



Letter

Thermal treatment and chemical doping of semi-transparent graphene films



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ARTICLE INFO

Article history:

Received 7 November 2014

Received in revised form 9 December 2014

Accepted 13 December 2014

Available online 12 January 2015

Keywords:

Graphene

Work function

Doping

Graphene oxide

Liquid-phase exfoliated graphene

ABSTRACT

Graphene transparent conductive films have been proposed as indium tin oxide (ITO) modifiers for application in optoelectronic devices. Here thermal and chemical treatments of graphene-based transparent films are systematically investigated with a view to increasing their conductivity and tuning their work function. We look at two different types of graphene, obtained either via spin-coating of graphene oxide (GO) aqueous dispersions, or vacuum-filtration of liquid-phase exfoliated (LPE) graphene in highly volatile, non-toxic solvents such as isopropanol and ethanol. As-deposited films are relatively resistive, but we are able to lower their sheet resistance by up to three orders of magnitude for both LPE and GO, so as to reach values of $\sim 10^5 \Omega/\square$ via thermal treatments at temperatures of $\sim 350/400^\circ\text{C}$ at pressures of $\sim 10^{-6}/10^{-4}$ mbar. Most importantly, the physisorption of the molecule $(\text{CF}_3\text{SO}_2)_2\text{NH}$ (trifluoromethanesulfonimide) results in an increase of the films work function by up to 0.5 eV, to yield a value of ~ 5.3 eV. This is comparable or slightly better than what can be achieved with poly(3,4-ethylene dioxathiophene) doped with poly(styrene sulfonate) (PEDOT:PSS), depending on PSS concentration, thereby confirming the potentially beneficial role of chemical doping of liquid dispersions of graphene-derivatives for application to organic electronics.

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1. Introduction

Graphene is one of the most interesting candidate materials for the production of transparent conductive films for flexible optoelectronic applications such as light-emitting diodes (LEDs) or photovoltaics. Graphene is a monoatomic layer of carbon atoms arranged in a honeycomb lattice. It combines a good transparency (2.3% transmittance for a single layer for wavelengths higher than ~ 400 nm [1]), good charge carrier mobility [2] ($\sim 10^5 - \text{cm}^2 \text{s}^{-1} \text{V}^{-1}$) and promising mechanical properties [3].

Thanks to a strong ambipolar field-effect, the tuning of the Fermi energy of either sign causes a variation in the charge carrier concentration and hence of the electrical conductivity of graphene [4]. As a consequence of this, for a single layer of graphene the sheet resistance can be reduced from $\sim 6 \text{ k}\Omega/\square$ for the undoped graphene to few hundreds of Ω/\square via intentional or serendipitous chemical doping with molecules such as H_2O , NO_2 and NH_3 , or by applying a gate voltage of ~ 100 V or so [5,6].

Since it was first isolated in 2004, different production methods have been developed for graphene. They all result in products with slightly different physical properties depending on the size of the graphene flakes, the integrity of the honeycomb lattice and the presence of chemical

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defects [7,8]. The application of graphene in optoelectronic devices requires films with areas up to several cm^2 and a production method that can be scaled-up for massive production. Only few of the existing synthetic approaches meet these requirements.

The chemical vapor deposition (CVD) method is generally reported to produce multi-crystalline films of graphene, with domains of up to $50\ \mu\text{m}$ or larger [9,10]. In a basic configuration methane and hydrogen gas are passed through a reactor at high temperature ($\sim 1000\ \text{C}^\circ$) to activate the growth of graphene domains on a thin copper foil ($25\ \mu\text{m}$) as a catalytic substrate [11]. A polymer layer is then deposited on the film and the copper foil is etched in a FeCl_3 solution. The graphene is transferred onto the final substrate and the polymer layer is washed away. Large-area films with a sheet resistance as low as $\sim 200\ \Omega/\square$ have been obtained with a roll-to-roll adaptation of this method [12]. The use of high temperatures reactors, an ignitable gas and the dependence on an expensive metal as copper are the main shortcomings of this method that need to be considered when upscaling the process toward industrial production.

Less expensive and highly-scalable methods for the production of graphene are based on the exfoliation of graphite powder in a solvent to obtain liquid dispersions of mono and multi-layer graphene flakes [13–15]. The exfoliation process is based on the surface energy matching between the graphene sheets and the solvent [13]. Interestingly, the range of suitable solvents can be usefully extended by using a variety of surfactants, also with a view to using water as a dispersant [16–18]. In the liquid-phase exfoliation approach, a low-power bath sonication provides enough energy to intercalate solvent molecules between the graphene planes and to exfoliate them mechanically. Alternatively, exfoliation can also be achieved after chemical modification of graphite via extensive oxidation to separate the graphene sheets [19,20]. The formation of oxygen functional groups on the graphene lattice increases drastically the affinity of the flakes for polar solvents such as water. Liquid-phase exfoliated (LPE) graphene and graphene oxide (GO) are characterized by flakes with sizes up to several microns [13,19]. Crucially, and differently from CVD graphene, LPE and GO dispersions can be obtained in large quantities (easily up to kilograms) via scalable processes and relatively low costs. This is of enormous technological significance, because the liquid dispersions can be used as conductive inks with already existing ink-jet and roll-to-roll printing technology for printable electronics [21,22].

Nevertheless, although technologically very appealing, films obtained by deposition of either LPE or GO are constituted by a number of overlapping flakes. The charge transport in such films occurs via hopping between consecutive flakes and constitutes one of the main limits to the conductivity. In addition, oxidation of graphite typically introduces a number of lattice defects, leading to a lower quality graphene in terms of charge mobility and thus conductivity, also in relation to the need of charge to hop between domains [13,23]. Several methods have been proposed to reduce the amount of such defects and restore the properties of graphene, at least partially. They generally

involve either high temperatures annealing (typically $> 1000\ \text{C}^\circ$ for few hours), lower temperatures but extremely long times (e.g. several days at $80\ \text{C}^\circ$), electrochemical treatments or even chemical reduction of GO with hydrazine [23–28].

In this work we report the tuning of the work function of thin transparent films of LPE and GO after thermal treatments at relatively mild temperature ($350/400\ \text{C}^\circ$) for only few hours, which also significantly increase their conductivity. The ability to control the work function of thin films is of paramount importance for applications as components of electronics devices [29,30]. To this purpose we studied the effect of chemical p-type doping on LPE and reduced GO films for the tuning of the electrical properties. In particular we used the electron-withdrawing molecule 1,1,1-trifluoro-N-(trifluoromethyl)sulfonyl-methanesulfonamide (TFSA, see Fig. 1 panel A) as a p-doping agent on graphene [31–33]. By decreasing the electron density of graphene, TFSA shifts the Fermi level toward lower energies where the density of states (DOS) is higher, thereby increasing the conductivity of the material. Interestingly, by TFSA deposition we managed to increase the work function of our films by $0.5\ \text{eV}$ to a final value of about $5.3\ \text{eV}$.

2. Experimental

2.1. Liquid dispersion of graphene oxide

We prepared a GO water dispersion via a modified Hummers method [19] obtaining a final concentration of about $1\ \text{g L}^{-1}$.

2.2. Liquid-phase exfoliated graphite

We prepared two LPE graphene dispersions via low power ($\sim 50\ \text{W}$) bath-sonication of graphite flakes (Sigma–Aldrich 332461) in low boiling point organic solvents such as isopropanol and ethanol. For the preparation of the dispersion LPE(1), graphite was added to isopropanol at a concentration of $3\ \text{g L}^{-1}$. A second dispersion, LPE(2), was prepared with the same concentration of graphite in ethanol and with the addition of $0.1\ \text{g L}^{-1}$ of a sulfonated perylene diimide derivative (PDI, see Fig. 1 panel B) as a surfactant and exfoliation agent provided by

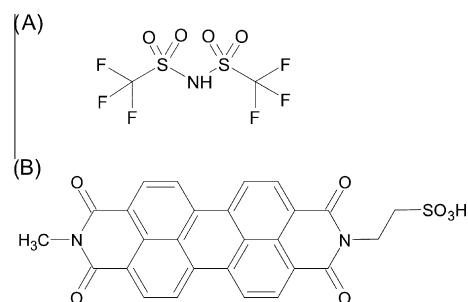


Fig. 1. (A) Molecular formula of bis(trifluoromethanesulfonyl)amide (TFSA) used as p-doping agent. (B) Molecular formula of the sulfonated perylene diimide derivative (PDI) used as surfactant for the exfoliation of graphite in ethanol.

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