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Preparation of highly conductive, transparent, and flexible graphene/silver nanowires substrates using non-thermal laser photoreduction

Badawi Anis [a,*], A.M. Mostafa [a], Z.A. El Sayed [a], A.S.G. Khalil [b], A. Abouelsayed [a]

[a] Spectroscopy Department, Physics Division, National Research Centre, 33 El Bohouth st. (former El Tahrir st.), P.O. 12622, Dokki, Giza, Egypt
[b] Physics Department and Center for Environmental and Smart Technology, Faculty of Science, Fayoum University, 63514 Fayoum, Egypt

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ABSTRACT

We present the preparation of highly conducting, transparent, and flexible reduced graphene oxide/silver nanowires (rGO/SNWs) substrates using non-thermal laser photoreduction method. High quality monolayers graphene oxide (GO) solution has been prepared by the chemical oxidation of thermally expanded large area natural graphite. Silver nanowires was prepared by using the typical polyol method. Uniform hybrid GO/silver nanowires (GO/SNWs) was prepared by growing the nanowires from silver nuclei in the presence of GO. Uniform and high-quality rGO/SNWs thin films were prepared using a dip-coating technique and were reduced to highly electrically conductive graphene and transparent conductive films using non-thermal laser scribe method. The laser scribed rGO/SNWs hybrid film exhibited 80% transparency with 70 $\Omega\,\square^{-1}$ after 20 min of dipping in GO/SNWs solution.

1. Introduction

Transparent conductive electrodes (TCEs) are very important candidates for a numerous flexible optoelectronic devices such as organic solar cells, light-emitting diodes, photodetectors, liquid crystal displays, and touch screens [1–4]. In addition to being electrically conductive and optically transparent, electrode materials of next-generation flexible electronic devices are required to be robust under extreme conditions and compatible with large-scale manufacturing [5]. Indium tin oxide (ITO) electrodes are the most common TCEs today owing to its low sheet resistance (Rs = 10 $\Omega\,\square^{-1}$) coupled with high transmittance (T = 80% @ 550 nm) [6,7]. However, ITO suffers from several limitations: high cost due to indium scarcity, the ceramic nature, and instability of ITO toward acidic or basic conditions, and mechanical brittleness. These disadvantages are limiting the applicability of ITO in flexible electronic devices [8,9]. A flexible substitutive material for ITO with a similar performance but lower cost is evidently needed. Recently, the researchers have focused on the development of thin layers of highly transparent conductive films based on metallic nanowires [10], carbon nanotubes (CNTs) [11–13], and conductive polymers [13–15]. However, TCEs composed of metallic nanowires suffer from large surface roughness, CNTs films have limitations due to high contact resistances between nanotube bundles; finally, conductive polymers are not stable upon exposure to high temperature, humidity, or UV radiation [16]. Recently, graphene, a two-dimensional carbon nanoscale material, brought a new alternative to commercially available ITO electrodes. Graphene is a single atomic monolayer of sp^2 bonded carbon atoms with a zero band-gap. In graphene, the electrons delocalize over the complete sheet, which provides ballistic charge transport with very little optical absorption [17,18]. Moreover, the graphene films exhibit a higher transmittance over a wider wavelength range than ITO [9].

One method of making graphene is by mechanical cleavage of graphite. This method can only produce small area of graphene films with dimensions of a few tens of micrometers and is not scalable. Graphene prepared by chemical vapor deposition (CVD) allows obtaining samples up to several centimeters. However, the process of preparation and transfer of CVD graphene needs a lot of effort and time [19]. The solution processing of graphene oxide (GO) is the most commonly used method to date, mainly due to the high throughput preparation, low cost, and the simplicity of the fabrication technique. This method is based on solution-

* Corresponding author.
E-mail address: badawi.ali@daad-alumni.de (B. Anis).

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casting of GO, synthesized from inexpensive graphite powders onto a substrate, followed by reduction to graphene through chemical reducing agents and/or high-temperature annealing [20–23]. However, the GO-reduction methodologies are not compatible with flexible substrates, such as polyethylene terephthalate (PET), since PET cannot stand high temperature and typically melts at 250 °C.

Currently, one dimensional (1D) metals such silver nanowires (SNWs) thin films exhibit high performance as a transparent conductive substrates [10,24–27]. As most of the 1D materials, SNWs can be constructed in network structure using vacuum filtration [10], casting [28], coating [29], and transferring [26] methods. In spite of the fascinating properties of the SWNs films, many challenges facing the implementation of SNWs films in the commercial applications, such as low oxidation resistance, poor adhesion to many substrates, and low stability in harsh environments [24].

The addition of SNWs into the 2D graphene network resulted in a new hybrid films. The resulting hybrid films overcome the transparency-conductivity constraint of pure graphene or metallic nanowires networks [24,30,31]. Different methods have been used to GO reduction including, thermal [1], chemical [32], microwave [33], photo-catalytical [34], and Electrochemical [35]. Using these methods will reduce GO to graphene but it will destroy the metal nanowires and hence decrease the total conductivity of the hybrid structure. Therefore, multi-steps fabrication methods have been used to overcome this problem [24,30,31]. Laser scribe reduction [36] have been used to produce reduced graphene (rGO) films with a much higher conductivity, and rGO patterns can be drawn directly by commercial a pre-programmed computer dvd drive or commercial CO_2 laser cutter.

Here we present a novel facile and rapid methodology to prepare transparent and highly conductive graphene layers, produced by dip-coating of GO/silver nanowires (GO/SNWs) on flexible substrates. Such layers were realized through in situ CO_2-laser induced non-thermal reduction of the dip-coated GO/SNWs films on PET substrates. The laser writing technique will be used in the preparation of large-area flexible reduced-GO/SNWs films without practically affecting the integrity of the thermally sensitive substrate underneath. The effect of GO/SNWs film thickness on the sheet resistance will be tested. The four-probe technique will be used to measure the sheet resistance.

2. Experiment

Highly oxidized graphene mono-layers with high lateral sizes of graphene sheets was prepared using improved method by Marcano et al.[37]. Briefly, dry expandable graphite flakes (3772, Asbury Graphite Mills USA) were first thermally treated at 1050 °C for 15 s. Then 3.0 g of the thermally expanded graphite was added to a 9:1 mixture of concentrated H_2SO_4 (96–98%)/H_3PO_4 (85%) (360:40 mL) in ice bath. Then 18 g of $KMnO_4$ was added very slowly to the mixture. The graphite/acids solution was then mechanically stirred at room temperature for 5 days continuously. Then the graphite/acids solution was poured very slowly onto ice mixture of 400 ml deionized water and 5 ml 30% H_2O_2. The solution then turned to bright golden color, indicating the formation of highly oxidized graphite. The graphite oxide suspension was then washed with 1:10 HCl (35%) solution (5 L) on a filter paper. Then the formed paste was collected from the filter paper and dried at 60 °C. The solid was dispersed into deionized water in static state for 2–3 h and then slightly stirred by glass bar. The suspension was filtered and washed with deionized water, until the PH is nearly 7 [38]. The graphene oxide powder was obtained by drying at 60 °C for 6 h under vacuum. The GO powder is dispersed into water by ultra-sonication. The obtained brown dispersion is then subjected to 30 min of centrifugation at 5000 rpm to remove any un-exfoliated GO.

Graphene Oxide/Silver Nanowires (GO/SNWs): Silver nanowires were prepared by using typical polyol method [39]. In atypical experiment, 0.4125 g of PVP (sigma aldrich, mol. wt 40,000) was dissolved in 55 ml ethylene glycol at 160 °C. The PVP/ethylene glycol was stirred at this temperature for 1 h. Then 0.3 g silver nitrate and 1.125 g potassium chloride in 5 ml ethylene glycol was added to the PVP solution. The solution turned dark gray indicating the formation of silver nuclei. Then 40 ml of 0.068 mol of silver nitrate in ethylene glycol was injected to the silver nuclei solution. The reaction was continued for 30 min. A 60 mg of GO was dispersed in 20 ml ethylene glycol using ultra-sonication for 2 h in ice bath. Then the GO solution was heated to 160 °C for 1 h, to this solution 10 mg (calculated by atomic absorption) of hot ethylene glycol silver nanowires solution was added to GO solution and thermally stabilized at 160 °C for 1 h. Then solution was cooled down and the GO/silver nanowires was then precipitated with acetone and centrifuged at 1000 rpm for 10 min. The supernatant containing the GO/nanowires (GO/SNWs) was washed many times with ethanol through centrifugation at 5000 rpm. Then the solution was dispersed in 20 ml of deionized water.

Laser-Scribed Graphene: The GO/SNWs thin films were prepared using simple dip-coating method. First the GO/SNWs solution was heated at 80 °C and, then the film will be formed at the air/water interface. The PET substrate was inserted carefully inserted into the GO/SNWs surface and the PET substrate subsequently was removed from the solution. The GO/SNWs thin film on the PET substrate was dried at 180 °C for 30 min in Oxygen atmosphere. The thickness of the GO film was controlled by varying the heating time. The GO/SNWs - coated PET films were reduced using commercial laser cutter. The power of the laser cutter was adjusted to 6 watt and scan rate of 35 mm/s. This laser scribing process converts the brown insulating GO/SNWs into metallic gray conducting laser-scribed graphene/silver nanowires (LSG/SNWs).

Samples Characterization: The samples were investigated by high resolution scanning electron microscope (HRSEM), Quanta EFI 250 - Philipes Company - Netherlands. High resolution transmission images were taken by a Jeol -JEM-1011 high resolution transmission electron microscope (HRTEM). The microscope was operated at 100 kV. The Samples were dispersed in distilled water using an ultra- sonic probe and subsequently few two drops were put onto a copper TEM grid coated with amorphous carbon. A double beam Jasco V-630 UV–vis spectrophotometer was used for recording the absorption spectra. The infrared reflectance measurements were carried out at room temperature in the energy range 500–4000 cm^{-1} using a bruker vertex 70 Spectrophotometer coupled with diamond attenuated total reflection unit. Programmable Keithley 4200 was used for sheet resistance measurements.

3. Results and discussion

It has been known that the graphite has compact and very close graphene layers with a distance of ≈0.35 nm between each layer [40]. As graphite is intercalated with sulfuric acid, the layers distance has been enlarged. The sudden heating of the intercalated graphite at 1050 °C results in the loose of the forces between the graphite layers and a marked volume increase of the graphite was observed as shown in Fig. 1(a). One can observe from Fig. 1 (a) that the expanded graphite has worm-like, and graphite layers have been opened mostly in direction of c-axis. A magnified SEM of such worm-like structure is shown in Fig. 1(b). The worms-like still has layered structure but the distances between the carbon layers have been increased. It means the interacting graphite forces