FUDMA Journal of Sciences (FJS)
ISSN online: 2616-1370
ISSN print: 2645 - 2944
Vol. 5 No. 1, March, 2021, pp 47 – 56
DOI: https://doi.org/10.33003/fjs-2021-0501-536

THE EFFECT OF THERMAL ANNEALING AND PULSE LASER ANNEALING IN THE REDUCTION OF GRAPHENE OXIDE

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ABSTRACT

The discovery of Graphene and its unique properties has attracted great interest. Unfortunately, the synthesis of graphene in large scale is challenging, for this reason the derivative of graphene such as graphene oxide (GO) and reduce graphene oxide (rGO) have become alternative sources. The reduction of graphene oxide is an alternative route to obtain graphene-like behavior. This study is aim at examining the similarities and difference between thermal reduction technique and pulse laser method of reduction of (GO). The method utilizes a pulse laser beam for reduction of GO layers on glass substrates and thermal reduction technique. Using the pulse laser method, conductivity of reduced GO was found to be 2.325E-2(1/ohm) which is six times higher than conductivity values reported for GO layers reduced by thermal means at 400°C which was 3.740E-3(1/ohm). A higher transmittance was observed for the pulse laser annealed which holds promising application in a lot technological research. The scanning electron microscope (SEM) result reveals the evenly distribution of the GO around the substrate. The non-thermal nature of the pulse laser method combined with its simplicity and scalability, makes it very attractive for the future manufacturing of large-volume graphene-based optoelectronics

Keywords: Laser Annealing, Reduced Graphene Oxide and Thermal Annealing.

INTRODUCTION

The discovery of graphene with it extraordinary thermal, Opto-electrical and mechanical properties[1], these unique properties have attracted a lot of attention from scientist all around the world. However, the applications of graphene are face with a lot of challenges such as the production of highly pure graphene in large quantities[2,3]. In fact for large scale applications few layer graphene, multi-layer graphene of graphite are typically used instead of the pure single atom-thick graphene[4].

The properties of graphene material change dramatically with increase in the number of layers[5,6] and or the presence of defect [(7,8,9)], it is of importance to measure the effective properties instead of assuming the reported for graphene from literature. For this reason, the discovery of graphene to its derivatives such as graphene oxide (GO) and reduced graphene oxide (rGO) which are relatively easy to produce on large scale.

Graphene oxide is considered as the oxidize form of graphene which was discovered way before the discovery of graphene. However, until the discovery of graphene it became an alternative source of graphene[10]. The synthesis of GO is mainly carried out by the top-down approach which include the oxidation of graphite with strong oxidant or sulfuric acid and potassium permanganate and mechanical peeling method. However, it is also possible to obtain through bottom-up synthesis methods such as chemical vapordeposition (CVD)[11]. The level of oxidation strongly affect the chemical structure of the GO sheets, GO shows low electrical conductivity causing it to behave like an insulator or semi-conductor depending on the degree of oxidaion[12]. Other properties such as mechanical strength, hydrophilicity and the optical transparency are also affected greatly.

The reduction of graphene oxide is an alternative route to graphene like behavior. Chemical, thermal and photo-thermal (LASER) reduction methods are used to obtain reduce graphene oxide structure. Basically we call it r-GO when we are getting the product by reducing the graphene (GO) starting from graphite as a carbon source. This is because it is practically impossible to remove all the oxygen functional groups from GO by reduction either by chemical reduction or thermal reduction. Hence the name of the obtained product is r-GO is where r stands for "reduced". It is noteworthy that this terminology is for the product obtained by reduction of graphene oxide only not from other carbon sources. Chemical reducing agent such as NaB or organics, such as phenyl hydrazine hydrate or hydroxilamine[13]. The thermal reduction occurs in an inert or reducing atmosphere at temperatures between 300^0C- 2000^0C. Finally the photo thermal reduction of GO can be done with a direct laser beam at wavelength under 300nm (energy greater than 3.2eV)[14]

Thermal annealing

Thermal annealing occurs by the diffusion of atoms within a solid material, so that the material progresses towards its equilibrium state. Heat increases the rate of diffusion by providing the energy needed to break bonds. The movement of atoms has the effect of redistributing and eradicating the dislocations in materials especially metals and ceramics. Thermal treatment will result in higher reduction degree than that from chemical reduction treatment, restoring sp^2 carbon domains and improving the electrical properties of GO. This is due to the prompt release of CO or CO_2 gases from the decomposition of functional groups of GO during heating [15,16]. The more the increase in annealing temperature the more the formation of graphene crystal leading to the improvement of electrical conductivity. To produce high-quality graphene, high annealing temperature is needed which will help to repair the defects in RGO to improve the crystal structure[17]. The highest quality of RGO film with an electrical conductivity of 3112 $\Omega^{-1}S^{-1}$cm which was prepared through a joule heating process of about (2750K)[17]. A high-temperature graphitization of about (3000K) will restore all defects content to gain perfect ∏-∏ conjugation network in graphene whose I_D/I_G is almost zero. However, these high temperature requirement has called for great concern because of high technological equipment requirement to carry them out and time interval required.

LASER Annealing

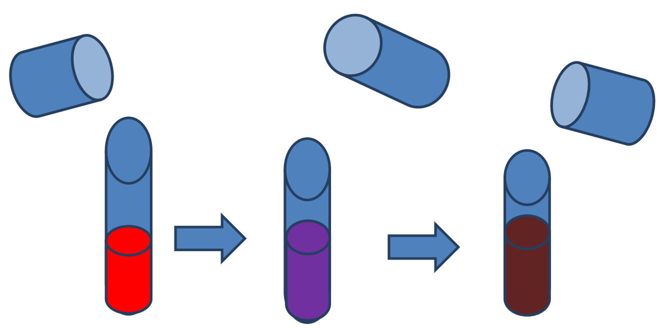
Theterm "laser annealing" came to limelight after initial studies of Gerasimenko in 1957, He observed that using pulsed LASER irradiation the structural damage in ion-implanted c-Si can be removed and the electrical activation of doped layers can be affected increasingly. In pulsed LASER annealingfor the processing to be done in a single shot the available beam size must be sufficiently large enough with high power density, the energies use is usually in the order of 1J/cm^2. However, the LASER beam is not made of matter particles but "light particles (photons)", the particle "photons" which have no mass i.e. a LASER beam and has no temperature. The photon (light particles) transfers their energy to the atomic or molecular structure of the material, which in turn causes the material to heat up. Considering the high melting point of graphene which is about 4000-6000^{0}C and the melting point of reduced graphene oxide which is about 3600^{0}C. The LASER annealing will be very good to annealing graphene since it has no initial temperature and the exposure will be for a very short time.

MATERIALS AND EQUIPMENT

The main materials used in this study are Graphite (MERCK), titaniumnanoxide D/SP (solaronix), Acetyl Acetone (Guangdong guanghuaSci-tech co Ltd), Potassium per Manganate [$KMnO_4$] (Merck), Concentrate. Tetraoxosulphate VI acid [H_2SO_4] (produce by LOBA Chemie), Hydrochloric Acid [HCL] (sigma Aldrich),hydrogen peroxide[H_2O_2] (MERCK), Phosphoric Acid [H_3PO_4] (BDH chemicals Ltd), Microscope Glass slide, sodium Hydroxide [NaOH], distilled water. The equipment areHot Air Blower, sonicator, Glove Box, industrial hot box plate, magnetic hot plate stirrer, spin-coating centrifuge, electronic weighing balance, beakers and test tubes, scanning electron microscope SEM, UV-spectroscopy, Hall Effect, profilometer, solar simulator, IR Thermometer, PIB Temperature Controller, Masking Tape, Filter paper and 15000MW DIY LASER.

Preparation of the Samples

Graphene was produce using the modified hummer's method called the Tours method. Ina bid to meet with local needs and materials available,360ml of H_2SO_4 (solvent) was mixed with 40ml of H_3PO_4 (additive). 3g of graphite was gradually added to avoid an explosive oxidation reaction. The resulting mixture was placed in a water bath at 35^{o}C on a magnetic stirrer hot plate while 18g of $KMnO_4$ was gradually added to the solution while the temperature was monitored not to exceed 50^{0}C. The careful dropping of $KMnO_4$ allowed the control of possible occurrence of a destructive combustion that can emanate due to the presence of $KMnO_4$ as the process was gassy. However, a color change to greenish purple was observed.



3g graphite+$KMnO_4$ H_2O_2+$H_2OH_2SO_4$+ H_3PO_4 360ml: 40ml

Figure 1.1: Preparation of graphene samples

While stirring, the resulting dispersion was first heated to 40^{0}C for 1 hour and later raised to 50^{0}C for 12 hours during which a thick greyish dispersion was observed. While H_3PO_4 allows more graphitic basal plane, $KMnO_4$ helps to obtain a higher oxidation degree. 400ml of ice and 3ml of H_2O_2 was added after stirring to enhance the eliminating of manganese from the colloid[18]. A color change from dark brown to light brown accompanied the addition of deionized water and H_2O_2. The colloid was allowed to sediment for 48 hours with subsequent decantation through a filter paper. The filter was cleansed severally following the sequence below:

a. With 200ml of HCL (PH of 1)
b. With 200ml of H_2O

c. With 200ml of methanol for easy drying at 50^oC over night

To make graphene oxide solution the powder form of the graphene through Redispertion 70% of Acetone $(CH_3)_2CO$ 58.08M and 30% water to 15mg per ml of dried graphene and ultra-sonicate to convert graphene oxide to reduce graphene at about 180^0C.

Pulsed Laser Reduction process of GO Films

For the purpose of this research, the pulsed laser setup consists of a 15000MW DIY LASER engraver machine, 15W LASER (λ=500 nm) operating at 80 fs pulses with a repetition rate of 1 kHz. The laser beam was concentrated down to 170 µm onto the GO film using a 10-mm lens. For this research work, the laser output power was varied within the range of 1.0–10 mW. GO films were mounted on a high-precision X−Y translation stage normal to the incident laser beam. A mechanical shutter was added in other to provide a uniform exposure of the sample area to a constant number of pulses.

Three samples of graphene oxide where prepared, in each case the doctor blading approach was use to lay the reduce graphene oxide RGO on the glass substrate against the spin coating method in other to get a thick good film in the shortest possible time. Sample A is two-layer Unannealed graphene oxide, Sample B is a two-layer thermally annealed at 400^oC graphene oxide and Sample C is a two-layers LASER annealed graphene oxide.

RESULTS AND DISCUSSION

Raman Spectroscopy Result Analysis

In this study, the Raman spectroscopy was carried out to identity the molecular composition of the samples prepared. All the Raman spectra were recorded with high resolution Jobin-Yyon Horiba T64000 micro-Raman spectroscopy equipped with a triple monochromatic system to eliminate contribution from Rayleigh scattering. To identify the functional groups of the synthesized GO Pro-Raman-L-785-BIS with serial number 196166 was utilized and the resulting spectra shows active Raman bands. The sample was excited using the 514nm wavelength of an argon excitation laser with power of 1.5Mw at the source. This was done in center for Genetic and Engineering Research Center, Bosso, Federal University of technology Minna, Nigeria.

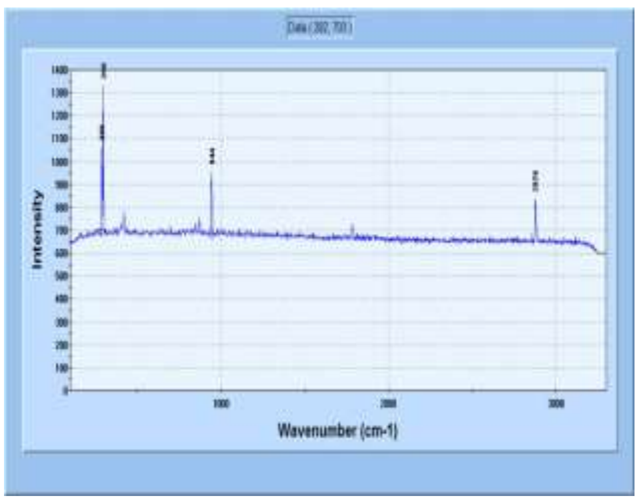


Figure 1.3: Graph showing the active Raman band of reduces graphene oxide

The prominent Raman signal at 944cm^{-1} designated by the G-band is attributed to the strong presence of *sp* hybridization of carbon atoms (C≡C).The D-band at 296cm^{-1} is ascribed to the presence of defects in the *sp* lattice and related to defects (edge, vacancy and ripples) in the graphene structure which confirms the analysis from the SEM image of the unannealed GO. The 2D band peak observed at 2876cm^{-1} is credited to the oxidation of the graphene structure with the of oxygen and hydrogen functional group. The intensity ratio of the D/G band (I_D/I_G) and intensity ratio 2D/G band (I_{2D}/I_G) may provide valuable information about the structure of graphene and graphene materials. The I_D/I_G represents the defects density[19]while I_{2D}/I_G denotes the numbers of the layers[20] in graphene. The position of the D-band,G-band and 2D-band correspond to carbon material called graphene oxide.

Hall Effect Measurement Analysis

Hall Effect is basic solid-state equipment suitable for characterizing the nature if positive or negative charge carriers, corresponding density, mobility, conductivity and resistivity of materials. The ECOPIA HMS-300 was used to characterize the RGO at different annealing conditions.

TABLE 1.2: Showing the electrical properties of the three samples of RGO from the Hall Effect measurement

S/N	Electrical properties	Sample A Unannealed	Sample B Thermally annealed	Sample C LASER annealed
1	Bulk concentration(/cm^3)	2.215E+13	4.392E+12	-1.03E+12
2	Mobility (cm^2/Vs)	8.358E+1	5.317E+3	2.715E+4
3	Sheet-Resistance(ohm)	1.124E+8	1.337E+7	1.955E+6
4	Resistivity (ohm)	3.373E+3	2.673E+2	4.300E+1
5	A-C Cross Hall Coefficient (cm^3/C)	-1.039E+6	1.900E+5	1.433E+5
6	Magneto-Resistance (ohm)	7.577E+7	1.064E+8	1.603E+7
7	Sheet Concentration (/cm^2)	6.644E+8	8.783 E+7	-1.176E+8
8	Conductivity (1/ohm)	2.965E-4	3.740E-3	2.325E-2
9	Average Hall Coefficient (cm^3/C)	2.819E+5	1.421E +6	-1.167E+6
10	B-D Cross Hall coefficient (cm^3/C)	1.603E+6	2.653E+6	-2.476E+6
11	Ratio of vertical/horizontal	-1.678E-1	-7.535E-1	-2.714E+0

Hall Effect measurement was used to characterize the nature and properties of the following: charge carriers, bulk concentration, mobility, resistivity, sheet concentration, conductivity etc. of the reduced graphene oxide at different annealing condition. The results above agree with the theoretical propose values on the properties of graphene that makes it suitable for solar device application at the Nano-particle scale. The two-layer LASER annealed graphene according to theoretical results have better results. The sheet resistance of the two-layer LASER annealed was found to be 1.955E6 which is lower than others because the LASER annealing leads to the flattening of the graphene layers which account for the improvement in the electrical properties of the graphene such as the conductivity and others. The considerable reduction in the sheet resistance confirms the assessment: electrical transport in graphene films is dominated by the junction resistance of the inter-flakes and the number of junctions along the percolation paths[21]. As the graphene films are flattened, the overlapping flakes/ the junction area increases compared to the un-annealed and the inter flakes resistance reduces drastically. Therefore, the percolation path is reduced and these leads to the reduction in the sheet resistance.

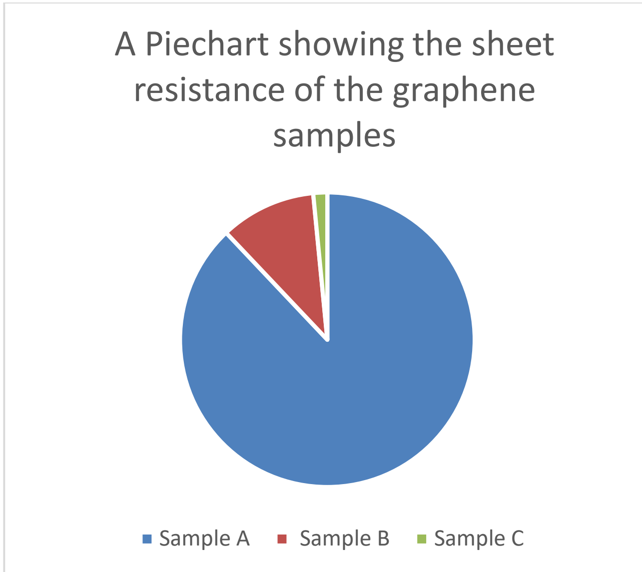


Figure 1.4: A pie chart showing the sheet resistance of the different graphene samples

In addition to flattening of the layer of graphene films, the LASER annealing may have help in removing the remaining polymer (ethyl cellulose) that are trapped between the flakes on the film by local heating. The flow of heat in the graphene layers and graphite cross-plane direction has strongly the inter plane van der waals forces which may also be the reason for the improve conductivity of the graphene.

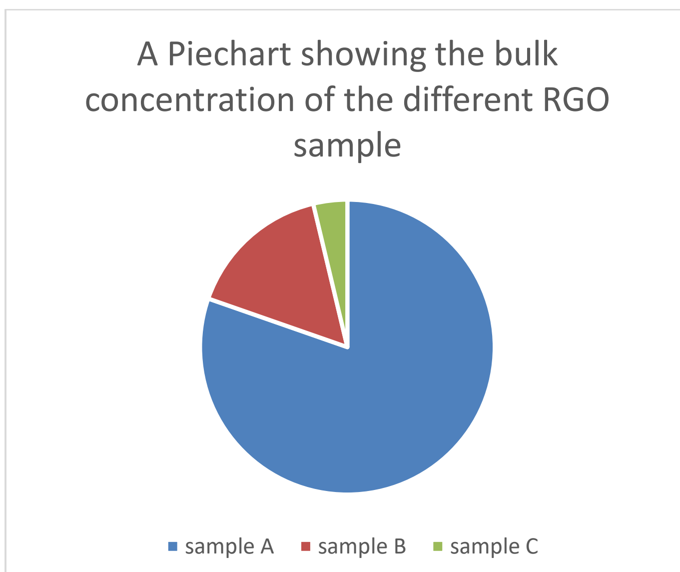


Figure 1.5: A pie chart showing the bulk concentration of the different RGO samples

From the figure above the two layer unannealed has a bulk concentration of 2.22E+13 which is 86.8% of the total bulk concentration. There is significant reduction of the GO sheets is evidenced by the reduction in the bulk concentration, the GO exhibits three components that can be attributed to carbon atoms in different functional groups: The C in C–O bonds, the non-oxygenated ring C,and carboxylate carbon (C=O). It is observed that the carbon content bonded to oxygen is reduced from 95.5% in the initial unannealedGO to 4.5% in LrGO indicating that the majority of oxygen groups and other polymer group were removed.With the pulse laser annealing It is observed that such improvement can be achieved without any apparent damage in the structural, mechanical properties and integrity of the RGO substrate, the bulk concentration of the LASER two-layer graphene oxide was found to be -1.03E+12 which is 4%, to conform the reduction in the graphene oxide.

The conductivity of a semiconductor depends on the product of mobility and concentration of the charge carriers. The two quantities are independent.mobility is the drift velocity per unit electric field and depends only slightly with temperature but concentration of charge carriers increases exponentially with temperature.

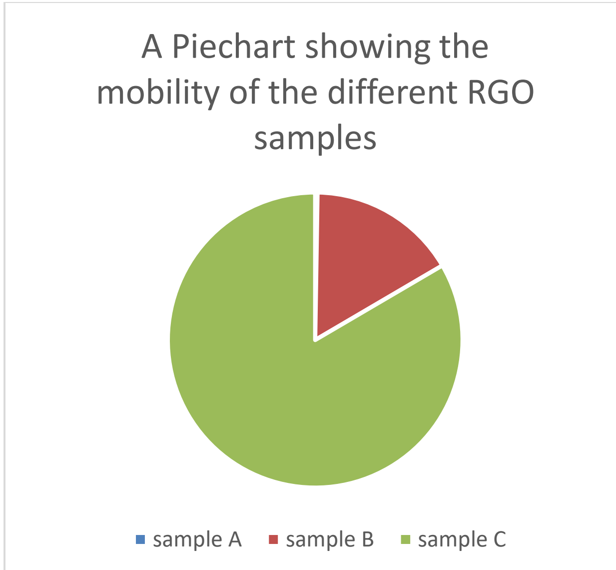


Figure 1.6: A pie chart showing the mobility of the different RGO Samples

The mobility increases with temperature because the field of the substrate surface phonons is effectively screen by the additional graphene layer and the mobility is dominated by coulomb scattering. The two-layer LASER annealed graphene having the maximum mobility of 2.72E+04 which is 83.4% compared to others, the two-layer annealed thermally at 400^{0}C has mobility of 5.32E+03 which is 16% while the least mobility was observe in two-layer unannealed which was found to be 8.328E+1 which is insignificant compared to the others. The mobility of the un-annealed sample might due to the high presence of impurities and resistance of the component of the impurity.

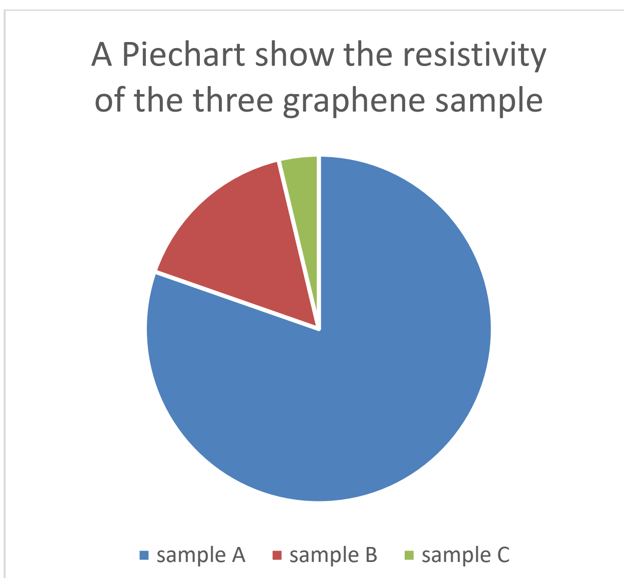


Figure 1.7: A pie chart showing the resistivity of the different samples of RGO

The pie chart above shows the resistivity of the different sample of graphene. We observe that the resistivity of two-layer LASER annealed is the least which is 4.30E+01, almost 0% compared to the others. Two layer thermally annealed at 400^{O}C follows the expected trend which the resistivity of graphene decreases with increase in temperature.

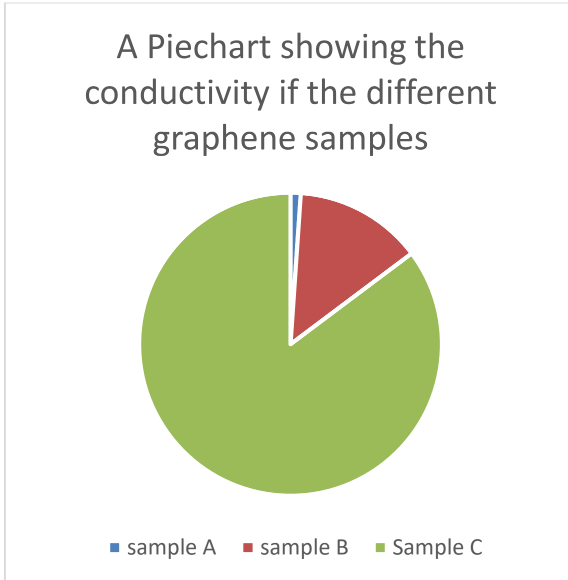


Figure 1.8: A pie chart showing the conductivity of the different RGO sample

The electrical conductivity is a measure of the ease at which an electric current passes through a material mathematically it the reciprocal of resistivity and it is measured in the reciprocal ohm meters. The electron mobility has been increased with increased in temperature, the conductivity of graphene has been found to depend on the temperature, electric field, magnetic field etc. The only variable here is the temperature. The conductivity of two-layer LASER annealed graphene was found to have the biggest conductivity with value 2.33E-02 which is 85% of the total conductivity.

The two-layer LASER annealed graphene has been found to have better values in terms of electrical.

ANALYSIS OF THE UV-VIS SPECTROPHOTOMETRY RESULT

The absorptivity transmittance and reflectance of the four samples of reduce graphene oxide were investigated using UV-750 series between 230-1200nm wave lengths. The graphical representation of each configuration as deposited on FTO glass slides for necessary investigation are represented below. However, the absorption as reported was normalized by dividing through by the highest peak Absorbance, transmittance, and reflectance thereby in a range from 0 and 1.

Sample A

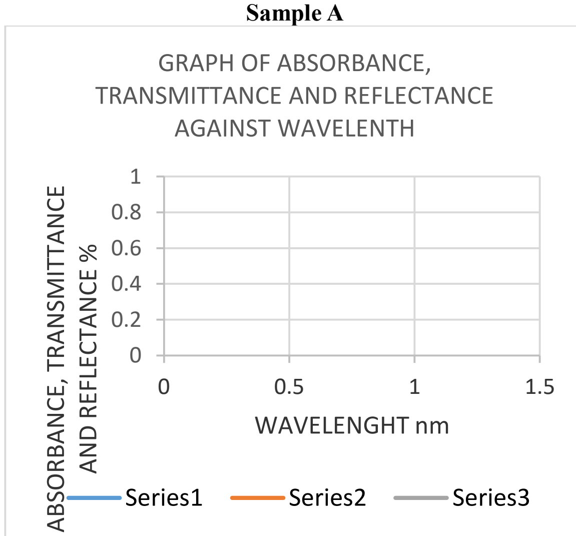


Figure 1.9.1: Showing the Graphical Representation for the Absorbance, Transmittance and Reflectance of The 2 Layer Un-Annealed Reduced Graphene Oxide.

From the above result gotten from the two layer of Un-annealed reduce graphene oxide, the Absorbance is 7.23%, Transmittance is 3.88% and Reflectance is 88.88%

Sample B

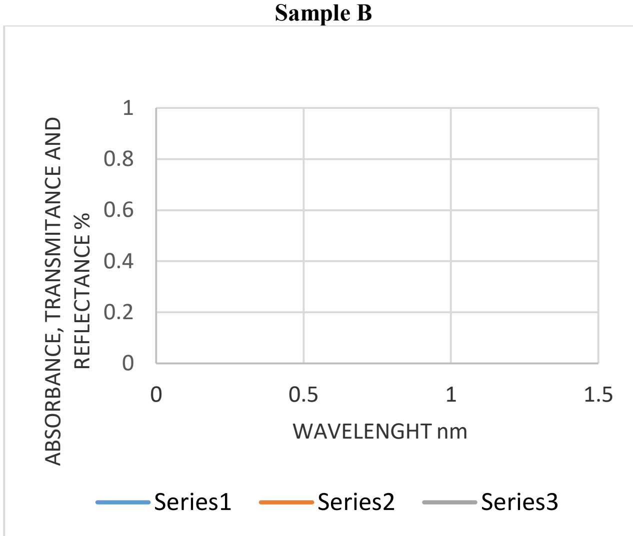


Figure 1.9.2: Showing the Graphical Representation for the Absorbance, Transmittance and Reflectance of the 2 Layer Annealed at 400^{0}C Reduced Graphene Oxide.

From the above result gotten from the two layer Annealed at 400^{0}C of reduce graphene oxide, the Absorbance is 57.4%, Transmittance is 35.48% and Reflectance is 7%.

Sample c

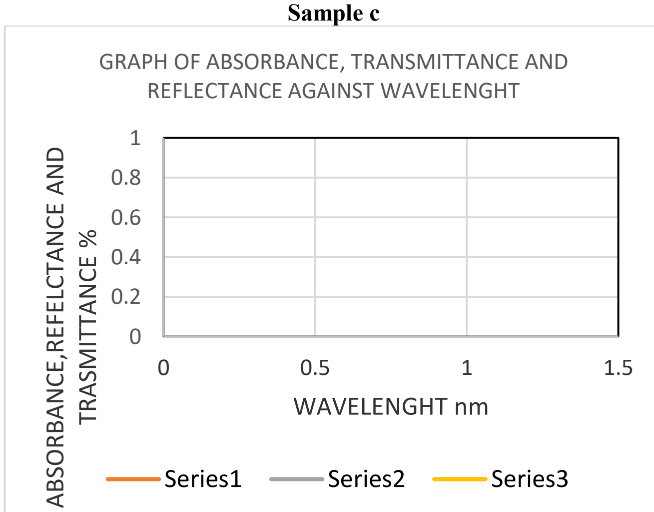


Figure 1.9.3: Showing the Graphical Representation for the Absorbance, Transmittance and Reflectance of the 2 Layer Laser Annealed Reduced Graphene Oxide.

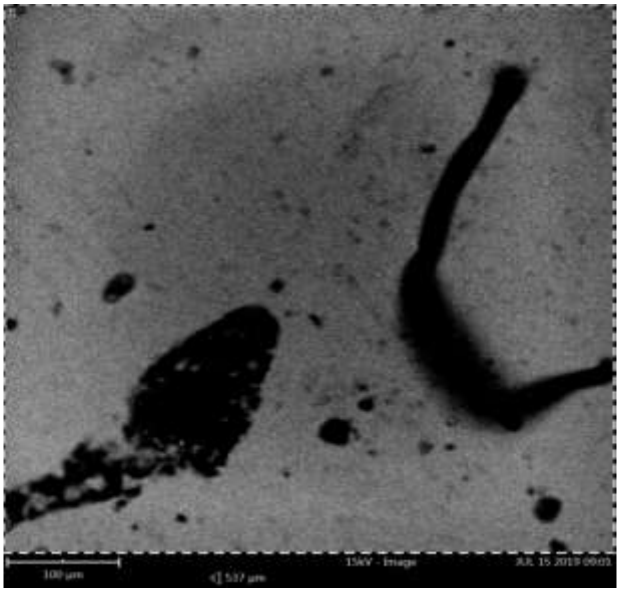
From the above result gotten from the two layer of LASER annealed reduce graphene oxide, the Absorbance is 21.08%, Transmittance is 58.86% and Reflectance is 21.08%.

From the graph of absorbance against wavelength for the three samples of reduced graphene the absorbance increases with increase in the annealing temperature. The lowest absorbance was observed in the un-annealed sample while the highest was observe in two-layer annealed at 400^{o}C sample. The absorbance peak of all the samples was less than 300nm, this absorbance peak is due to electronic transition between the molecule having an intermediate ionic degree in conformity with those of the synthesized molecular material. At such a wavelength, no visible light can be absorbed since graphene is absorbing within the ultra-violet region. The absorbance increase with increase in the annealing temperature is due to the fact that the increase in temperature helps in reducing the graphene oxide and reducing the excess impurity.

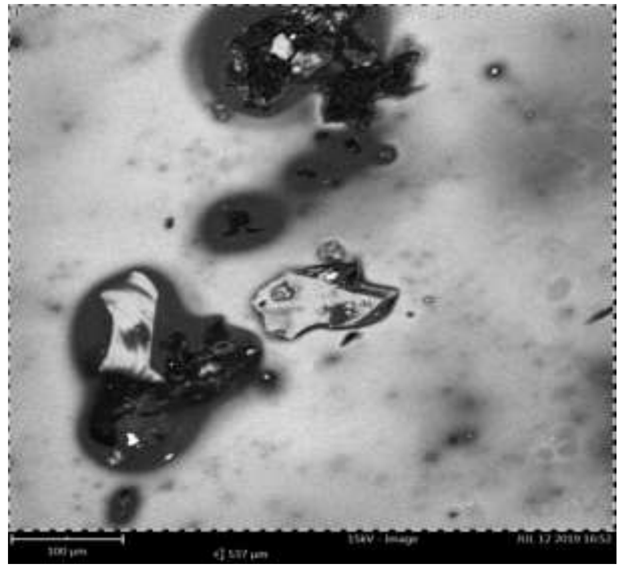
The major advantage of the LASER annealing technique over the thermal reduction method is that the combination of short laser pulses (fs) and the right repetition rate which help in the fast removal of the polymer and oxygen groups from the GO crystal without causing any damage thermally to the graphene lattice and the deposition substrate. However, the two-layer LASER annealed has a greater transmittance compared to the others which is very important to numerous applications in technology.

The SEM Measurement

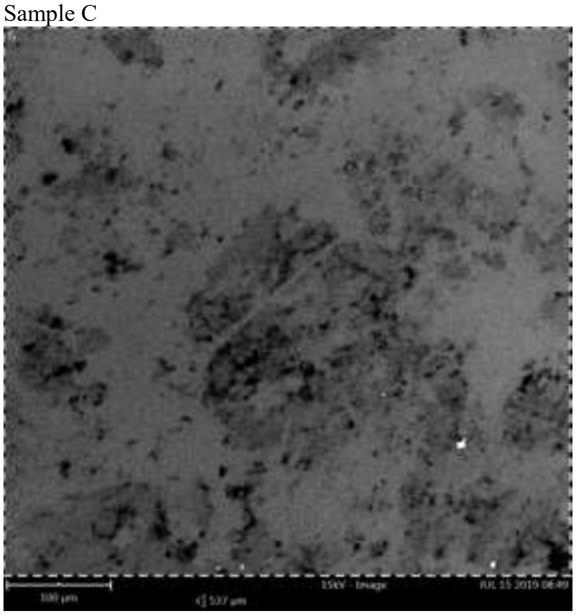
Sample A



Sample B



Sample C



From the morphological image of the different samples of RGO, we observe that the graphene where evenly distributed around the substrate in the LASER annealing than the other samples. This shows that to ensure the evenly distribution and reduction in the sheet resistance the LASER annealing is a step forward in technological application.

CONCLUSION

In conclusion, we are able to carry out an efficient laser-based method for the reduction of transparent GO Nano-layersthat were solution-processed. The results from both the laser annealing and the thermally method shows that the laser annealing is faster considering the application of the pulse laser method. Pulsed laser photo-reduction is a simple, fast, energy efficient, and free from poisonous material.

Furthermore, this method of reducing graphene oxide can be applied in a large scale for mass production of rGO because it is fastand large-area processing can be realized, hence, making this technique easily applicable in the product of flexible roll-to-roll mass manufacturing.

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