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Transparent conducting films made of different carbon nanotubes, processed carbon nanotubes, and graphene nanoribbons

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HIGHLIGHTS

- Transparent conducting films are fabricated of eight carbon nanotube materials.
- Carbon nanotubes for the films can bear many physicochemical transformations.
- Certain nanotube electronic properties can vary without losing film conductivity.
- Single-walled carbon nanotubes are sorted by the gel chromatography method.
- Graphene nanoribbons are also tested.

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ABSTRACT

Transparent conducting films (TCFs) are made of different single-walled (SW) or multi-walled (MW) carbon nanotubes (CNTs), some of them previously modified by chemical or physical processes. The TCFs are prepared by spray-coating of CNT surfactant dispersions over glass substrates. Among pristine CNTs, laser-grown SWCNTs lead to the lowest resistivity, even though good results can be achieved with other selected SW or MWCNTs. Ultracentrifugation of the SWCNT dispersions can be utilized for improving the characteristic SWCNT spectroscopic signals. Controlled oxidation, acid treatment, and covalent functionalization with aromatic organic groups can be applied to CNT solid powders without substantially increasing the resulting TCF resistivity. The oxidative transformation of arc-discharge MWCNTs into graphene nanoribbons relatively improves their TCF performance. The positive effects of TCF washing with water or oxidant acids are quantified for various SWCNT types. Red and green inks, enriched in metallic or semiconducting SWCNTs, are obtained by the gel-chromatographic method, all the fractions being useful for the preparation of TCFs. Thus, it is shown that different physical and chemical processes can be performed on CNTs before or after their deposition, demonstrating a great chemical versatility for CNT-TCFs.

1. Introduction

The fabrication of transparent conducting films (TCFs) is one of the most promising applications of carbon nanotubes (CNTs) (Ho and Wei, 2013). Based on the outstanding mobility properties and high aspect ratio of rolled-up graphene layers, CNT-TCFs have been successfully tested as components for different electronic and optical devices. First attempts of fabricating CNT-TCFs were done by solution casting and transferring to the desired substrate (Meitl et al., 2004; Wu et al., 2004). Other direct deposition methods were soon utilized including spray techniques (Kaempgen et al., 2005), rod-coating (Dan et al., 2009) and dip-coating (Mirri et al., 2012).

Commonly, CNTs are dispersed in water with the aid of surfactants. After the CNT-TCF fabrication, the residual surfactant may be removed by immersion in water, improving the network conductivity and the transparency (Kaempgen et al., 2005; Luo et al., 2013). It has been also recognized that chemical post-treatments with oxidant acids (HNO_3) or $SOCl_2$ further improve the

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conductivity, due to a complete surfactant removal or to CNT doping (Dan et al., 2009; Geng et al., 2008; Li et al., 2008; Paul and Kim, 2009; Majunder et al., 2010; Gao et al., 2013). More recently, many efforts have been directed towards improving film homogeneity and adhesion to the substrate (Cho et al., 2014; Meng et al., 2014; Li et al., 2014). In this sense, the presence of surfactants and other additives may be beneficial for the CNT-TCF surface homogeneity, robustness and adhesion (De et al., 2009; Jung et al., 2011; Jung et al., 2013).

The CNT characteristics, including number of walls, synthesis method, quality, length and diameter, can influence the resulting TCF performance (Mirri et al., 2012). Single-walled carbon nanotubes (SWCNTs) usually perform better than multi-walled carbon nanotubes (MWCNTs) (Kaempgen et al., 2005; Li et al., 2008), although certain double-walled carbon nanotube (DWCNT) materials have demonstrated to be superior to SWCNTs prepared by a similar synthesis method (Mirri et al., 2012). Among the SWCNTs, those produced by laser ablation usually make up more conductive networks than the others (Kaempgen et al., 2005; Li et al., 2008). In addition, it is expected that metallic SWCNTs show an improved performance compared with the raw SWCNT material, which typically contains a mixture of metallic and semiconducting SWCNTs (Green and Hersam, 2008).

During the last years, new protocols have been developed for the purification, chemical functionalization, and sorting of CNTs. Those treatments usually have clear effects on the individual CNT electronic properties, which could be transferred to macroscopic systems built of CNTs. However, the effect of CNT processing on the resulting TCFs has been seldom reported. In the present work, the influence of some of those treatments on the CNT-TCF film performance is studied. Ultracentrifugation of CNT dispersions, various oxidative treatments, and two protocols for grafting chemical moieties are considered. An oxidative method for transforming arc-discharge MWCNTs into graphene nanoribbons is also tested. Finally, a gel chromatography process for the separation of SWCNTs into different electronic types is tested. The studies are carried out using a wide selection of commercial and home-made CNT materials that usually appear in the existing scientific literature and can be easily available for researchers and companies.

2. Experimental

2.1. Raw CNT powder materials

The raw CNT powder materials are listed in Table 1, including nomenclature and a brief description. The characterization details are extracted from the respective manufacturer websites and from references (Benito et al., 2005) and (Martinez-Rubi et al., 2012). Four different SWCNT samples, three MWCNT samples and a DWCNT sample were utilized. The AP-SW material was purchased from Carbon Solutions Inc. (AP-SWNT grade) and it was synthesized by the electric arc-discharge method with Ni/Y catalysts. The HiPco-SW material was purchased from Carbon Nanotechnologies Inc. (later Unidym and NanoIntegris) and it was synthesized through high pressure carbon monoxide (HiPco) pyrolysis with an iron catalyst. The SG76-SW material was purchased from Sigma-Aldrich; it was produced by South West Nanotechnologies (SWeNT, SG-76 grade) through the CoMoCAT method. The L-SW material was synthesized by a laser ablation method (Kingston et al., 2004) at the National Research Council (NRC) Canada, Ottawa. A DWCNT sample (NC2100 grade), a thin MWCNT sample (NC3100 grade) and an industrial grade MWCNT material (NC7000) were purchased from Nanocyl; they were synthesized by chemical vapor deposition (CVD) methods. Another MWCNT material was home-produced at ICB-CSIC by the arc-discharge method (Benito et al., 2005).

2.2. Surface modification of CNTs

The nomenclature for the modified samples is summarized in Table 2, together with a brief description of the preparation protocol. A series of modified CNTs was prepared from the AP-SW material by different oxidation or acid treatments. The AP-SW/Air material was prepared by thermal oxidation in an air atmosphere at 350 °C for 2 h. The AP-SW/HCl sample was obtained from the AP-SW/Air by 2 h acid treatment in a 3 M HCl reflux. The AP-SW/SN material was prepared from the AP-SW/HCl by 2 h reflux in a 3 M 1:3 HNO_3:H_2SO_4 mixture. Another material, hereafter called the AP-SW/HNO_3 sample, was directly prepared from the AP-SW material by reflux in 1.5 M HNO_3 for 2 h. Similarly, the NC7000-MW/HNO_3 material was prepared through the reaction of NC7000-MW CNTs with 1.5 M HNO_3 for 2 h.

Functionalization with *p*-nitrophenyl moieties was carried out through the reaction with 4-nitrobenzenediazonium tetrafluoroborate (O_2N–$C_6H_4N_2^+BF_4^-$, Aldrich 294438) in an aqueous medium at room

Table 2
Nomenclature and description of the modified CNT materials.

Modified sample	Starting material	Treatment	Representative functional groups
AP-SW/Air	AP-SW	350 °C, 2 h, static air	–C=O
AP-SW/HCl	AP-SW/Air	3 M HCl, 2 h reflux	–C=O, –C–OH
AP-SW/SN	AP-SW/HCl	3 M 3:1 H_2SO_4:HNO_3, 2 h reflux	–COOH
AP-SW/HNO_3	AP-SW	1.5 M HNO_3, 2 h reflux	–COOH
AP-SW/NO_2	AP-SW	NO_2–C_6H_4–$N_2^+BF_4^-$	–C_6H_4–NO_2
HiPco-SW/BPO	HiPco-SW	Na/naphthalene, $C_{14}H_{10}O_4$	–C_6H_5
NC7000-MW/HNO_3	NC7000-MW	1.5 M HNO_3, 2 h reflux	–COOH
AD-MW/15	AD-MW	H_2SO_4:$KMnO_4$, 15 min, 65 °C	–COOH
GNR	AD-MW	H_2SO_4:$KMnO_4$, 15 min, 65 °C + N_2H_4, 95 °C, 2 h	–C=O

Table 1
Nomenclature and characteristics of the raw CNT materials. Data are extracted from the respective manufacturer websites and from references (Benito et al., 2005) and (Martinez-Rubi et al., 2012).

Sample	Synthesis method	Manufacturer	Diameter [nm]	Length [μm]	TGA residual mass
AP-SW	Arc discharge	Carbon Solutions	1.4	> 1	< 30%
HiPco-SW	CVD (HiPco)	CNTI (Unidym)	0.8–1.2	0.1–1	< 35%
SG76-SW	CVD (CoMoCAT)	SWeNT	0.9	~9	≤ 10%
L-SW	Laser ablation	NRC Canada	1.2–1.5	> 1	11%
NC2100-DW	CVD	Nanocyl	3.5	1-10	< 10%
NC3100-MW	CVD	Nanocyl	9.5	1.5	< 5%
NC7000-MW	CVD	Nanocyl	9.5	1.5	~10%
AD-MW	Arc discharge	ICB	10–40	~1	–