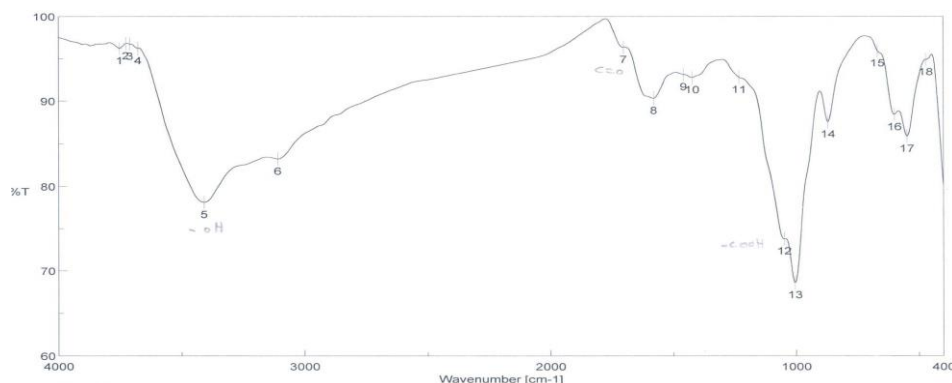


Fig (10): Effect of ozonation 2LO₃\min 15min on introducing oxygenated groups to graphene at 90 °C

Figs (7,8 ,9 ,and10) shows the (GO) modification with ozone flow rate 2L O₃ /min in presence of reducing agent K₂HPO₄ at different temperatures 60°C , 70°C , 80°C and 90°C.

Fig (7) where treatment was performed at temperature 60°C. The peaks at (1560 cm⁻¹, 1526 cm⁻¹ and 1624 cm⁻¹) indicates increase C-H group with increasing temperature while sharp peak at (1004 cm⁻¹– 1050 cm⁻¹) corresponding for C-O group COOH indicate more intensity .Fig (8) shows ozone treatment at temperature 70°C indicating more intensity of –OH attached groups compared to peaks appeared at previous Figure.

Fig (9) and Fig (10) where ozone treatment worked at 80°C and 90°C as higher temperatures shows decrease in oxygenated groups. Heat treatment decreased –OH at(3408 cm⁻¹ and 3409 cm⁻¹) respectively and increased C=O at (1399 cm⁻¹– 1610 cm⁻¹) and (1457 cm⁻¹– 1579 cm⁻¹– 1702 cm⁻¹) respectively.

The decrease in -COOH and OH groups intensity at ($1007\text{ cm}^{-1} - 1059\text{ cm}^{-1}$) and ($1004\text{ cm}^{-1} - 1047\text{ cm}^{-1}$) during increasing temperature of reaction from 80°C up to 90°C was investigated.

A significant decrease for -OH peaks at ($3116\text{ cm}^{-1} - 3423\text{ cm}^{-1}$) appears in the chart while an increase for C=O and C-O at ($1473\text{ cm}^{-1} - 1634\text{ cm}^{-1}$) respectively besides the increase of -COOH groups. i.e. The reduced (GO) showed O-H and C=O stretching vibrations and observed C-O group which become more sharp after K_2HPO_4 reduction.

Scan Electron Microscope (SEM) and Energy dispersive X-Ray spectrometer (EDX)

The surface morphology of graphite and samples and those modified with ozone oxidation were studied by (SEM) and (EDX).

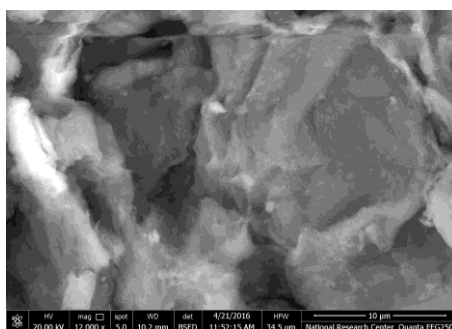


Fig (11)a: SEM image of graphite without chemical treatment

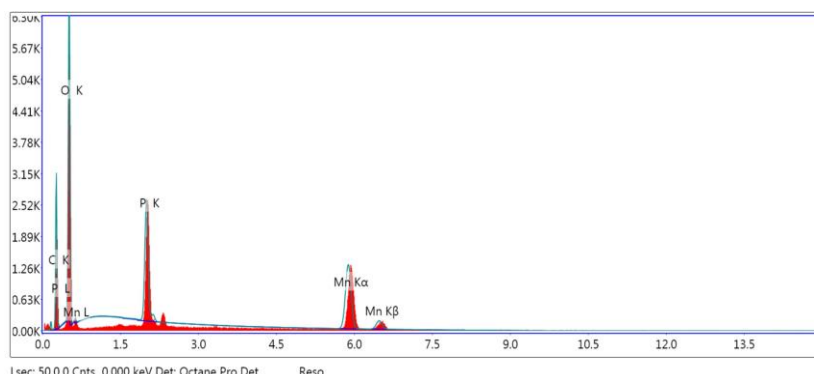
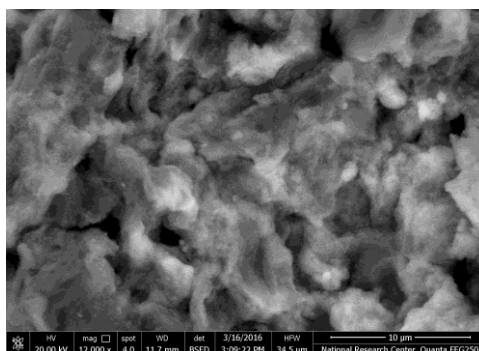


Fig (11)b: EDX of original graphite before thermal treatment

Table(1) oxygen content 10% in prepared graphite before chemical treatment

Element	Weight %	Atomic %	Net Int.	Error %
C K	9.55	26.3	177.62	9.68
O K	10.52	21.76	519.33	6.21
P K	8.13	8.68	372.26	4.41
MnK	71.81	43.25	337.23	5.98



Fig(12)_a: SEM image of graphene with chemical treatment

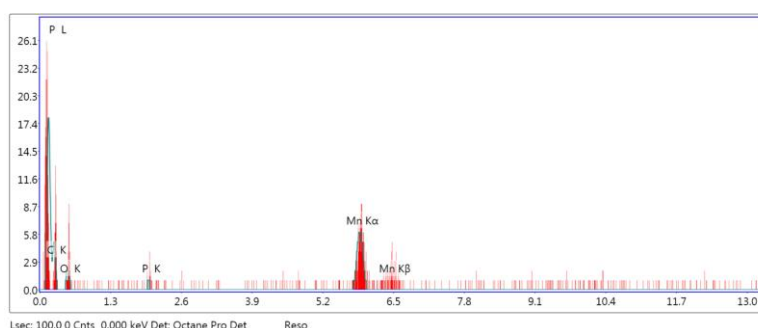


Fig.(12)_b: EDX of graphene chemically treated

Table (2): oxygen content 17.22% in prepared graphene after chemical treatment

Element	Weight %	Atomic %	Net Int.	Error %
C K	41.1	64.82	0.78	20.8
O K	17.22	20.39	0.44	28.94
P K	1.6	0.98	0.19	76.8
MnK	40.08	13.82	1.98	11.97

The original sample of graphite, graphene oxide and graphene were studied by (SEM) image showing porous surface area with fluppy sheets with 10.52 weight % for oxygen, before exfoliation, and reviled 17.22 weight % for oxygen present which is related to oxygenated groups attached after chemical treatment.

The ozone 2LO₃/min flow rate was studied at different time treatment 5,10,15 and 20 min in presence of KH₂PO₄ as reducing agent to modified thermally treated graphene oxide. The (SEM) images **Fig (11)_a** and **Fig(11)_b**, **Fig (12)_a** and **Fig(12)_b**, **Fig(13)_a** and **Fig(13)_b**, and **Fig(14)_a** and **Fig(14)_b** showed nearly the same fluppy sheets of graphene oxide. But, the (EDX) illustrated increase in oxygen weight % as time of ozonation changes from 5 min up to 20 min treatment indicating that , 15 min > 5min >10 min> 20min ozonation reviling more oxygenated groups by 48.71 weight % > 46.55 weight % > 45 weight % > 42.87 weight % respectively.

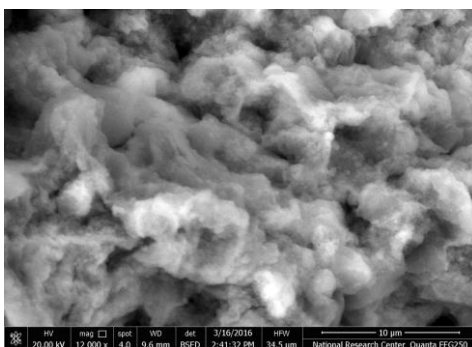


Fig (13)_b:SEM of graphene illustrated increase fluphy sheets after 5 min ozonation

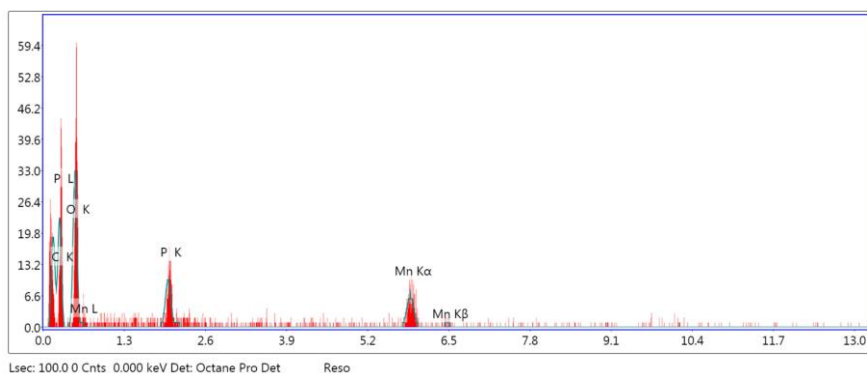


Fig (13)_b: EDX of graphene illustrated increase 46.55 oxygen weight % after 5 min ozonation

Table (3): oxygen content 46.55intreated graphene after ozonation 5 min

Element	Weight %	Atomic %	Net Int.	Error %
C K	40.05	51	3.34	14
O K	46.55	44.5	5.15	14.45
P K	3.56	1.76	1.94	17.59
MnK	9.83	2.74	1.98	18.7

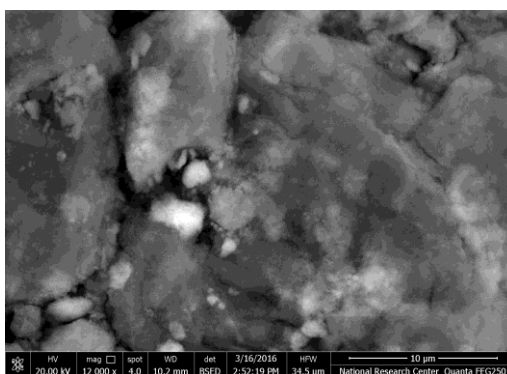


Fig (14)_a: SEM image of graphene with ozone treatment 10 min

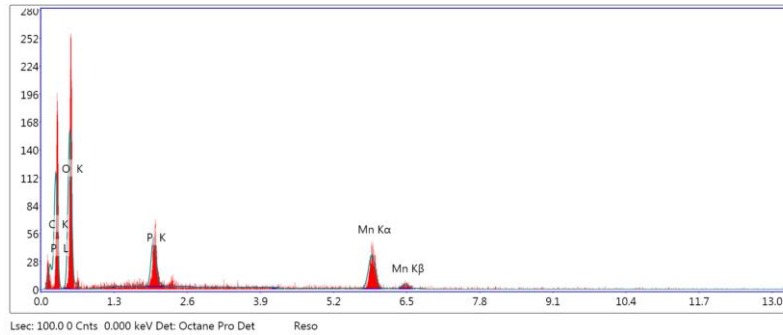


Fig (14)_b: EDX of graphene illustrated increase 45.63 oxygen weight % after 10 min ozonation

Table (4): oxygen content in treated graphene 45.63 % after ozonation 10 min

Element	Weight %	Atomic %	Net Int.	Error %
CK	40.81	51.89	16.88	9.95
OK	45.63	43.56	24.63	11.1
PK	3.62	1.78	9.76	9.39
MnK	9.95	2.77	9.95	8.5

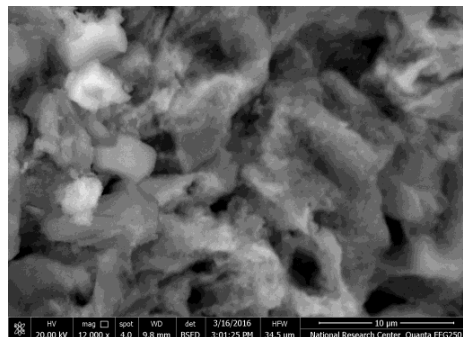


Fig (15)_a: SEM image of graphene treated with ozone 15 min

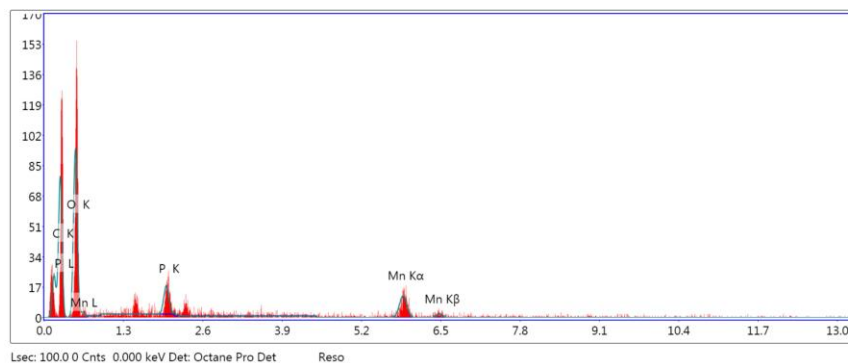


Fig (15)_b: EDX of graphene illustrated increase 48.71 oxygen weight % after 15 min ozonation

Table (5): oxygen content 48.71% in treated graphene after 15 min ozonation

Element	Weight %	Atomic %	Net Int.	Error %
C K	42.96	52.58	11.49	9.99
O K	48.71	44.75	14.6	11.97
P K	2.13	1.01	3.29	15
MnK	6.19	1.66	3.5	16.33

The (SEM) showed more fluppy sheet shaped and EDX showed 42.87 % oxygen content and more pores appeared with fluppy sheets as in Fig (16)_a and Fig (16)_b.The ozone treatment introduced for the exfoliate sample decreases the aggregation of the nano-carbon material prepared and improves its H₂ absorbance.

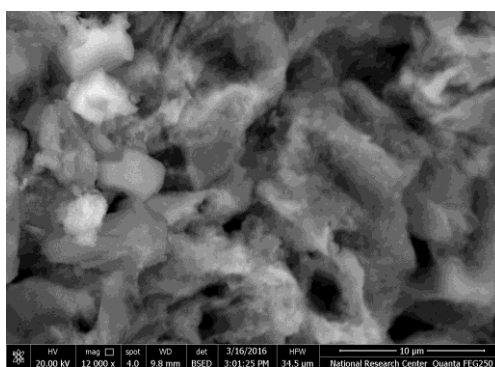


Fig (16)_a: SEM image of graphene after treatment with ozone 20 min showing wide pores

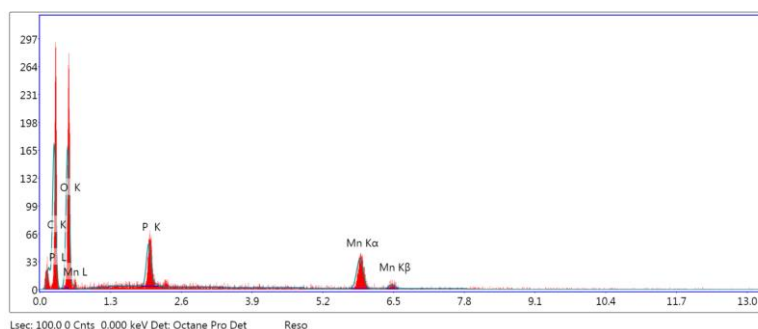


Fig (16)_b: EDX of graphene illustrated increase 42.87 oxygen weight % after 20 min ozonation

Table (6): oxygen content 42.87% in treated graphene after zonation 20 min ozonation

Element	Weight %	Atomic %	Net Int.	Error %
C K	45.64	56.45	24.91	9.09
O K	42.87	39.81	25.91	11.24
P K	3.03	1.45	10.11	9.52
MnK	8.47	2.29	10.35	9.08

The (SEM) and (EDX) for chemical treated reduced graphene showing more crystallinity where UV/light 40 Wt was used to enhance the modification process in presence of KH_2PO_4 and ozone treatment at $2\text{LO}_3/\text{min}$ for 15 min reaction at ambient temperature Fig (17)_a and Fig (17)_b.

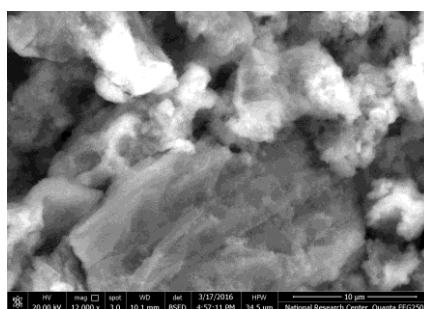


Fig (17)_a: SEM image of graphene with more crystallinity appeared after Ozone treatment 15 min and UV light

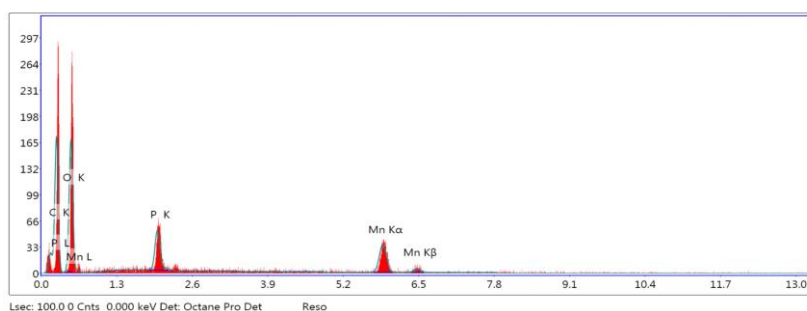


Fig (17)_b: EDX of graphene illustrated increase 42.87 oxygen weight % after 15 min ozonation and UV light

Table (7): oxygen content 42.87% in treated graphene after 15 min ozonation and UV light

Element	Weight %	Atomic %	Net Int.	Error %
C K	45.64	56.45	24.91	9.09
O K	42.87	39.81	25.91	11.24
P K	3.03	1.45	10.11	9.52
MnK	8.47	2.29	10.35	9.08

To insure the effect of KH_2PO_4 reduction the ozone modification treatment was repeated with different ozone dose of $4\text{LO}_3/\text{min}$, $6\text{LO}_3/\text{min}$ and $8\text{LO}_3/\text{min}$. The reaction time was fixed at 15 min and in presence of double distilled water (DDW). The first $4\text{LO}_3/\text{min}$ dose revealed oxygen content 27.81 weight % and $6\text{LO}_3/\text{min}$ dose showed 37.59 weight % while $8\text{LO}_3/\text{min}$ achieved 35.96 weight% oxygen groups only Fig (18)_a and Fig (18)_b, Fig(19)_a and Fig(19)_b and Fig(20)_a and Fig(20)_b.

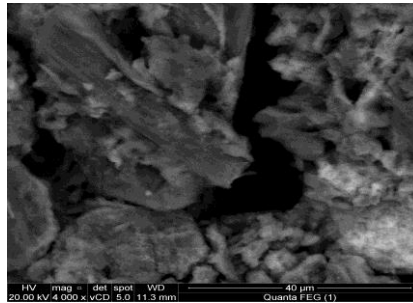


Fig (18)a: SEM image of graphene with fluppy sheets after ozonation 4LO₃\min15 min in distilled water

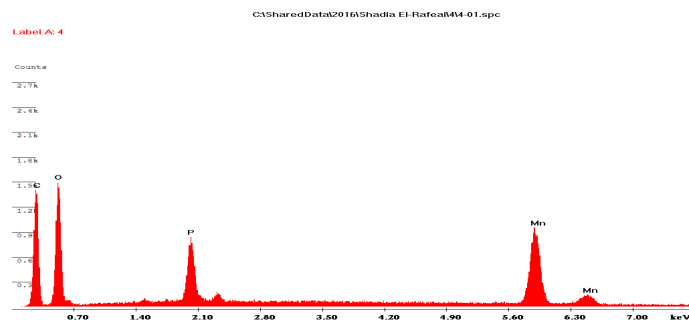


Fig (18)b: EDX of graphene illustrated increase 27.81 oxygen weight % only after ozonation 4LO₃\min15 min in distilled water

Table (8): oxygen content 27.81% in treated graphene with ozone 15 min in distilled water

Element	Wt %	At %	K-Ratio	Z	A	F
C K	38.57	56.87	0.1186	1.0570	0.2907	1.0004
O K	27.81	30.78	0.0766	1.0393	0.2649	1.0008
P K	6.04	3.45	0.0481	0.9600	0.8285	1.0018
MnK	27.58	8.89	0.2414	0.8633	1.0137	1.0000
Total		100.00	100.0			

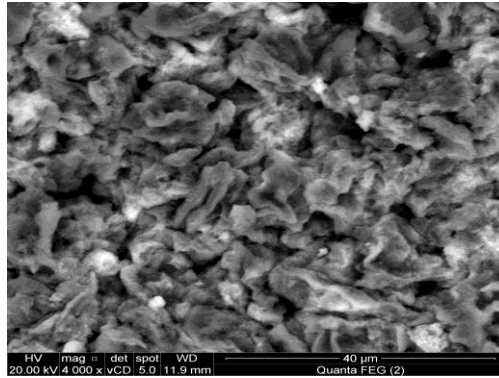


Fig (19)_a: SEM image of graphene with fluppy sheets after ozonation 6LO₃\min15 min in distilled water

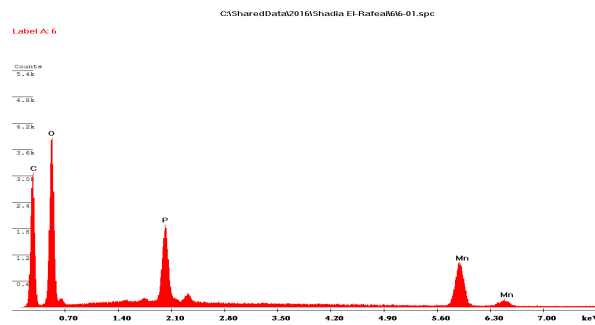


Fig (19)_b: EDX of graphene illustrated increase 37.81 oxygen weight % only after ozonation 6LO₃\min15 min in distilled water

Table (9): oxygen content 237.81% in treated graphene with ozone 6LO₃\min15 min in distilled water

Element	Wt %	At %	K-Ratio	Z	A	F
C K	40.19	54.18	0.1291	1.0385	0.3093	1.0004
O K	37.14	37.59	0.1009	1.0211	0.2660	1.0005
P K	6.81	3.56	0.0555	0.9418	0.8648	1.0012
MnK	15.85	4.67	0.1363	0.8468	1.0154	1.0000
Total		100.00	100.0			

The 6O₃/min dose shows the best ozone dose without UV-light to increases oxygenated groups but shows lower crystallinity in material as in SEM images Fig (19)_a and Fig(19)_b.

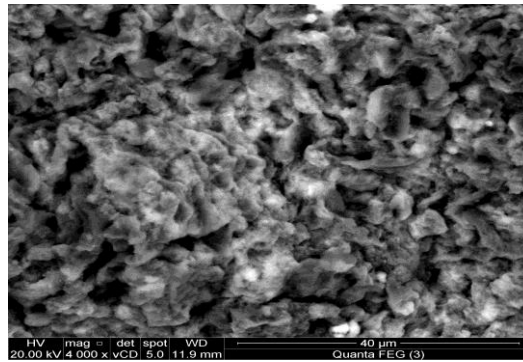


Fig (20)_a: SEM image of graphene with fluppy sheets Ozonation 8LO₃\min15 min in distilled water

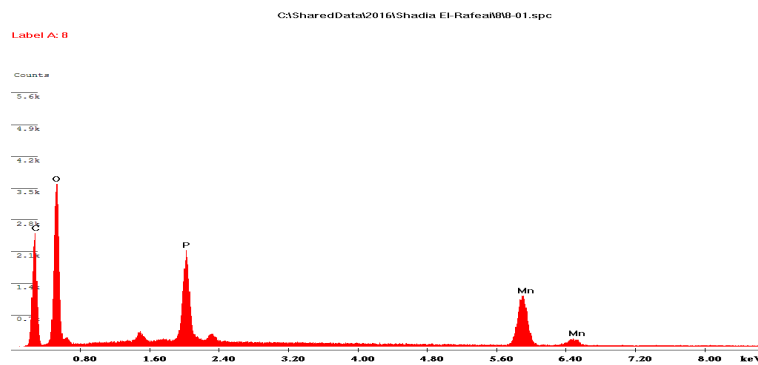


Fig (20)_b: EDX of graphene illustrated increase 35.96 oxygen weight % only after Ozonation 8LO₃\min15 min in distilled water

Table (10): oxygen content 35.96% in treated graphene with ozone 8LO₃\min15 min in distilled water

Element	Wt %	At %	K-Ratio	Z	A	F
C K	37.37	52.22	0.1107	1.0443	0.2835	1.0004
O K	35.96	37.72	0.1003	1.0269	0.2716	1.0005
P K	8.08	4.38	0.0655	0.9475	0.8549	1.0013
MnK	18.60	5.68	0.1607	0.8520	1.0139	1.0000
Total			100.00	100.00	counts	

This indicated that 2LO₃/min ozone treatment is an efficient dose at 15 min with KH₂PO₄ and UV-irradiation enhanced (GO) modification. The platelet sheets are illustrated clearly with the UV-light and ozone in situ treatment. Also-the present present pores in graphene SEM images revealed increase with increasing time of ozone treatment.

The X- Ray diffraction (XRD);

This analysis shows the changes of graphite, graphite oxide and reduced graphene with ozone treatment effect.

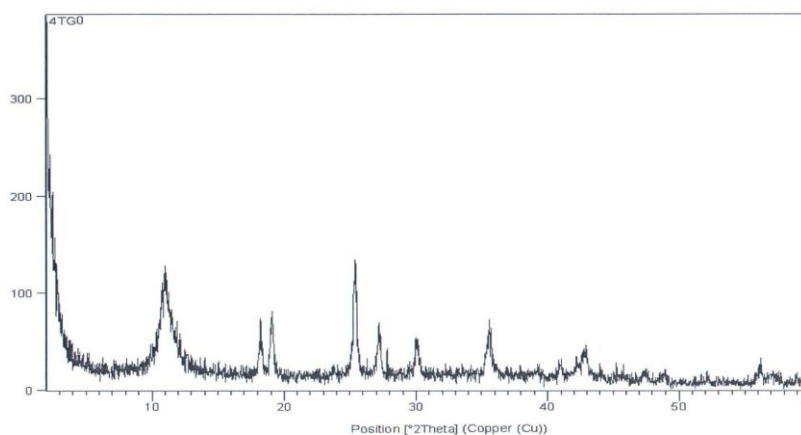


Fig (21): XRD Chart of Graphene (GO) treated with 6LO₃/min for 15 min in presence of K₂ HPO₄.3H₂O counts

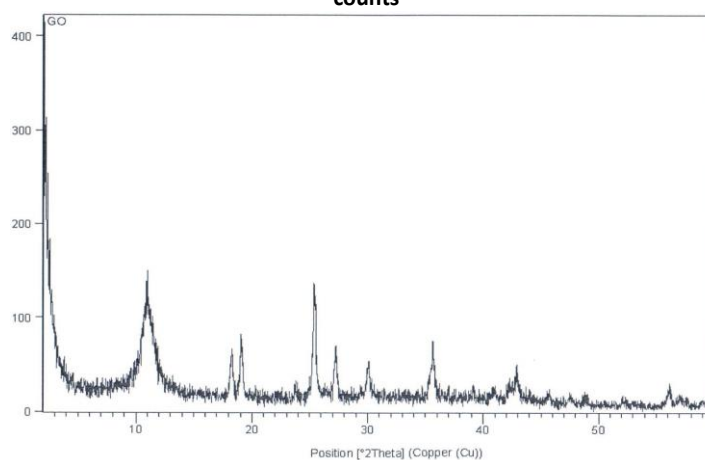


Fig (22): XRD Chart of Graphene (GO) treated with 2LO₃/min for 15 min in presence of K₂ HPO₄.3H₂O counts

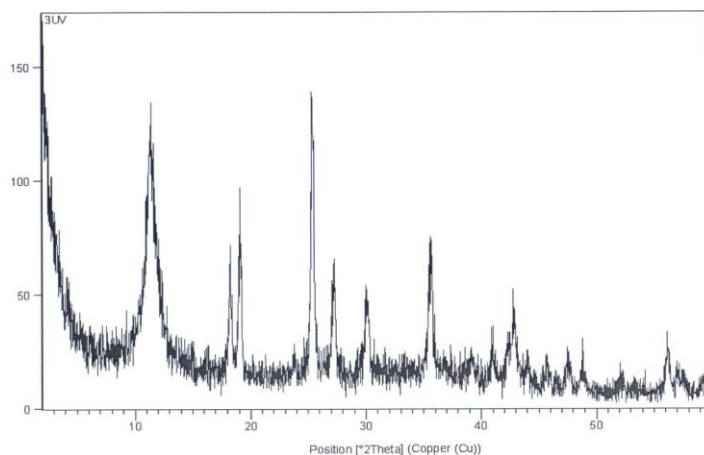


Fig (23): XRD Chart of Graphene (GO) treated with 2LO₃/min for 15 min in presence of UV Light and K₂ HPO₄.3H₂O

Graphene (GO) treated with 6LO₃/min for 15 min shows broad peak at $2\Theta=11^\circ$. The interlayer spacing at 0.79nm d- spacing confirms the presence of oxygen functional groups on the (GO) sheets surface. Another sharp peak at $2\Theta = 25$ appears confirming the reduction of K₂ HPO₄.3H₂O during treatment reaction with d-spacing 0.35 nm Fig(21).

Graphene (GO) treated with $2\text{LO}_3/\text{min}$ for 15 min shows nearly the same trend in XRD-chart Fig (22) where a broad peak at $2\theta = 10.9^\circ$ with d-spacing 0.8 nm for the inter layer spacing. Another sharp peak at $2\theta = 25.4^\circ$ with d-spacing 0.35nm confirming the K_2HPO_4 reduction effect.

Fig (23) showing the $2\text{LO}_3/\text{min}$ treatment in presence of both $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ and UV-light 40 wt. The broad peak at 11.3° appeared more sharp than in previous treatment with interlayer spacing at 0.77nm. The sharp peak appeared at $2\theta = 25.4^\circ$ confirming the reduction process with 0.35nm too.

The appearance of both broad and sharp peak indicating decrease interlayer spacing of 0.35 nm compared to 0.79 nm, 0.8 nm and 0.77nm, for $6\text{LO}_3/\text{min}$, $2\text{LO}_3/\text{min}$ and $2\text{LO}_3/\text{min}$ in presence of UV-light respectively at fixed time 15 min treatment process. The decrease in interlayer spacing at 0.77nm indicated the inter calculation of oxygenated groups into the interlayer spacing of graphene. The ozone and UV-light modification reflects the conjugated graphene network establishment.

CONCLUSION

- The synthesis of exfoliated graphene oxide (GO) and modified graphene by ozone successfully showed graphene Nano-sheets.
- The use of UV-light 40 wt./h in presence of KH_2PO_4 assist ozone treatment showing effective in-situ modification of reduced graphene oxide network.
- The FTIR, SEM, EDX and XRD results showed the introduction of oxygenated groups via (such as C=O, -COOH and C-O) via ozone treatment are best improvement at normal temperature.
- The percentage of oxygenated groups was increased up to 48.71 weight % from 10.52 weight % without exfoliation and 17.22 weight % after chemical treatment.
- The ozone modification successfully increased the oxygenated group up to 31.5 % more over the chemically thermal treatment of (GO) with best flow rate $40\text{L}/\text{min}$ for 15 min ozone treatment

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