MRS Advances © 2017 Materials Research Society
DOI: 10.1557/adv.2017.621

Solvent Interface Trapping as an Effective Technique to Fabricate Graphite-Nanomaterial Composite Thin Films

Medini Padmanabhan, Rachel Meyen, Kerri Houghton and Miles St. John

Department of Physical Sciences, Rhode Island College, Providence, RI-02908, U.S.A.

ABSTRACT

Natural graphite can be exfoliated into thin films by trapping it at the interface between water and heptane [S. J Woltornist, A. J. Oyer, J-M. Y. Carrillo, A.V. Dobrynin, and D.H. Adamson, ACS Nano 7, 7062 (2013)]. In this work, we add functional elements into these graphitic thin films by introducing additives into the water phase prior to exfoliation. We report the successful incorporation of ZnO nanoparticles thereby enabling the composite films to act as effective ultraviolet photodetectors. In a similar manner, integration of silver nanowires is achieved, which results in an enhancement of the electrical conductivity of graphite.

INTRODUCTION

A unique combination of desirable electrical, optical and mechanical properties makes graphene an attractive candidate for myriad technological applications [2]. Fabrication techniques which produce large area graphene sheets are highly sought after. Room temperature solution processing routes are especially attractive since they tend to be cost effective and scalable. The technique of solvent interface exfoliation yields large area thin films of graphene consisting of one to four layers of carbon [1]. The method exploits the unique value of the surface energy of graphene which falls between the values of surface tension for water and heptane. As a result, graphite is naturally exfoliated and a stable graphene film is formed at the interface. The resulting thin film readily climbs up any hydrophilic surface such as glass coating it uniformly with graphene. The lack of any chemical modification ensures that the individual graphene flakes are pristine and maintain their desirable optical and electrical properties [1].

The range of application of graphene thin films is significantly enhanced by the addition of functional elements which impart desirable optoelectronic properties. Covalent and non-covalent functionalization of graphene has resulted in its widespread use in devices such as solar cells, super capacitors and sensors [3].

In this work, we show that the technique of solvent interface exfoliation can be modified to yield graphite-nanomaterial composite thin films. Specifically, we show that nanoparticles of ZnO (ZnO-NP) can be incorporated into these films which then act as effective ultraviolet (UV) photodetectors. We also present the fabrication of graphite-silver nanowire (Ag-NW) composite films. The inclusion of silver enhances the conductivity of graphite which would then have potential applications as transparent conducting electrodes.

EXPERIMENT

We roughly follow the procedure outlined in reference [1]. A small amount (~0.5-5.0 mg) of commercially available natural graphite flakes (Asbury Carbons) is suspended in 1.2 ml of n-heptane and sonicated in a bath sonicator. The suspension is allowed to sit for 30-300 seconds and 1 ml of aliquot is removed into a glass vial. About 1 ml of water is then added to the vial. The desired additive is separately dispersed in water and then added to the mix ensuring a 1:1 volume ratio between water and heptane. The additives used in this study are: ZnO nanoparticles (Sigma Aldrich 721077), silver nanowires (Sigma Aldrich 807826) and rhodamine-6G (Sigma Aldrich 252433). The contents of the vial are sonicated in a bath or horn sonicator for approximately 30 seconds. A thin film of carbon is observed to climb the walls of the container. In the absence of Raman or AFM studies to confirm the thickness of the flakes, we refer to these films as graphitic thin films instead of graphene.

The thin film is then transferred to a pre-cleaned glass slide by inserting the slide into the vial right after sonication. Often, a gentle squeezing of the thin film is necessary for achieving optimal electrical contact between adjacent flakes. This is achieved by dipping a cotton applicator in isopropanol and bringing it to a close proximity of the film. The low surface tension of isopropanol has the effect of pushing the carbon flakes together.

These thin films are contacted electrically using conductive silver paste (Sigma Aldrich 735825). They are annealed at 120 °C for 20 minutes to harden the silver paste. Electrical measurements are performed using a Keithley 2400 source meter unit in a 2-probe configuration. To record the photoresponse of the graphite-ZnO-NP composite films, a commercial UV-LED of 365 nm wavelength is used as the illumination source.

DISCUSSION

Effect of the additive on the ease and quality of composite formation

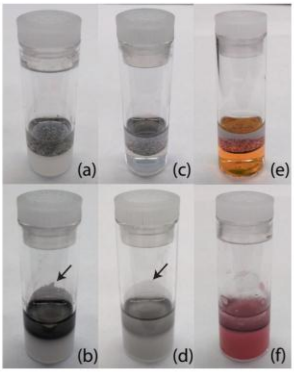

Figure 1. Glass vials showing formation of graphene-nanomaterial composite films using the solvent interface exfoilation technique. ZnO-NP ((a) and (b)), Ag-NW((c) and (d)) and rhodamine-6G dye ((e) and (f)) are explored as possible additives to graphite thin films. Top and bottom panels show the vials before and after sonication respectively.

In figure 1 we show photographs of glass vials where graphite is trapped at the oil-water interface. Here we compare three additives: 1) ZnO-NP 2) Ag-NW and 3) rhodamine 6G dye. The top panels show the glass vials right before sonication. In all cases, the lower phase is water with the additive dispersed in it and the upper phase is heptane with graphite flakes suspended in it. The bottom panels show the same vials after ~30 s sonication in a bath sonicator.

In figure 1(b) we see a thin film climbing up the walls of the container. Later, we show that the film is a composite consisting of graphite and ZnO-NPs closely integrated with each other. The composition of the film can be tuned from carbon-rich to ZnO-rich by changing the relative amount of carbon and ZnO in the liquids. The transparency of the films is partly determined by the percentage of the substrate that is not covered by carbon flakes. The opto-electronic characterization of these films is presented below.

Incorporation of Ag-NWs into graphite films is shown in figure 1(d). In this case our objective is to obtain a transparent film. The procedure of inserting a glass slide and pulling it out to obtain a coating of graphite on it can be repeated multiple times. With each successive pull, we observe lesser percentage of large carbon flakes resulting in more transparent films.

In figure 1(f), we see that the rhodamine dye seems to strongly favor the formation of a water-oil emulsion. We do not observe a carbon film climbing the walls of the container. The emulsion shown in figure 1(f) is stable over a period of many hours. Once the droplets coalesce, we do observe a graphitic thin film floating at the interface. This indicates that the interaction of rhodamine with the interface is different from that of the inorganic nanomaterials. More studies need to be performed before the nature of this interaction can be completely understood.

Graphite-ZnO ultraviolet photodetectors

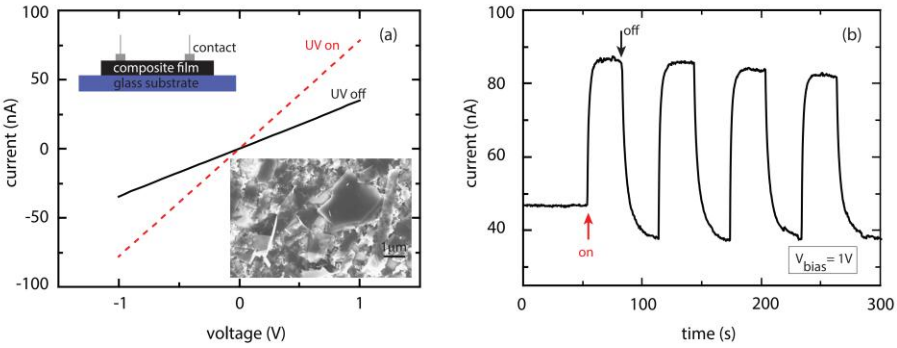

Figure 2. Optoelectronic characterization of graphite-ZnO-NP composite films. (a) Current-voltage measurement. Bottom right inset: SEM of a similar sample. Top-left inset: schematic of the measurement set-up. (b) Modulation in the current as light is turned on and off.

The bottom right inset of figure 2(a) shows an SEM image of a graphite-ZnO-NP composite film formed by solvent interface trapping. It shows that the two constituent materials are well-mixed. In some locations, the ZnO particles are visible through the graphite flakes thereby suggesting high degree of exfoliation and the existence of graphene.

Electrical characterization of one such sample is shown in figure 2(a) with the schematic in the top left inset. The current-voltage relationship is linear attesting to the Ohmic nature of conduction. In the presence of UV-light we observe a significant increase in the conductivity of the sample. This photoconductivity is further studied by applying a constant voltage and monitoring the current through the sample as light is successively turned on and off. As shown in figure 2(b), we observe a response time of the order of a few seconds.

Ultraviolet photodetectors using a combination of graphene and ZnO-NPs is widely studied in literature [4-7]. While some approaches involve deposition of ZnO-NPs over a layer of graphene, others have tried to encapsulate ZnO-NPs with graphene flakes resulting in a wide range of responsivity and response time scales. Here, we emphasize that our method is facile, cost-effective, scalable and produces response levels and response times comparable to values reported in literature.

Graphite-Ag nanowire transparent conducting sheets

In figure 3 we show Ag-NWs being incorporated into graphite films. Similar to the case of ZnO-NPs, we see significant intermixing of the two components as shown by the SEM image in the bottom right inset. Electrical characterization shows Ohmic conduction with resistance values as low as 200 Ω in some samples. Data from a typical sample is shown in figure 3 with a resistance of 15.4 kΩ. A photograph of this sample is shown in the top-left inset.

Addition of silver nanowires to graphene has been explored in the literature as a way of fabricating transparent conducting electrodes [8,9]. The presence of graphene protects silver from atmospheric degradation [10] thereby preserving its high conductivity. In our samples, although we observe an enhancement in conductivity of graphite as a result of the addition of Ag-NWs, we are unable to achieve high levels of transparency. Preliminary measurements also show that the effect of atmospheric exposure is not completely eliminated by the presence of graphite. More studies are needed before we can gain a better understanding of this system.

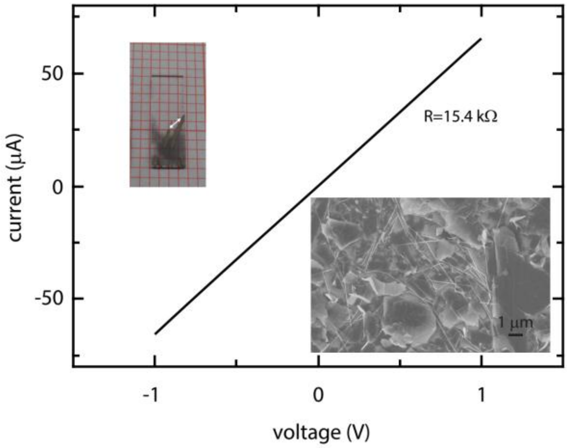

Figure 3. Current-voltage characteristics of a typical grahite-Ag-NW composite thin film. A photograph of the sample is shown in the top left inset. An SEM image of a similar sample is shown in the bottom right inset.

CONCLUSIONS

We explore the feasibility of fabricating graphite-nanoparticle composite thin films by trapping then at an oil-water interface. We find that ZnO nanoparticles and Ag nanowires can be integrated into graphitic thin films with relative ease. The resulting films can function as technologically relevant entities such as photodetectors and transparent conducting electrodes.

ACKNOWLEDGMENTS

MP is thankful to Prof. Douglas Adamson, University of Connecticut for help with the technique of solvent interface trapping. We thank Asbury Carbons, NJ for providing us with natural graphite. We are grateful to Mr. Charles Simson for help with lab set up and IMNI, Brown University, for access to SEM imaging facility.

This work is supported in part by the National Science Foundation (grant # OIA-1538893). MP acknowledges support of Rhode Island College, Rhode Island College Foundation and Rhode Island College Alumni Affairs Office.

References

[1] S. J. Woltornist, A. J. Oyer, J-M. Y. Carrillo, A.V. Dobrynin, and D.H. Adamson, *ACS Nano* **7**, 7062 (2013).
[2] A. C. Ferrari, F. Bonaccorso, V. Fal'ko, K. S. Novoselov, S. Roche, P. Bøggild, S. Borini, F. H. L. Koppens, V. Palermo, N. Pugno, J. A. Garrido, R. Sordan, A. Bianco, L. Ballerini, M. Prato, E. Lidorikis, J. Kivioja, C. Marinelli, T. Ryhänen, A. Morpurgo, J. N. Coleman, V. Nicolosi, L. Colombo, A. Fert, M. Garcia-Hernandez, A. Bachtold, G. F. Schneider, F. Guinea, C. Dekker, M. Barbone, Z. Sun, C. Galiotis, A. N. Grigorenko, G. Konstantatos, A. Kis, M. Katsnelson, L. Vandersypen, A. Loiseau, V. Morandi, D. Neumaier, E. Treossi, V. Pellegrini, M. Polini, A. Tredicucci, G. M. Williams, B. H. Hong, J -H Ahn, J. M. Kim, H. Zirath, B. J. van Wees, H. van der Zant, L. Occhipinti, A. Di Matteo, I. A. Kinloch, T. Seyller, E. Quesnel, X. Feng, K. Teo, N. Rupesinghe, P. Hakonen, S. R. T. Neil, Q. Tannock, T. Löfwander and J. Kinaret, *Nanoscale* **7,** 4598 (2015).
[3] X. Gong, G. Liu, Y. Li, D. Y. W. Yu, and W. Y. Teoh, *Chem. Mater.*28, 8082 (2016).
[4] D. I. Son, H. Y. Yang, T. W. Kim, and W. Il Park, *App. Phys. Lett.* **102**, 021105 (2013)
[5] W. Guo, S. Xu, Z. Wu, N. Wang, M. M. T. Loy, and S. Du, *Small* **9,** 3031 (2013)
[6] D. Shao, M. Yu, H. Sun, T. Hu, J. lian and S. Sawyer, *Nanoscale* **5**,3664 (2013)
[7] S. Safa, R. Sarraf-Mamoory and R. Azimirad, *J Sol-Gel Sci Technol* **74**, 499 (2015)
[8] D. Lee, H. Lee, Y. Ahn, Y. Jeong, D -Y Lee and Y. Lee, *Nanoscale* **5**, 7750 (2013)
[9] R. Chen, S. R. Das, C. Jeong, M. R. Khan, D. B. Janes and M.A. Alam, *Adv Funct Mater* **23**, 5150 (2013)
[10] J. C. Reed, H. Zhu, A. Y. Zhu, C. Li, and E. Cubukcu, *Nano Lett.* **12**, 4090 (2012)