

Study of Surface Morphology with Electrical and Optical Properties of GO and rGO

Aniruddha Mondal^{1,2}, Dilip K. Maiti^{3,*}, Hari Shankar Biswas^{1,†}

¹ Department of Chemistry, Surendranath College, 24/2, Mahatma Gandhi Road, 700009 Kolkata, India

² Harindanga High School, Harindanga, Falta 743504 West Bengal, India

³ Department of Chemistry, University of Calcutta, University College of Science, 92, A. P. C. Road, 700009 Kolkata, India

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Graphene oxide (GO) thin film possesses a 2D sheet structure and was synthesized indigenously via the enhanced solvothermal Hummer method. Conventionally, the redox approach can be a characteristic technique to fabricate GO films on an expanded scale. AFM characterization shows GO film had a 2D lamellar layer structure and a thickness between 3 to 5 nm. Heat treatment reduces the GO film to reduced graphene oxide (rGO). The crystallinity of GO thin film was recognized by XRD study. The typical characteristic 2θ peak appeared at 9.85 corresponding to (001) of the GO sheet for carbon with a d -spacing of 0.9 nm. Atomic force microscopy (AFM), scanning electron microscopy (SEM), and Fourier Transform Infrared Spectroscopy (FTIR) were employed to characterize the morphological and optical properties of the GO and rGO thin films. The electrical properties of the thin films were studied with current-voltage (I - V) properties. It is seen that the rGO thin film shows higher conductivity than GO and the value $\approx 5.1 \times 10^{-4}$ S/cm, and also changes the morphology and optical properties. The morphological and optical properties change indicates that GO loses oxygen groups to form rGO. The reason behind the change of conductivity is the reduction of GO at 280 °C temperature and decreased oxygen functional groups as compared to GO confirmed by FTIR.

Keywords: GO, rGO, XRD, AFM, SEM, Surface morphology, I - V characteristics.

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1. INTRODUCTION

A crystalline important allotrope of carbon is graphite. The structure of graphite contains a layer-by-layer hexagonally arrangement of carbon bonded to three coplanar surrounded atoms by the covalent bond of length 1.42 Å and layer-to-layer distance is 3.35 Å. The single layer of graphite is known as graphene. Andre Geim and his team prepared graphene from graphite first in 2004 at Manchester University by a simple peeling of the top layer of pyrolytic graphite with the tape scotch method. Andre Geim and Konstantin Novoseloy jointly won the Nobel Prize in Physics in 2010 for their work on graphene. This single-layer graphene is a 2D nanomaterial graphite structure that contains a layer-by-layer hexagonally arrangement of carbon bonded to three coplanar surrounded atoms by the covalent bond of length 1.42 Å and layer-to-layer distance of al 100 % sp^2 hybridized carbon atom with several distinct properties and has exploded with interest. It is recognized as a feasible alternative to silicon.

In the production of graphene, the graphene oxide (GO) is the main originator [1] that consists of a two-dimensional network of sp^2 and sp^3 covalent bonded atoms [2].

Restoration of the structure of pristine graphene will be practically attainable by the reduction of GO [3]. Thus GO will be reduced by a chemical process, thermal reduction, and multistep reduction so as to get free of the O-containing groups [4]. The number of residual O-containing groups affected the electrical performance of rGO that it depends on the useful teams that remain

once reduced. The rGO has wonderful electrical, thermal, and mechanical properties. It's a really promising material for several applications, like as the development of energy-storage capacitors, pseudocapacitor [5-6], energy-related materials [7], field-effect transistors [8], medical specialty applications [9], sensors [10], making of catalyst for specific organic transformation [11], paper-like materials and skinny films, as substrates, as a coating layer, and as clear conductive thin films [12].

2. EXPERIMENTAL

The enhanced Hummer technique was used to prepare the GO thin film [13] [14]. In detail, 4 g of graphite flake, 2.5 g of KNO_3 , and 110 mL H_2SO_4 (98 %) were mixed in a 1000 ml volumetric flask and kept under the ice bath (0°-6 °C) with stirring continuously for 2 hrs. Next, 8 g of $KMnO_4$ was slowly added so that the temperature of the mixture remained below 5 °C. The suspension was then reacted for 2 h in an ice bath and stirred for 60 min before again being stirred in a 40 °C water bath for 60 min. The temperature of the mixture was adjusted to a constant 98 °C for 60 min. Deionized water was used so that the amount of the suspension was 400 ml and after five minutes noted temperature was 25 °C. 10 mL of H_2O_2 was added after 5 min. The reaction product was centrifuged and washed with deionized water and 5 % HCl solution repeatedly then a small amount of ethanol was added to it [15]. After filtration, it was poured into a Petri dish as well as on mica foil and dried in a vacuum chamber. Finally, a

* dkmchem@caluniv.ac.in

† harishankarb7@gmail.com

graphene oxide thin film was obtained as a brown film. Then reduced graphene oxide was obtained by annealing of GO at 280 °C temperature.

The sheet resistance and I-V characteristics of the GO and rGO films were measured by using Keithley 2635 source meter. FTIR spectrum of the sample was obtained by Infrared Fourier Vacuum Spectro-meter Vertex 70v (Bruker Optik GmbH Germany) and X-Ray diffraction (Philips Analytical PW-1710X-ray powder diffractometer with Bragg-Brentano goniometer geometry and Cu-K α X-ray radiation source ($\lambda = 1.5418 \text{ \AA}$). Scanning Electron Microscopy (SEM, ZEISS, Supra 40VP) was employed to take the surface morphology of the GO and rGO. A surface morphological image of the surface of the Graphene oxide was obtained by using atomic force microscope (AFM, Agilent AFM 5500 series, USA.) in a noncontact mode having a multipurpose small scanner with a low coherence laser (670 nm wave-length (<50 μm), 1 mW power, scan range: XY; 0-10 μm ; noise level; XY < 0.1 nm RMS, Z: 0-2 μm , Z < 0.02 nm RMS.

3. RESULT AND DISCUSSION

The surface of the GO mostly contains coherent domains of sp^3 C-H, C-OH, and sp^2 C = O groups (non-conductor) carbons which are resistive in nature. The crystallinity of GO thin film was recognized by XRD study. X-ray diffraction patterns of GO and rGO are shown in Figure 1. The typical characteristic 2θ peak appeared at 9.85 corresponding to (001) of the GO sheet for carbon with a d-spacing of 0.9 nm which is in good conformity with GO in the existing literature [16]. Initially this XRD result confirmed the typical production of GO thin films. After reduction by annealing, the peak of 9.85 completely disappeared and generated a new peak at 26.2 which corresponded to (002) with a d-spacing of 0.5nm which is a very good agreement of the interlayer spacing of grapheme [17] [18].

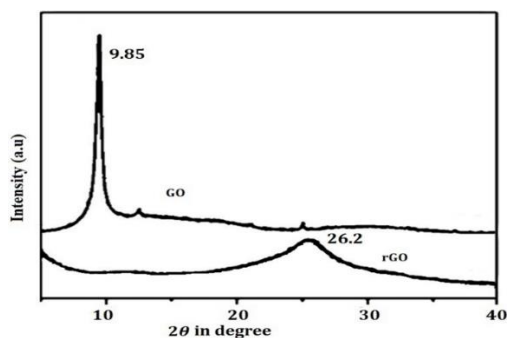


Fig. 1 – XRD pattern of GO and rGO

Figure 2(a, b) shows the FTIR spectra of graphene oxide (GO) and rGO. A broad peak at 2900 cm^{-1} to 3500 cm^{-1} in the FTIR spectrum of GO due to the stretching mode of the carboxyl O-H groups is shown in Figure 2(a). The absorption peaks near 1620 cm^{-1} and 1630 cm^{-1} correspond to conjugated ketone groups and unsaturated C = C stretching. The peak position 3405 cm^{-1} in GO and 3440 cm^{-1} in rGO corresponding to normal polymeric primary O-H stretching and H-bonded O-H stretching [19]. The tentative peak at

2960 cm^{-1} indicates sp^3 C-H asymmetric stretching arises due to the reduction of GO. The presence of functional groups like carboxylic, carbonyl, and hydroxyl groups indicates the successful full oxidation of graphite flakes.

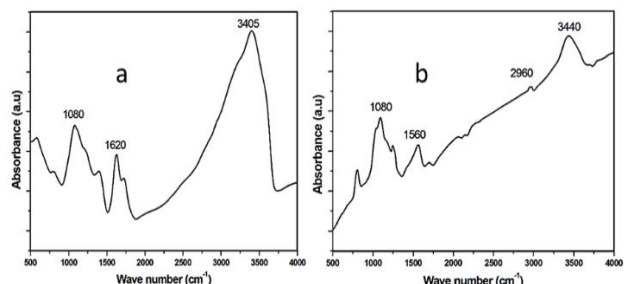


Fig. 2 – FTIR spectrum of (a) GO and (b) rGO

It is seen that the broad peak with high intensity of the hydroxyl group in rGO is diminished compared to pristine GO. The reason behind this is due to the reduction of GO at 280 °C temperature and decreased hydrophilicity. The oxygen functional groups were removed from the GO surface during heat treatment and the properties of GO were changed for the reduction as shown in Figure 2(a, b).

The surface morphology of GO and rGO were characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Figure 3 (a) illustrated the existence of a cabbage or crumple-like structure of GO. It is expected due to the exploitation of graphite flake conversion to GO. Figure 3 (b) shows that distorted cabbage-like shape due to the formation of reduced graphene oxide after annealing.

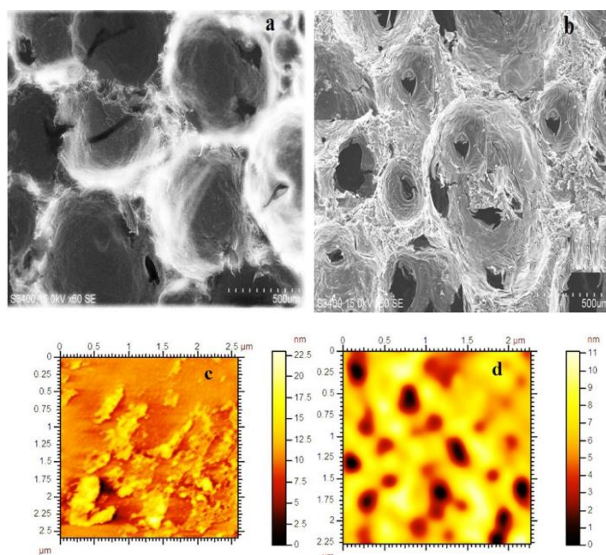


Fig. 3 – SEM images of (a) GO and (b) rGO and AFM images of (c) GO and (d) rGO

Figure 3 (c, d) indicates the contact mode AFM images of GO synthesized by enhanced Hummers method and rGO prepared from GO by annealing respectively. Fig. 3c shows the wrinkled and folded nature of GO sheets. Both images show an almost smooth surface spread over a large area. The important thing is the color variation on the surface. It is due to the

presence of a large number of oxygen-containing groups in GO and fewer oxygen-functional groups in rGO. The GO films seemed to be broken down to create trenches in the scrap sheet on heat

The nature of the GO sheet is an insulator due to the presence of various oxygen functional groups. The typical *I-V* characteristic curves of the graphene oxide and reduced graphene oxide thin films are shown in Fig.4. It is seen that the current (5.31×10^{-4} A) in rGO is about a thousand times higher than that of the current (7.52×10^{-7} A) of GO. The cause of enhancement of the current is due to the formation of rGO by losing oxygen with heat treatment [6]. The sheet resistance of rGO is 14 K Ω – 15 K Ω and sheet resistance of GO is $\sim 1.6 \times 10^4$ K Ω and area were 1.2 cm \times 1.2 cm for both GO and rGO. Shi H.F. et al. has shown that the sheet resistance decreases after the reduction of GO and the value they have mentioned was 58 K Ω [20].

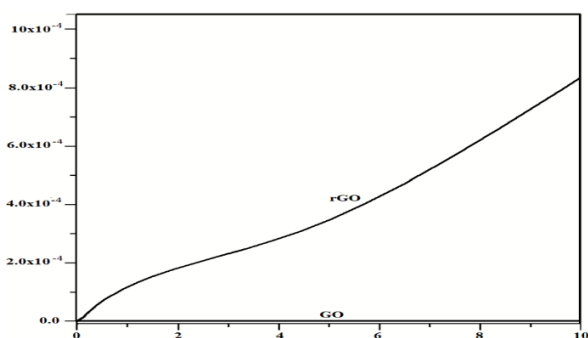


Fig. 4 – *I-V* characteristic curves of the graphene oxide and reduced graphene oxide thin films

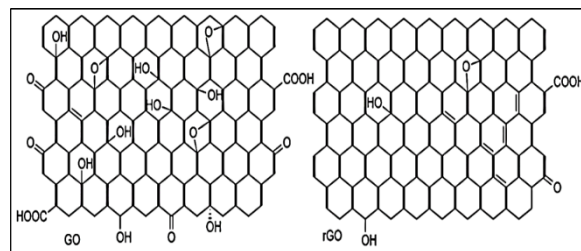


Fig. 5 – Schematic drawing of GO and rGO structures

CONCLUSION

The graphene oxide thin film was successfully synthesized by the enhanced Hummer method. Then reduced graphene oxide was obtained by annealing of GO at 280 °C temperature. It is seen that rGO thin films show a very good electrical conductivity rather than GO. The reason behind this change is the reduction of GO at 280 °C temperature and decreased oxygen functional groups as compared to GO. Again the AFM and SEM characterization supports the surface morphology of GO and rGO. XRD and FTIR also confirmed the difference in oxygen functional groups in GO and rGO

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REFERENCES

- Z. Liu, Y. Wang, X. Zhang, Y. Xu, Y. Chen, J. Tian, *Appl. Phys. Lett.* **94**, 021902 (2009).
- G. Venugopal, K. Krishnamoorthy, R. Mohan, S. Kim, *Mater. Chem. Phys.* **130** No 1, 29 (2012).
- V.G. Sreeja, G. Vinitha, R. Reshmi, E.I. Anila, M.K. Jayaraj, *Opt. Mater. (Amst.)* **66**, 460 (2017).
- A. Shalaby, D. Nihtianova, P. Markov, A.D. Straneva, R.S. Iordanova, Y.B. Dimitriev, *Bulg. Chem. Commun.* **47** No 1, 291 (2015).
- P. Mandal, S. Bala, S. Poddar, S. Sarkar, H.S. Biswas, *Mater. Today: Proc.* **65** No 2, 1001 (2022).
- M.D. Stoller, S. Park, Z. Yanwu, J. An, R.S. Ruoff, *NanoLett.* **8** No 10, 3498 (2008).
- Y. Zhu, S. Murali, W. Cai, X. Li, J.W. Suk, J.R. Potts, R.S. Ruoff, *Adv. Mater.* **22** No 35, 3906 (2010).
- L.Y. Wang, Y. Park, P. Cui, S. Bak, H. Lee, S.M. Lee, H. Lee, *Chem. Commun.* **50**, 1224 (2014).
- L. Cardenas, J. MacLeod, J. Lipton-Duffin, D.G. Seifu, F. Popescu, M. Sijaj, D. Mantovani, F. Rosei, *Nanoscale* **6** No 15, 8664 (2014).
- J.T. Robinson, F.K. Perkins, E.S. Snow, Z. Wei, P.E. Sheehan, *Nano Lett.* **8** No 10, 3137 (2008).
- P. Mandal, R.A. Molla, A.P. Chattopadhyay, S. Poddar, H.S. Biswas, *Inorg. Chem. Commun.* **144**, 109825 (2022).
- D. Kim, S.J. Yang, Y.S. Kim, H. Jung, C.R. Park, *Carbon* **50** No 9, 3229 (2012).
- M. Sohail, M. Saleem, Sana Ullah, Noor Saeed, Ayesha Afridi, Majid Khan, M. Arif, *Mod. Electron. Mater.* **3** No 3, 110 (2017).
- D.A. Jasima, H. Boutinc, M. Fairclough, C. Ménard-Moyon, C. Prenant, A. Bianco, K. Kostarelos, *Appl. Mater. Today* **4**, 24 (2016).
- H.S. Biswas, S. Bala, A.K. Kundu, I. Saha, S. Poddar, S. Sarkar, P. Mandal, *Inorg. Chem. Commun.* **139**, 109356 (2022).
- N.A.C. Ferrari, J. Robertson, *Phys. Rev. B* **61**, 14095 (2000).
- D.C. Marcano, D.V. Kosynkin, J.M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L.B. Alemany, W. Lu, J.M. Tour, *ACS Nano* **4**, 4806 (2010).
- V. Singh, D. Joung, L. Zhai, S. Das, S.I. Khondaker, S. Seal, *Prog. Mater. Sci.* **56**, 1178 (2011)
- L. Shahriary, A.A. Athawale, *Int. J. Renew. Energy Environ. Eng.* **2** No 1, 58 (2014).
- H.F. Shi, C. Wang, Z.P. Sun, Y.L. Zhou, K.J. Jin, G.Z. Yang, *Sci. China-Phys. Mech. Astron.* **58**, 1 (2015).

Вивчення морфології поверхні з електричними та оптичними властивостями GO та rGOAniruddha Mondal^{1,2}, Dilip K. Maiti³, Hari Shankar Biswas¹¹ *Department of Chemistry, Surendranath College, 24/2, Mahatma Gandhi Road, 700009 Kolkata, India*² *Harindanga High School, Harindanga, Falta 743504 West Bengal, India*³ *Department of Chemistry, University of Calcutta, University College of Science, 92, A. P. C. Road, 700009 Kolkata, India*

Тонка плівка оксиду графену (GO) має двовимірну листову структуру та була синтезована власним шляхом за допомогою вдосконаленого сольвотермічного методу Хаммера. Традиційно окисно-відновний підхід може бути характерною технікою для виготовлення плівок GO у розширеному масштабі. АСМ-характеристика показує, що плівка GO має двовимірну структуру пластинчастого шару та товщину від 3 до 5 нм. Термічна обробка відновлює плівку GO до відновленого оксиду графену (rGO). Кристалічність тонкої плівки GO була визнана за допомогою XRD. Типовий характерний пік 2θ з'явився на $9,85^\circ$, що відповідає (001) листа GO для вуглецю з d-відстанню 0,9 нм. Атомно-силова мікроскопія (AFM), скануюча електронна мікроскопія (SEM) та інфрачервона спектроскопія з перетворенням Фур'є (FTIR) були використані для характеристики морфологічних і оптичних властивостей тонких плівок GO і rGO. Електричні властивості тонких плівок досліджували за допомогою вольт-амперних (ВАХ). Видно, що тонка плівка rGO демонструє вищу провідність, ніж GO і значення $\approx 5.1 \times 10^{-4}$ См/см, а також змінює морфологію та оптичні властивості. Зміна морфологічних і оптичних властивостей вказує на те, що GO втрачає кисневі групи з утворенням rGO. Причиною зміни провідності є зменшення GO при температурі 280°C і зменшення функціональних груп кисню порівняно з GO, підтвердженням FTIR.

Ключові слова: GO і rGO, XRD, AFM, SEM, Морфологія поверхні, ВАХ.