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Conductive graphene coatings synthesized from graphenide solutions

Yu Wang [a, b], Kai Huang [a, b], Alain Derré [a, b], Pascal Puech [c], Stéphan Rouzière [d], Pascale Launois [d], Celia Castro [c, 1], Marc Monthioux [c], Alain Pénicaud [a, b, *]

[a] CNRS, Centre de Recherche Paul Pascal (CRPP), UPR 8641, F-33600 Pessac, France
[b] Université de Bordeaux, CRPP, UPR 8641, F-33600 Pessac, France
[c] Centre d'Elaboration des Matériaux et d'Etudes Structurales (CEMES), UPR-8011 CNRS, Université de Toulouse, Toulouse, France
[d] Laboratoire de Physique des Solides, CNRS, Univ. Paris-Sud, Université Paris Saclay, 91405 Orsay Cedex, France

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ABSTRACT

A simple preparation procedure to produce conductive graphene coatings from graphenide solution under inert atmosphere is achieved. The obtained graphene films exhibit reasonably low surface resistivity of 5 kohms/Square at 60% transmittance at 550 nm that can be largely improved by thermal treatment. XPS, Raman spectroscopy and X-ray diffraction measurements demonstrate that annealing vastly improves the quality of the graphene films. Heat treatment at low temperature (120 °C) demonstrates a 60% resistivity decrease, an impressive and promising improvement for films deposited onto flexible polymer substrate.

1. Introduction

Graphene, the basal plane of graphite, has been the subject of intense research since its first isolation in 2004 [1,2]. Graphene has demonstrated many fascinating properties such as high carrier mobility [3,4], good optical transparency and high mechanical strength [5,6], making it an excellent candidate for a number of applications [7]. Graphene can be produced by micromechanical exfoliation of bulk graphite [1], thermal rearrangement of SiC [2], chemical vapor deposition (CVD) [8,9] and liquid-phase routes [10]. Transparent conductive graphene films produced by CVD process show the best performances reaching very low resistivity with good transparency [8,9]. However, high cost and transfer challenges limit the use of CVD based graphene in industrial applications. Graphene solutions (aqueous or organic) produced by liquid-phase routes have good opportunities for making cheaper graphene films in large scale applications, because they can be easily manipulated via simple techniques such as vacuum filtration [11–13], spray-coating [14], dip-coating [15,16], spin-coating [17,18] or Langmuir-Blodgett method [19]. Up to this time, the preparation of graphene films via a solution route has been reported from reduced graphene oxide or dispersion of graphite powders in organic solvents or surfactant-containing aqueous dispersions using sonication. The former has the problem of remaining oxygen atoms and/or holes within the graphene skeleton [20] whereas the latter compromises between exfoliation efficiency and lateral size [21].

Over the last decade, a number of materials have been explored to produce transparent conductive electrodes, such as metal nanowires and carbon nanotubes (CNTs). Transparent conductive films synthesized from both materials demonstrate very good electrical and optical properties [22,23]. Mirri et al. reported a nanotube film prepared with long CNTs (~10 μm) that displays a sheet resistivity of ~100 Ω/sq for a transmittance of ~90% [24], which surpasses the minimum industrial standards required for transparent conductor application. Likewise, transparent conductive electrodes synthesized with metal nanowire/mesh show excellent electrical properties but they still confront some challenges, such as price, longer-term stability, uniformity etc. Being atom thick two-dimensional material, graphene is the ultimate membrane. As such, besides conductivity, transparency, flexibility and chemical inertness (shared with CNTs), it may offer low oxygen diffusion rate, hence protect devices such as organic light emitting diodes (OLEDs) and organic solar cells if used as replacement for indium tin oxide (ITO) electrode, and thus perform as a multifunctional material. Moreover, the roughness of the films, an often overlooked parameter, should be smoother with graphene than with filamentous objects such as silver nanowires [25].

* Corresponding author. CNRS, Centre de Recherche Paul Pascal (CRPP), UPR 8641, F-33600 Pessac, France.
E-mail address: penicaud@crpp-bordeaux.cnrs.fr (A. Pénicaud).
[1] Present address: Normandie Univ, UNIROUEN, INSA Rouen, CNRS, Groupe de Physique des Matériaux, 76000 Rouen, France.

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Besides dispersion as mentioned above, another approach to produce graphene consists in using graphite intercalation compounds. $FeCl_3$ intercalated graphite exposed to H_2O_2 yields high quality few layer graphene [26]. Likewise, the spontaneous dissolution of graphite intercalation compounds (GICs) [27,28] in organic solvents without the need for (defect-inducing) sonication, yields fully exfoliated graphenide (negatively charged graphene) solutions [29–37]. Recently, it has been shown that transferring graphenide solution to water yields a stable dispersion of single layer graphenes in water without surfactants, so-called "eau de graphene" [38–40]. In this contribution, we report on the use of the same graphenide solutions to directly produce conductive coatings. The films show a reasonably low resistivity vs transparency ratio. Furthermore, a simple thermal annealing procedure, without any chemical treatment involved, improves considerably the electrical properties of the as-prepared graphene films, ranking them among the best performing conducting films among those prepared by solution routes.

2. Experimental section

2.1. Preparation of graphenide solutions

Graphenide solutions were prepared according to literature [29–32]. The process consists of two steps: (i) production of graphite intercalation compounds (GICs) and (ii) dissolution of GICs. First, potassium was intercalated into graphite to produce stage-1 GICs KC_8 by vapor transport technique: K and graphite in stoechiometric amounts (C:K = 8) were placed together in a sealed evacuated pyrex tube and heated at 250 °C for 48 h to give golden KC_8. X-ray diffraction patterns for both the starting graphite and KC_8 intercalation compound can be found in Supplementary data (Fig. S1). They are both consistent with literature data. Then, 200 mg of KC_8 was dissolved at room temperature in 100 ml of freshly distilled tetrahydrofuran (THF) with a glass-coated magnetic stirring bar under inert atmosphere. After stirring for 5 days, a mild centrifugation (780 g) for 20 min was applied to remove insoluble material. The solution obtained contains only negatively charged graphenes and potassium counter ions. From a dry extract of the solution, the concentration of the graphenide solution was estimated around 0.15 mg/ml.

2.2. Preparation of graphene films

Graphene films were prepared under inert atmosphere by filtering [41–43] a certain amount (15–30 ml) of graphenide solutions in THF. Graphenide solutions were filtered onto Al_2O_3 membrane (Anodisc 47, 0.02 μm, Whatman) and dried in an argon-filled glove-box. The films were taken out of the glove-box and exposed to dry air. The Al_2O_3 membranes were then dissolved in a 1.5 M NaOH aqueous bath. After complete dissolution of the membrane, transparent homogeneous films were floating on the liquid surface and several washing steps with pure H_2O were done until the pH value of the washing bath was 7. Free-standing films were transferred to a desired substrate, such as polyethyleneterephtalate (PET) film, glass, Si/SiO_2 wafer etc. The transferred films were then dried at 50 °C in oven overnight and stored under ambient laboratory conditions for further characterization.

2.3. Thermal treatment

Films were prepared with 30 ml of graphenide solution and transferred onto glass substrates for further thermal treatment. To better control and understand the thermal treatment process, films were placed into a thermogravimetry apparatus (TG, SETARAM Setsys) under constant Ar flow at 450 °C for 1 and 2 h respectively. Both heating and cooling speed were 5 °C/min. One film transferred on glass substrate was preserved under ambient lab condition as a reference film without any treatment.

2.4. Characterization

Graphene solutions and graphene deposits from them were characterized by UV-vis absorption spectroscopy, transmission electron microscopy (TEM), thermogravimetric analysis (TGA), X-ray Photoelectron spectroscopy (XPS) and Raman spectroscopy. Raman spectra were obtained with a Raman spectrometer HORIBA Xplora with 532, 638 and 785 nm wavelength incident laser light. The incident laser power was carefully tuned by using filters so that the laser power on the film surface was inferior to 1 mW to avoid sample modification due to laser-induced heating. Atomic force microscopy (AFM) images were obtained in tapping mode (Digital Instruments NanoScope MultiMode Scanning Probe Microscope) using 8 nm radius tips MPP-111000. Scanning electron microscopy (SEM) images were obtained using a JEOL 6700F high resolution instrument. For transmission electron microscopy (TEM), Lacey carbon grids (NetMesh™ Grids, 300mesh, copper) were used for the preparation of samples. 50 μL of graphenide solution was deposited on the grid. The grid was dried in air, then washed by MillQ H_2O, acetone and isopropanol. Large view images and selected area electron diffraction pattern were obtained with a thermionic LaB6 TEM (CM30 Philips) operating at 150 keV and high resolution images were performed with a field emission Cs corrected TEM (FEI Tecnai F20) operating at 100 keV. After transferring the films to the substrates, four gold contacts were deposited onto them through a mask, and then the surface resistivity of films was measured by four-point method. Current-voltage curves were measured with Keithley 6220 and 2000 Multimeters. The optical transmittance of the films at 550 nm was characterized by UV–Visible–NIR Microspectrophotometer (CRAIC 20/20 PVTM Dual Microspectrophotometer). X-ray photoelectron spectroscopy (XPS) measurements were performed with a VG 200i XL ESCALAB spectrometer. All spectra were taken using a Mg monochromatized source (1253.6 eV) at 200 W. Typical operating pressure was 2×10^{-7} Pa. Both starting graphite and graphene films were stamped on the XPS sample holder by using conductive copper adhesive tape. Thermogravimetric analysis (TGA) was performed with a SETARAM Setsys. X-ray scattering measurements were performed on a rotating anode X-ray generator and under vacuum, to optimize the signal over background ratio, using monochromatized MoKα radiation (λ = 0.711 Å). For X-ray scattering experiments, graphene films were deposited onto an ultra thin silicon wafer (~10 μm thick), to minimize scattering from the substrate.

3. Results and discussion

Typical picture of a transparent graphene film on PET substrate is shown in Fig. 1a. Film morphology was investigated by SEM (Fig. 1b) and AFM (Fig. 1c). Both techniques demonstrate that in a typical film, graphene flakes are stacked randomly together to form a continuous film. Transmittance at 550 nm and surface resistivity of films were measured (Fig. 1d). Smaller surface resistivity and decrease of transmittance were observed for films prepared from larger amounts of graphenide solution. Films prepared with 30 ml of graphenide solution had a surface resistivity of 1700 Ω/sq for a transmittance of 33% at 550 nm. These data were transferred to figures of merit (FoMs) [44]. The film prepared using 30 ml of graphenide solutions has a FoM value of ca 1900 (Table 1).