

# Research Journal of Pharmaceutical, Biological and Chemical Sciences

## Synthesis of Reduced Graphene Oxide from Graphite and its Application on Supercapacitor

Dinesh Kumar Mani<sup>1\*</sup>, and Bharath Suresh<sup>2</sup>.

<sup>1</sup>Department of Chemical Engineering, Kongu Engineering College, Perundurai, Erode

<sup>2</sup>Department of Chemical Engineering, Sri Venkateswara College of Engineering, Pennalur, Sriperumbudur

### ABSTRACT

Reduced graphene oxide based supercapacitor have been synthesized by simple chemical methods using graphite oxide as a precursor. The structural, morphological and functional group properties of the synthesized reduced graphene oxide were analyzed using X-ray diffraction (XRD), scanning electron microscope (SEM) and Fourier transform Infra-red spectroscopy (FTIR). XRD pattern shows the presence of both graphite oxide and graphene oxide peak and crystallite size was found to be 12 nm. The supercapacitor was fabricated with the synthesized reduced graphene oxide powder and capacitance value with respect to thickness of graphene oxide layer were also investigated.

**Keyword:** Graphite oxide, Reduced graphene oxide, Thickness, Supercapacitor

*\*Corresponding author*

## INTRODUCTION

Supercapacitor or ultra-capacitor, are capable to store electrical charge hundreds times more than when compared to available standard capacitors and it can safely charge or discharge with extremely long cycle life (4100 000 cycles) within seconds [1]. A basic operation of standard capacitor is consists of two electrode (i) positive and (ii) negative, these positive and negative electrode was separated by an insulator or dielectric. During charging cycle, the electrons are stored in one electrode and depart from the other electrode. So, one side of the conductor built up with positive charge and other side gains negative charge. The insulator disturbs the natural pull of the negative charge towards the positive one, and that tension creates an electric field. Once electrons are given a path to the other side, discharge occurs. In the case of the supercapacitor the electrodes are made with highly porous materials and immersed in the solution as known as electrolyte which contain both positive and negative ions. Since the electrode was made with nano based porous material it significantly improve the charging and discharging capacity of the capacitor due to presence of higher surface area of the electrode, so it can able to adsorbed more charge carrying ions towards the electrode [2]. The developed supercapacitor with high power density, fast charging – discharging time and long life time will finds application in the automobiles, memory backup systems, transportation, medical and portable electronic devices [3].

Due to the low cost, non-toxic and high theoretical specific capacitance value of transition metal oxide nanoparticles are employed to prepare the supercapacitor such as NiO [4], carbon aerogel [5], CuS [6], copper oxide decorated on reduced graphene oxide [7], cobalt oxide hybrid nanostructure [8], Ni(OH) [9], nickel sulfide on nickel cobalt nanoplate array [10], iron oxide core – shell [11], MnO<sub>2</sub> [12]. But the main disadvantage of these materials are high electrical resistivity and lack, short life time [13]. The other main problem in supercapacitor is the low energy density, the energy density of the supercapacitor was given by  $E = \frac{1}{2} CV^2$  where, C is the toatal capacitance of the electrode and V is the operating voltage. In order to improve the energy density of supercapacitor steps has to be taken to improve the increasing the operating voltage of the system and have to choose high capacitance value of the electrode materials [14].

Nowadays, the graphene and related materials attracted many researcher interest towards supercapacitor application. Graphene is one of the famous two-dimensional material and composed of all-sp<sup>2</sup>-hybridized carbons atoms which exhibiting most interesting properties such as high electrical conductivity, thermal conductivity, highly tunable surface area (up to 2675 m<sup>2</sup> g<sup>-1</sup>), strong mechanical strength (~1 TPa) chemical stability, high optical transparency (97.7 %), lightweight [15] and large theoretical specific surface area ( 2630 m<sup>2</sup> g<sup>-1</sup>) [16]. These outstanding properties of the graphene materials find applications in various fields such as flexible electronics, gas sensors, hard coatings, solar cells, fuel cells, batteries and so on.

In the present work, we have prepared graphene oxide from graphite oxide through hummer method. The properties of synthesised graphene oxide was studied using XRD, SEM, FTIR. The supercapacitor was fabricated using direct coating technique on the cleaned aluminum sheet and capacitance values were measured with help of LCR meter.

## MATERIALS AND METHODS

### Synthesis of Graphene Oxide:

Graphene oxide was prepared from purified natural graphite powder according to the hammer's method [17–19]. In details graphite powder (3g), O-H<sub>3</sub>PO<sub>4</sub> (23mL) and KMnO<sub>4</sub> (12g), were slowly added to a concentrated H<sub>2</sub>SO<sub>4</sub> solution (200 mL) within an ice bath. After removing the ice bath, the above mixture was intensely stirred in magnetic stirrer for 6 hours. After the reaction was completed, deionised water was added to the above mixture at the temperature of 980 °C for 15 minutes, followed by reducing the temperature to 600 °C with the addition of warm deionised water and H<sub>2</sub>O<sub>2</sub> (30 %, 100 mL) while stirring continuously for stopping the reaction and kept it for 3 to 4 hours for settling. After the settling, the solution is taken to the centrifuge process to separate the immiscible substances. The obtained mixture was centrifuge to collect the solid product and washed with ammonia hydrate solution 5 times and then with deionised water until the pH of the supernatant was neutral. The centrifuged product is separated and allowed to dry at hot air oven to

obtain as a moisture free materials and dried material is crushed to obtain the loose powder. Finally the graphene oxide powder is obtained.

**Reduction of Graphene Oxide to Reduced Graphene Oxide:**

At first the equimolar of graphene oxide and ascorbic acid mixed with de-ionized water and mixer was ultrasonicate for 30 min. The obtained ultrasonicate product was centrifuge to remove the supernatant particles. After the centrifuge the obtained product was mixed with hydrogen peroxide and heated with 180 °C for 12 hours. As results of heat treatment reduced graphene oxide powder was precipitated. The obtained reduced graphene oxide precipitate was washed several times and finally tried in hot air oven at temperature of 70 °C for 24 hours.

**CHARACTERIZATION TECHNIQUES**

The structural properties of reduced graphene oxide was analyzed using X-ray diffraction (XRD). The XRD measurement was recorded by Rigaku, Ultima III, Japan with CuK $\alpha$  radiation of 1.5406 Å. The sample was analyzed at 2 $\theta$  scan range of 15-80° with scan rate of 0.02°. Scanning electron microscope (SEM) JEOL, JSM-7401 was employed to study the surface morphology of the synthesis of reduced graphene oxide. The functional groups were analyzed using Fourier transform infra-red spectroscopy (FTIR) Perkin Elmer, the measurement was taken on pellet containing reduced graphene oxide and KBr with wavenumber range of 400-4000 cm<sup>-1</sup>. The electrical capacitance was studied with help of LCR - Q meter (Yokogawa).

**RESULTS AND DISCUSSIONS**

**Structural Properties:**

The XRD pattern of synthesis reduced graphene oxide is shown in Fig. 1. The XRD pattern confirmed that the prepared reduced graphene from graphite oxide was crystalline in nature. The diffraction peak at 2 $\theta$  = 10.25° is corresponds to the (002) plane due to presence of carbonyl and hydroxyl group located on the graphene plane [20]. Further, the diffraction peaks at 2 $\theta$  = 26.6 and 42.2° confirms the presence of graphite phase. In diffraction pattern no other peaks other than graphite oxide and graphite which indicate that the synthesis reduced graphene oxide was highly free from impurity.

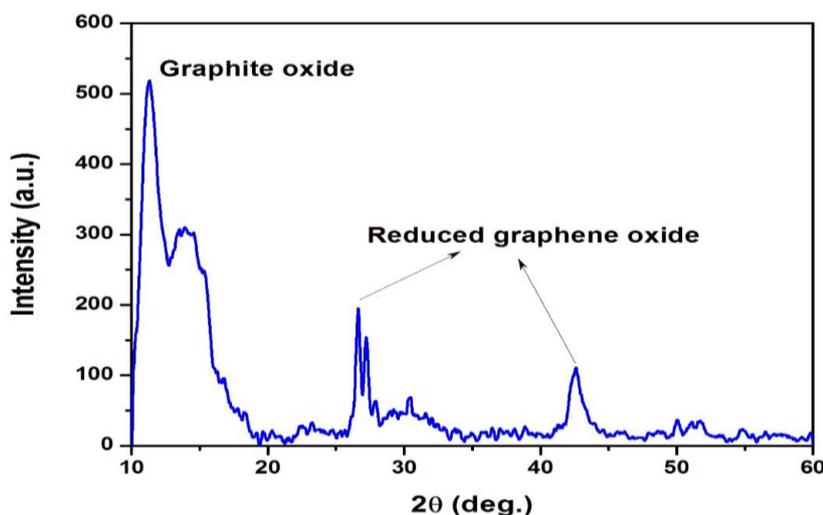


Figure: 1. XRD pattern of reduced graphene oxide

The crystallite size was calculated using Debye Scherrer’s formula [21] is given below,

$$D = \frac{k\lambda}{\beta \cos\theta} \text{ ---- (1)}$$

Where  $k$  is the shape factor,  $\lambda$  is the wavelength of the incident X-ray beam,  $\beta$  is the full width at half maxima of the diffracted peak,  $\theta$  is the angle of diffraction. The crystallite size was found to be 12 nm.

**Surface Morphology:**

The surface morphology of the reduced graphene oxide from graphite oxide as shown in Fig. 2 (a and b). The synthesized reduced graphene oxide powder showed aggregated sheet like morphology and each sheet size was about 50 nm. In addition the SEM images clearly showed that the aggregated sheets are closely associate with neighboring sheets which leads to uniform morphology.

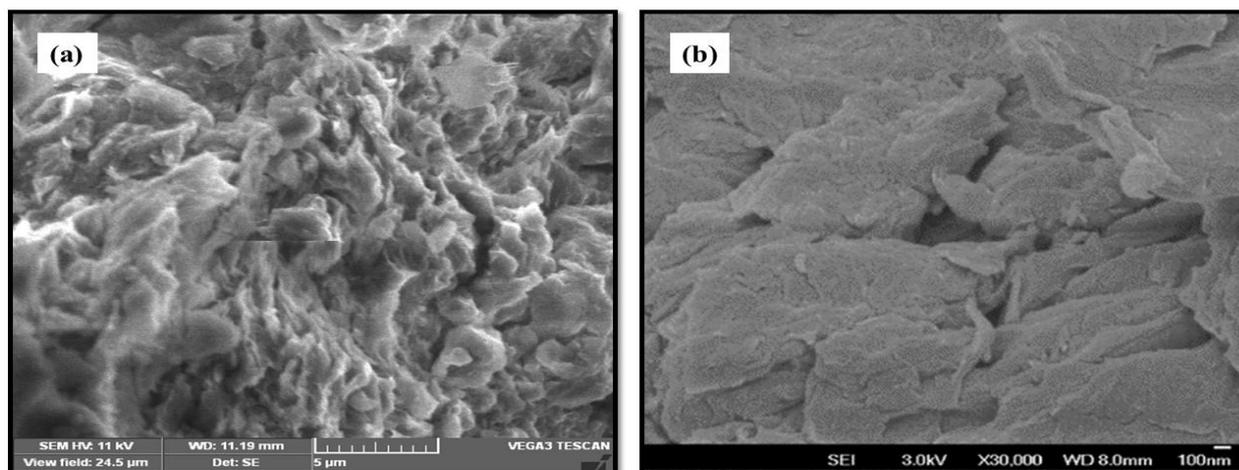


Figure: 2 (a) low and (b) high magnification of SEM images of reduced graphene oxide

**Functional Group analysis:**

The FTIR analysis of reduced graphene oxide was taken in the transmission mode and it is shown in Fig. 3. In FTIR spectra the transmittance value is recorded in the wavenumber ranges from 400 to 4000  $\text{cm}^{-1}$ . At 1634  $\text{cm}^{-1}$  the finger print peak of C=C of carbon atom was observed which corresponds to  $\text{sp}^2$  hybridization. The peak at 3447  $\text{cm}^{-1}$  are assigned to the stretching vibration of hydroxyl group it indicate trace level of water in the reduced graphene oxide from graphite oxide. The carbonyl group stretching vibration was observed at 1724  $\text{cm}^{-1}$  and 1399  $\text{cm}^{-1}$  peak indicate the presence of methyl groups [22,23].

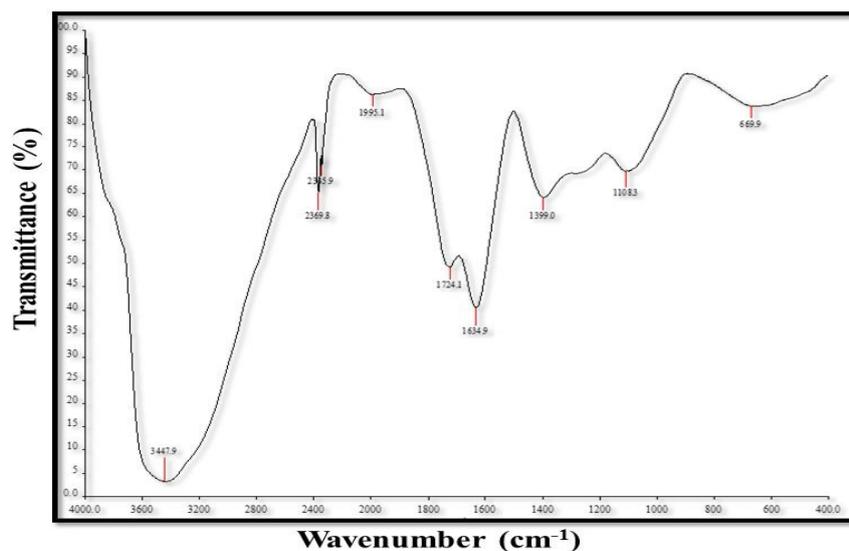


Figure: 3 FTIR spectrum of reduced graphene oxide

**Supercapacitor measurement:**

Reduced graphene oxide supercapacitor was fabricated using direct coating method [24] on to the aluminum sheet. The schematic representation of fabrication of supercapacitor is shown in Fig. 4. Initially the aluminum sheet was scrubbed with fine grade of emery to make the surface rough and clean. The synthesized reduced graphene oxide powder was mixed with binding agent to make it as a paste. After that the fine layer of paste was applied on the surface of the aluminum sheet. The coated aluminum sheet was allowed to dry in atmosphere for 24 hours. After the atmospheric drying the coated sheets are taken kept parallel to make capacitor arrangement and sealed with electrolyte of ortho-phosphoric acid. The external copper contacts were made by using wire binder on the both side of the capacitor. The capacitance value was measured by varying the thickness of the reduced graphene oxide on the aluminum sheet and thickness values were found to be 500, 1000 and 2000  $\mu\text{m}$  and it is shown in Fig. 5.

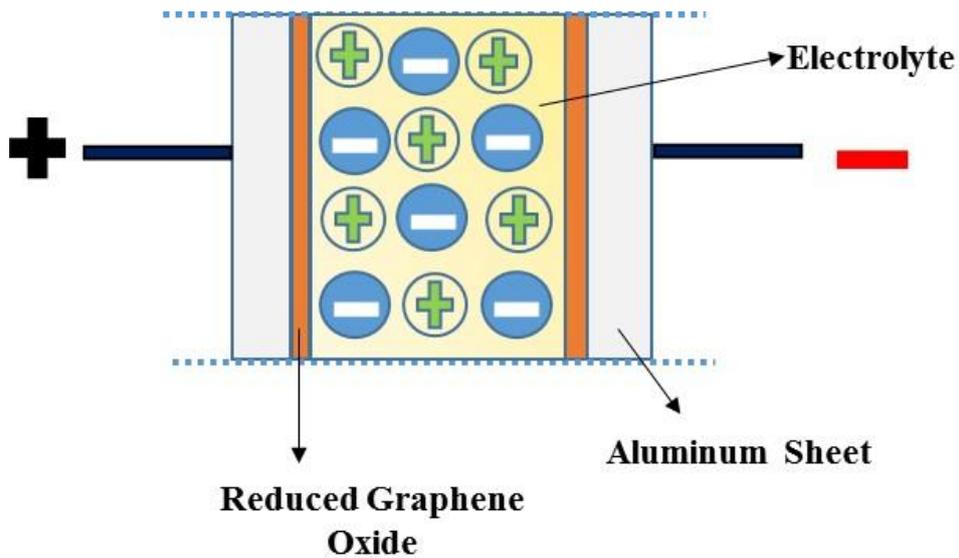


Figure: 4 Schematic representation of fabricated supercapacitor

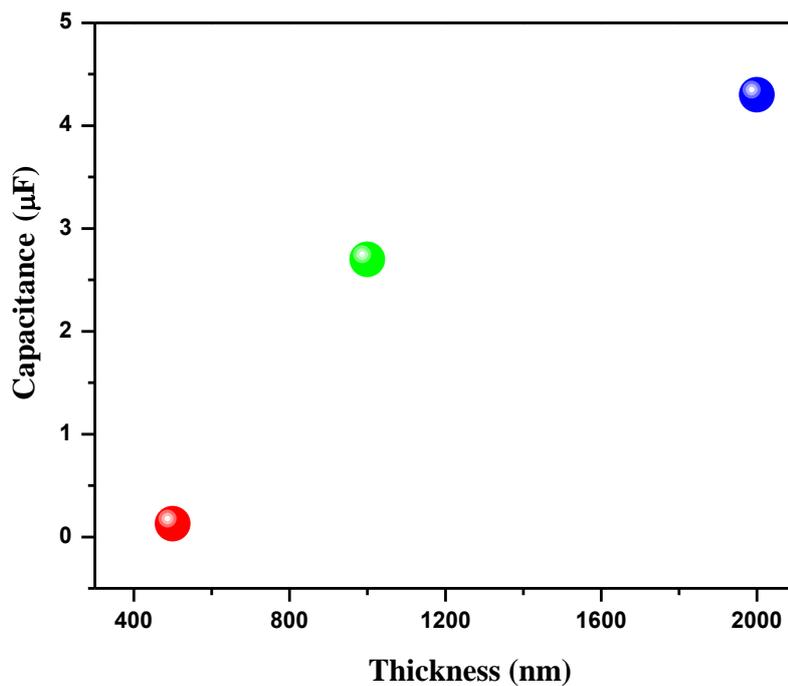


Figure: 5 The variation of capacitance value with respect to thickness

From the graph, it was observed as the reduced graphene oxide layer thickness increases the capacitance value tend to increase from 0.127 to 4.30  $\mu\text{F}$ . This might be attributed due to that more possible of electrolyte will be reacting with the reduced graphene oxide layer which leads to higher capacitance value. Still future investigation will be needed to know what are mechanisms involves between electrolyte and reduced graphene oxide layers.

### CONCLUSION

In this work, reduced graphene oxide was synthesis using modified hummer method. After that the obtained graphite oxide is reduced to high purity graphene. SEM micrograph showed the synthesized graphene from reduced graphene oxide possessed aggregated sheet like morphology. FTIR results confirms presence of characteristics peak of C=C which confirms the presence of  $\text{sp}^2$  hybridization of graphene. Initial supercapacitance studies were carried out the fabricated supercapacitor, capacitance values were increased with increasing graphene layer thickness on the aluminum sheet. The maximum capacitance value is found to be 4.30  $\mu\text{F}$ . In future work has been devoted to improve the supercapacitor value by doping with some polymer based materials and several studies need to be considered to understand the proper mechanism between the reduced graphene oxide layer and the electrolyte materials.

### REFERENCES

- [1] Y. Shao, M. F. El-kady, L. J. Wang, Q. Zhang, Y. Li, H. Wang, F. Mousavi and R. B. Kaner, *Chem. Soc. Rev.*, 2015, 44, 3639–3665.
- [2] W. Yang, M. Ni, X. Ren, Y. Tian, N. Li, Y. Su and X. Zhang, *Curr. Opin. Colloid Interface Sci.*, 2015, 20, 416–428.
- [3] S. Bag, A. Samanta, P. Bhunia and C. R. Raj, *Int. J. Hydrogen Energy*, 2016, 41, 22134– 22143.
- [4] X. Zhang, W. Shi, J. Zhu, W. Zhao, J. Ma, S. Mhaisalkar and T. L. Maria, *Nano Res.*, 2010, 3, 643–652.
- [5] J. Li, X. Wang, Q. Huang, S. Gamboa and P. J. Sebastian, *J. Power Sources*, 2006, 158, 784–788.
- [6] S. Peng, L. Fan, C. Wei, X. Liu, H. Zhang, W. Xu and J. Xu, *Carbohydr. Polym.*, 2017, 157, 344–352.
- [7] K. Wang, X. Dong, C. Zhao, X. Qian and Y. Xu, *Electrochim. Acta*, 2015, 152, 433–442.
- [8] X. Pan, F. Ji, L. Kuang, F. Liu, Y. Zhang, X. Chen, K. Alameh and B. Ding, *Electrochim. Acta*, 2016, 215, 298–304.
- [9] W. Sun, X. Rui, M. Ulaganathan and S. Madhavi, *J. Power Sources*, 2015, 295, 323–328.
- [10] Q. Chu, W. Wang, X. Wang, B. Yang, X. Liu and J. Chen, *J. Power Sources*, 2015, 276, 19–25.
- [11] X. Tang, R. Jia, T. Zhai and H. Xia, *Appl. Mater. Interfaces*, 2015, 7, 27518–27525.
- [12] Z. Yu, B. Duong, D. Abbitt and J. Thomas, *Adv. Mater.*, 2013, 25, 3302–3306.
- [13] H. Reza, P. Norouzi, M. Reza and H. Gholipour-ranjbar, *Powder Technol.*, 2016, 302, 298–308.
- [14] F. Sun, J. Gao, X. Pi, L. Wang, Y. Yang, Z. Qu and S. Wu, *J. Power Sources*, 2017, 337, 189–196.
- [15] Q. Ke and J. Wang, *J Mater.*, 2016, 2, 37–54.
- [16] Z. Yang, S. Chabi, Y. Xia and Y. Zhu, *Prog. Nat. Sci. Mater. Int.*, 2015, 25, 554–562.
- [17] P. Karthika, N. Rajalakshmi and K. S. Dhathathreyan, *Soft Nanosci. Lett.*, 2012, 2, 59– 66.
- [18] T. Fan, W. Zeng, Q. Niu, S. Tong, K. Cai, Y. Liu, W. Huang, Y. Min and A. J. Epstein, *Nanoscale Res. Lett.*, 2015, 10, 1–8.
- [19] M. Kim, C. Lee, Y. D. Seo, S. Cho, J. Kim, G. Lee, Y. K. Kim and J. Jang, *Chem. Mater.*, 2015, 27, 6238–6248.
- [20] T. Kim and S. Park, *J. Colloid Interface Sci.*, 2017, 486, 287–295.
- [21] P. Dhivya and M. Sridharan, 2013, vol. 1.
- [22] B. Zahed and H. Hosseini-monfared, *Appl. Surf. Sci.*, 2015, 328, 536–547.
- [23] R. Kumar, D. K. Avasthi and A. Kaur, *Sensors Actuators B. Chem.*, 2017, 242, 461–468.
- [24] W. K. Chee, H. N. Lim, Z. Zainal, N. M. Huang, I. Harrison and Y. Andou, *J. Phys. Chem. C*, 2016, 120, 4153–4172.