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.

Key words: carbon nanotubes; doping; electrical conductivity

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

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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.
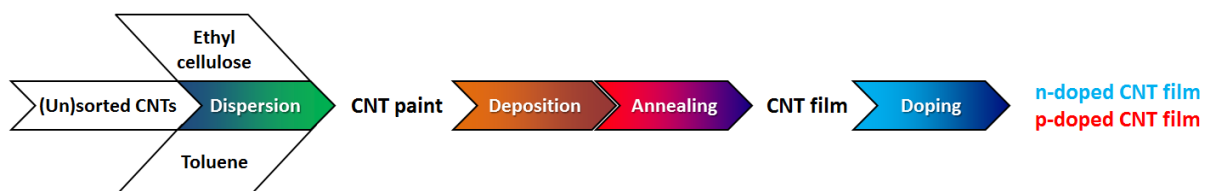
1. Experimental

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

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 second [27]. Three types of SWCNTs were used to prepare the films: unsorted Tuball[TM] 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.

Raman spectroscopy (inVia Raman Ramascope λ=633 nm) was used to probe the surface chemistry and electronic structure. 10 spectra from different positions were recorded for each sample. The given plots represent their average.

Electrical resistance measurements were carried out using a four probe method (Keithley 2000 multimeter). 10 μm x 30 mm x 30 mm samples were attached to custom-designed sample holders with electrical terminals made of Cu tape. Ag conductive paste was used to minimize the influence of contact resistance. I-V curves were recorded up to about 100°C (measured by an on-line pyrometer) caused by resistive heating of the samples. A relation between specimen's temperature and sheet resistance is given to observe how permanent the doping with the increase in temperature is. 10 samples were measured for each treatment.

2. Results

To get an insight how dopant addition influences the electronic structure of the CNTs, Raman spectroscopy was carried out on unsorted (Fig. 2) and sorted CNT films (Fig. 3 – (7,6), Fig. S1 – (6,5)). Data regarding (6,5) CNT films is given in the Supplementary information

file. Materials of very high purity in terms of I_D/I_G ratios were selected to have a precise overview on the doping action. The unsorted SWCNT films had exceptionally low level of disorder ($I_D/I_G=0.02$), which was only slightly affected by the action of BF_3 ($I_D/I_G=0.03$, Fig. 2c) and N_2H_4 ($I_D/I_G=0.03$, Fig. 2e), what indicates a non-destructive character of the doping method. Most importantly, a strong charge transfer effect was observed, which gives an indirect proof that doping was successful. It was manifested by a shift of G or 2D peak position relative to the parent spectra.
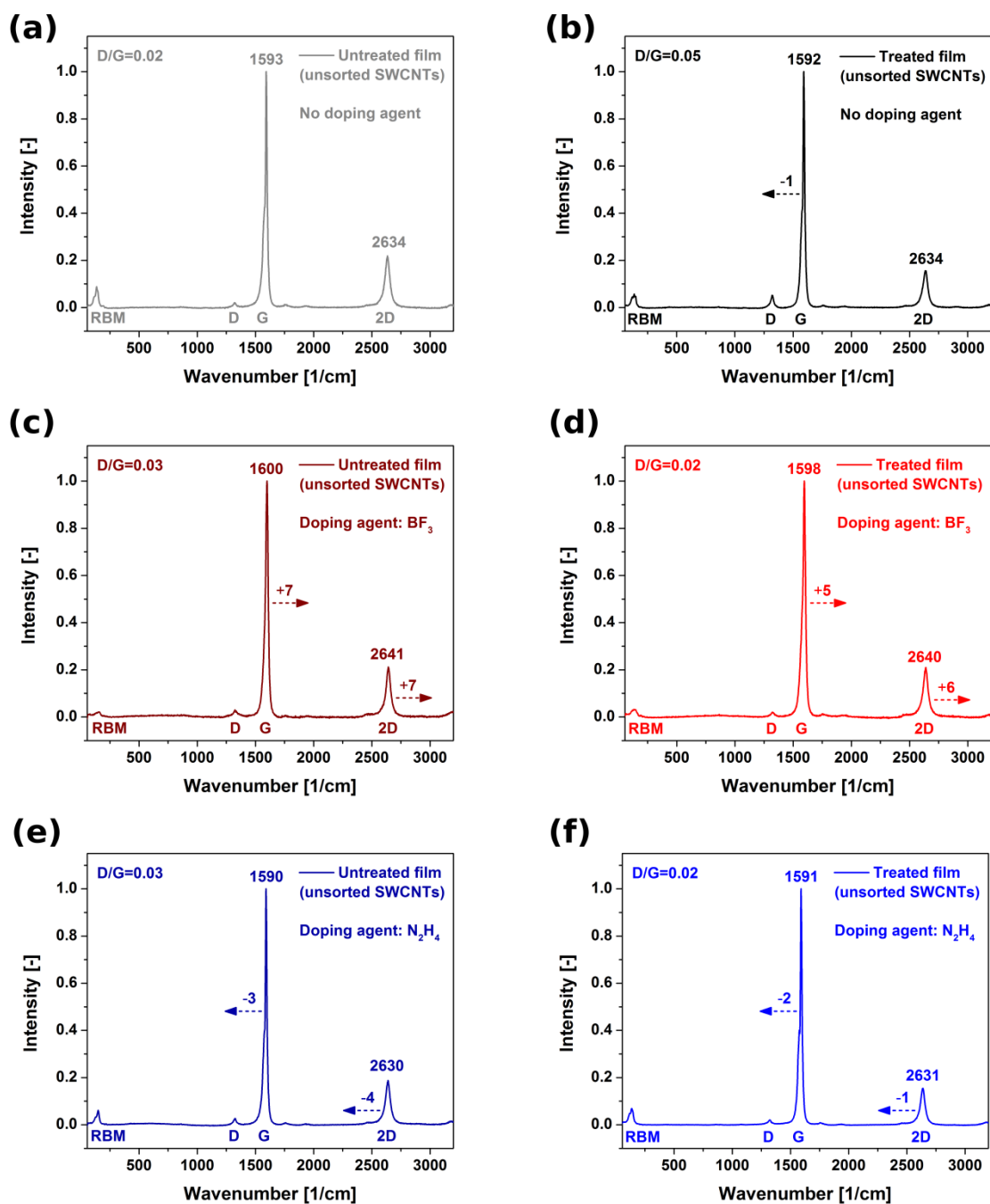
Fig. 2 Raman spectra of untreated (left column) and electrically treated to 100°C (right column) films made from unsorted SWCNTs. The films used were (a,b) as made, (c,d) doped with BF_3 and (e,f) doped with N_2H_4.

Red-shift and blue-shifts are indicative of n-doping and p-doping, respectively [28, 29]. In the case of unsorted SWCNT films, the peaks shifted by up to 7 cm^{-1} for BF_3 and 4 cm^{-1} for N_2H_4. CNTs kept in the ambient are naturally p-doped due to the presence of oxygen [30]. As

a consequence, the shift caused by hydrazine is smaller because it counteracts the electron-withdrawing effect of oxygen adsorbed on the surface.

Furthermore, the as-made and doped unsorted SWCNT films were heated up to 100°C during I-V characterization and Raman spectra were recorded again to see whether the doped material can withstand elevated temperature. It was found that electrical treatment itself causes negligible red-shift (1 cm^{-1}, Fig. 2b), which slightly counteracts the action of p-doping (Fig. 2d), but reinforces n-doping (Fig. 2f). Most importantly, even after high temperature treatments the shifts remain significant, so the dopants are not desorbed under these conditions. Because unsorted material contains also metallic CNT (insensitive to doping), SWCNT films from predominantly (6,5) and (7,6) CNTs were manufactured and characterized (Fig. 3, Fig. S1). Materials composed of predominantly semiconducting chiralities are much more suited for this purpose.

In this case, shifts to the G and 2D peaks have also been observed and for some of the samples they were even stronger. (7,6)-rich SWCNT films were particularly responsive to p-doping BF_3 (Fig. 3c,d). Initially, a blue-shift as large as 14 cm^{-1} was recorded, which decreased to 7 cm^{-1} after the electrical treatment, what is still a remarkable performance. N-doping action of N_2H_4 was observed in both (6,5) and (7,6) SWCNT films (Fig. 3e,f and Fig. S1e,f, respectively), but again the action was not as powerful as in the case of BF_3.
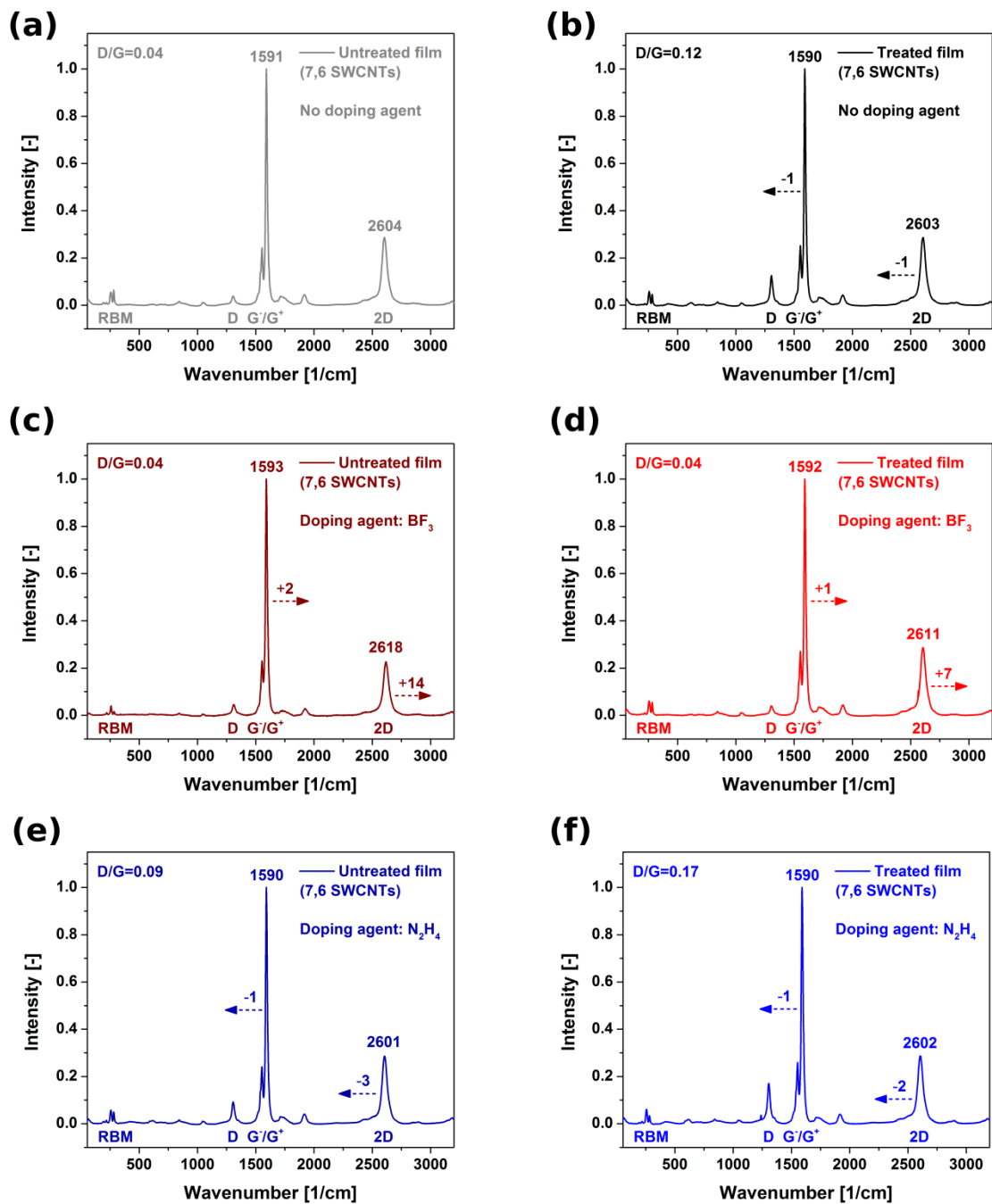
Fig. 3 Raman spectra of untreated (left column) and electrically treated to 100°C (right column) films made from (7,6) SWCNTs. The films used were (a,b) as made, (c,d) doped with BF$_3$ and (e,f) doped with N$_2$H$_4$.

As a final step evaluation how the doping influenced electrical conductivity of the SWCNT films in terms of sheet resistance was done (Fig. 4 – (7,6), Fig. S2 – (6,5)). Significant decrease of sheet resistance was registered, both in the case of unsorted and sorted material. Two effects are in accordance Raman spectroscopy results. Firstly, BF_3 is a much stronger dopant than N_2H_4.
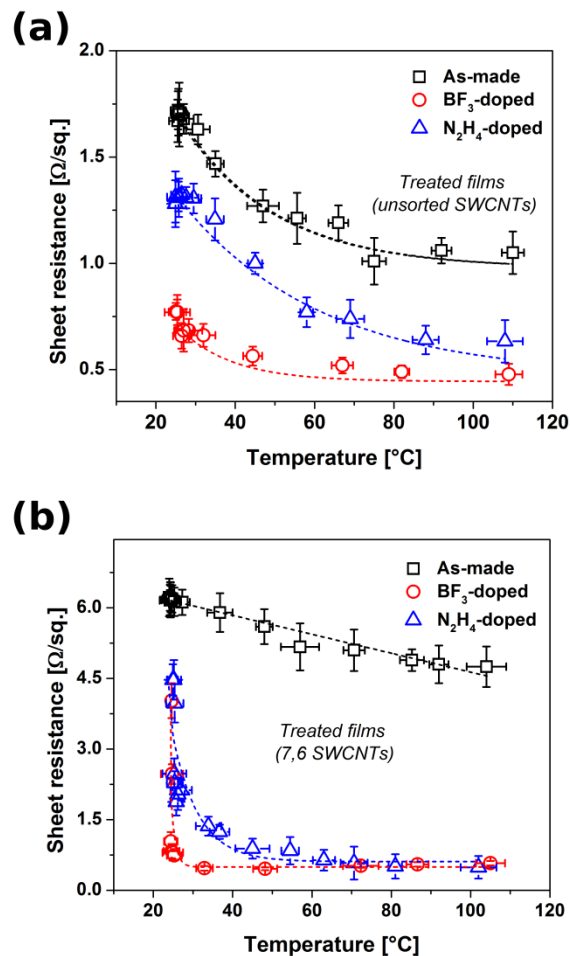

Fig. 4 Relation between temperature and sheet resistance for (a) unsorted and (b) predominantly (7,6) SWCNT films. As-made as well as p/n-doped samples were characterized.

Secondly, the doping effect is more profound in the case of predominantly (7,6) and (6,5) SWCNT films (Fig. 4b – (7,6) and Fig. S2 – (6,5)), which are of semiconducting character

rather than unsorted SWCNT film (Fig. 4a), which also contains metallic CNTs (as revealed by a Breit-Wigner-Fano left shoulder to the G peak rather than a developed Lorentzian lineshape as in the case of (6,5) and (7,6) SWCNTs). Moreover, the doping was found to intensify with temperature, but in most of the cases it tended to a particular asymptotic value. The most significant decrease in sheet resistance was observed in the case of BF_3 doped (7,6) SWCNT film. It was lowered from 4.59 to 0.50 Ω/sq (compared at about 100°C), what was a reduction by almost an order of magnitude. Doping of (6,5) SWCNTs by BF_3 resulted in similarly strong action and its sheet resistance was reduced from 3.76 to 0.47 Ω/sq. In both cases the reduction was slightly smaller than in the case of N_2H_4 treatment.

3. Conclusions

A strategy how to prepare free-standing SWCNT films of high electrical conductivity with predetermined type of predominant charge carriers was proposed. By n-doping with N_2H_4 or p-doping with BF_3 it was possible to decrease the sheet resistance of macroscopic assemblies of SWCNTs by almost an order of magnitude. What is important, such enhancement of electrical conductivity was not achieved at the expense of surface chemistry caused by unnecessary functionalization.

There is a growing need to create semiconductors with high performance for microelectronics. In particular, rapid development in the field of wearable and flexible conductors still lacks functional materials that could step in to solve the problems and circumvent the limitations of the currently used components. Nanocarbon materials such as CNTs or graphene are a viable light-weight, flexible alternative to reach the level of performance unachievable by silicon or ITO even with any further advances to their technologies. As shown by the results of this study, further progress in the preferential synthesis of particular types of CNTs coupled with appropriate methods to tune their

electrical conductivity is a direction, which can take us closer to the application of nanocarbon devices in the real life.

Acknowledgements

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