J Mater Sci: Mater Electron (2017)28: 1038-1041
DOI 10.1007/s10854-016-5626-7

Effect of thermal reduction temperature on the optical and electrical properties of multilayer graphene

Marjoni Imamora Ali Umar[1] · Chi Chin Yap[2] · Rozidawati Awang[2] · Muhamad Mat Salleh[3]

Received: 11 June 2016 / Accepted: 24 August 2016

Abstract Multilayer graphene was prepared by thermal reduction of graphene oxide film at various temperatures (200, 400 and 500 °C) in argon atmosphere for an hour. The graphite oxide was first synthesized by using modified Hummers method and spin coated on quartz substrate to form graphene oxide film. X-ray diffraction, field emission scanning electron microscopy, UV–Vis spectroscopy and four point probe measurement were used to characterize the resultant multilayer graphene. The transmittance and sheet resistance decreased with the thermal reduction temperature. The lowest sheet resistance of 91.6 ± 0.3 kΩ/sq was obtained at temperature of 500 °C, showing almost 100 times improvement compared to that prepared at 200 °C.

1 Introduction

Graphene, a low cost material with a monolayer of carbon in 2D honeycomb lattice with a 0.34 nm thickness [1], has been found useful in solar cell application due to its good electrical and optical transmission properties [2–6]. Especially in dye sensitized solar cells (DSSC) devices, graphene has been used widely as a counter electrode. Graphene in this study is provided by means of chemical method through oxidation of graphite using modified Hummer methods. Hummers method has become a famous technique of graphene oxide preparation because it is a low cost and simple method by which large scale of graphene oxide can be obtained easily [7, 8]. Graphene can be produced via thermal reduction of graphene oxide film deposited on substrate [9]. However, it has been reported that, the sheet resistance of graphene film is much larger than that of platinum for the same optical transmittance [10]. This could be due the poor interconnection with neighboring ones which limits the electronic conduction across the sheets. Although a thicker or multilayer graphene film can be deposited to ensure the individual graphene sheets are connected to each other and hence lower sheet resistance, the optical transmittance will decrease accordingly [11].

Multilayer graphene has been successfully synthesized from graphite oxide prepared by using modified Hummers method with a relatively small amount of oxidizing agent and short-time processing at ambient temperature in previous work [7]. However, the high temperature (600 °C) applied during thermal reduction of graphene oxide is not suitable if the multilayer graphene is to be used as low-cost counter electrode deposited on glass substrate in dye sensitized solar cell application. Therefore, the present work was carried out to investigate the effect of using lower thermal reduction temperature (200, 400, and 500 °C) on the electrical and optical properties of multilayer graphene. The transmittance and sheet resistance of multilayer graphene decreased with the temperature. The lowest sheet resistance of 91.6 ± 0.3 kΩ/sq was obtained at temperature of 500 °C, showing almost 100 times increase as compared to that of 200 °C.

✉ Marjoni Imamora Ali Umar
marjoniimamora@gmail.com

1 Department of Physics Education, Faculty of Tarbiyah and Education, Institut Agama Islam Negeri (IAIN), Batusangkar 27213, West Sumatera, Indonesia

2 School of Applied Physics, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia

3 Institute of Microengineering and Nanoelectronics (IMEN), Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia

Published online: 29 August 2016

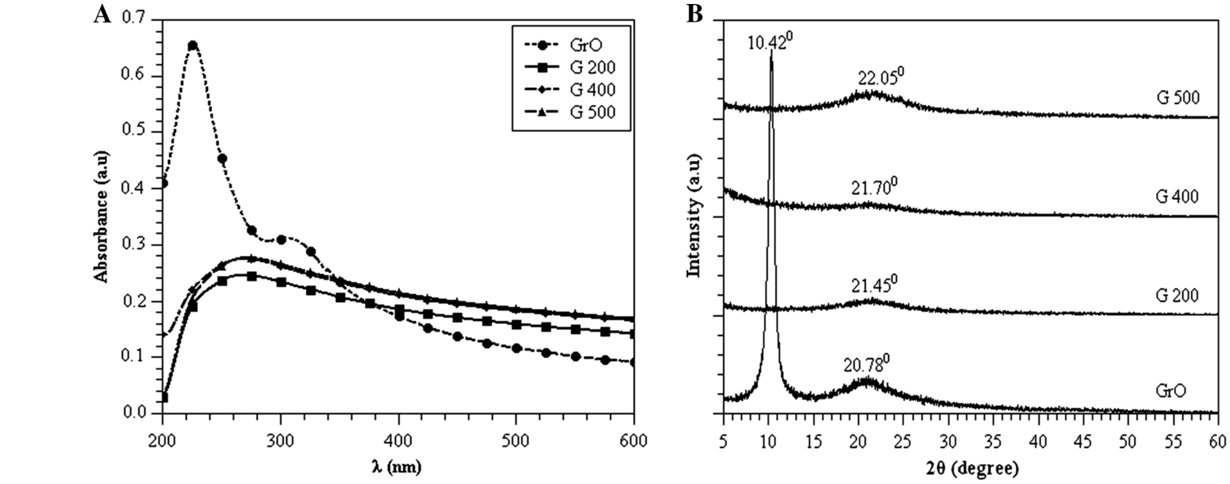

Fig. 1 Absorption (**a**) and XRD (**b**) spectra of graphene oxide and multilayer graphene films prepared at different thermal reduction temperatures

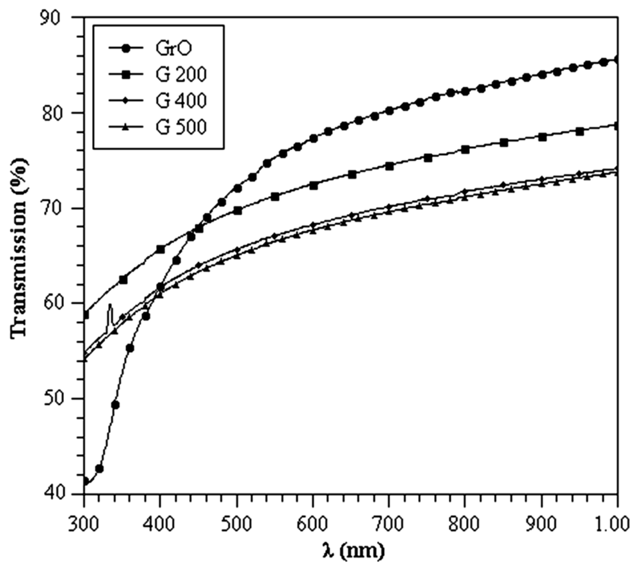

Fig. 2 Transmission spectra of graphene oxide and multilayer graphene films prepared at different thermal reduction temperatures

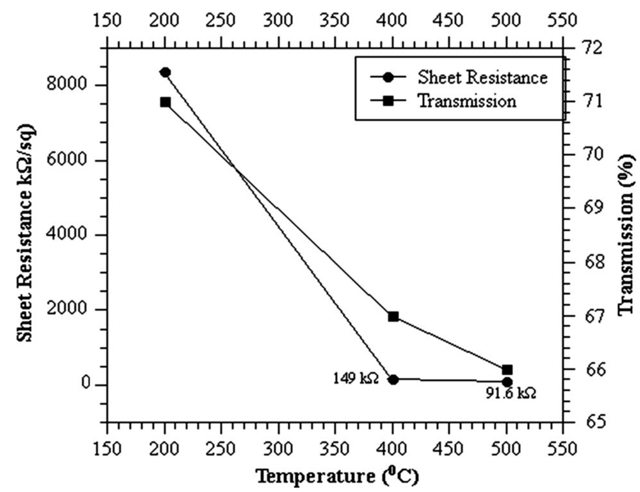

Fig. 3 The sheet resistance and optical transmittance of multilayer graphene films as a function of thermal reduction temperature

2 Experimental

Multilayer graphene was synthesized from graphite oxide prepared by using modified Hummers method [12]. The details of the graphite oxide flake synthesis were described elsewhere [7]. The typical preparation of graphene oxide film is shown below: small amount of graphite oxide flake was dissolved in deionized water at a concentration of 10 mg ml^{-1} by sonication for 30 min followed by stirring for 2 h. Then, the resultant solution was spin-coated by using Chemat Technology Spin-Coater KW-4A on quartz substrates to form graphene oxide film. Next, they were annealed at 200, 400, and 500 °C in argon atmosphere for 1 h to form MLG film. The resultant samples were then denoted as G200, G400, and G500, respectively.

The optical transmission characterization of graphene oxide and multilayer graphene films was carried out by using Halo DB-20 UV–Vis spectrophotometer. The crystal-structure of the films was characterized by using BrukerD8 Advanced X-ray diffraction (XRD) with CuKα radiation at a scan rate of 0.025°/0.1 s. The morphology of the samples was obtained by using Zeiss Supra 55VP field emission scanning electron microscope (FESEM) at an acceleration voltage of 3 kV. Lastly, the sheet resistance of MLG films was studied via Four Point Probe measurement by using Keithley 2401 source meter.

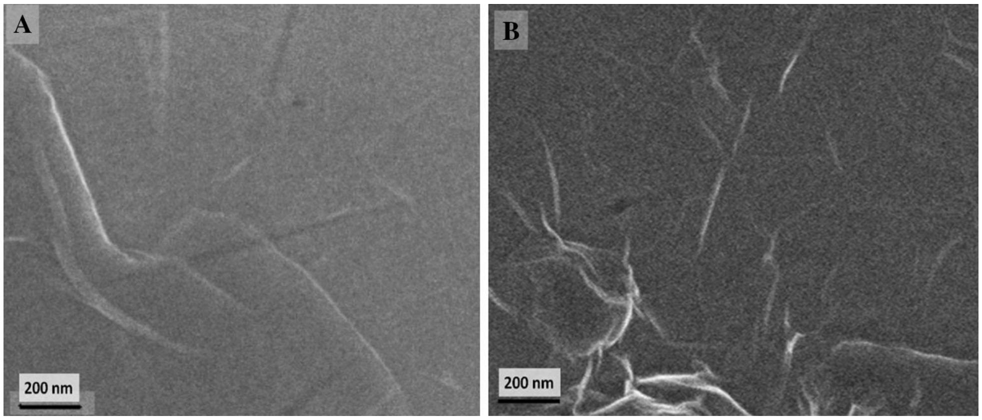

Fig. 4 FESEM images of multilayer graphene prepared at **a** 400 °C, and **b** 500 °C

3 Results and discussion

Optical absorption spectra of graphene oxide and multilayer graphene films prepared at different thermal reduction temperatures are shown in Fig. 1a. It was found that graphene oxide exhibited a maximum absorption peak at 226 nm and a shoulder peak at 310 nm. The absorption peak red-shifted to 270 nm as the thermal reduction temperature increased, indicating part of conjugated C=C bonds have been restored as an effect of heating process applied [7].

X-ray diffraction spectra of graphene oxide and multilayer graphene films are shown in Fig. 1b. A significant diffraction peak at $2\theta = 10.42°$ corresponding to interlayer distance of 0.886 nm was observed in the XRD spectrum of graphene oxide. The weakening of Van der walls force [8, 13] and the presence of functional groups such as hydroxyl, epoxy, and carboxyl during the oxidation step [14–16] contributes to the increase in interlayer distance. In addition, a weak diffraction peak detected at $2\theta = 20.78°$ indicates incomplete oxidation and intercalation of graphite [7]. After thermal reduction at 200 °C, the diffraction peak shifted to $2\theta = 21.45°$, indicating interlayer distance was reduced to 0.411 nm due to the removal of water molecules and functional groups [9]. The interlayer distance decreased further to 0.406 nm and 0.401 nm at temperature of 400 and 500 °C, respectively. The decrease in interlayer distance with thermal reduction temperature suggests more functional groups could be removed at higher heating temperature.

The optical transmission spectra of graphene oxide and multilayer graphene films are shown in Fig. 2. The transmittance of multilayer graphene decreased significantly with increasing thermal reduction temperature. The graphene oxide film showed a transmittance of 79 % at $\lambda = 550$ nm. After thermal reduction, the transmittance decreased to 54 %, indicating the formation of multilayer graphene (±19 layer or 6.46 nm in thickness) since absorbance of each individual graphene layer is approximately 2.3 % [17]. Besides that, the decrease in transmittance could be attributed to partial restoration of conjugated C=C bonds in the graphene structure [18]. Figure 3 shows the optical transmittance at $\lambda = 550$ nm and sheet resistance of the corresponding films as a function of thermal reduction temperature. Both sheet resistance and optical transmittance decreased as the temperature increased. The multilayer graphene prepared at temperature of 500 °C exhibited the lowest sheet resistance of 91.6 ± 0.3 kΩ/sq, almost 100 times improvement as compared to that prepared at 200 °C. The lowest sheet resistance obtained in this work was slightly higher than that obtained from graphene (70 kΩ/sq) with similar transmittance of 65 % [19].

Figure 4 shows the typical FESEM images of multilayer graphene prepared at thermal reduction temperature of 400 and 500 °C. The wrinkle observed in G500 was more significant than that in G400, probably due to escape of more functional groups at higher temperature. Besides, increase in thermal reduction temperature also results in graphene aggregation due to stronger attractive force between layers [20].

4 Conclusions

The effect of thermal reduction temperature on the optical and electrical properties of multilayer graphene has been investigated. The interlayer distance of graphene decreased with the temperature, indicating more water molecules and functional groups were removed. The transmittance and sheet resistance of multilayer graphene decreased with increasing temperature due to partial restoration of conjugated C=C bonds in the graphene structure. The lowest sheet resistance of 91.6 ± 0.34 kΩ/sq was achieved at temperature of 500 °C, exhibiting almost 100 times improvement compared to that of 200 °C.

Acknowledgments This work has been carried out with the financial support of the Malaysian Ministry of Higher Education (MOHE), under the Research funding ERGS/1/2011/STG/UKM/02/62. The authors would like to thank Assoc. Prof. Dr. Akrajas Ali Umar (IMEN, UKM), Mrs. Fitri Yenni, M.Sc., Tan Sin Tee, Mr. Md. Nizam bin Mohammed for their contribution in this work, and Mr. Muhammad Hasnul Naim B. Abdul Hamid and Mr. Idris Sharif in FESEM characterization.

References

1. F. Akbar, M. Kolahdouz, S. Larimian, B. Radfar, H. Radamson, J. Mater. Sci. Mater. Electron. **26**, 4347 (2015)
2. H. Choi, H. Kim, S. Hwang, W. Choi, M. Jeon, Sol. Energy Mater. Sol. Cells **95**, 323 (2011). doi:10.1016/j.solmat.2010.04.044
3. W. Hong, Y. Xu, G. Lu, C. Li, G. Shi, Electrochem. Commun. **10**, 1555 (2008). doi:10.1016/j.elecom.2008.08.007
4. E. Kymakis, E. Stratakis, M. Stylianakis, E. Koudoumas, C. Fotakis, Thin Solid Films **520**, 1238 (2011)
5. X. Li, Y. Zhu, W. Cai et al., Nano Lett. **9**, 4359 (2009)
6. H. Park, J.A. Rowehl, K.K. Kim, V. Bulovic, J. Kong, Nanotechnology **21**, 505204 (2010). doi:10.1088/0957-4484/21/50/505204
7. M.I. Ali Umar, C.C. Yap, R. Awang, M. Hj Jumali, M. Mat Salleh, M. Yahaya, J. Mater. Sci. Mater. Electron. **24**, 1282 (2013). doi:10.1007/s10854-012-0920-5
8. Z. Osváth, A. Darabont, P. Nemes-Incze, E. Horváth, Z. Horváth, L. Biró, Carbon **45**, 3022 (2007)
9. S.H. Huh, H.M. Ju, S.H. Choi, J. Korean Phys. Soc. **57**, 1649 (2010)
10. J.D. Roy-Mayhew, D.J. Bozym, C. Punckt, I.A. Aksay, ACS Nano **4**, 6203 (2010)
11. C.M. Weber, D.M. Eisele, J.P. Rabe et al., Small **6**, 184 (2010)
12. W.S. Hummers Jr., R.E. Offeman, J. Am. Chem. Soc. **80**, 1339 (1958)
13. Y. Si, E.T. Samulski, Nano Lett. **8**, 1679 (2008)
14. T. Zhou, F. Chen, K. Liu et al., Nanotechnology **22**, 1 (2011)
15. K.-S. Kim, S.-J. Park, Electrochim. Acta **56**, 6547 (2011). doi:10.1016/j.electacta.2011.04.092
16. Y. Wu, B. Wang, Y. Ma et al., Nano Res. **3**, 661 (2010)
17. M.J. Allen, V.C. Tung, R.B. Kaner, Chem. Rev. **110**, 132 (2009)
18. S. Stankovich, R.D. Piner, S.B.T. Nguyen, R.S. Ruoff, Carbon **44**, 3342 (2006)
19. G. Eda, Y.Y. Lin, S. Miller, C.W. Chen, W.F. Su, M. Chhowalla, Appl. Phys. Lett. **92**, 233305 (2008)
20. T.V. Cuong, V.H. Pham, Q.T. Tran et al., Mater. Lett. **64**, 765 (2010)