GRAPHENE TRANSPARENT AND CONDUCTIVE ELECTRODE FOR LIGHT HARVESTING SOLAR CELLS

Wei Zhou[1,2] , Amare Benor Belay[1,2] , Kris Davis[1] , Rodica Khugler[1,3], Nicoleta Sorloaica-Hickman[1,2]
[1] Florida Solar Energy Center – University of Central Florida, Orlando Fl
[2] NanoScience and Technology Center - University of Central Florida, Orlando, Fl
[3] Industrial Engineering & Management Systems - University of Central Florida, Orlando Fl

ABSTRACT

Transparent and conductive coatings were achieved on glass by dissolving graphene oxide into dionized water followed by spray-coating on preheated substrate, chemical and thermal reduction. SEM shows the spray-coating graphene oxide coatings and the reduced graphene oxide coatings are uniform. No obvious aggregation was observed. UV-vis transmission spectra shows 65% transmittance at 550 nm of the graphene coatings with 15 kΩ/□.

INTRODUCTION

For more than 5 years, the poly(3-hexylthiophene):1-(3-methoxycarbonyl)propyl-1-phenyl[6,6]C_{61} (P3HT:PCBM) blend has been dominating the organic-solar-cell research. Although the material blend is well known and investigated, there are still discussions on the practical efficiency one may expect from that system [1]. However, a standard planar organic solar cell cannot make full use of the light since the Al electrode will always reflect part of the light. We have designed a photovoltaic device with transparent electrodes (like graphene and ITO) to capture more light.

Graphene has focused a great deal of attention due to its unique electrical properties. The exfoliation of graphite oxide is efficient and results in high yields of single-layered graphene oxide (GO). Oxygen functionalities of four kinds are known to exist in GO: epoxide (-O-), hydroxyl (-OH), carbonyl (-CdO), and carboxyl (-COOH). These functional groups make graphene oxide sheets strongly hydrophilic and decrease the interaction energy between the graphene layers. Hence the individual GO sheets can then be readily deposited on virtually any substrate over large areas using solution based methods and transfer printing [2].

GO is electrically insulating and must be reduced to make it electrically active [3]. Although other methods have been reported, the most widely used chemical route to reduce GO in solution as well as after deposition onto substrates is exposure to hydrazine vapor. To further improve the electrical properties of reduced GO, the hydrazine treatment is usually followed by thermal annealing (200–500 °C) [4].

In this paper, we employed spray coating to deposit the GO films and attempted several methods, like hydrazine vapor treatment, ultraviolet (UV) treatment, and thermal annealing under high purity Argon (Ar), to reduce the GO films. As a result of the hydrazine vapor treatment, cracks were spotted on the RGO films. An alternative reducing method without damaging the RGO films is thermal treatment. We also found that UV radiation can reduce the GO films. Finally, UV radiation and thermal treatment were combined to reduce the GO films.

EXPERIMENT

GO can be readily obtained from exfoliation of graphite through oxidation. A stable 1 mg/mL GO aqueous dispersion was obtained by adding GO into DI water followed by 1 h sonication. In order to achieve a highly uniform deposition, we employed a motor controlled two dimension airbrush spray coating to deposit the GO dispersion onto a preheated glass substrate. The GO coatings in different thickness were achieved by 1, 2, 3, and 4 runs of spray with a certain N_2 presure. The as prepared GO coatings were reduced by hydrazine vapor at 100 °C and followed by annealing under Ar atmosphere at 400 °C for 30 min.

RESULTS AND DISCUSSION

Optical properties of as sprayed GO coatings were studied as shown in Fig. 1. The GO coatings showed very high light transmittance. Even the GO coating sample with 8 runs spray still gave a transmittance around 80% (Fig.1a) at 550 nm which is related with P3HT absorption band [5]. After reduction, the transmittance of graphene could show a small decrease. For example, a 92% transmittance was observed on the 4 runs spray coating GO sample at 550 nm. However, after UV reduction, the transmittance at 550 nm dropped to 65%, and a slight decrease was also observed after the following thermal reduction, resulting into a 63% transmittance (Fig.1b), indicating a very strong reduction effect by UV radiation. In our case, a photothermal energy conversion was generated by UV radiation to initiate the thermal deoxygenating reactions [6]. Since GO has a high absorption at UV band comparing to visible band, UV radiation is an environment friendly and low cost solid state reduction method.

978-1-4244-9965-6/11/$26.00 ©2011 IEEE

We also tried to deposit the GO coatings with drop coating and spin coating methods. However, these experiments all resulted in aggregation of the GO platelets as the droplets of water evaporated and became smaller. Since possessing lots of hydrophilic –COOH and -OH groups, GO tends to concentrate in water instead of depositing on glass substrate, resulting into a nonuniform coating. Only spray coatings on hot substrate generate a uniform coating that show almost the same transmission spectra at different position of one GO Coating. It might be explained that the small droplets and immediate evaporation prevent the GO platelets from aggregating.

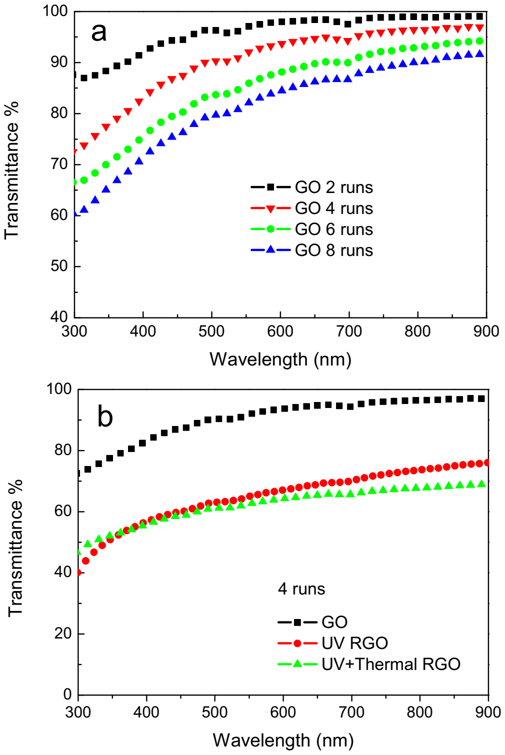

Figure 1 Transmittance spectra of (a) GO coatings with 1, 2, 3 and 4 spray runs, and (b) 4 run GO samples before and after UV and thermal treatments.

At the same time, the electric properties were characterized by four-point probe measurement. The surface resistance of the reduced GO (rGO) film sprayed 2, 4, 6, and 8 runs was measured to be 49, 15, 13, 13 kΩ/□, respectively, after UV and thermal reduction. It seems the surface resistance almost does not increase after 6 runs spray coating, while the 4 runs spray coating sample already shows both an excellent surface resistance (15 kΩ/□) and a high transmittance (65% at 550 nm). Surface resistance of hydrazine treated rGO film smaples was also measured to compare with that of UV treated rGO film samples. The suface resistance of UV treated rGO film was too high to meature, while Hydrazine treated rGO film provided ~200 MΩ/□ suface resistance. However, after additional thermal treatment under Ar, the results are comparable.

Fig.2 shows the scanning electron microscopy (SEM) images of rGO 8 run spay coatings by different reduction methods. The SEM images indicate a homogeneous morphology of rGO coatings. No obvious aggregation of Graphene has been observed even in the magnified TEM images. Hydrazine and thermal treated rGO film exhibits typical wrinkled structure with corrugation and scrolling as shown in Fig. 2a, which is intrinsic to graphene due to van der Waals forces during drying and maintaining high surface area [7,8]. However wrinkled structure was not obvious on UV and thermal treated rGO film sample, instead, some pieces of graphene sheets were observed (Fig. 2b). It might be explained that the rGO film was soaked by hydrazine vapor and generated more wrinkle structures. In addition, hydrazine vapor removed the small graphene pieces attached on the rGO film. On the other hand, UV radiation was a solid state treatment and kept the rGO film structure unchaged.

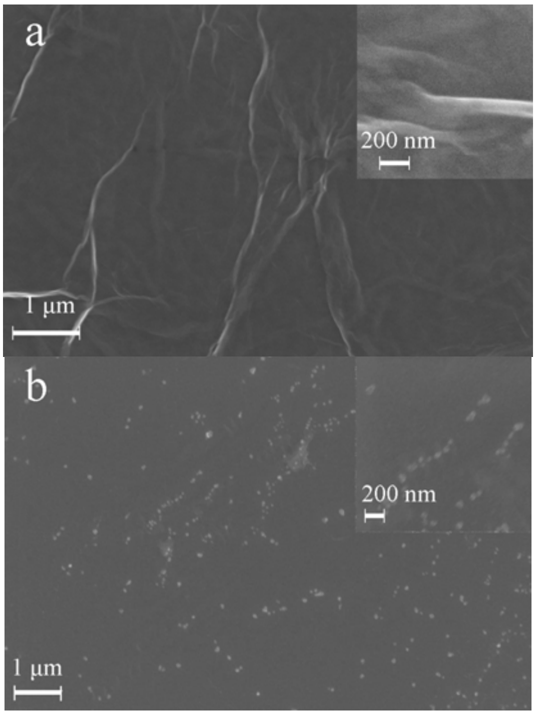

Figure 2 SEM images of (a) hydrazine and thermal reduced GO coating, and (b) UV and thermal reduced GO coating.

CONCLUSION

In summary, we report a spray coating method to deposit uniform and controllable GO coatings. Homogeneous rGO coatings were achieved by combined reduction with UV radiation and annealing under Ar atmosphene. Excellent transparency and sheet resistance were achieved on the rGO coatings. The graphene coatings show promissing applications on transparent and conductive electrodes. We will employ graphene coatings to fabricate the enhanced light harvesting solar cells in further work.

REFERENCES

[1] G. Dennler, M.C. Scharber, C.J. Brabec, "Polymer-fullerene bulk- heterojunction solar cells." *Adv. Mater.* **21**, 2009, pp, 1323-1338.

[2] X. Gao, J. Jang, S. Nagase, “Hydrazine and Thermal Reduction of Graphene Oxide: Reaction Mechanisms, Product Structures, and Reaction Design.” *J. Phys. Chem. C***,** **114**, 2010*,* pp, 832–842

[3] S. Gijie, S. Han, M. Wang, K. L. Wang, R. B. Kaner, “A chemical route to graphene for device applications.” *Nano Lett.* **7**, 2007, pp, 3394–3398.

[4] C. Mattevi, G. Eda, S. Agnoli, S. Miller, K. A. Mkhoyan, O. Celik, D.Mastrogiovanni, G. Granozzi, E. Garfunkel, M. Chhowalla, “Evolution of Electrical, Chemical, and Structural Properties of Transparent and Conducting Chemically Derived Graphene Thin Films.” *Adv. Funct. Mater.* **19**, 2009, pp, 2577–2583.

[5] J.-J. Yun, J. Peet, N.-S. Cho, G. C. Bazan, S. J. Lee, M. Moskovits, “Insight into the Raman shifts and optical absorption changes upon annealing polymer/fullerene solar cells” *Appl.Phys.Lett.* **92**, 2008, pp, 251912-1--251912-3.

[6] D. Li, M. B. Müller, S. Gilje, R. B. Kaner, G. G. Wallace, “Processable aqueous dispersions of graphene nanosheets” *Nature Nanotechnology.* **3**, 2008, pp, 101-105.

[7] M.J. McAllister, J.L. LiO, D.H. Adamson, H.C. Schniepp, A.A. Abdala, J. Liu, M. Herrera-Alonso, D.L. Milius, R. CarO, R.K. Prud’homme, I.A. Aksay, “Nitrogen-doped graphene and its electrochemical applications.” *Chem of Mater.* **19**, 2007, pp, 4396-4944.

[8] R. Kou, Y.Y. Shao, D.H. Wang, M.H. Engelhard, J.H. Kwak, J. Wang, V.V. Viswanathan, C.M. Wang, Y.H. Lin, Y. Wang, I.A. Aksay, J. Liu, “Enhanced Activity and Stability of Pt Catalysts on Functionalized Graphene Sheets for Electrocatalytic Oxygen Reduction.” *Electrochem. Commun.* **11**, 2009, pp, 954.