

Physical Properties of Reduced Graphite Oxide Prepared via Chemical Reduction by Using Ammonia solution as a Reducing Agent

Intesar R. Hussain^{*,1,2}, A.B. Dayang Radiah², Faten H. Kamil^{2,3}, F. Mohd Yasin², S. Kamarudin², H.M. Yusoff²

¹State Commission for Dams and Reservoir, Ministry of Water Resources, Baghdad, Iraq.

²Department of Chemical and Environmental Engineering, Universiti Putra Malaysia Selangor, Malaysia.

³Chemical and Petrochemical Research Center, Commission for Research and Industrial Development, Ministry of Industry and Minerals, Baghdad, Iraq.

*Corresponding Author. Email: Intesar_eng2005@yahoo.com

Abstract. This research studied the synthesis of graphite oxide and reduced graphite oxide via a low- cost manufacturing method. The process started with the chemical oxidation of commercial graphite powder into graphite oxide by Staudenmaier's method, followed by the chemical reduction of graphite oxide in ammonium hydroxide vapor. Subsequently, graphite oxide and reduced graphite oxide were assembled into a thin film, and microscale liquid droplets were placed into the film surface for measurement of wettability and contact angle. It is found that a graphite oxide sheet is hydrophilic while a reduced graphite oxide is hydrophobic with a contact angle equal to 120°C and 53°C respectively.

1. Introduction

The discovery of two-dimensional graphene by Novoselov and his coworker in 2004, has attracted a lot of research attention due to its excellent thermal, mechanical and electrical properties [1]. Reduced graphite oxide is a sp^2 -hybridized carbon monolayer that has a great deal of interest in recent years owing to its fundamental electronic and mechanical properties [1,2]. One of the greatest challenges in the large-scale production of rGO is seeking for the economical and environmentally friendly route. Up to date, several techniques have been employed for the synthesis of graphene. Amongst these several techniques, the oxidation, and reduction of graphite have been identified as one of the most attractive and cost-effective routes for the large-scale production of GO and rGO papers [8]. The reduction of graphite oxide (GO) is a vast field of study [3] by itself. Up to date, several techniques have been employed for the synthesis of reduced graphite oxide (rGO). Amongst these several techniques, the oxidation, and reduction of graphite have been identified as one of the most attractive and cost-effective routes for the large-scale production of GO and rGO papers. However, rGO can be produced from GO via chemical reduction method under a mild temperature [29, 30]. This process is accompanied by the release of gases during chemical reduction of GO which aid in the formation of a compact GO layered films as well as a porous graphene structures. In order to prevent re-staking of converting the graphene sheets produced via chemical reduction, Yang et al. applied water as an effective spacing agent [31]. The synthesis of rGO through chemical reduction method has been performed using various reducing agent such as hydrazine [4], hydriodic acid (HI) [5], vitamin C [6], sodium boron hydride ($NaBH_4$) [7, 8], hydroquinone [9], Nascent Hydrogen [10], alumina powder [11], sodium bisulfite [12], and diethylaminosulfur (DAST) [13] with focus on two-dimensional (2D)



constructs. RGO could be produced also by a thermal modification of GO [14]. Presently, the synthesis of three-dimensional (3D) rGO based structures has been the main focal point of active research in material science [15].

Therefore, focus of this study is to investigate the synthesis of a 3D rGO papers using a cost effective and environmental friendly techniques by using ammonia solution as a reducing agent, and identified its physical properties.

2. Experimental Section

To perform the reduction process of GO which prepared by modified Staudenmaier's method based on that described by [16], to rGO, GO was placed in a cellulose extraction thimble, and was exposed to Ammonia solution (30%) that was heated @ 90°C. The process was conducted for 10 hr. Here, the GO powder had a direct contact with the vapor of the ammonia solution only. The reduced GO was allowed to cool for about 15 minutes. The suspension obtained from the preparation via the dispersion of rGO in 100 ml of DI water was filtered using vacuum assisted unit equipped with an MCE membrane filter. The filtered sample was allowed to dry on the membrane for 24 h. The peeled off sheet was characterized as required.

3. Results & Discussions

3.1 Physical observation of the liquids

It is to be noted that during the oxidation process of graphite in a modified Staudenmaier method, graphite underwent a significant change in its physical properties. To illustrate, Fig. 1 shows the excellent dispersions of GO in water compared to that of graphite particles. Graphite particles settled down at the bottom of the flask in less than 10 minutes, whilst the changes in bond configurations in GO allowed water intercalation making them highly hydrophilic and thus dispersed well in the water. Fig 1(a) shows homogenous dispersion of GO in DI water. This phenomenon indicates strong hydrophilic nature of the particles due to the presence of negative charge on the surface. Similar scenario was described by [17] on their GO product. However, when the graphite oxide was reduced in ammonia, black precipitates were formed as shown in Fig 1(b). This is a typical hydrophobic characteristic of rGO with less polar functionality on the surface of the sheets, compared to that of GO based on those described by [18]; and [19].

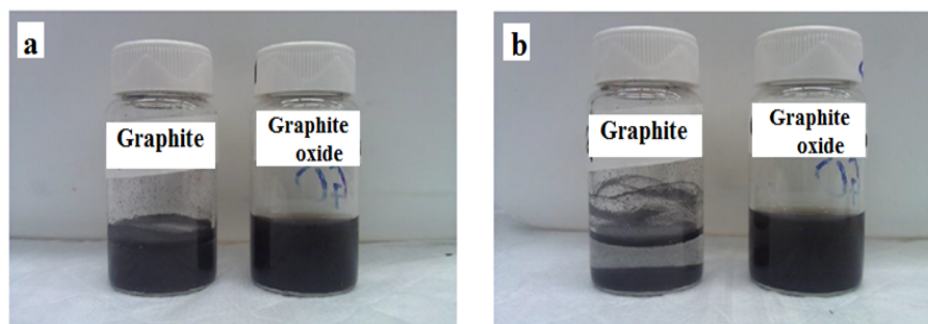


Figure 1. Solubility of graphite and GO in water (a) Graphite and GO in water (b) Graphite and GO in water after 10 minutes.

3.2 The Physical Observation of the Prepared Paper

The ideal product of rGO paper should be a metallic look black thin membrane with mirror smooth surface. Chen ; described similar appearance of their rGO product [20]. Also, compared to GO paper, rGO paper did not have aggregated carbon particles on the surface [20]. Fig. 2(c), shows the rough surface of GO film due to the formation of particles aggregates on the surface of GO paper. The reduced films, on the other hand, have a metallic look [21]. In addition, the obtained freestanding rGO paper is uniform, dark brown under white light and almost black for thick samples as that displayed in

Fig. 2(e). In addition, is the sheet was also flexible and can be rolled as shown in Fig. 2(f). However, it is impossible to re-disperse the rGO once dried.

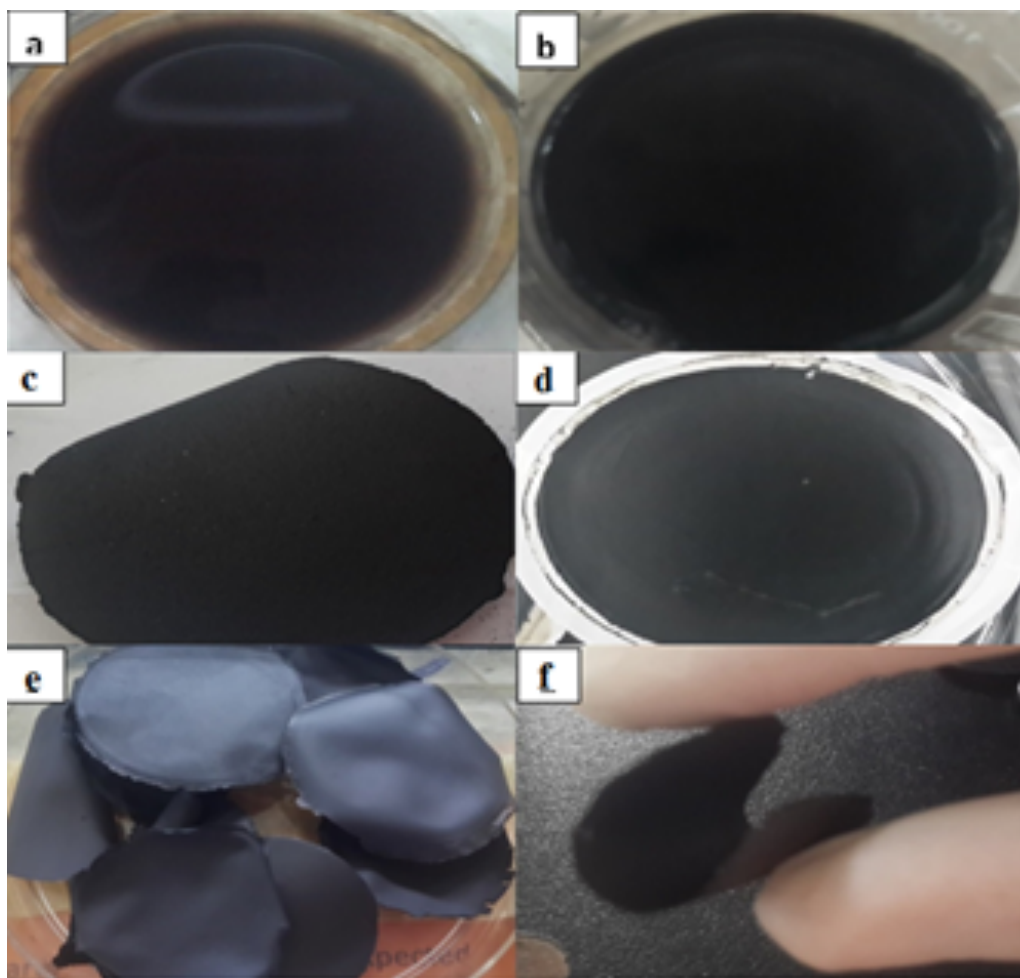


Figure 2. Physical properties of the obtained rGO (a) GO dispersion, (b) rGO dispersion, (c) GO film (d) wet rGO paper, (e) rGO paper and (f) flexible rGO paper

3.3 Ultraviolet – Visible (UV-Vis) Spectroscopy

GO absorption spectrum is characterized by two bands assessed to π - π^* (C=C) and n - π^* (C=O) transitions. During the oxidation of graphite, oxygen attached to the graphite layers and thereby increased the polarity of the layers which in turn increased their solubility in water [22].

Fig. 3 shows the UV-Vis absorption spectrum of GO and rGO sample. The image was focused only between 200 to 500 nm. The rest of the area follows the same trends up to 800 nm but does not bring any other useful information. The absorption peaks showed maximum absorption around 229 nm and a shoulder band around 300 nm, which is consistent with findings reported by Kuchlyan et al. [23]; and Marciano et al., [24]. The removal of large amount of oxygenated functional groups in rGO results in the transfer of electrons between π - π conjugations. When the electron is transferred between n - π^* conjugation more energy will be absorbed as compared to π - π^* conjugations. Therefore, the shift was observed for rGO as some of the conjugated C=C bonds were restored due to the reduction process [25].

When GO was reduced, the absorption band assigned of GO at 229 nm, had been shifted to a higher wavelength to 261 nm for rGO sample and the shoulder band disappeared. This can be attributed to the removal of oxygen atoms that were attached of the oxygen functional groups and an increase in aromatic rings. All of these factor caused electrons to be easily excited at a lower energy level [26]. The color of the solution was also changed from dark brownish to black due to the reduction

process this feature was consistent with that described in literature [19]. These indicate that a substantial reduction of graphite oxide had been taken place.

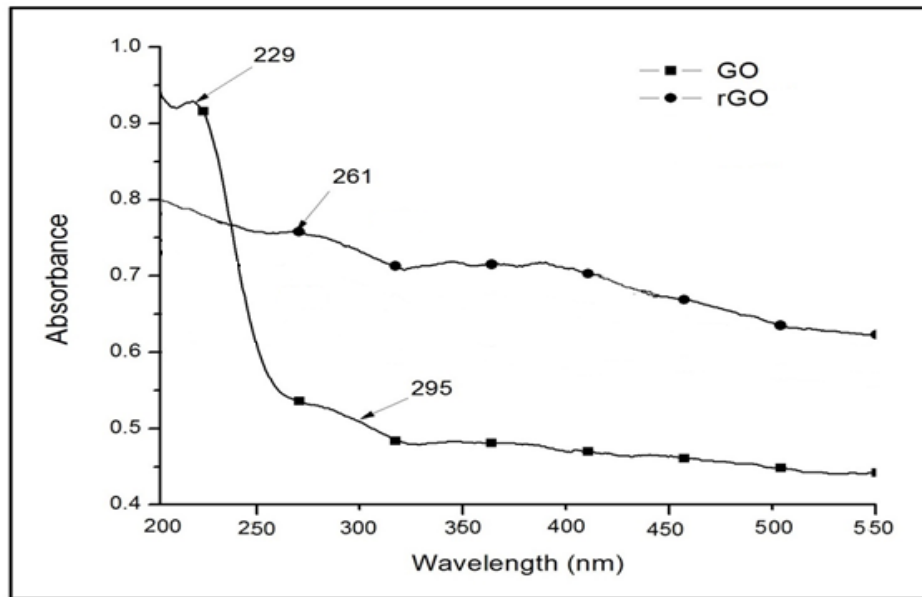


Figure 3. UV absorption spectra of GO, & rGO from 200 nm to 550nm

3.4 Wettability of Reduced Graphite Oxide Paper

GO, and chemically reduced GO, were assembled into a thin film by the filtration process as described in the literature [27], [28]. The wettability of the GO and rGO paper were tested by measuring its static contact angle with water. GO film was made from oxidized and intercalated graphite. The measurement indicated that the static contact angle is 53.0° ($< 90^\circ$) as illustrated in Fig. 4 (a). Hence, GO shows a good hydrophilic property. Meaning that the GO surface was grafted with hydroxyl and epoxy groups. The presence of the polar groups altered the graphite properties from hydrophobic to hydrophilic. After a chemical reduction of GO by ammonia, hydroxyl and epoxy groups were eliminated. This is in agreement with the findings reported in literature on work reduction of a colloidal suspension of exfoliated graphene oxide sheets in water with hydrazine hydrate [18], [17]. The experimental results indicated that the contact angle is 120.0° as shown in Fig. 4(b). It is interesting to note that this contact angle is larger than that of graphite film and water as mentioned by Wang et al., [27]; and Mukherjee et al., [29]. The static contact angle for graphite film and water is 98° and is attributed to the presence of carbon atoms without any polarity which also demonstrates the hydrophobic properties of graphite.

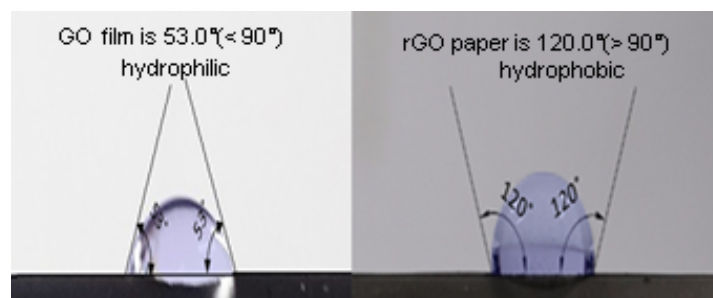


Figure 4. A water droplet on the flat of (a) graphite oxide paper and (b) reduced graphite oxide paper to measure the contact angle.

4. Conclusions

The objective of this research is to describe a simple synthetic route for the preparation of reduced graphite oxide (rGO) papers from graphite oxide (GO) using ammonia solution by contact with vapor phase. The wettability and the contact angles of the prepared paper were measured. It was found that a graphite oxide sheet is hydrophilic whilst the reduced graphite paper is hydrophobic with a contact angle about 120°. In summary, a simple low temperature process that utilized a less toxic material, *i.e.* Ammonia, had been developed and proved to be successfully reduced the GO and modified its properties.

5. Acknowledgment

This work was supported by the Fundamental Research Grant sponsored by the Ministry of Higher Education, Universiti Putra Malaysia (No. frgs/03-02-14-1522fr). The authors wish to thank the staff of Material Characterization: Laboratory, Department of Chemical and Environmental Engineering (UPM) for providing the analytical services.

References

- [1] K. S. Novoselov, a. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and a. a. Firsov, "Electric Field Effect in Atomically Thin Carbon Films," *Science* (80., vol. 306, pp. 666–669, 2004.
- [2] D. R. Dreyer, R. S. Ruoff, and C. W. Bielawski, "From conception to realization: An historical account of graphene and some perspectives for its future," *Angew. Chemie - Int. Ed.*, vol. 49, no. 49, pp. 9336–9344, 2010.
- [3] F. T. Johra, J. W. Lee, and W. G. Jung, "Facile and safe graphene preparation on solution based platform," *J. Ind. Eng. Chem.*, vol. 20, no. 5, pp. 2883–2887, 2014.
- [4] Z. Fan, J. Yan, L. Zhi, Q. Zhang, and T. Wei, "A Three-Dimensional Carbon Nanotube/Graphene Sandwich and Its Application as Electrode in Supercapacitors," *Adv. Mater.*, vol. 10, no. 22, pp. 3723–3728, 2010.
- [5] S. Pei and H.-M. Cheng, "The reduction of graphene oxide," *Carbon N. Y.*, vol. 50, no. 9, pp. 3210–3228, 2012.
- [6] S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S. T. Nguyen, and R. S. Ruoff, "Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide," *Carbon N. Y.*, vol. 45, no. 7, pp. 1558–1565, Jun. 2007.
- [7] B. Y. Zhu, S. Murali, W. Cai, X. Li, J. W. Suk, J. R. Potts, and R. S. Ruoff, "Graphene and Graphene Oxide : Synthesis , Properties , and Applications," *Adv. Mater.*, pp. 1–19, 2010.
- [8] X. Yang, J. Zhu, L. Qiu, and D. Li, "Bioinspired effective prevention of restacking in multilayered graphene films: Towards the next generation of high-performance supercapacitors," *Adv. Mater.*, vol. 23, no. 25, pp. 2833–2838, 2011.
- [9] G. G. Wallace, R. B. Kaner, M. Muller, S. Gilje, and D. Li, "Processable aqueous dispersions of graphene nanosheets," *Nat. Nanotechnol.*, vol. 3, pp. 101–105, 2008.
- [10] S. Jin, Q. Gao, X. Zeng, R. Zhang, K. Liu, X. Shao, and M. Jin, "Diamond & Related Materials Effects of reduction methods on the structure and thermal conductivity of free-standing reduced graphene oxide films," *Diam. Relat. Mater.*, vol. 58, pp. 54–61, 2015.

- [11] X. Gao, J. Jang, and S. Nagase, "Hydrazine and thermal reduction of graphene oxide: Reaction mechanisms, product structures, and reaction design," *J. Phys. Chem. C*, vol. 114, no. 2, pp. 832–842, 2010.
- [12] W. Gao, L. Alemany, L. Ci, and P. Ajayan, "New insights into the structure and reduction of graphite oxide," *Nat. Chem.*, vol. 1, no. 5, pp. 403–408, 2009.
- [13] Q. A. Khan, A. Shaur, T. A. Khan, Y. F. Joya, M. S. Awan, Q. A. Khan, A. Shaur, T. A. Khan, Y. F. Joya, and M. S. Awan, "Characterization of reduced graphene oxide produced through a modified Hoffman method," *Cogent Chem.*, vol. 3, pp. 1–9, 2017.
- [14] J. Yang, B. Wang, G. Wang, J. Yang, J. Park, X. Gou, B. Wang, H. Liu, and J. Yao, "Facile Synthesis and Characterization of Graphene Nanosheets," *J. Phys. Chem. C*, vol. 112, no. 22, pp. 8192–8195, 2008.
- [15] Q. Zhuo, J. Tang, J. Sun, and C. Yan, "High Efficient Reduction of Graphene Oxide via Nascent Hydrogen at Room Temperature," *Materials (Basel)*, vol. 11, no. 340, pp. 1–12, 2018.
- [16] A. Pruna, D. Pullini, and D. Busquets, "Structure and Properties of Chemically-reduced Functionalized Graphene Oxide Platelets," *J. Mater. Sci. Technol.*, vol. 31, no. 5, pp. 458–462, 2015.
- [17] X. Gao and X. S. Tang, "Effective reduction of graphene oxide thin films by a fluorinating agent : Diethylaminosulfur trifluoride," *Carbon N. Y.*, vol. 6, pp. 2–9, 2014.
- [18] S. N. Alam, N. Sharma, and L. Kumar, "Synthesis of Graphene Oxide (GO) by Modified Hummers Method and Its Thermal Reduction to Obtain Reduced Graphene Oxide (rGO) *," *Sci. Res. Publ.*, vol. 6, pp. 1–18, 2017.
- [19] S. Nardecchia, D. Carriazo, M. L. Ferrer, M. C. Gutiérrez, and F. del Monte, "Three dimensional macroporous architectures and aerogels built of carbon nanotubes and/or graphene: synthesis and applications," *Chem. Soc. Rev.*, vol. 42, no. 2, pp. 794–830, 2013.
- [20] D. W. Lee and J. W. Seo, "Preparation of carbon nanotubes from graphite powder at room temperature," *arXiv Prepr. arXiv*, vol. 1007, no. 1062, 2010.
- [21] S. Park and R. Ruoff, "Chemical methods for the production of graphenes," *Nat. Nanotechnol.*, vol. 4, no. 4, pp. 217–224, 2009.
- [22] V. Loryuenyong, K. Totepvimarn, P. Eimburanaprat, W. Boonchompoo, and A. Buasri, "Preparation and characterization of reduced graphene oxide sheets via water-based exfoliation and reduction methods," *Adv. Mater. Sci. Eng.*, vol. 2013, 2013.
- [23] J. Chen, K. Sheng, P. Luo, C. Li, and G. Shi, "Graphene Hydrogels Deposited in Nickel Foams for High-Rate Electrochemical Capacitors," *Adv. Mater.*, vol. 24, no. 33, pp. 4569–4573, 2012.
- [24] G. Eda and M. Chhowalla, "Chemically Derived Graphene Oxide: Towards Large-Area Thin-Film Electronics and Optoelectronics," *Adv. Mater.*, vol. 22, no. 22, pp. 2392–2415, 2010.
- [25] A. Balandin, S. Ghosh, and W. Bao, "Superior thermal conductivity of single-layer graphene," *Nano Lett.*, vol. 8, no. 3, pp. 902–907, 2008.

- [26] J. Kuchlyan, N. Kundu, D. Banik, A. Roy, and N. Sarkar, "Spectroscopy and Fluorescence Lifetime Imaging Microscopy To Probe the Interaction of Bovine Serum Albumin with Graphene Oxide," *Langmuir*, vol. 31, no. 51, pp. 13793–801, Dec. 2015.
- [27] D. C. Marcano, D. V Kosynkin, J. M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L. B. Alemany, W. Lu, and J. M. Tour, "Improved Synthesis of Graphene Oxide," *ACS Nano*, vol. 4, no. 8, pp. 4806–4814, 2010.
- [28] S.-H. Liao, P.-L. Liu, M.-C. Hsiao, C.-C. Teng, C.-A. Wang, M.-D. Ger, and C.-L. Chiang, "One-Step Reduction and Functionalization of Graphene Oxide with Phosphorus-Based Compound to Produce Flame-Retardant Epoxy Nanocomposite," *Ind. Eng. Chem. Res.*, vol. 51, no. 12, pp. 4573–4581, Mar. 2012.
- [29] F. Thema and M. Moloto, "Synthesis and characterization of graphene thin films by chemical reduction of exfoliated and intercalated graphite oxide," *J. Chem.*, vol. 2013, p. 150536, 2012.
- [30] H. Wang, J. T. Robinson, X. Li, and H. Dai, "Solvothermal Reduction of Chemically Exfoliated Graphene Sheets," *J. Am. Chem. Soc.*, vol. 131, no. 29, pp. 9910–9911, 2009.
- [31] J. Qiu, C. Zhang, B. Wang, and R. Liang, "Carbon nanotube integrated multifunctional multiscale composites," *Nanotechnology*, vol. 18, no. 27, p. 275708, 2007.
- [32] A. Mukherjee, P. Rozelle, and S. V. Pisupati, "Effect of hydrophobicity on viscosity of carbonaceous solid–water slurry," *Fuel Process. Technol.*, vol. 137, pp. 124–130, 2015.