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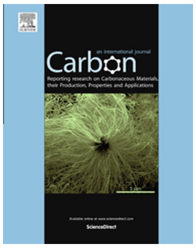

Electronic transport in composites of graphite oxide with carbon nanotubes

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ABSTRACT

We show that the presence of electrically insulating graphite oxide (GO) within a single wall carbon nanotube (SWCNT) network strongly enhances electrical conductivity, whereas reduced graphite oxide, even though electrically conductive, suppresses electrical conductivity within a composite network with SWCNTs. Measurements of Young's modulus and of Raman spectra strongly support our interpretation of the "indirect" role of the oxide groups, present in GO within the SWCNT-GO composite, through electronic doping of metallic SWCNTs.

1. Introduction

Electronic transport in low-dimensional graphitic carbon structures is determined firstly by the dimensionality (0, 1 or 2) of the system. The significance of electronic transport for the zero-dimensional carbon form – fullerene – is negligible, as these tend to avoid double bonds in the pentagonal rings, resulting in poor electron delocalisation, whereas carbon nanotubes, with dimensionality "quasi-one", as well as entirely 2-dimensional graphene, are well appreciated for their electrical conduction with ballistic transport. Regarding carbon nanotubes, it is a network of carbon nanotubes that is most likely to be used in technological applications, as electronic circuits are rarely formed from individual nanotubes. But then we have to ask: to what extent transport properties entirely bound to an individual carbon nanotube can still be preserved in a macroscopic network? Various factors control electronic transport through a nanotube network, such as the network's packing density, the length and orientation of the tubes and, most importantly, the interactions between the nanotubes at their contacts [1,2]. For current to efficiently pass along the network, strong inter-tube interactions are necessary. Electronic doping is a powerful way to enhance the tunneling of charges through the inter-tube contacts [3,4].

In that sense, the same situation holds for graphene as well; here also the phenomena appreciated in graphene's electronic and magneto-transport properties [5,6] are confined inside a single graphene crystal, while they are hardly expected to be observed in an ensemble of weakly bound graphene flakes. Graphene-flake networks are relevant for many application of graphene in the large-scale. The "scotch-tape" method, so successful in the first experiments, cannot be used anymore; instead, techniques for large-scale preparation of graphene had to be developed. One of them

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uses exfoliation of graphitic powders through chemical oxidation [7,8], that produces graphitic sheets with high efficiency; but the oxide groups covalently attached to the graphene's surface (graphite oxide (GO)) cause strong electron localization, shutting down the charge transport. Electrical conductivity recovers, after the oxide groups are reduced. When measuring electronic transport through devices fabricated of a single layer of rGO, Kaiser et al. [9,10] showed that 2-dimensional variable-range hopping (VRH) is employed at electronic transport, whereas 3-dimensional VRH fitted better when a thin GO film based device was investigated [11,12].

The main aim of this work is to investigate the electronic transport mechanism in composite networks of 1-dimensional SWCNTs mixed with 2-dimensional flakes of graphite oxide (in its oxidized and reduced form), through measuring the temperature dependence of electrical conductivity.

As a surprising result, we find that a composite network of SWCNTs and GO (which is electrically insulating) shows a higher conductivity than pure SWCNTs or GO by itself. This is interpreted as an effect of electron transfer (doping) from GO to SWCNTs, as evidenced also by Raman spectroscopy.

2. Experimental

We have studied electronic properties of networks of SWCNTs, rGO, and, in particular, of composite networks formed by SWCNTs + GO and SWCNTs + rGO. All samples were prepared by vacuum filtration from a solution, or mixtures of solutions. Besides the electronic transport measurements at variable temperature which form the central aspect of this work, the samples were characterized by Raman spectroscopy, scanning electron microscopy, high-resolution transmission electron microscopy, and mechanical testing as detailed below.

2.1. *Sample preparation*

2.1.1. *GO synthesis*

Natural graphite powder of microcrystal grade, purity of 99.9995% and size of 2–15 μm was purchased from Alfa Aesar. Sulfuric acid (350 ml) was mixed with graphite (2 g) at 0–5 °C for 15 min. Potassium permanganate (8 g) and sodium nitrate (1 g) were added portion-wise at 0 °C and stirred for 30 min, then for 30 min at 35 °C. Water (250 ml) was added via a dropping funnel and the reaction mixture was heated to 98 °C for 3 h. The reaction was terminated by adding 500 ml of water deionized and 40 ml of 30% H_2O_2. The mixture was filtered off through a nylon filter, washed with diluted HCl (10%) in order to remove metal ions and then with water until the pH of the filtrate is about 7, and dried at 75 °C.

2.1.2. *Chemical reduction*

Deionized water (150 ml) was added to GO (1 g) and vigorously stirred for 24 h at room temperature. The suspension was then sonicated in the ultrasonic bath cleaner for 3 h, then sonicated with a horn sonicator for 30 min and, finally, for 1 h in the bath sonicator. The mixture was mixed with ammonia (1.5 ml) and hydrazine monohydrate (3 ml) and stirred vigorously at 85 °C for 24 h under the reflux condenser. After cooling, the suspension was filtered off through nylon filter, washed with deionized water (500 ml) and with methanol (50 ml). The cake was dried at 75 °C in the oven for 24 h.

2.1.3. *Thermal reduction*

A GO free-standing film was inserted into a quartz tube centered in a cylindrical furnace. After evacuation, the sample was slowly heated up to 700 °C under Ar/H_2 atmosphere for 2 h.

2.1.4. *Preparation of networks*

Free-standing SWCNT and GO based papers were prepared from a suspension by vacuum filtration. For SWCNTs (prepared by the Laser Ablation method), a *N*-methyl-2-pyrolidone (NMP) based suspension was used, whereas GO was suspended in water. The composite of SWCNT with GO was prepared by mixing 50 wt% of SWCNT and 50 wt% of GO in a 1 wt% SDS/water solution, while the composite of SWCNT with chemically reduced graphite oxide (rGO) was prepared by mixing SWCNT and rGO at same weight ratio in the NMP based suspension. The surface morphology of the papers imaged by SEM is illustrated in Fig. 1b.

2.2. *Characterization*

2.2.1. *Scanning electron microscopy*

The samples' morphology was examined by SEM JEOL JSM-7500F. Fig. 1 presents four samples studied in this work: (a) SWCNTs showing the typical spaghetti-like morphology at approximately 10-times higher magnification than the other images containing GO flakes; (b) thermally-reduced rGO; (c) composite SWCNT-GO; and (d) composite SWCNT-rGO – all of them in a similar scale. In the composites, the carbon nanotubes are well intercalated into the GO flakes.

Fig. 1 clearly demonstrates an important difference in the morphologies between SWCNT-GO and SWCNT-rGO: While the SWCNTs are tightly integrated in the layers of densely packed GO sheets (Fig. 1(c)), the structure of SWCNT-rGO in Fig. 1(d) is loose. The interactions between the particles, well demonstrated in the SEM images, determine all the properties studied in this paper.

2.2.2. *Transmission electron microscopy*

TEM investigations were carried out using a Philips CM200 microscope operating at an accelerating voltage 80 keV and selected-area diffraction (SAD) patterns taken from areas of 1 μm diameter were recorded on a CCD camera.

While SEM provided a picture of the cross-section of a bulk sample, for TEM a small piece of material was pulled out of the bulk and the edge layer was imaged. Imaging more detailed morphology in the transmission mode helps to better understand particle interactions within the composite. Fig. 2(a) shows a top view of the composite SWCNT-GO. Here a percolating SWCNT network is mostly intercalated with GO-flakes often smaller than a micrometer size, while high density GO areas and large GO flakes are marked by a dashed red line. SEM in Fig. 1 indicated also significantly larger graphitic platelets. The inset shows electron diffraction; the smeared ring is formed due to a background of randomly oriented GO-flakes of a small size, whereas the bright spots decorating