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Powerful doping of chirality-sorted carbon nanotube films

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ABSTRACT

A fast and convenient method to create n-doped or p-doped carbon nanotube (CNT) films of improved electrical conductivity is presented herein. Free-standing thin flexible films made from unsorted CNTs and composed of predominantly (6,5) or (7,6) chiral angle were exposed to hydrazine (N_2H_4) or boron trifluoride (BF_3) solutions, which decreased the sheet resistance by almost up to an order of magnitude. Analysis of the CNT films surface chemistry indicates that despite benign influence of the dopants on their composition, they strongly, but favorably affected electronic structure. Depending on the type of employed dopant, the Fermi level was strongly shifted upwards or downwards to enhance conduction of electrons or holes for employed n-doping and p-doping agents, respectively. This work provides an effective approach for the formation of CNT or graphene-based macroscopic assemblies such as films or fibers of high electrical conductivity with predetermined type of predominant charge carriers without excessive processing.

1. Introduction

Ever since carbon nanotubes (CNTs) and graphene have revealed their excellent electrical [1–3], thermal [4–6] and optical [7–9] properties, they have been the subject of intensive and extensive research all around the world. In particular, the progress in the field of portable electronics, which rapidly approaches the limits of currently used materials, has been one of the driving forces for the development of nanocarbon technology [10]. We need a next generation of conductive materials, which would be light, durable, flexible and offer much higher performance than materials used at present such as aluminium/copper (wires, interconnects) [11] or indium tin oxide (touch panels, LCDs) [12]. CNTs can already be assembled into macroscopic objects [13–16], but their performance still has to be optimized.

To improve electrical conductivity of CNTs both p-dopants (halogens [17], interhalogens [18,19], strong acids [20]) and n-dopants (nitrogen-bearing polymers [21] or compounds [22], alkali metals [23]) can be employed. For the doping strategy to be feasible, it needs to have a strong and permanent influence on electrical conductivity of nanocarbon materials. It is especially important that the method of doping is as benign as possible and does not deteriorate the structure of individual CNTs by unnecessary functionalization.

In this paper, a convenient method is demonstrated, using which one can create n-doped or p-doped free standing CNT films. It is showed that addition of small amount of hydrazine (known for its electron-donating properties [24,25]) or boron trifluoride can decrease the sheet resistance by up to an order of magnitude. The best results have been obtained with CNT films based on chirality sorted (6,5) and (7,6) material. The presented method of doping is powerful while it does not degrade the individual CNTs. To the best of my knowledge, this is the first report of using boron trifluoride as a doping agent for nanocarbon materials.

2. Experimental

The CNT films were produced by a previously reported method [26] (Fig. 1). Herein, single-wall carbon nanotubes (SWCNTs) were dispersed in toluene using ethyl cellulose. Next, CNT dispersion was deposited onto Nomex and detached from its surface upon evaporation of the solvent. Finally, binder was removed by flash annealing of the sample in air by igniting the film with a lighter for 1 s [27]. Three types of SWCNTs were used to prepare the films: unsorted Tuball™ purchased from OCSiAl and predominantly (6,5) or (7,6) CNTs purchased from SouthWest NanoTechnologies.

For the doping, an appropriate amount of N_2H_4 aqueous solution (50% w/w) or BH_3 methanol solution (50% w/w) was dripped onto the CNT films to fully soak them with the dopant. The samples were then kept in the ambient for 3 days to fully evaporate the solvent and any unabsorbed dopant.

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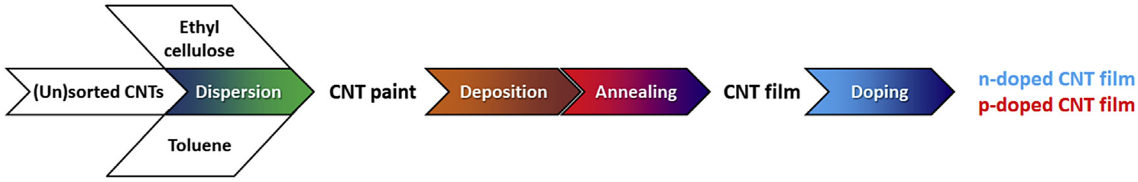

Fig. 1. Method of production of CNT films used in the study.

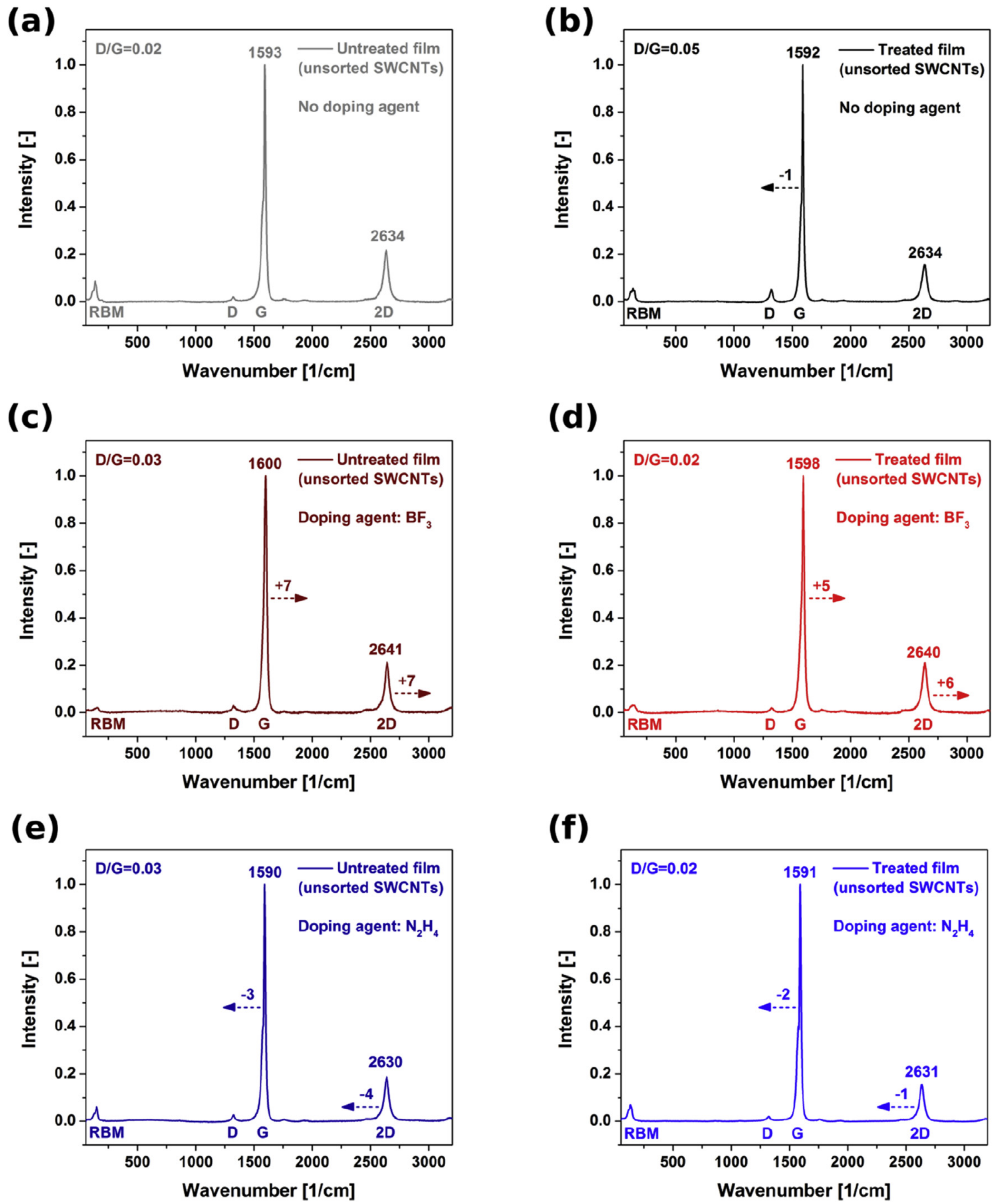

Fig. 2. Raman spectra of untreated (left column) and electrically treated to 100 °C (right column) films made from unsorted SWCNTs. The films used were (a,b) as made, (c,d) doped with BF_3 and (e,f) doped with N_2H_4.