Copyright © 2016 Tech Science Press CMC, Vol.52, No.3, pp.173-184, 2016

Structural and Optical Properties of Graphene Oxide Prepared by Modified Hummers' Method

N. Selvakumar[1,2], Uday Pradhan[1], S.B. Krupanidhi[2] and Harish C. Barshilia[1*]

Abstract Graphene oxide was synthesized from graphite flakes using modified Hummers' method. The interlayer spacings of graphite, graphite oxide and graphene oxide were measured using X-ray diffraction technique. The C/O atomic ratios of graphite oxide and graphene oxide were calculated from XPS measurements. The transformation of graphite to graphite oxide and finally to graphene oxide was clearly observed from the micro-Raman spectroscopy data and was confirmed from the FESEM micrographs. UV-VIS-NIR spectrophotometer was used to study the absorbance of graphene oxide and reduced graphene oxide samples. Finally, the chemically reduced graphene oxide was heat-treated in air to obtain chemically modified graphene.

Keywords: Graphene oxide, Graphite, modified Hummers' method, thermal annealing, optical properties.

1 Introduction

Graphene is a single atom thick, sheet of rigid two dimensional hexagonal lattice structure consisting of sp^2 hybridized carbon atoms [Geim and Novoselov (2007)]. It has been a material of great interest due to its excellent properties like high mechanical strength, thermal conductivity, optical and electrical conductivity. Graphene also finds potential applications in the field of sensing, metamaterials, solar cells, photonics, plasmonics, photodetectors and optoelectronics [Bonaccorso and Sun (2010; Yang and Kim (2013) Liu and Jackson (2010))]. Due to this, various methods such as mechanical exfoliation, annealing of SiC under ultrahigh vacuum, chemical vapor deposition (CVD), reduction of graphene oxide (GO), etc. have been used to prepare graphene [Aissa and Memon (2015); Mattevi and Kim (2011)]. In 2004, Geim and Novoselov have produced graphene by micromechanical cleavage of bulk graphite. However, this technique can produce graphene flakes only in limited quantities. To fulfill the present demand of graphene for various applications, mass production is very much required. Even though several methods have been proposed to produce graphene, chemical reduction of graphene oxide is the best method to produce chemically modified graphene in large

---

[1] Nanomaterials Research Lab, Surface Engineering Division, CSIR-National Aerospace Laboratories, Bangalore – 560017, India

[2]Materials Research Center, Indian Institute of Science, Bangalore – 560012, India

* harish@nal.res.in

quantities. In this approach, graphite is chemically oxidized to graphite oxide using different kinds of oxidizing reagents such as $KMnO_4$, $NaNO_3$ [Staudenmaier (1898)], $KClO_3$ [Brodie (1859)] etc. in an acidic medium. In graphite oxide, the oxygen functional groups like epoxy (C-O-C), carbonyl (C=O), carboxyl (COOH), hydroxide (OH) [Hummers and Offeman (1958)] are formed between the graphite interlayers and at the edges. Graphite oxide is the intermediate product between graphite and graphene oxide and it can be used as a precursor to produce reduced graphene oxide (RGO). The role of oxide functional groups is to weaken the Vander Waal's force between the graphite layers by increasing the interlayer spacing from 0.34 nm to 0.8 nm [Dreyer and Park (2009)]. The simple ultrasonication and stirring of colloidal graphite oxide in deionized water can easily exfoliate graphite oxide to single layer or few layers of graphene oxide (GO). The graphene oxide layer size and extent of oxidation depends upon different factors such as size of graphite flakes, quality of graphite, oxidation time, temperature, and the quantity of oxidizing agents [Some and Kim (2013)].

The synthesis of graphite oxide has been widely studied in the past. In 1859, Brodie et al. reported preparation of graphite oxide, in which $KClO_3$ (potassium chlorate) was used to oxidize graphite to graphite oxide in fuming HNO_3 (Nitric acid). In 1898, Staudenmaier simplified Brodie method, by adding concentrated sulphuric acid (H_2SO_4) in place of fuming HNO_3. The major drawback of these methods is that the oxidation of graphite takes long time. The most widely used method for synthesis of graphene oxide was proposed by Hummers and Offeman in 1958. They oxidized graphite with concentrated sulphuric acid, sodium nitrate and potassium permanganate. Chen and Yao et al. (2013) have slightly modified the Hummers' method and proposed an eco-friendly method for the synthesis of graphene oxide. In the modified Hummers' method, $NaNO_3$ has been avoided since it produces toxic gases like NO_2/N_2O_4 during oxidation [Chen and Yao et al. (2013); Marcano and Kosynkin (2010); Pei and Cheng (2011)]. Various researchers have used the modified Hummers'method to produce graphene oxide [Eda and Fanchini et al. (2008); Fan and Wang et al. (2010); Guo and Wang et al. (2003); Shahriary and Athawale (2014); Tung and Allen et al. (2009); Wu and Gao et al. (2013); Zhang and Li et al. (2014)]. However, to the best of our knowledge, the reflectance value of graphene oxide has not been reported in the literature.

In the present work, we have synthesized graphene oxide using modified Hummers' method. The as-prepared graphite oxide was reduced using hydrazine hydrate in order to obtain reduced graphene oxide. Using hydrazine hydrate, the epoxy (C-O-C), carboxyl (COOH) and carbonyl (C=O) groups attached to graphene oxide can be easily reduced. However, it is difficult to remove the OH groups from graphene oxide. In order to achieve this, thermal annealing in air at different temperatures was carried out. The variations in the surface morphology of graphite oxide and graphene oxide samples were studied using field-emission scanning electron microscope (FESEM). The structural and chemical properties of these samples have been studied using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and micro-Raman spectroscopy techniques. UV-VIS-NIR spectrophotometer was used to measure the absorbance and reflectance of graphene oxide.

2 Experimental

Graphene oxide was prepared through modified Hummers' method from graphite flakes (98% purity, 60 mesh, Loba Chemie Pvt. Ltd.). The synthesis of GO involves the following steps. First, 3 g of graphite was added into 70 ml of H_2SO_4 (98% concentrated) and the solution was stirred vigorously for 30 min at room temperature. Subsequently, the beaker with graphite and H_2SO_4 was kept in an ice bath at temperature below 0°C, followed by addition of potassium permanganate ($KMnO_4$, 98.5% concentrated). The solution temperature was kept below 5°C and stirred continuously for 30 min. After addition of the oxidant, the temperature of the solution was raised to 45°C by a hot plate and stirred for 24 hr. In the next step, deionized water was added slowly into the solution, which leads to an increase in the process temperature. During this step, the process temperature was maintained at 95°C using a hot plate. In order to stop the oxidation reaction, 400 ml of deionized water and 15 ml of H_2O_2 (30%) were added.

The as-prepared graphite oxide solution was allowed to settle down and water at the top was removed without disturbing the graphite oxide at the base of the beaker. The obtained graphite oxide was filtered by Whatman filter paper (42 grade, 0.2 µm). Subsequently, the graphite oxide was washed several times in dilute HCl (35%) in order to remove the metal ions. By rinsing it with deionized water for several times using centrifugation, the pH of graphite oxide was increased to 6. The dark brown gel of graphite oxide was vacuum dried at 60°C for 4 hr. The obtained dark brown product was allowed to dry in air and the powder was mixed with 400 ml of deionized water and stirred for 1 hr. The yellowish brown solution was kept for ultrasonification for 2 hrs in order to exfoliate the graphite oxide to graphene oxide (i.e., mono or multi layers).

Reduced graphene oxide was obtained by both chemical and thermal annealing methods. In the chemical method, hydrazine hydrate (80%) was added as a reducing agent in the graphite oxide solution. 400 µL of hydrazine hydrate was added drop wise in the solution and then heated to 95°C for 3 hr with continuous stirring. The formation of black precipitation indicates the reduction of graphene oxide. The solution was again filtered and air dried at 60°C. In thermal annealing method, the powder of graphite oxide was heat-treated in air in the range of 400-700°C for 30 min to obtain reduced graphene oxide.

The interlayer spacings of graphite, graphite oxide and reduced graphene oxide were studied using powder X-ray diffraction technique (Bruker D8 Advance). The atomic C/O ratios of the graphite oxide and graphene oxide were characterized by X-ray photoelectron spectroscopy (SPECS) using non-monochromatic MgK_α radiation (1253.6 eV). A DILOR-JOBIN-YVON-SPEX integrated micro-Raman spectrometer (Model Labram) was used to obtain the Raman spectra. UV-VIS-NIR (Perkin-Elmer, Lambda 950) spectrophotometer was used to measure the absorbance of the graphite oxide and graphene oxide samples for a wavelength range of 0.25-0.8 µm. A 150 mm Spectralon® integrating sphere attachment was used to measure the total reflectance of graphene oxide in the UV-VIS-NIR region (i.e., 250-2500 nm). The absorptance (α) of the graphene oxide sample was calculated from the reflectance data using the selected ordinates method. The emittance (ε) of the reduced graphene oxide pellet was measured using emissometer of M/s Devices and Services, USA.

3 Results and Discussion

3.1 X-ray Diffraction

Figure 1(a-c) shows the XRD patterns of graphite powder (Fig. 1a), graphite oxide (Fig. 1b) and reduced graphene oxide (Fig. 1c) samples. The XRD pattern of graphite flakes (Fig. 1a) shows a sharp peak at $2\theta = 26.5°$ (d spacing - 0.335 nm) [Jeong and Jin (2009)]. After oxidation of graphite, the (002) peak of graphite disappeared and a peak at $2\theta = 8.98°$ (d spacing - 0.98 nm, Fig. 1b) was formed, which confirms the complete oxidation of graphite to graphite oxide. The increase in the interlayer spacing (i.e., from 0.335 nm to 0.98 nm) weakens the Vanderwaals force between the layers, which allows easy exfoliation of graphite oxide to monolayer or few layers of graphene oxide.

Figure 1

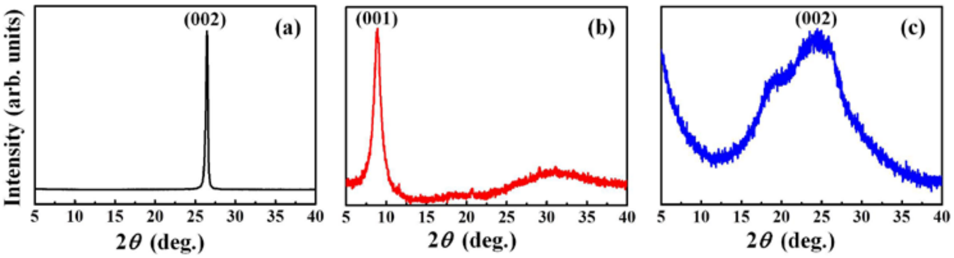

Figure 1: XRD patterns of (a) graphite, (b) graphite oxide and (c) reduced graphene oxide samples

Further reducing the graphite oxide with hydrazine hydrate resulted in a broad peak at 24.5° (Fig. 1c). The broad peak indicates the nanocrystalline/amorphous nature of reduced graphene oxide and this may be due to the defects formed by removal of some of the oxide functional groups. The interlayer spacing for reduced graphene oxide was approximately 0.363 nm. Even though, the hydrazine hydrate is efficient in removal of epoxy (C=O, C-O-C) groups, it cannot remove the hydroxyl (OH) groups from graphene oxide. The shoulder peak at $2\theta = 19°$ may be due to presence of -OH groups or other functional groups which were not reduced by the reducing agent [Jeong and Jin (2009)]. The XRD data clearly shows the presence of graphite oxide and graphene oxide. This data was supported by micro-Raman spectroscopy data and is discussed below.

3.2 Micro-Raman Spectroscopy

Figure 2

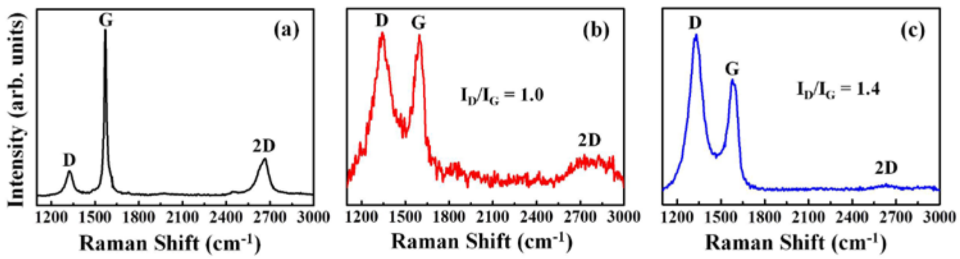

Figure 2: Micro-Raman spectra of (a) graphite, (b) graphite oxide and (c) reduced graphene oxide samples.

Raman spectroscopy is widely used to study the defects, disorder and crystal structure of carbon based materials. The Raman spectrum of graphite (Fig. 2a) shows three major peaks D, G and 2D at 1324, 1570 and 2667 cm^{-1}, respectively. Figure 2b and 2c show the Raman spectra of graphite oxide and reduced graphene oxide, respectively. The D peak of graphite oxide and graphene oxide situated at 1342 and 1331 cm^{-1}, respectively and the presence of D band is due to defect induced breathing mode of sp^2 carbon rings. Similarly, the G peak is located at 1596 cm^{-1} for graphite oxide and 1579 cm^{-1} for RGO and the presence of G peak is due to first order scattering of the E_{2g} optical phonon of sp^2 hybridized (C=C) aromatic carbon rings [Yang and Velamakkani (2009)].

The 2D peak is considered as second order peak and arises on account of zone boundary phonons. The blue shift of G peak in graphite oxide (i.e., from 1325 cm^{-1} to 1343 cm^{-1}) indicates the formation of alternating sp^2 and sp^3 bonds or domains [Yang and Velamakkani (2009)]. Furthermore, red shift of G peak towards the original peak position of graphite was observed in reduced graphene oxide sample which indicates the recovery of sp^2 bonds. The relative intensity ratio (I_D/I_G) measures the degree of disorder and is inversely proportional to the average size of the sp^2 clusters. The I_D/I_G ratio of graphene oxide (1.4) is larger than graphite oxide (1.0) and it is due to the formation of new or more graphitic domains and also from the increase in the number of sp^2 cluster after reduction.

It has also been reported that the increase of the D peak intensity indicates formation of more sp^2 domains [Sobon et al. (2012)]. The Raman data clearly shows the transformation of graphite to graphite oxide and finally to graphene oxide. The XRD and Raman results were further confirmed by the X-ray photoelectron spectroscopy data.

3.3 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy technique was used to study the bonding structure of graphite oxide and graphene oxide samples. Figure 3 (a and d) show the survey spectra of graphite oxide and reduced graphene oxide samples and it is clearly evident from the figures that the C/O ratio is greater for reduced graphene oxide than graphite oxide. The atomic ratio of carbon to oxygen was calculated from the survey spectrum and the values are 1.59 and 4.44 for graphite oxide and graphene oxide, respectively. These values clearly showed that reducing the graphite oxide with hydrazine hydrate removed some of the oxygen containing functional groups, which resulted in increase in the C/O ratio. Deconvolution of the C 1s and O 1s spectra was performed using a Gaussian peak shape after performing a Shirley background correction. Figure 3b shows the deconvoluted high resolution C 1s spectrum of graphite oxide. The peak centered at 284. 4 eV corresponds to C-C bonding of sp^2 carbon atoms. Whereas, peaks centered at 285.9 and 286.4 eV correspond to C-OH and C=O, respectively [Yang and Velamakanni (2009)]. Figure 3e shows the C 1s spectrum of reduced graphene oxide and it is clearly evident from the figure that the intensity of C-OH peak was reduced. Furthermore, the C=O peak disappeared and a broad peak centered at 288.3 eV was observed, which is attributed to O=C=OH peak. The O 1s spectra of graphite oxide and reduced graphene oxide are shown in Figure 3c and 3f, respectively. The peaks centered at 531.5 and 533.4 eV correspond to C-O and C=O, respectively. After reduction, the O 1s peak intensities were considerably reduced (Figure 3f).

3.4 Field Emission Scanning Electron Microscopy

Figure 4 (a-c) shows the FESEM micrographs of graphite oxide, graphene oxide and reduced graphene oxide solutions dried on SS substrates. Single flakes of graphite oxide are clearly visible in Figure 4a. The ultrasonication of the graphite oxide solution for 30 min resulted in few layers of graphene oxide and is clearly evident from Figure 4b. Further reducing the graphene oxide solution with hydrazine hydrate resulted in RGO and the graphene like islands are observed in Figure 4c.

Figure 3

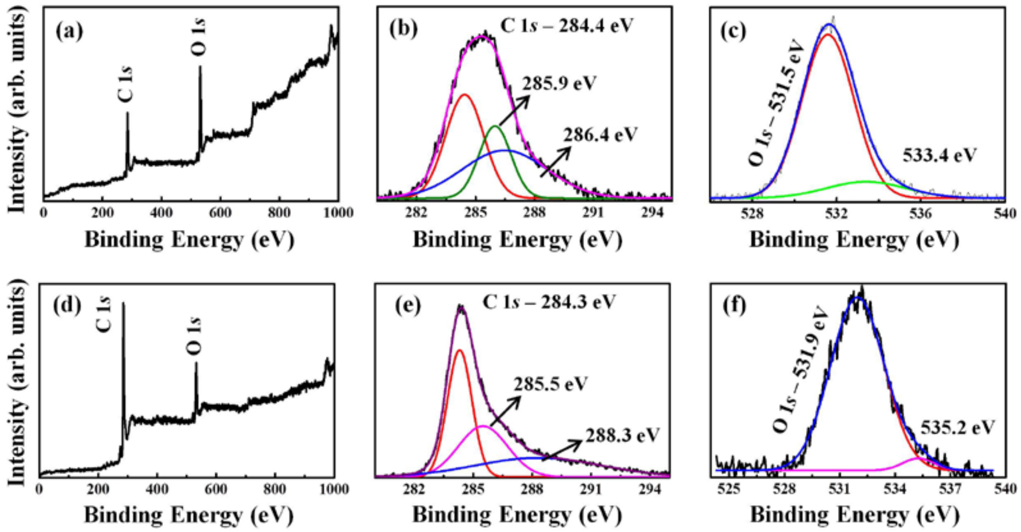

Figure 3: High resolution XPS spectra of (a) survery spectrum, (b) C 1s and (c) O 1s of graphite oxide; similarly (d) survery spectrum, (e) C 1s and (f) O 1s of reduced graphene oxide.

Figure 4

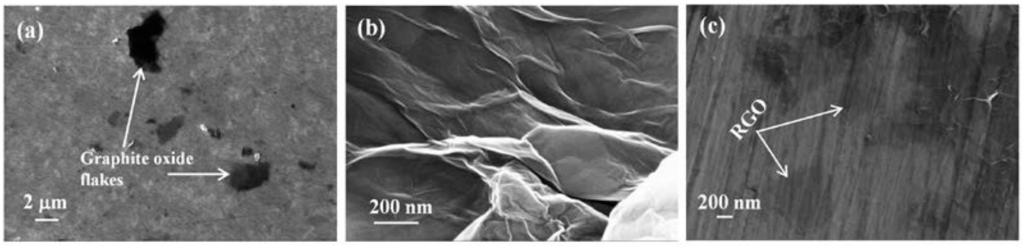

Figure 4: FESEM micrographs of (a) graphite oxide (b) graphene oxide and (c) reduced graphene oxide deposited on SS subtrates.

3.5 Optical Properties

In order to study the optical properties, the GO and RGO powders were dissolved in deionized water and the solutions were taken in quartz cuvette for absorbance measurements. Figure 5 (a and b) shows the absorbance spectra of graphene oxide (1 mg/ml) and reduced graphene oxide (RGO) (0.5 mg/ml) solution. The GO absorbance peak appears at 235nm and a shoulder peak is observed at 300 nm, which are due to the π to π* transition in C=C bonds of aromatic rings and n-π* transition of C=O bonds, respectively [Lai et al. (2012)]. In reduced graphene oxide, (Figure 5b), the red shift of absorbance peak was observed (i.e., from 235 nm to 277 nm) which indicates the increase in π-electrons concentration and recovery of sp^2 structural ordering [Lai et al. (2012)]. Furthermore, the absorbance shoulder peak of GO at 300 nm disappears which indicates the decrease in C=O concentration [Lai et al. (2012)]. The intensity of absorbance depends upon the concentration of dispersed GO in solution. The dispersion concentration of GO is greater than that of RGO due to its hydrophilic nature imparted by the oxygen functional groups.

The reflectance of the reduced graphene oxide sample was carried out using an integrating sphere attachment in the Lambda 950 UV-VIS-NIR spectrophotometer. Figure 6 shows the total reflectance spectrum of RGO pellet in the wavelength range of 250-2500 nm. The α of the sample was calculated from the selected ordinates method. The α and ε of the RGO sample were 0.96 and 0.92, respectively. Further studies are currently underway to reduce the emittance of RGO samples. The reflectance data clearly showed that the chemically reduced graphene oxide can be used as an absorber for solar thermal applications.

Figure 5

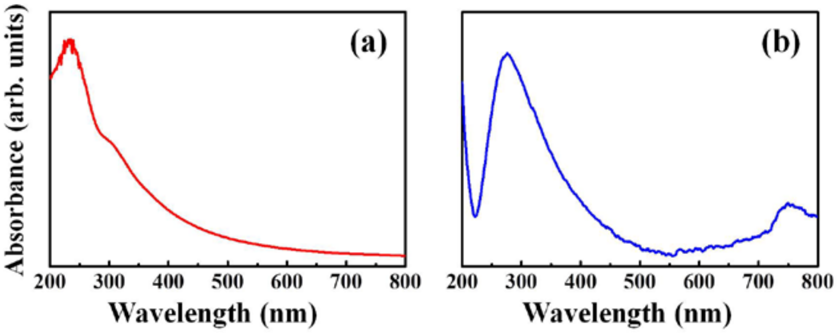

Figure 5: Absorbance spectra of (a) graphene oxide and (b) reduced graphene oxide solutions.

3.6 Thermal Annealing in Air

Even though graphene oxide was reduced using hydrazine hydrate, some hydroxyl functional groups attached to graphene oxide were not reduced. In order to remove these functional groups and also to achieve chemically modified graphene, the chemically reduced graphene oxide was further annealed in air at temperatures in the range of 400-

Figure 6

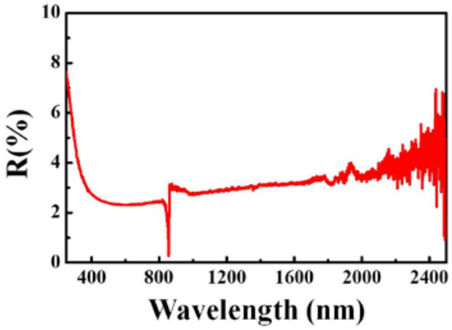

Figure 6: Reflectance spectrum of reduced graphene oxide pellet.

Figure 7

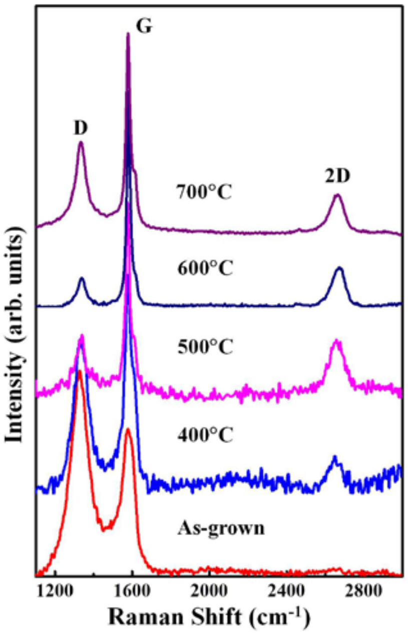

Figure 7: Composite Raman spectra of chemically reduced graphene oxide sample heat-treated in air at different temperatures for 30 minutes.

700°C. Figure 7 shows the Raman spectra of RGO samples heat-treated in air at different temperatures. The Raman study of these samples shows significant decrease in (I_D/I_G) ratio, due to the removal of amorphous carbon and oxygen functional groups with an increase in annealing temperatures. The presence of sharp G and 2D peaks at higher wavenumber compared to flat 2D peak of chemically reduced graphene oxide indicates the presence of multilayer graphene [Ferrari et al (2006)]. It has to be mentioned that at higher annealing temperatures such as 600 and 700°C, the yield of multilayer graphene obtained after reducing the RGO is very low when compared to 400 and 500°C.

4 Conclusions

The structural and optical properties of graphene oxide synthesized using Modified Hummers' method were studied. The decrease in the interlayer spacing for RGO (0.36 nm) when compared to GO (0.98 nm) confirmed the recovery of sp^2 carbon atoms and the reduction of functional groups in GO. The higher C/O atomic ratio for RGO (4.44) than GO (1.59) obtained from the XPS data clearly showed that reducing the graphite oxide with hydrazine hydrate reduced the oxygen containing functional groups. The transformation of graphite oxide to reduced graphene oxide was evident from the I_D/I_G ratios of GO (1.0) and RGO (1.4) evaluated from the micro-Raman spectroscopy data. The increase in the I_D/I_G ratio for RGO confirmed the formation of more sp^2 domains. The presence of GO and RGO was further substantiated by the absorbance peaks observed at 235 and 277 nm, respectively. The α and ε of the RGO sample were 0.96 and 0.92, respectively. Chemically modified multilayer graphene was obtained after thermal annealing of chemically reduced graphene oxide in air at temperatures in the range of 400-700°C. These results clearly showed that the graphene oxide can be used as a potential candidate for solar thermal applications.

Acknowledgement The authors thank the Director, NAL for giving permission to publish these results. We thank Mr. G. Srinivas and Mr. Siju for carrying out X-ray diffraction and FESEM studies.

References

Aissa B.; Memon N.K.; Ali A.; Khraisheh M.K. (2015): Recent progress in the growth and applications of graphene as a smart material: a review, *Front Mater* vol. 2, article no. 58.

Bonnaccorso F.; Sun Z., Hasan T.; Ferrari A.C. (2010): Graphene photonics and optoelectronics, *Nature Photon* vol. 4 pp. 611-622.

BRODIE B. C. (1859): On the Atomic Weight of Graphite. Philos Trans R. Soc. London, vol.14, pp.249-252.

Chen J.; Yao, B.; Li C.; Shi G. (2013): An improved Hummers method for eco-friendly synthesis of graphene oxide. *Carbon*, vol.64, pp. 225-229.

Dreyer D.R.; Park S.; Bielawski C.W.; Ruoff R.S. (2010): The chemistry of graphene oxide, *Chem. Soc. Rev*, vol. 39, pp. 228-240.

Eda G.; Fanchini G.; Chhowalla M. (2008): Large-area ultrathin films of reduced graphene oxide as a transparent and flexible electronic material, *Nature Nanotechnology*. vol.3, pp.270-274.

Fan Z.; Wang K.; Wei T.; Yan J.; Song L.; Shao B. (2010): An environmentally friendly and efficient route for the reduction of graphene oxide by aluminum powder. *Carbon* vol.48, pp.1670 –1692.

Ferrari A.; Meyer J.C.; Scardaci V.; Casiraghi C.; Lazzeri M.; Mauri F.; et al. (2006): Raman spectrum of graphene and graphene layers, *Phys. Rev. Lett.* vol. 97, pp. 187401-1 – 187401-4.

Geim A.K. ;Novoselov K.S (2007): The rise of graphene. *Nature Materials*, vol.6, pp.183-191.

Guo H.L; Wang X.F; Qian Q.Y; Wang F.B; Xia X.H (2003): A Green Approach to the Synthesis of Graphene Nanosheets. *ACS Nano.* vol.3, no. 9, pp. 2653–2659.

Hummers W.S.; Offeman R.E. (1958): Preparation of Graphitic Oxide, *J Am Chem Soc*, vol. 80, no.6, pp. 1339.

Jeong H.K.; Jin M.H.; So K.P.; Lim S.C.; Lee Y.H. (2009): Tailoring the characteristics of graphite oxides by different oxidation times, *J. Phys. D. Appl. Phys*. vol. 42, pp. 065418.

Lai Q.; Zhu S.; Luo X.; Zou M.; Huang S. (2012): Ultraviolet-visible spectroscopy of graphene oxides, *AIP adv*. vol. 2, art. No. 032146.

Liu W.; Jackson B.L.; Zhu J.; Miao C.Q.; Chung C.H.; Park Y.J. et al. (2010): Large scale pattern graphene electrode for high performance in transparent organic single crystal field-effect transistors. *ACS NANO*, vol. 4, pp. 3927-3932.

Marcano D.C.; Kosynkin D.V.; Berlin J.M.; Sinitskii A.; Sun, Z.; Slesarev A.; Alemany L.B.; Lu W.; Tour J.M. (2010): Improved synthesis of graphene oxide. *ACS Nano.*,vol. 4, no.8, pp. 4806-4818.

Mattevi C.; Kim H.; Chhowalla M. (2011) A review of chemical vapor deposition of graphene on copper, *J. Mater. Chem*. vol. 21, pp. 3324-3334.

Pei S.; Cheng H.M. (2011): The reduction of graphene oxide, *Carbon*, vol. 50, no. 9, pp. 3210-3228.

Shahriary L.; Athawale A.A (2014): Graphene Oxide Synthesized by using Modified Hummers Approach. *International Journal of Renewable Energy and Environmental Engineering.* vol. 02, pp. 58-63.

Sobon G.; Sotor J.; Jagiello J.; Kozinski R.; Zdrojek M.; Holdynski M.; Paletko P.; Boguslawski J.; Lipinska L.; Abramski K.M. (2012): Graphene oxide vs reduced graphene oxide as saturable absorbers for Er-doped passively mode-locked fiber laser, *Opt. Exp*. vol. 20, no. 17 pp. 19463-19473.

Some S.; Kim Y.; Yoon Y.; Yoo H.; Lee S.; Park Y.; Lee H. (2013): High quality reduced graphene oxide by a dual function chemical reduction and healing process *Sci Rep.* vol. 3, pp. 1-5.

Staudenmaier L. (1898)**:** Verfahren zur Darstellung der Graphitslure, *Ber Dtsch Chem Ges*, vol.31, no.2, pp.1481-1487.

Tung V.C; Allen M.J; Yang Y; Kaner R.B (2009): High throughput solution processing of large scale graphene, *Nature nanotechnology*. vol.4, pp. 25-29.

Wu T.; Gao J.; Xu X.; Wang W.; Gao C.; Qiu H. (2013): A new rapid chemical route to prepare reduced graphene oxide using copper metal nanoparticles. *Nanotechnology*, vol.24, pp. 215604-215614.

Yang D.; Velamakanni A.; Bozoklu G.; Park S.; Stoller M.; Piner R.D.; Stankovich S.; Jung I.; Field D.A.; Ventrice C.A.; Ruoff R.S. (2009): Chemical analysis of graphene oxide films after heat and chemical treatments by X-ray photoelectron and Micro-Raman spectroscopy, *Carbon*, vol. 47, pp. 145-152.

Yang G.; Lee C.; Kim J.; Ren F.; Pearton S.J.; (2013): Flexible graphene based chemical sensors on paper substrates, *Phys Chem Chem Phys*, vol. 15 pp. 1798-1801.

Zhang W.; Li Y..; Peng S.; Cai X. (2014): Enhancement of photocatalytic H_2 evolution of eosin Y-sensitized reduced graphene oxide through a simple photoreaction. *Beilstein J. Nanotechnol.* vol.5, pp.801–811.