THE USE OF TRIPLE-TAILS CUSTOM-MADE SURFACTANT IN THE PRODUCTION OF GRAPHENE OXIDE THIN FILM AS TRANSPARENT CONDUCTIVE ELECTRODE

Muqoyyanah[1,2], A. B. Suriani[1,2*], A. Mohamed[1,3], N. Hashim[1,3], M.H. Mamat[4], M.F. Malek[4,5], and M.K. Ahmad[6]
*e-mail: absuriani@yahoo.com

[1]Nanotechnology Research Centre,
[2]Department of Physics,
[3]Department of Chemistry,
Faculty of Science and Mathematics, Universiti Pendidikan Sultan Idris,
35900 Tanjung Malim, Perak, Malaysia.
[4]NANO-ElecTronic Centre (NET), Faculty of Electrical Engineering,
[5]NANO-SciTech Centre (NST), Institute of Science (IOS),
Universiti Teknologi MARA (UiTM), 40450 Shah Alam, Selangor, Malaysia.
[6]Microelectronic and Nanotechnology–Shamsuddin Research Centre (MiNT-SRC),
Faculty of Electrical and Electronic Engineering, Universiti Tun Hussein Onn Malaysia,
86400 Parit Raja, Batu Pahat, Johor, Malaysia.

ABSTRACT

In this work, graphene oxide (GO) and reduced GO (rGO) thin films were fabricated from GO and rGO using the custom-made and commercial surfactants, which were sodium 1,4-bis (neopentyloxy)-3-(neopentyloxycarbonyl)-1,4-dioxobutane-2-sulphonate and sodium dodecyl sulphate, respectively. The GO solution was synthesized using electrochemical exfoliation method followed by reduction process utilizing hydrazine hydrate to produce rGO solution. The GO and rGO transfer process were done using spraying deposition method on fluorine-doped tin oxide substrate. The fabricated GO and rGO thin films consists of several layers resulted in high transparency over 85% with maximum transmittance of 93.69%. Based on several characterizations, the fabricated GO and rGO thin films have potential to be applied as transparent conductive electrode.

Key words: Custom-made, Surfactant, Electrochemical, Spraying, Electrode.

ABSTRAK

Dalam penelitian ini, film tipis grafin oksida (GO) dan grafin oksida yang direduksi (rGO) difabrikasi dari GO dan rGO menggunakan surfaktan yang dibuat khusus dan surfaktan komersial yaitu secara berurutan adalah sodium 1,4-bis (neopentyloxy)-3-(neopentyloxycarbonyl)-1,4-dioxobutane-2-sulphonate dan sodium dodecyl sulphate. Larutan GO disintesis menggunakan metode eksfoliasi elektrokimia diikuti dengan proses reduksi menggunakan hidrazin hidrat untuk menghasilkan larutan rGO. Proses transfer GO dan RGO dilakukan dengan menggunakan metode deposisi penyemprotan diatas substrat oksida timah oksida dengan doping florin. Film tipis GO dan rGO yang difabrikasi terdiri dari beberapa lapis dengan transparansi tinggi

mencapai 85% dengan transmitansi maksimum sebesar 93,69%. Berdasarkan beberapa karakterisasi, film tipis GO dan rGO ini memiliki potensi untuk diaplikasikan sebagai elektroda konduktif transparan.

Kata Kunci: dibuat khusus, surfaktan, elektrokimia, penyemprotan, elektroda

INTRODUCTION

Graphene becomes a popular material to be investigated in recent years due to its excellent electrical, optical, mechanical, and physical properties since its discovery in 2004 [Gee, *et.al.,* 2013; Choi, *et.al.,* 2010; Park and Ruoff, 2009; Zhu, *et.al.,* 2010]. Graphene is the basic form of another graphitic structure, such as fullerenes, carbon nanotubes, and graphite [Geim and Novoselov, 2007]. The first method to produce graphene is via mechanical exfoliation using scotch tape. This simple method produce defect free and high purity graphene. Unfortunately, this method is limited if applied for mass production [Zhu, *et.al.,* 2010; Zheng, *et.al.,* 2011; Pati, *et.al.,* 2011]. Several methods are developed in order to produce high quality graphene, such as epitaxial growth on SiC, Brodie or Hummers method, and chemical vapor deposition. However, those methods involve chemical materials which are highly toxic and unsafe, high synthesis temperature as well as complex synthesis step thus make it time consuming [Celebi, *et.al.,* 2012; Mikhailov, 2011; Gilje, *et.al.,* 2007].

The fabrication of graphene thin film also becomes a challenge which need to be further developed. Transfer process onto desired substrate need to be considered in order to avoid the degradation of graphene quality. Several transfer process such as chemical etching, roll-to-roll, spin and dip coating are usually used and have their own advantages and disadvantages [Chen, *et.al.,* 2013; Bae, *et.al.,* 2010; Kymakis, *et.al.,* 2011; Wobkenberg, *et.al.,* 2011]. In this work, we synthesize GO in the solution form using electrochemical exfoliation method which are simple and have great potential to be applied in large scale production [Alanyalıoğlu, *et.al.,* 2012; Wang, *et.al.,* 2014; Ambrosi, *et.al.,* 2014]. Different ionic custom-made and commercially available surfactants were used to assist exfoliation process and study their effect in the production of GO. Reduction process was further done to produce reduced graphene oxide (rGO) by utilizing hydrazine hydrate as reducing agent. Finally, GO and rGO solution were transferred using a simple spraying deposition method on fluorine-doped tin oxide (FTO) substrate [Ham, *et.al.,* 2010; Beidaghi, *et.al.,* 2012]. The samples were then analyzed by using field emission scanning electron microscopy (FESEM), micro-Raman spectroscopy, UV-Vis spectroscopy, *I-V* measurement using four point probes to investigate the morphology, crystallinity, and electrical performance of the fabricated films.

MATERIALS AND METHOD

The first step in GO and rGO thin films fabrication was preparing GO in the solution form which was synthesized by electrochemical exfoliation in an electrolyte solution assisted by different surfactants [Suriani, *et.al.,* 2016]. In this work, we used sodium 1,4-bis (neopentyloxy)-3-

(neopentyloxycarbonyl) -1,4-dioxobutane-2-sulphonate, known as TC14 and sodium dodecyl sulphate (SDS) which were custom-made and commercially available surfactants, respectively. The electrolyte solution was prepared by dissolving them into DI water to obtain 0.1 M concentration. Two graphite rods were used as electrodes and connected to 7 V for 24 hours to perform electrochemical exfoliation.

The second step was on the rGO production which was done by chemical reduction utilizing hydrazine hydrate [Tong, *et.al.*, 2014; Low, *et.al.*, 2013]. Hydrazine hydrate of 0.5 ml was dropped to 50 ml of GO solution then maintained at ~95℃ temperature under constant stirring. The reduction process was performed for 24 hours. The last step was transferring the produced GO and rGO solution onto FTO substrate using spraying deposition method. FTO with 2×1 cm^2 size which was cleaned by acetone, methanol, and DI water for 5 minutes for every sonication step were preheated on hot plate at 120℃ for another 5 minutes. GO and rGO solution were then sprayed at 10 cm distance between airbrush nozzle and FTO substrate followed by annealing at 400℃ in argon ambient. Morphological, optical, and electrical properties of fabricated GO and rGO thin films were determined by field emission scanning electron microscopy (FESEM), micro-Raman spectroscopy, UV-Vis spectroscopy, and *I-V* measurement using four-point probes.

RESULTS AND DISCUSSIONS

FESEM images shown in Fig. 1 presents the morphology of the fabricated GO and rGO thin films. Based on Fig. 1 (a), the morphology of the produced rGO thin film from SDS (SDS-rGO) shows a thick layer at the edge side. Some GO agglomeration were also observed in some part of the film shows that the solution was less stabilized by SDS surfactant. In addition, SDS surfactant also seen to be less effective to exfoliate graphite indicated by the thick layer produced in the sample. This finding was similar to GO thin film from triple-tail surfactant TC14 (TC14-GO) which also demonstrated thicker layer at the edge side. This is believed due to the existence of oxygen functional groups on GO compared to rGO solution.

After the reduction process, rGO thin film from TC14 (TC14-rGO) shows thinner layer compared to SDS-rGO and TC14-GO samples as shown in Fig. 1 (c). This results show that TC14 surfactant was more efficient in exfoliation process of GO production. This also confirmed by the less GO agglomeration on TC14-rGO sample. Better exfoliation process done by TC14 was believed due to the triple-tails branch of TC14 structure as compared to SDS which only has single-tail. The successful oxidation process on electrochemical exfoliation was also confirmed by fold-up layer in all samples [Suriani, *et.al.*, 2016].

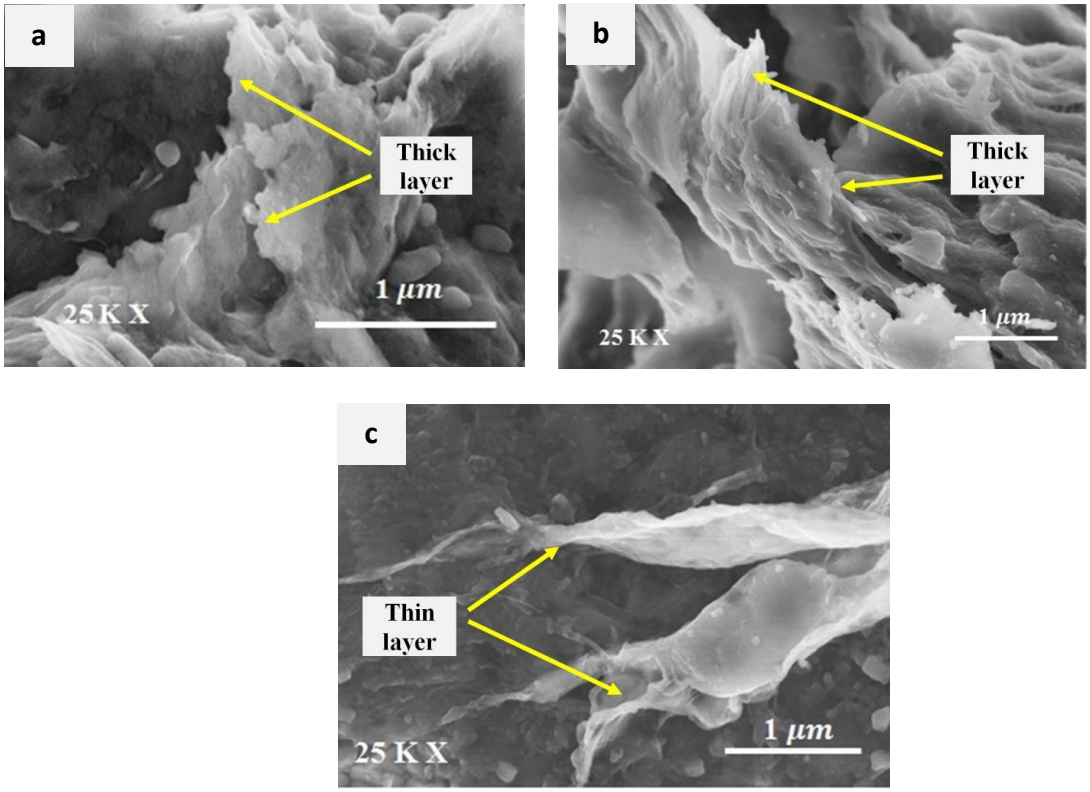

Fig. 1. FESEM images of fabricated; (a) SDS- rGO, (b) TC14-GO, and (c) TC14-rGO thin films.

The crystallinity of fabricated GO and rGO thin films were then investigated using micro-Raman spectroscopy. Fig. 2 presents the micro-Raman spectra of fabricated GO and rGO thin films which show the D-, G-, and 2D-band peaks. Those three peaks are in similar range for the whole samples in the range of 1355-1378, 1584-1589, and 2715-2723 cm^{-1} respectively. The graphene layers number can also be determined by the G-band peak position. The G-band peak for every samples were seen to be shifted from graphite's peak (1581.72 cm^{-1}) at which 1585, 1584, and 1589 cm^{-1} for SDS-rGO, TC14-GO, and TC14-rGO samples, respectively. The shifted peak of TC14-GO and TC14-rGO were caused by oxidation during exfoliation and reduction process. The most shifted peak of TC14-rGO sample indicated that the film has the lowest layers number compared to other samples confirming the result from FESEM images in Fig. 1 (c). An additional peak, called G^{+}-band around 1615-1624 cm^{-1} were also observed in the whole samples, which is believed due to the edge defects. However, this additional peak was slightly disappearing in SDS-rGO and TC14-rGO samples, which show a higher crystallinities.

The crystallinity of the samples were also determined by I_D/I_G ratio. Based on calculation, the I_D/I_G ratio of SDS- rGO, TC14-GO, and TC14-rGO samples were 0.55, 0.48, and 0.65, respectively. The I_D/I_G ratio for TC14-GO was found to be lower than TC14-rGO sample which was believed due to the effect of reduction process. The utilization of hydrazine hydrate as reducing agent was believed to increase the defect on the sample. In addition,

the higher I_D/I_G ratio of TC14-rGO compared to SDS-rGO sample shows the effectiveness of TC14 surfactant in dispersing GO sample as compared to SDS based sample. The result is consistent with the FESEM analysis where the rGO sample from TC14 produces thinner sample with better morphology [Low, *et.al.*, 2012; Yang, *et.al.*, 2009].

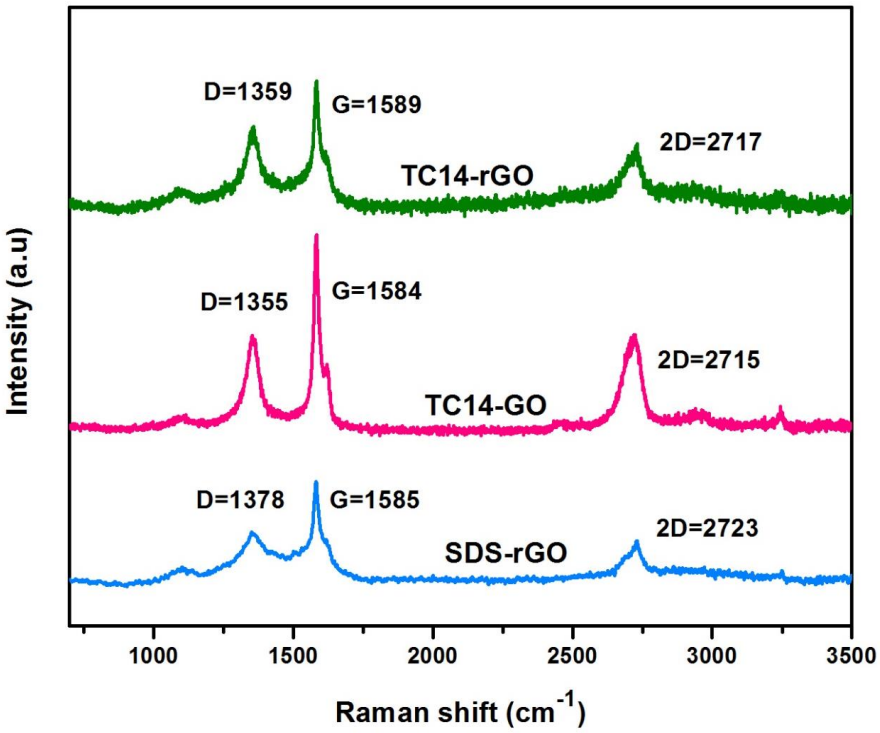

Fig. 2. Micro-Raman spectra of fabricated GO and rGO thin films by TC14 and SDS surfactants.

The transmittance of GO and rGO thin films were determined at 550 nm wavelength [Gee, *et.al.*, 2013]. The highest transmittance was achieved by TC14-GO which exhibit 93.69% transparency as shown in Fig. 3 followed by TC14-rGO and SDS-rGO which exhibit 90.25% and 86.12%, respectively. This results confirmed that the fabricated GO and rGO thin films are highly transparent and suitable to be applied as transparent conductive electrode.

The *I-V* measurement using four-point probes reveals the electrical resistivity of GO and rGO thin films. Based on the measurement, TC14-rGO sample has the lowest resistivity of 3.01 Ωcm. This value was found to be lower than TC14-GO sample which exhibit 3.82 Ωcm. The oxygen functional groups removal during reduction process might be the reason for this decrement and electrical conductivity improvement in rGO sample. The electrical resistivity of SDS-rGO was found to be higher (3.39 Ωcm) compared to TC14-GO sample. Unfortunately, the result was lower than TC14-rGO sample, confirms that TC14 plays a key role to stabilize the GO and rGO solution [Hu, *et.al.*, 2016].

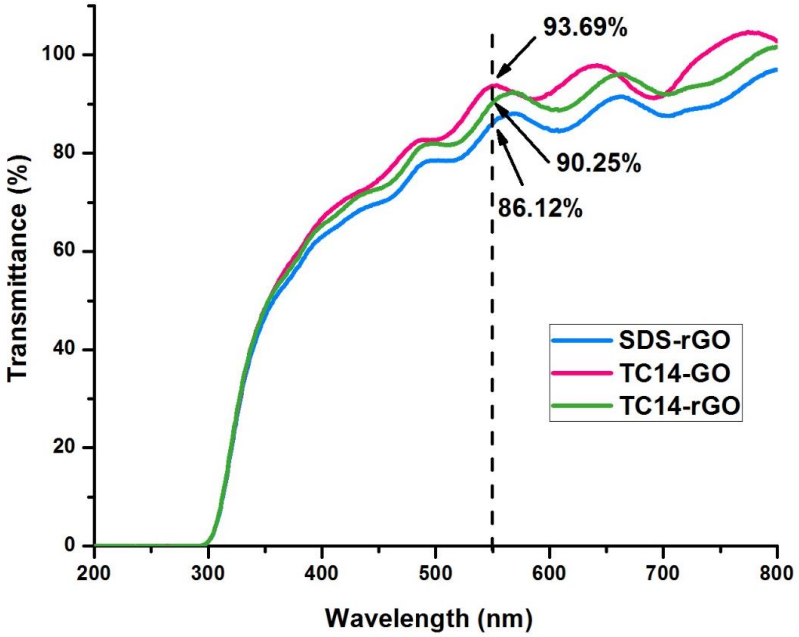

Fig. 3. The transmittance of fabricated GO and rGO thin films by TC14 and SDS surfactants.

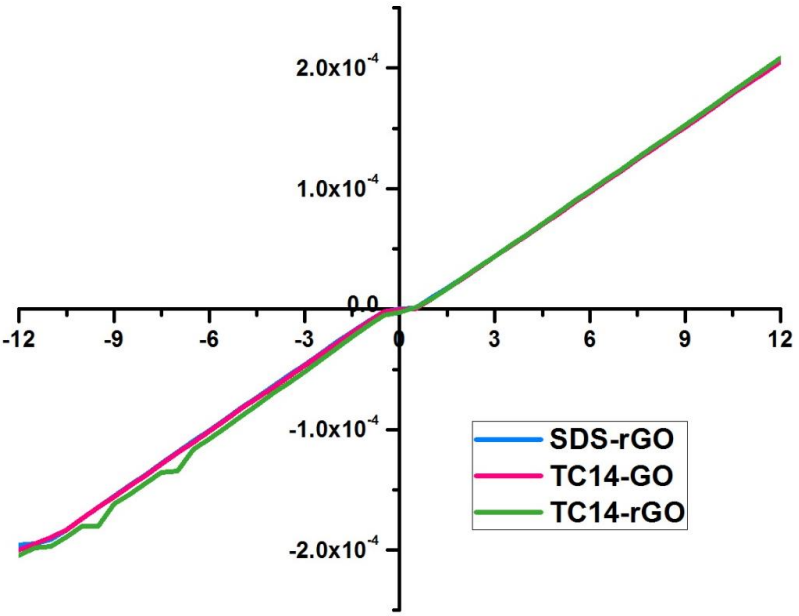

Fig. 4. The electrical resistivity based on *I-V* measurement of fabricated GO and rGO thin films by TC14 and SDS surfactants.

CONCLUSION

In this work, we have successfully fabricated the GO and rGO thin films by using different surfactants; custom-made TC14 and commercially available SDS surfactants. Based on several characterizations, TC14-rGO sample shows better quality and properties (optical and electrical) compared to the SDS-rGO and TC14-GO samples. The high transmittance of 90.25%, high I_D/I_G ratio of 0.65, and lowest electrical resistivity of 3.01 Ωcm makes TC14-rGO sample potential to be applied as transparent conductive electrode.

ACKNOWLEDGEMENT

The authors would like to express their appreciation to the TWAS-COMSTECH Research Grants (2017-0001-102-11), National Nanotechnology Directorate Division (2014-0015-102-03) and Fundamental Research Grant Scheme (2015-0154-102-02) for financial support on this project.

REFERENCES

Alanyalıoğlu, M., J. J. Segura, J. Oró-Solè, and N. Casañ-Pastora. 2012. *The Synthesis of Graphene Sheets with Controlled Thickness and order Using Surfactant-Assisted Electrochemical Processes*. Carbon.50:142-152.

Ambrosi, A., C. K. Chua, A. Bonanni, and M. Pumera. 2014. *Electrochemistry of Graphene and Related Materials*. Chemical Review.114:7150-7188.

Bae, S., H. Kim, Y. Lee, X. Xu, J. S. Park, Y. Zheng, J. Balakrishnan, T. Lei, H. R. Kim, Y. I. Song, Y.-J. Kim, K. S. Kim, B. Ozyilmaz, J.-H. Ahn, B. H., Hong, and S. Iijima. 2010. *Roll-to-Roll Production of 30-inch Graphene Films for Transparent Electrodes.* Nature Nanotechnology.5:574-578.

Beidaghi, M., Z. Wang, L. Gu, and C. Wang. 2012. *Electrostatic Spray Deposition of Graphene Nanoplatelets for High-Power Thin-Film Supercapacitor Electrodes*. Journal of Solid State Electrochemistry.16:3341-3348.

Çelebi, C., C. Yanık, A.G. Demirkol, and İ. Kaya. 2012. *The Effect of A SiC Cap on The Growth of Epitaxial Graphene on SiC in Ultra High Vacuum*. Carbon.50:3026-3031.

Chen, X.-D., Z.-B. Liu, C.-Y. Zheng, F. Xing, X.-Q. Yan, Y. Chen, and J.-G. Tian. 2013. *Electrochemical Approaches to The Production of Graphene Flakes and Their Potential Applications.* Carbon.56:271-278.

Choi, W., I. Lahiri, R. Seelaboyina, and Y. S. Kang. 2010. *Synthesis of Graphene and It's Applications: A Review*. Critical Review in Solid State and Materials Sciences.35:52-71.

Gee, C.-M., C.-C. Tseng, F.-Y. Wu, H.-P. Chang, L.-J. Li, Y.-P. Hsieh, C.-T. Lin, and J.-C. Chen. 2013. *Flexible Transparent Electrodes Made of Electrochemically Exfoliated Graphene Sheets from Low-cost Craphite Pieces.* Displays.34:315-319.

Geim, A. K., and K. S. Novoselov. 2007. *The Rise of Graphene*. Nature Materials.6:183-191.

Gilje, S., S. Han, M. Wang, K. L. Wang, and R. B. Kaner. 2007. *A Chemical Route to Graphene for Device Applications*. Nano Letters.7:3394-3398.

Hu, C., R. Zhou, C. Fan, and X. Zhou. 2016. *Influence of Reducing Reagent Combination in Graphene Oxide Reduction.* Micro and Nano Letters 11 (4) (2016) 215-220.

Kymakis, E., E. Stratakis, M. M. Stylianakis, E. Koudoumas, and C. Fotakis. 2011. *Spin Coated*

Graphene as The Transparent Electrode in Organic Photovoltaic Devices. Thin Solid Films.520:1238-1241.

Low, C. T. J., F. C. Walsh, M. H. Chakrabarti, M. A. Hashim, and M. A Hussain. *Electrochemical Approaches to The Production of Graphene Flakes and Their Potential Applications*. Carbon.54:1-21.

Mikhailov, S. 2011. *Physics and Applications of Graphene-Experiments.* InTech:Croatia.

Park, S. and R. S. Ruoff. 2009. *Chemical Methods for the Production of Graphenes.* Nature Nanotechnology. Doi:10.1038/ nnano.2009.58.

Pati, S. K., T. Enoki, and C. N. R. Rao. 2011. *Graphene and Its Fascinating Attributes*. World Scientific Publishing Co. Pte. Ltd.

Pham, V. H., T. V. Cuong, S. H. Hur, E. W. Shin, J. S. Kim, J.S. Chung, and E. J. Kim. 2010. *Fast and Simple Fabrication of Large Transparent Chemically-Converted Graphene Film by Spray-Coating*. Carbon.48:1945-1951.

Sobon, G., J. Sotor, J. Jagiello, R. Kozinski, M. Zdrojek, M. Holdynski, P. Paletko, J. Boguslawski, L. Lipinska, and K. M. Abramski. 2012. *Graphene Oxide vs. Reduced Graphene Oxide as Saturable Absorbers for Er-doped Passively Mode-locked Fiber Laser.* The Optical Society.20(17):19463-19473.

Suriani, A. B., M. D. Nurhafizah, A. Mohamed, A. K. Masrom, V. Sahajwalla, and R. K. Joshi. 2016. *Highly Conductive Electrodes of Graphene Oxide/Natural Rubber Latex-Based Electrodes by using a Hyper-Branched Surfactant*. Materials and Design.99:174-181.

Tong, Y., S. Bohm, and M. Song. 2014. *Graphene Based Materials and Their Composites as Coatings*. Journal of Nanomedicine and Nanotechnology.1(1):1003.

Wang, L.-J., L. Li, J. Yu, Y. Wu, H. He, X. Ouyang, X. Zhao, Y.-C. Yen, and L. J. Lee. 2014. *Large-Area Graphene Coating via Superhydrophilic-Assisted Electro-hydrodynamic Spraying Deposition.* Carbon.79:294-301.

Wobkenberg, P. H., G. Eda, D.-S. Leem, J. C. de Mello, D. D. C. Bradley, M. Chhowalla, and T. D. Anthopoulos. 2011. *Reduced Graphene Oxide Electrodes for Large Area Organic Electronics*. Advanced Materials.23:1558-1562.

Yang, D., A. Velamakanni, G. Bozoklu, S. Park, M. Stoller, R. D. Piner, S. Stankovich, I. Jung, D. A. Field, C. A. Ventrice Jr., and R. S. Ruoff. 2009. *Chemical Analysis of Graphene Oxide Films After Heat and Chemical Treatments by X-Ray Photoelectron and Micro-Raman Spectroscopy*. Carbon.47:145-152.

Zheng, Q., W. H. Ip, X. Lin, N. Yousefi, K. K. Yeung, Z. Li, and J.-K. Kim. 2011. *Transparent Conductive Films Consisting of Ultralarge Graphene Sheets Produced by Langmuir-Blodgett*

Assembly. American Chemical Society Nano.5(7):6039-6051.

Zhu, Y. W., S. Murali, W. Cai, X. Li, J. W. Suk, J. R. Potts, and R. S. Ruoff. 2010. *Graphene and Graphene Oxide: Synthesis, Properties, and Applications*. Advanced Materials.22:3906-3924.