Opt Quant Electron (2016) 48:319
DOI 10.1007/s11082-016-0591-1

Transparent and conductive films from liquid phase exfoliated graphene

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Received: 5 November 2015 / Accepted: 6 May 2016 / Published online: 14 May 2016

Abstract We describe transparent and conductive films of liquid-phase exfoliated graphene deposited with the Langmuir–Blodgett (LB) method. Graphene sheets (GS) were exfoliated from graphite by ultrasonic treatment in N-Methyl-2-pyrrolidone (NMP) and N, N-dimethylacetamide (DMA) solvents. For comparison, graphene sheets were also exfoliated in a water solution of surfactants. We confirm a higher exfoliation rate for surfactant-based processing compared to NMP and DMA. Furthermore, we demonstrate that our films exfoliated in NMP and DMA, deposited with LB and annealed have a higher optical transmittance and lower sheet resistance compared to films obtained with vacuum filtration, which is a necessary step for GS exfoliated in water solutions. The structural, optical and electrical properties of graphene layers were characterized with scanning electron microscopy, atomic force microscopy, UV/VIS spectrophotometry and sheet resistance measurements. Our facile and reproducible method results in high-quality transparent conductive films with potential applications in flexible and printed electronics and coating technology.

Keywords Graphene · LPE · Langmuir–Blodgett assembly

1 Introduction

Transparent conductors are an essential part of many optical devices. Many of the thin metallic or metal oxide films used as transparent conductors (Granqvist 2007) exhibit nonuniform absorption across the visible spectrum (Phillips et al. 1994), or they are

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This article is part of the Topical Collection on Advances in the Science of Light.

Guest Edited by Jelena Radovanovic, Milutin Stepic, Mikhail Sumetsky, Mauro Pereira and Dragan Indjin.

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chemically unstable, or both (Scott et al. 1996; Schlatmann et al. 1996). The experimental discovery of graphene (Novoselov et al. 2004) brought a new alternative to this field. Graphene is a material with high optical transparency, large carrier mobility, good chemical stability, and mechanical strength, making it an excellent choice for transparent electrodes in various optoelectronic devices (Blake et al. 2008).

Although graphene is a natural choice for transparent conductive films (Bonaccorso et al. 2010), the feasibility of its mass production is essential for applications. In order to produce large quantities of graphene Blake et al. (Blake et al. 2008) and Hernandez et al. (2008) developed a method of graphene production using solvent assisted exfoliation (or liquid phase exfoliation, LPE) of bulk graphite, which is simpler and less costly than chemical vapor deposition and returns a higher yield than mechanical exfoliation (Novoselov et al. 2004, 2005). LPE allows the possibility to scale up the synthesis of graphene making it economically available in a large amount, presenting a promising route for large-scale production (Paton et al. 2014).

Numerous research efforts followed up to increase the concentration and quality of the graphene flakes produced. One of the most promising synthesis routes for LPE graphene is non-covalent exfoliation using solvents that have surface energy values comparable to that of graphite (Hernandez et al. 2008). Typically ultrasound assists the separation of graphene flakes from graphite powder in solvent. Exfoliation conditions such as the initial concentration of graphite powder, sonication time (Khan et al. 2010), solvent type (O'Neill et al. 2011; Bourlinos et al. 2009; Hernandez et al. 2010; Lotya et al. 2009; Guardia et al. 2011), and possible filtration (Khan et al. 2011) were tuned in order to optimize the yield and quality of graphene dispersions. These graphene dispersions can be used to form films by various methods, for example spray coating (Blake et al. 2008), vacuum filtration (Hernandez et al. 2008; Lotya et al. 2009) or Langmuir–Blodgett assembly (LBA) (Cote 2009; Kim et al. 2013; Li et al. 2008).

In this study, graphene sheets (GS) were exfoliated from graphite by ultrasonic treatment in organic solvents with high boiling points, N-Methyl-2-pyrrolidone (NMP), N, N-dimethylacetamide (DMA), and for comparison, in a water solution of surfactant, sodium dodecylbenzenesulfonate (SDBS) and Pluronic P-123 (P-123). The graphene dispersions from NMP and DMA were used to form films by controlled deposition of few-layer graphene using the Langmuir–Blodgett (LB) method on a water–air interface. We confirm a higher exfoliation rate for surfactant-based processing, but demonstrate that our films exfoliated in organic solvents with high boiling points and deposited with LB have a higher optical transmittance and lower sheet resistance compared to films obtained with vacuum filtration, which is a necessary step for GS exfoliated in water solutions. The structural, optical and electrical properties of graphene layers were characterized with scanning electron microscopy, atomic force microscopy, UV/VIS spectrophotometry and sheet resistance measurements.

2 Experimental procedure

All chemicals used were purchased from Sigma Aldrich: graphite powder (product number 332461), N-Methyl-2-pyrrolidone (product number 328634), N, N-dimethylacetamide (product number 38840), sodium dodecylbenzenesulfonate (product number 289957) and Pluronic P-123 (product number 435467). The particular graphite powder product was chosen for its large initial flake size, which should result in the largest possible graphene flakes after exfoliation. Stock solutions of SDBS and P-123 of different concentrations were prepared in deionized water (resistivity 18 MΩ) by stirring overnight. A range of graphene dispersions were prepared. A typical sample was prepared by dispersing graphite in the desired solvent using from 30 min to 14 h of sonication in a low power sonic bath. The resulting dispersion was centrifuged for 60 min at 3000 rpm in order to reduce the amount of unexfoliated graphite.

The graphene sheets exfoliated from graphite by ultrasonic treatment in NMP were used to form films at a water–air interface. Beakers filled with deionized water, 10 mL volume, were used for film formation. A 1.5–2 vol% of GS + NMP was added to the interface with a continuous flow rate of 5–10 mL/s (Fig. 1a). This set of parameters provides enough surface pressure for the film to be close-packed. After the film is formed, it is slowly scooped onto the targeted substrate (Fig. 1b), as shown in our previous work (Matković et al. 2016). PET and SiO_2/Si were used as substrates. As it has been shown that annealing decreases sheet resistance due to solvent evaporation (Hernandez et al. 2008; Lotya et al. 2009), some of these deposited films were annealed. Annealing was carried out in a tube furnace at 250 °C in an argon atmosphere for 2 h.

For optical characterization, UV–VIS spectra were taken using a SUPER SCAN Varian spectrophotometer with quartz cuvettes. The resistance of each sample was measured in a two-point probe configuration, and the sheet resistance was obtained by including the sample geometry factors. AFM measurements were taken with an atomic force microscope, NTEGRA Spectra, in tapping mode. SiO_2/Si was chosen as a substrate for AFM due to its low surface roughness. The lateral profile of graphene flakes was analyzed with a Tescan MIRA3 field-emission gun SEM.

3 Results and discussion

We optimized for high graphene concentration and large flake size, tuning exfoliation conditions such as initial graphite concentration, sonication time and solvent type. The Lambert–Beer law was applied to UV–VIS absorption spectra to find graphene concentration. The concentration was estimated from the absorbance at 660 nm by using the extinction coefficient of graphene ($\alpha = 13.90$ mL mg^{-1} m^{-1}) previously determined in surfactant/water solutions (Hernandez et al. 2008; Lotya et al. 2009; Guardia et al. 2011) and ($\alpha = 24.60$ mL mg^{-1} m^{-1}) in NMP and DMA solutions (Hernandez et al. 2008). Figure 2a depicts a higher final concentration for surfactant-based processing for all initial concentrations of graphite powder, from 0.5 to 18 mg mL^{-1}. The most commonly used deposition technique for LPE GS is vacuum filtration. This is a necessary step for GS exfoliated in water solutions. For GS films formed by evaporation of a high boiling point

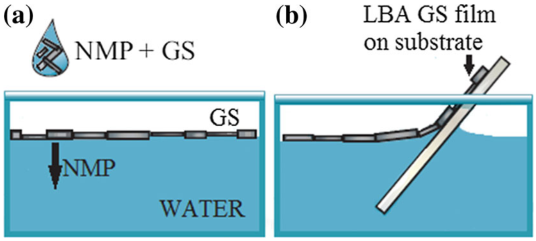

Fig. 1 Schematic representations of **a** LBA GS film formation, **b** scooping of the film onto a targeted substrate

solvent, one of the biggest problems is that graphene flakes aggregate during evaporation (O’Neill et al. 2011) hindering fine control over the film thickness (Hernandez et al. 2008). This can be avoided by depositing with LB, which allows reliable and reproducible thickness control and prevents further agglomeration of graphene flakes during drying (Kim et al. 2013). We chose the dispersion in NMP with the highest graphene concentration (Fig. 2b) for experiments on LB films.

A single LB deposition resulted in films with an average thickness 3.3 nm, as measured with AFM, indicating an average GS thickness of 10 layers (Fig. 3).

Figure 4 shows optical transmittance versus sheet resistance for varying number of LB depositions on PET, compared to graphene film obtained with vacuum filtration of GS exfoliated from the same graphite precursor using the same experimental procedure (Hernandez et al. 2008; Lotya et al. 2009) before and after annealing. The highest transparency for a single LB film deposition prior to annealing was found to be about 83 %, which is between 20 and 40 % higher than the transmittance that can be accomplished with vacuum-filtration. The sheet resistance of one LB film deposition is between 70 and 250 kΩ/sq, 2–5 times lower than sheet resistance achieved with vacuum filtration without annealing. Increasing the graphene film thickness with additional LB depositions led to consistent increases in conductivity, but a decrease in transparency. Our graphene films for three LB depositions prior to annealing have comparable sheet resistance but higher optical transmittance compared to vacuum-filtered films after annealing.

The electrical conductivity is affected by the size and connectivity of the flakes as well as the thickness of the films. Our average GS diameter was is 120 nm, as measured with SEM (Fig. 5). SEM also revealed the presence of pinholes between flakes for a single LB deposition, which probably results in parasitic sheet resistance (Fig. 5a). In order to remove the residual solvent between the overlapping flakes, which may affect transport, we employed thermal annealing. Annealing does not repair the holes and other irreversible defects (Fig. 5b), but it can remove residual solvents, improving the coupling between graphene flakes and hence decreasing sheet resistance. For a single LB deposition, annealing reduced sheet resistance by about six times, without considerably decreasing transparency (Fig. 4). The sheet resistance of a singly deposited film after annealing was found to be between 10 and 20 kΩ/sq, a significant improvement over other published data. After annealing we performed a second LB deposition and achieved sheet resistance of

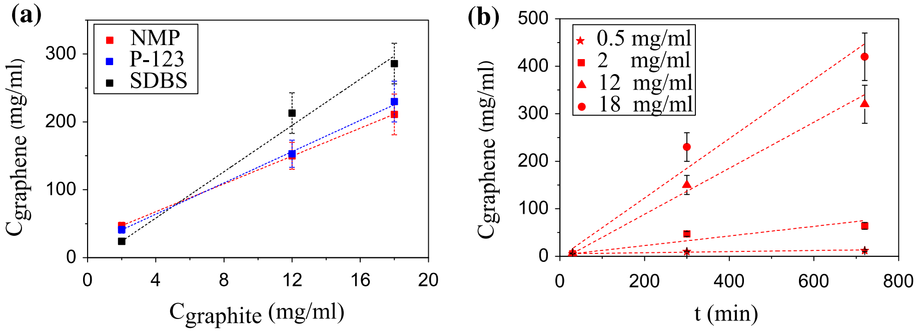

Fig. 2 Concentration of dispersed graphene: **a** in different solutions for different initial graphite concentration and sonication time of 5 h, **b** in NMP for different sonication time and different initial graphite concentration

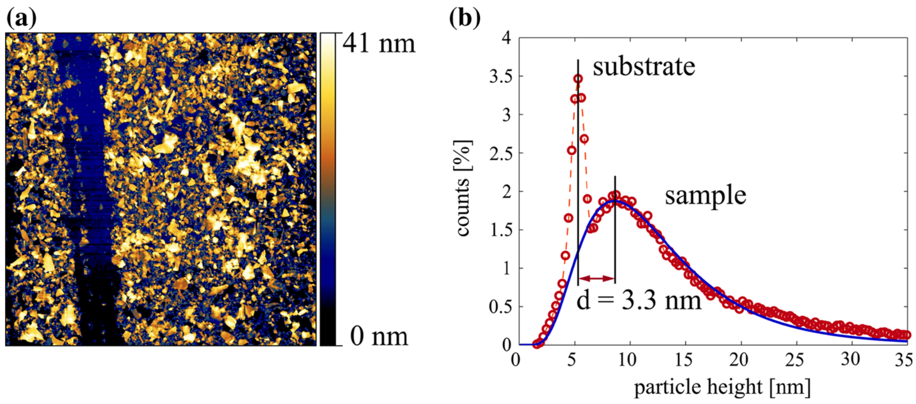

Fig. 3 **a** AFM image of a LB graphene film on a SiO_2/Si substrate, **b** an LB GS film/substrate height histogram fitted with a log-normal curve

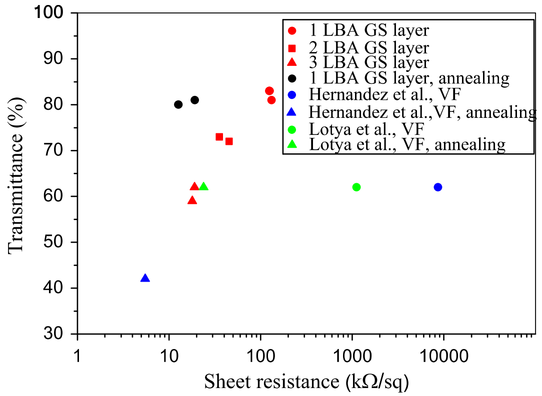

Fig. 4 Optical transmittance versus sheet resistance for varying number of LB deposition of graphene sheets on PET exfoliated in NMP before (*red*) and after annealing (*black*), compared to graphene films obtained with vacuum filtration in the same solvent (*blue*) (Hernandez et al. 2008) and graphene films obtained with vacuum filtration in surfactant/water solutions (*green*) (Lotya et al. 2009) before and after annealing. (Color figure online)

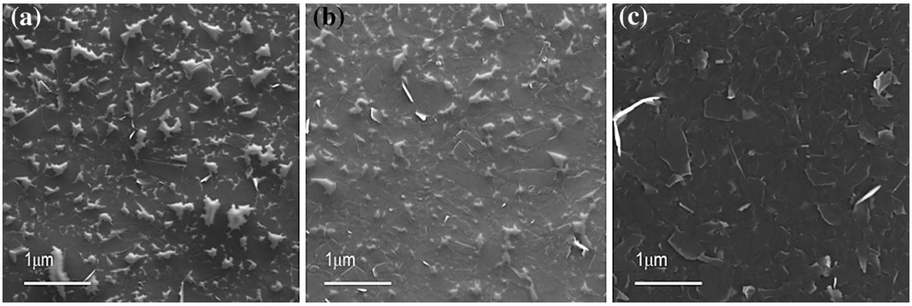

Fig. 5 SEM images of: **a** singly deposited LB film on a glass substrate, **b** the same film after annealing, **c** two LB depositions with an annealing step in between

3 kΩ/sq and a transparency of more than 70 %. Decreased resistance is the result of reduced density of pinholes (Fig. 5c) as well as increased film thickness.

4 Conclusion

In summary, we have shown that Langmuir–Blodgett assembly of multi-layer graphene sheets produced from liquid phase exfoliation of graphite powder in solvents can be used to fabricate transparent and conductive films. The sheet resistance of deposited LBA GS layers was found to be between 15 and 250 kΩ/sq, with transmittance between 60 and 85 %, depending on the number of deposited LBA graphene layers. The conductivity of these LBA films can be further increased by about six times with annealing, without considerably decreasing transparency. Optoelectronic properties of these films are much better compared to graphene films obtained with vacuum filtration of GS exfoliated with the same experimental procedure, which is the most commonly used deposition technique for LPE GS. Ours is a facile, reproducible and low-cost technique for transparent conductive films with potential applications in coating technology.

Acknowledgments This work was funded by the Serbian MPNTR through Projects OI 171005 and Innovation Project 451-03-2802-IP/1/167 and by Qatar National Research Foundation through Projects NPRP 7-665-1-125. The authors would like to express their gratitude to S. Novkovic for technical support with annealing.

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