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Effects of dielectric barrier discharge in air on morphological and electrical properties of graphene nanoplatelets and multi-walled carbon nanotubes

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ABSTRACT

Multi-walled carbon nanotubes (MWCNTs) and graphene nanoplatelets (GNPs) have been functionalized by dielectric barrier discharge (DBD) in air. The extent of functionalization of MWCNTs and GNPs reaches a maximum at the delivered discharge energy of 720 and 240 J mg^{-1}, respectively. Further exposure to plasma leads to reduction of functional groups from the surface of the treated nanomaterials. It has also been demonstrated that DBD plasma does not produce dramatic structural changes in MWCNTs, while flakes of the treated GNPs become thinner and smaller in the lateral size. Conductive thin films, obtained by drop casting a solution of the treated nanomaterials in *N*-methyl-1-pyrrolidone on poly(methyl methacrylate) substrate, show significantly lower sheet resistance.

1. Introduction

Because of their exceptional electronic, mechanical and structural properties, nanocarbon materials, such as graphene and carbon nanotubes (CNTs), have attracted enormous interest in recent years. Graphene is a one-atom-thick planar sheet of sp^2-hybridized carbon atoms densely packed in a honeycomb crystal lattice [1]. Carbon nanotubes (CNTs) consist of shells of sp^2-hybridized carbon atoms forming a hexagonal network which is itself arranged helically within a tubular motif resembling closed structure of "rolled up" graphene sheet [2,3]. Their numerous applications in progress include conducting nanowires, drug delivery vehicles and biology probes, electrochemical sensing and energy storage devices. However, the hydrophobic and inert nature of the nanotubes surface and formation of bundles, which are stabilized by van der Waals interactions between them, result in low dispersibility and difficult manipulation in different solvents or polymer matrices. Covalent functionalization of carbonaceous nanomaterials and nanotubes improves significantly their performance in most applications. Acid treatment (wet chemistry) and high-temperature vapors exposure are mostly used for introduction of various functional groups on surface of graphene or CNTs.

In this regard, several successful examples employing non-thermal plasma (*e.g.*, radio frequency, glow, microwave and dielectric barrier discharges) and in different gases such as O_2, CO_2, N_2, NH_3, and H_2O have been reported. The main characteristics of non-thermal atmospheric pressure discharges are high electron temperatures, in order of 1–10 eV, which provide a strong thermodynamic, non-equilibrium plasma at atmospheric pressure, and at moderate gas temperature of bulk gas. One of the most convenient atmospheric pressure discharges is dielectric barrier discharge (DBD), due to its simple arrangement, low cost and easy rescaling to large scale industrial installations [4]. A great flexibility with respect to their geometrical shape, working gas mixture and other operation parameters are decisive advantages for the wide field of applications [5]. DBD provides energetic electrons which are able to generate atoms, radicals and excited particles. Thus, processes in such discharges are determined by collisions of energetic electrons with bulk gas which lead to the formation of chemically active species and later reactions of such produced active species with molecules and atoms of the gas.

Among many possibilities for application of non-thermal plasma, one of the newest is functionalization of carbon

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nanomaterials. The efficient excimer formation in DBD is a three-body process and it is largely dependent on three conditions which should be provided: the bulk gas must be enriched with a significant amount of high energy electrons which is above the threshold for the metastable formation or ionization; the gas pressure in a reaction chamber must be high, the most favorably close to atmospheric pressure, in order to have a sufficiently high rate of three body collisions.

Due to the lack of energetic heavy particles, DBD discharge allows the addition of functional groups without significant disorder of CNT or graphene lattice. Plasma functionalization of MWCNTs in DBD plasma in presence of dry air offers the advantages of much shorter treatment time, and produces less damage when compared to acid treatment [6,7]. Furthermore, the amount of hydrophilic CO_x groups can be increased up to the amounts obtained by acid treatment by adjusting plasma parameters such as DBD power and treatment time. Wang et al. [8] have proposed the mechanism of oxidation under the O_2 DBD plasma treatment. Namely, O_2 plasma attacks defect sites, transforming the sp^2-hybridized carbons in the nanotube framework into sp^3 hybridization, and introduce mostly hydroxyl and carboxyl groups. Hydroxyl groups may be further converted to carboxyl groups, while carboxyl groups are oxidized to CO_2 and H_2O under excessive exposure time, causing the decrease of oxygen atom. Pourfayaz et al. [9] have functionalized MWCNTs in a DBD plasma reactor in the presence of CO_2 and an inert gas including He, Ar, or N_2. It has been demonstrated that dilution of CO_2 in an inert gas, up to a certain percentage, increases the amount of oxygen-containing functional groups formed on the nanotube surface, due to an enhanced charge and energy transfer mechanism to reactive species. The same authors have treated MWCNTs by DBD plasma followed by their exposure to NH_3 to introduce some nitrogen-containing functional groups on the nanotubes surface [10]. Poly(methyl methacrylate) (PMMA) based nanocomposites made from the functionalized MWCNTs have lower surface electrical resistivity than pristine and acid-treated ones. Fluorination of MWCNTs powder with a maximum fluorine content of 12% has been achieved by using home-made equipment for CF_4 plasma irradiation [11,12]. The fluorinated MWCNTs act as a good modifier for the poly(ethylene tereftalate) resin, which can be easily homogeneously dispersed in the PET matrix during the preparation process of *in situ* polycondensation.

Regarding utility of the plasma treatment of graphene, it has been demonstrated that O_2 plasma induces epoxy and hydroxyl-like groups in graphene and thus offers the possibility of tuning the electrical properties from metallic to semiconductor [13,14]. Fluorinated graphene sheets have been obtained by the plasma-assisted decomposition of CF_4 employing a radio-frequency plasma source, whereby fluorine in graphene can be further displaced by alkylamino and other functionalities which offers a possibility for graphenes to be integrated into the structure of different polymers [15].

Herein, we present modification of carbon nanomaterials, MWCNTs and GNPs, with active chemical species generated throughout the DBD in air. Nanomaterials were exposed to DBD in air for a different period of time in order to get information about the structural and morphological alteration of graphitic surface. The effect of DBD plasma on the time-dependent electrical properties at the increased and ambient temperature of the treated materials on glass substrate was studied. To promote the deposition rate of DBD treated MWCNTs and GNPs, *i.e.* to improve adhesion properties of PMMA surface, solvent etching and chemical treatment of PMMA were applied to provide uniform and controllable deposition (nanomaterial film) on the substrates at room temperature to obtain conductive and flexible thin film. Dispersion of DBD treated carbon nanomaterials was applied by drop-casting at the prepared substrate, and, through multiple steps of coatings, it was possible to control and tailor the desired film thickness and sheet resistance.

2. Materials and methods

2.1. Plasma functionalization

MWCNTs (Sigma), prepared by a chemical vapor deposition (CVD) method, and reagents were used as received without purification. The purity of MWCNTs was more than 95%, the outer and inner diameters were 20–30 and 5–10 nm, respectively, the length between 5 and 200 μm and specific surface area 40–600 $m^2\,g^{-1}$. GNPs (plasma-Argon) were purchased from Cheap Tubes with 99 wt% purity. The purity of *N*-methyl-1-pyrrolidone (NMP), purchased from Sigma-Aldrich, was more than 99% and the solvents, *p.a.* quality, was used as received. PMMA was supplied by Evonik Industries.

DBD of planar configuration with 4 mm gap was used for MWCNTs and GNPs treatments. The discharge cell (Fig. S1 in Supplementary material) consisted of two different dielectrics, glass plate with 1 mm thickness and alumina plate with 0.7 mm thickness. Between these two plates circular spacer of 40 mm in diameter, made of plastic, closed the discharge volume. Ground electrode was made of aluminum foil 40 mm in diameter and attached at one side of alumina. High-voltage electrode is 1 g L^{-1} solution of copper sulfate ($CuSO_4$) in water in direct contact with glass and it was edged with glass tube. This water tank, also 40 mm in diameter and with volume of 100 ml had an important role of preventing overheating of dielectrics. Such discharge cell, completely fulfilled by discharge, enabled homogeneous treatment of 10 mg samples of nanomaterials powder. Moderate dry air flow through the discharge was established by two pairs of inlet and outlet plastic tubes with 1 mm in diameter. Discharge was supplied by high-voltage sinusoidal signal from frequency generator driven transformer. Frequency and peak voltage were set at 300 Hz and 15 kV, respectively. Voltage was measured using a Tektronix P6015A probe. Current signals and transported charge were recorded by a resistor or a capacitor placed between the grounded electrode and grounding point, as shown in Fig. 1. Discharge power is calculated from the Lissajous figure. Characterization of the discharge was completed by optical emission and FTIR spectroscopy. Optical emission was recorded by an Ocean optics USB 4000 spectrometer in the range 200–900 nm with pixel-to-pixel resolution of 0.2 nm/pix and FWHM of the line from the spectral tube of 1.4 nm. FTIR spectra have been obtained by a 1 cm^{-1} resolution Bruker FTIR spectrometer equipped with 5 m gas cell.

2.2. Characterization

Fourier-transform infrared (FTIR) spectra were recorded in the transmission mode between 400 and 4000 cm^{-1} using a BOMEM (Hartmann & Braun) spectrometer with a resolution of 4 cm^{-1}. MWCNTs were pressed into a pellet with KBr and scanned. Elemental analyses were performed using a VARIO EL III Elemental analyzer. Scanning electron microscopy (SEM, model: JEOL JSM 6610LV), equipped with an energy dispersive spectrometer, was used for recording the images of the surfaces of MWCNTs and GNPs. Atomic force microscopy (AFM) was carried out in tapping mode at room temperature and ambient conditions in order to get the surface roughness of MWCNT films. Estimation of the DBD treated carbon nanomaterials film thickness was obtained from AFM analysis.

Field emission gun scanning electron microscopy (FEG-SEM) was performed with a field emission gun TESCAN MIRA3 XMU