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Controlling of the Oxidation Level of Graphite Oxide by Hydrogen Peroxide and γ-irradiation Treatment of Graphite

M. M. Atta[1], H. Reheim[1], H. A. Ashry[1] and G. M. Nasr [2] and M. Omar [2]

[1] National Center for Radiation Researches and Technology, Atomic Energy Authority, Cairo, Egypt
[2] Physics Department, Faculty of Science, Cairo University, Cairo, Egypt

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ABSTRACT

Influence of hydrogen peroxide and γ-irradiation on purification of graphite and oxidation level of descendant graphite oxides were studied. Treatment process carried out by dissolving different graphite samples in hydrogen peroxide followed by γ-irradiation doses of 0, 50, 150 and 280 kGy to be compared to untreated ones. Descendant graphite oxide obtained by oxidizing all precursor graphite samples using Hummer's method. The chemical structure and oxidation level of graphite oxides were proposed by analyzing the evolution of the functional groups with oxidation based on Fourier-transformed infrared Spectroscopy (FTIR), X-Ray diffraction (XRD), Raman spectroscopy and thermogravimetric analysis (TGA). The present study demonstrated that graphite attached functional groups impurities and defects are decreased by hydrogen peroxide treatment and irradiation dose. The Oxidation level of Descendant graphite oxides was affected by their parent graphite treatment. Where, the highest level of oxidation observed for whose parent graphite treated without irradiation, While lowest oxidation level for whose parent graphite untreated or treated and irradiated by 280 kGy. The thermal behavior of the graphite oxide samples was shown to be affected by their oxidation level.

Key words: Graphite oxide, oxidation, hydrogen peroxide, γ-irradiation, treatment

Introduction

Graphite oxide (GO) is a compound of carbon, oxygen, and hydrogen in variable ratios obtained usually by chemical oxidation of graphite using strong oxidizing agents. Oxygenated functionalities are introduced in the graphite structure which expands the layer separation and makes the material hydrophilic. This property enables the graphite oxide to be exfoliated in water and ultimately producing single or few layers using sonication, known as graphene oxide. Thus graphene oxide is a layer or few layer of graphite oxide. Graphene oxide has recently attracted substantial interest as a possible intermediate for the manufacture of graphene, a material with extraordinary electronic properties. The structure and properties of graphite oxide depend on oxidation degree and synthesis method. It preserves the layer structure of the parent graphite, but with increased interlayer spacing and buckled layers. Finally, graphite oxide used for wide range of applications such as preparation of graphene, water purification (Gao *et al*., 2011), coating (Su *et al*., 2014) and flexible rechargeable battery electrode (Lamuel *et al*., 2014).

In last years, the effects of γ-irradiation on the structure and physical properties of carbon material have been studied. The consequences of γ-irradiation depend on materials type, irradiation conditions, irradiation medium, and irradiation doses. A large number of examples showing different results after irradiating can be found in the literature (Xu *et al*., 2013). γ- Irradiation for activated carbons prepared from lignite lead to increased specific surface area (Erçin *et al*., 2005), γ-irradiation in different liquid media has been successfully utilized for the reduction of graphene oxide and for the synthesis of graphene composites. The mechanisms of those reactions are based on the generation of active radicals through the solvent radiolysis. Graphene oxide was reduced during γ -irradiation in ethanol/water under

Corresponding Author: M.M.Atta, Radiation Physics Department, National Center for Radiation Researches and Technology, Cairo, Egypt.
E-mail: mmatta2007@yahoo.com

an inert atmosphere, while the reduction reaction did not occur in pure water or under an oxygen atmosphere (Zhang *et al*., 2012).

Recent studies has focused on tailoring oxidation level of graphite oxide and controlling it through changing oxidation times (Jeong *et al*., 2009) or by changing amount of oxidant during graphite oxidation and study its effect on optoelectronic properties of organic solar cells (Wu *et al*., 2015).In another article the performance of dye-sensitized solar cells (DSCs) equipped with graphene counter electrode with different oxidation level controlled was thermally studied (Chien-Te Hsieh *et al*., 2012).

In the present study, effect of hydrogen peroxide and γ-irradiation on the graphite defects as well as oxidation level of descendant graphite oxides were proposed.

FTIR, RAMAN, XRD and TGA techniques were used for investigating graphite defects, oxidation level and thermal behaviors of descendant graphite oxides.

Materials and Methods

Materials

Graphite fine powder (<50µ m) was Purchased from Merk, Germany, H_2SO_4 (98%) purchased from Sigma-Aldrich, USA. $KMNO_4$, $NaNo_3$, H_2O_2 (35%), acetone (99%) and HCL purchased from El Nasr Pharmaceutical chemicals Company, Egypt.

Experiment

The preparation of samples was carried out in two steps:

A-Treatment of Graphite

Treatment of graphite was carried out in the following steps:

1-Four samples of graphite powder (each about 3 gram) immersed in 30 ml of H_2O_2 in sealed beaker and exposed to γ – rays doses zero, 50 ,150 and 280 kGy ; while the fifth untreated sample was kept as a reference one. γ – Rays source from a ^{60}Co source at National Center for Radiation Research and Technology (NCRRT), Egyptian Atomic Energy Authority (EAEA). All irradiations were carried out at room temperature and dose rate 2 kGyh^{-1}.

2- Unirradiated sample dissolved in H_2O_2 for about 24 hours.

3- Samples were filtered through porous filter paper and washed with water then dried.

B- Oxidation of Graphite

Graphite samples (treated and untreated) were oxidized based on Hummer's method discussed elsewhere (Park and Ruoff, 2009). The obtained graphite oxide was designated corresponding to precursor graphite treatment doses and untreatment as follow: GOuntreated (untreated), GOzero (zero KGy), GO50 (50 KGy), GO150 (150 KGy) and GO280 (280 KGy).

Characterization of Graphite and Graphite Oxide samples

Crystal structure of graphite and graphite oxides studied using X-ray diffraction analysis (XRD , Shimadzu X-Lab diffractometer) with a Cu-Kα radiation source (λ=1.54Å) in the range of 4–90° ,interlayer distance calculated based on Bragg's law :

$$n\lambda = 2d \sin(\theta) \qquad (1)$$

Where λWavelength of the X-ray, θ is scattering angle, n is integer representing the order of the diffraction peak and d is inter-plane distance of the lattices.

FTIR spectra were recorded using Shimadzu- Prestige 21 Fourier Transform Infrared spectrophotometer in the 2000-500 cm^{-1} range for graphite sample and the 4000-500 cm^{-1} for graphite oxide. The thermal behavior of graphite oxide was studied using a thermogravimetric analyzer (TGA, Shimadzu–50) at a heating rate of 5 ºC min^{-1} under a nitrogen atmosphere.

Raman spectroscopy was performed by Witec alpha 300 R confocal Raman microscopes with 532 nm laser excitation source.

Results and Discussion

FTIR Analysis

Figure (1 a) shows FTIR spectra for proposed graphite samples. From which, it is clearly shown that untreated graphite shows as stretching vibrations of C=O (carbonyl) groups observed at 1774 cm^{-1} (Meng *et al.*, 2010), 1630 and 1560 cm^{-1} assigned to aromatic C=C, 1170-1030 cm^{1} assigned to C-O (epoxide) stretching vibrations (Park and Ruoff, 2009).

By hydrogen peroxide treatment, C=O band intensity increased, C-O bands intensity decreased. New weak C-OH band at 1365cm^{-1} observed, C=C band at 1630 cm^{-1} intensity decreased while it increase at 1560 cm^{-1} as well as new C=C band observed at 1446 cm^{-1}suggesting reconstruction of graphite aromatic skeleton by hydrogen peroxide treatment (Zhang *et al.*, 2012).

Graphite irradiated by 50 kGy have similar behavior of unirradiated sample, by increasing dose to 150 KGy C=O, C=C bands destroyed, only one broad C-O observed , C-OH band intensity increased .by further raising dose to 280 KGy all bands disappeared .

Removal of attached functional groups by increasing γ-dose due to the reductive effect of free radicals and energetic electrons produced by radiolysis of H_2O_2 (Steensen *et al.*,1997).

Removal of functional group by γ-dose indicating reduced ratio of attached impurities and defects in graphite.

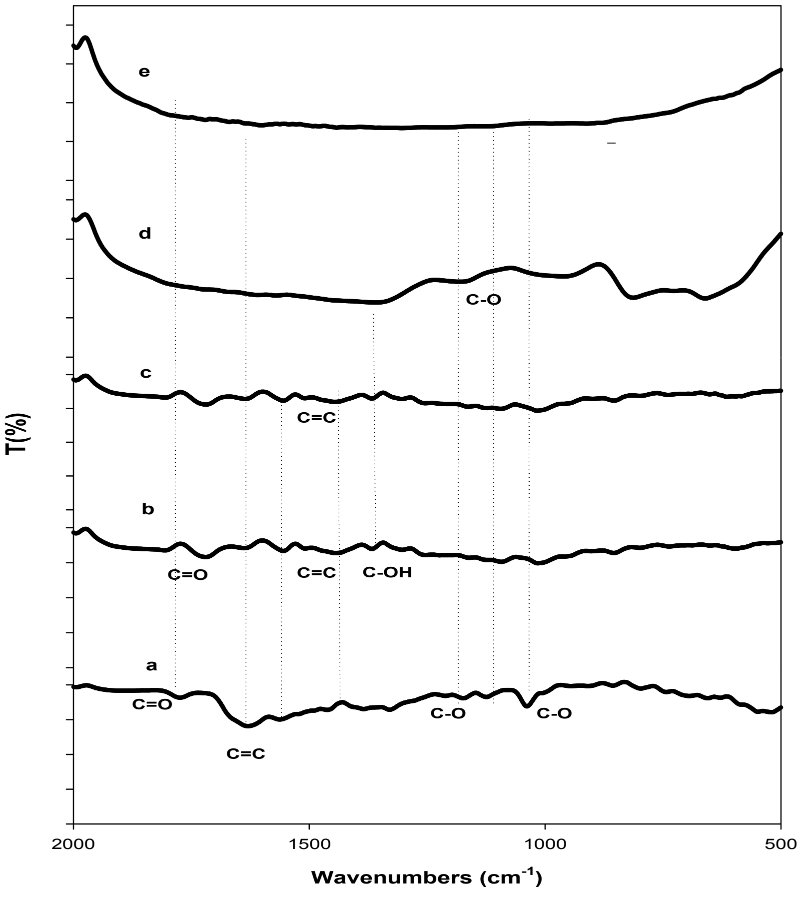

Fig. 1: FTIR spectra for untreated graphite (a) and graphite treated by hydrogen Peroxide and different absorbed doses of zero (b) 50 (c) 150 (d) 280 kGy (e).

Figure (2) shows FTIR spectra for graphite oxide samples , compared to its parent graphite , GOuntreated have a stronger O-H band around 3200 cm^{-1}, C=O and C=C bands ,two strong C-O bands at 1150 and 1035 cm^{-1} indicates that more oxygenated functional groups were attached to graphite basal plane during oxidation process. GOzero has C=C bands in range 1600-1450 cm^{-1} similar to its parent graphite. Compared to GOuntreated, GOzero has stronger and sharper C=O, C-O , as well as new C=O at about 1805 cm^{-1},indicating extra oxygenated functional groups attached to carbon basal plane and higher oxidation level. GO50 have similar behavior of GOzero with a slightly lower intensity of C=O band.

Increased level of oxidation in GOzero and GO50 compared to GOuntreated may be due to a reconstruction of C=C in their parent graphite by hydrogen peroxide as discussed above result in increasing no of C=C domains that in turn increase the ability to oxidation.

In GO150 reduced intensity of all functional groups detected and then further decreased in GO280 designate decreased oxidation level compared to GOzero and GO50, hence we conclude that GOzero has the highest oxidation level followed by GO50 then GO150, while GOuntreated and GO280 have the lowest level.

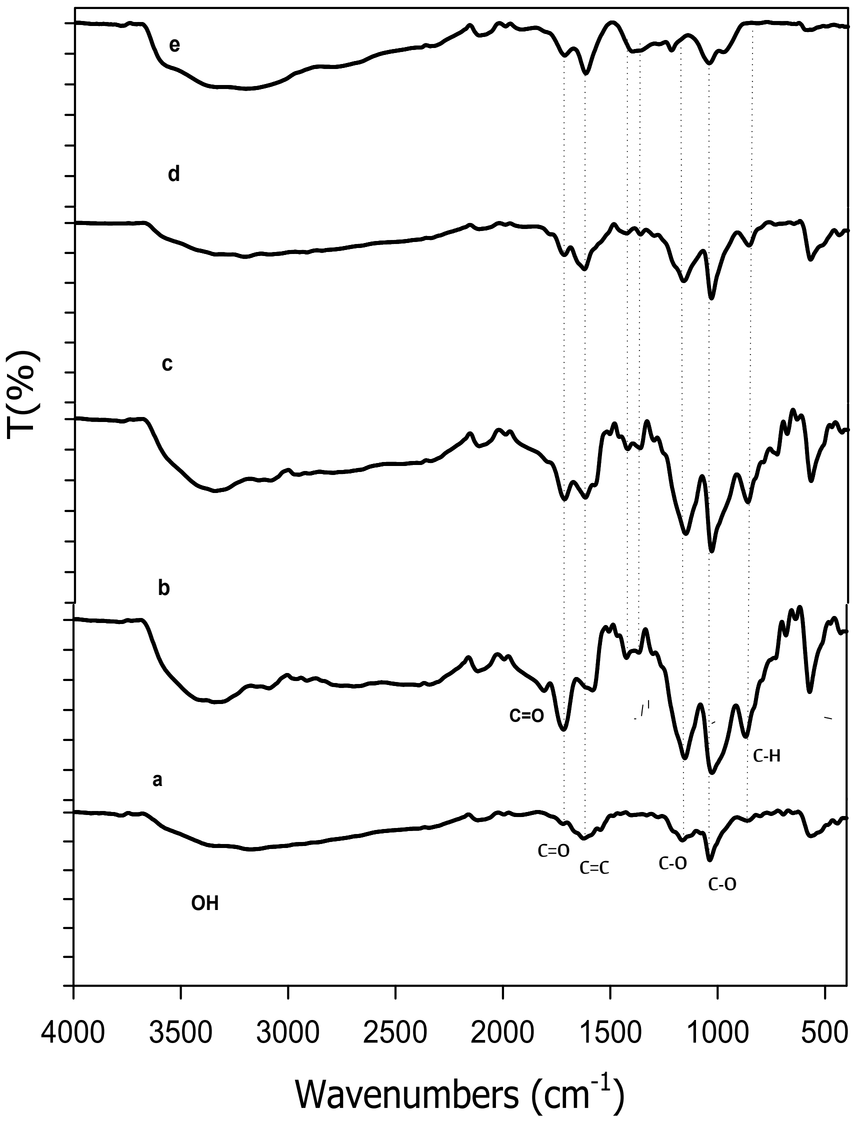

Fig. 2: FTIR spectra for graphite oxide samples: GOuntreated (a) GOzero (b), GO50 (c) GO150 (d) and GO280 (e).

Raman Spectroscopic Analysis

Raman spectroscopy is the most direct and non-destructive technique to characterize the structure and quality of carbon materials, particularly to determine defects as well as the ordered and disordered structures of graphite (Some *et al.*, 2012).As shown in Figure (3), Raman spectrum of graphite samples displays two mainly characteristic bands at 1580 cm^{-1}, 1350 cm^{-1} called the G band, D band respectively. The G band corresponding to the first-order scattering of the E_{2g} mode observed for sp^2 domains, D band is ascribed to edge planes and disordered structures and presence of sp^3 defects (Ferrari *et al.*, 2006; Thomsen *et al.*, 2000).

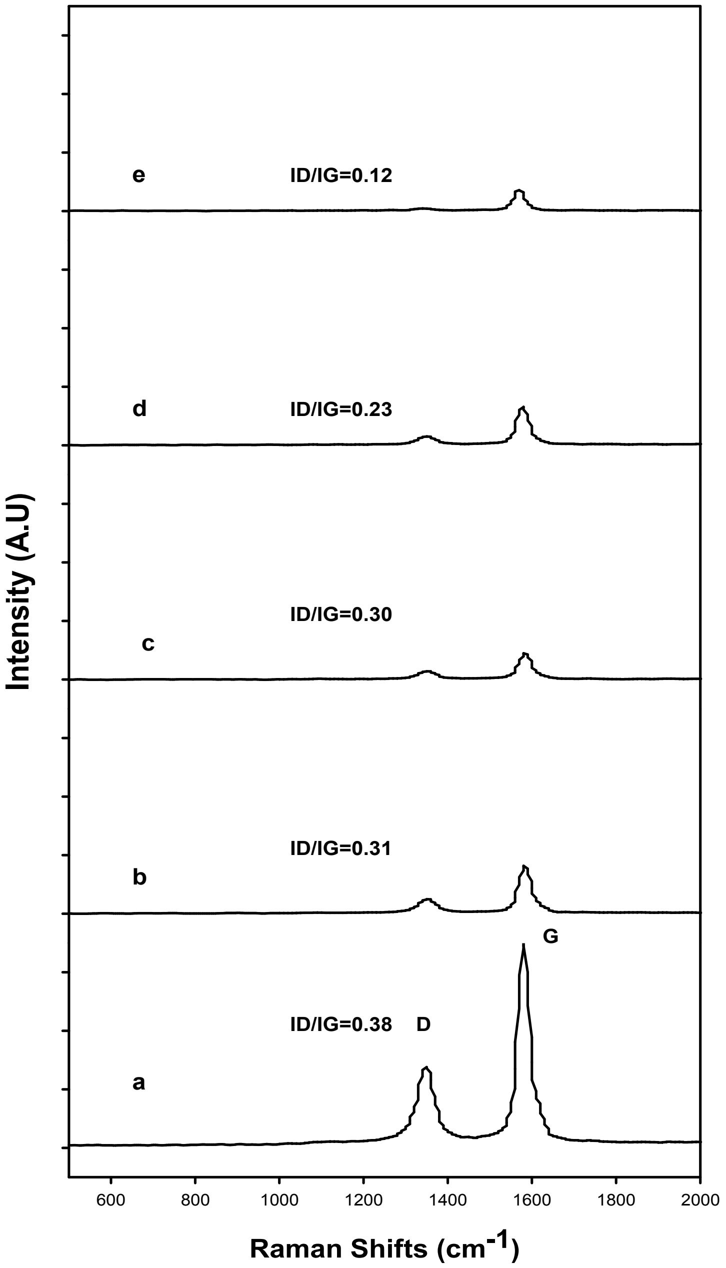

Fig. 3: Raman spectra for untreated graphite (a) and graphite treated by hydrogen peroxide and different absorbed gamma-doses (zero (b) 50 (c) 150 (d) 280 kGy (e)).

The empirical Tuinstra–Koenig relation (Tuinstra *et al.*, 1970) which is the ratio of the intensity of the D and G peaks (ID/IG) provides an indication of the degree of order across graphitic plans. ID/IG ratio of highly defective untreated graphite is found to decrease by treatment process and further decreased by irradiation dose indicating graphite purification which confirmed previously by FTIR.

In GO samples, G and D bands are broadened in all samples compared to their parent graphite, D band intensity increased compared to G band as shown in Figure (4), these phenomena could be attributed to the significant decrease of the size of the in-plane sp^2 domains due to oxidation process (Sasha *et al.*, 2007).

ID/IG ratio is found to increase in GOzero compared to GOuntreated then start to decrease in GO50, GOP150 till GO280 this behavior reflect oxidation level of different graphite in the order consistent with FTIR results.

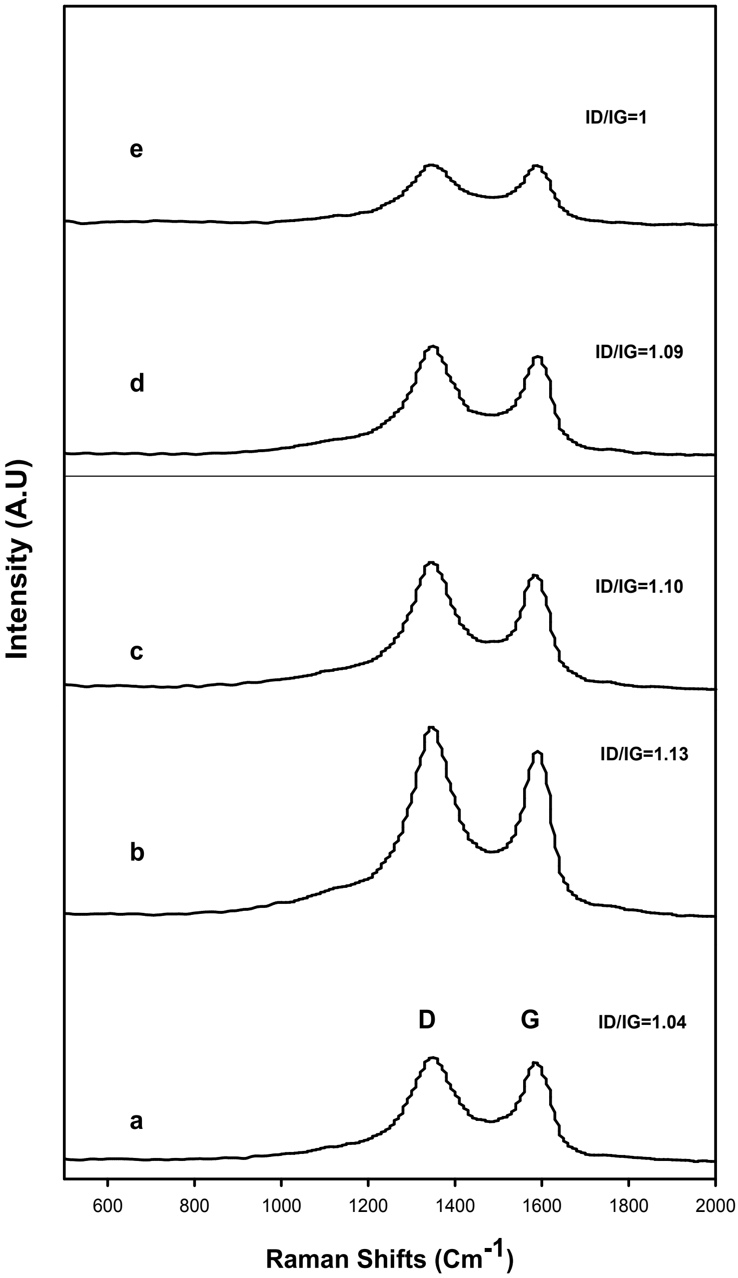

Fig. 4: Raman spectra for graphite Oxide Samples (a) GOuntreated, (b) GOzero, (c) GO50, (d) GO150 (e) GO280.

XRD Analysis

Figure (5) shows X-ray diffraction pattern of graphite and graphite oxide samples. Untreated graphite exhibits a basal reflection (002) peak at 2θ =26.32° corresponds to an interlayer spacing of 3.38 Å that represents tightly packed monolayer of carbon atoms. This very strong peak has no observed changes in treated graphite samples. In GO samples , graphite peak shifted to lower angle corresponding to a larger interlayer spacing which attributed the oxygen functional groups of GO as well as, water molecules held in the interlayer galleries of hydrophilic GO (Buchsteiner *et al.*, 2006).

Figure (5) also illustrates increased Interlayer spacing of GO zero compared to GO untreated indicating increased oxygen functional groups and hence oxidation level in GOzero.

Interlayer distance starts to decrease in irradiated samples compared to GOzero till an interlayer distance of GO280 became less than GO untreated. These reported behaviors confirm oxidation level of GO Samples in the same order confirmed by FTIR and Raman analysis.

There also another Peak around 2θ = 42.6° corresponding to an interlayer spacing of 2.12 Å, attributed to the turbostratic band of disordered carbon materials (Xu *et al.*, 2010).

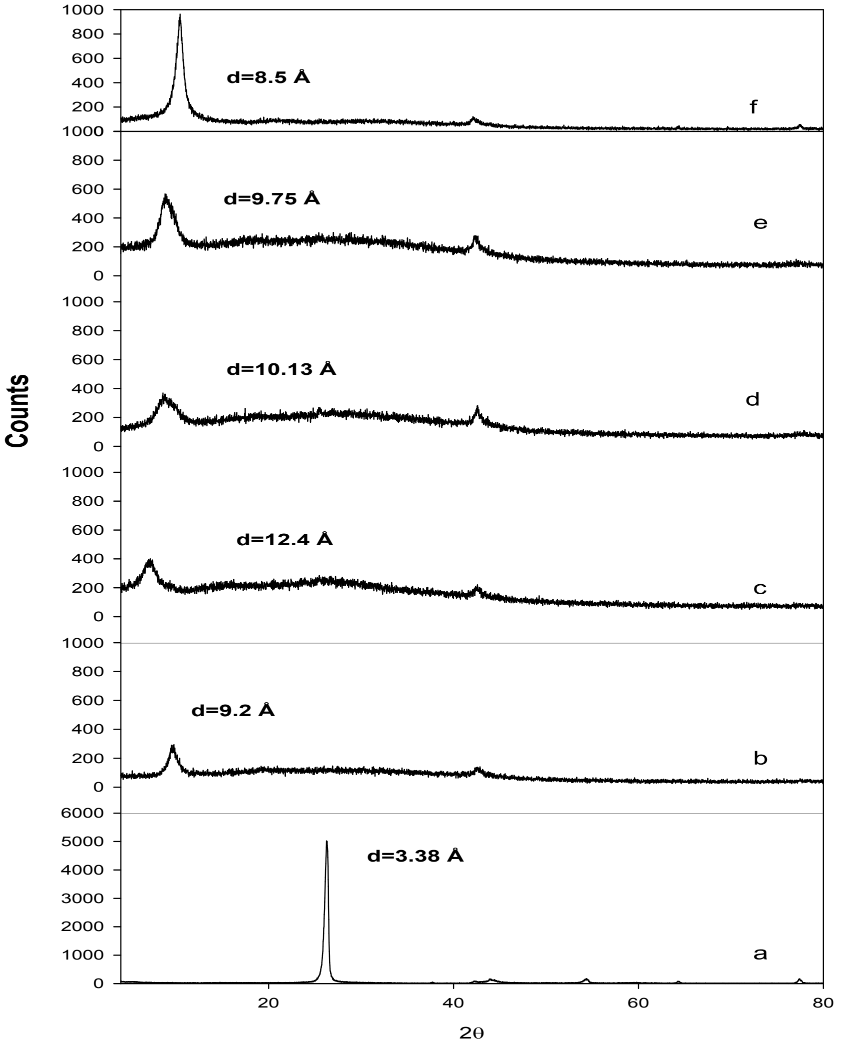

Fig. 5: XRD Analysis for (a) graphite, (b) GOuntreated, (c) GOzero, (d) GO50, (e) GO150 (f) GO280.

TGA analysis

Figure (6) shows the TGA for the investigated GO samples, it is clear that the weight profiles of all the graphite oxide samples exhibited similar thermal behavior. GO starts to lose mass upon heating even below 50 °C, which is associated with the elimination of loosely bound or adsorbed water and gas molecules. The second mass loss around 150 ^{0}C is due to the elimination of thermally-labile oxygen species. The major mass loss occurred at temperature span 460-530 °C for GOuntreated where loss 29% of its total weight, weight loss in this temperature span due to the sp^3 carbon backbones of the fully oxidized material (Jeong *et al.*, 2009).

Finally, major mass loss temperature slightly shifts in GOzero, GO50, and GO150 samples, where GOzero loss 32% of total mass at 540-620 ^{o}C, GO50 loss 31% in 520-620 ^{o}C and GO150 loss 30% in 520-585 ^{o}C this shifts indicating increased ratio of sp^3 carbon backbones of these material (Jeong *et al.*, 2009).Residual weights at 700 ^{o}C was 3,1,2 and 3 % for GOuntreated , GOzero, GO50 and GO150 respectively, While GO280 completely exhausted at short temperature span 545-570 ^{o}C and loss 32 %. This thermal behavior of graphite oxide samples also reflects their oxidation level in that order consistent with FTIR, Raman and XRD.

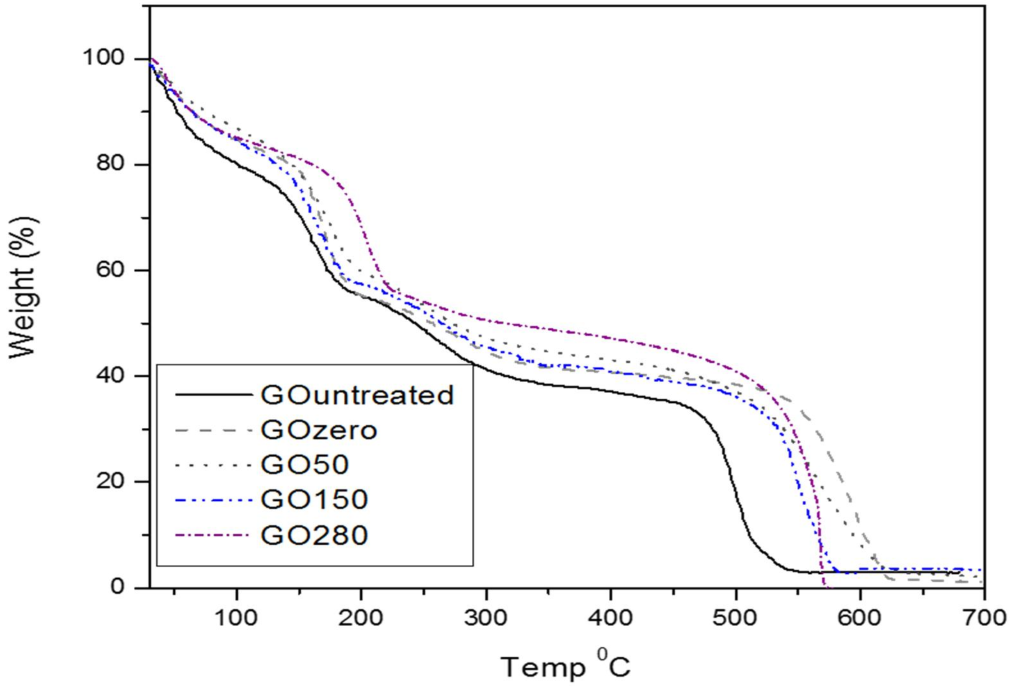

Fig. 6: TGA Analysis for different GO samples

Conclusion

Treatment of graphite by hydrogen peroxide and γ-irradiation led to reduce the ratio of attached functional groups impurities and defects with increasing dose. In other words purification of graphite achieved by hydrogen peroxide treatment and further increased by irradiation dose ,this results confirmed by FTIR and Raman Spectroscopy.

The oxidation levels of descendant graphite oxide were investigated by XRD, FTIR and Raman Spectroscopy. The level of oxidation of descendant graphite oxides are affected by parent's graphite treatment, the increase in the proportion of oxygenated functional groups, topological defects and interlayer distance observed for those samples treated without irradiation or with 50 kGy indicating highest level of oxidation. Lowest oxidation levels were observed for those samples untreated or treated and irradiated by 150 and 280 kGy of γ-Rays. TGA analysis reveals that major mass loss span of untreated graphite oxide Shift to higher temperature in treated samples and the samples with highest levels of oxidation have highest thermal shift.

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