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Corrigendum

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The authors would like to correct a line in the published paper.
Page 2, section 3, 11 lines after equation 1 should read:

Analysis of the films by vis-NIR spectroscopy using an
integrating sphere attachment confirms that the reflectance is
<1 %.

High conductivity transparent carbon nanotube films deposited from superacid

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Abstract

Carbon nanotubes (CNTs) were deposited from a chlorosulfonic superacid solution onto PET substrates by a filtration/transfer method. The sheet resistance and transmission (at 550 nm) of the films were 60 Ω /sq and 90.9% respectively, which corresponds to a DC conductivity of 12 825 S cm⁻¹ and a DC/optical conductivity ratio of 64.1. This is the highest DC conductivity reported for CNT thin films to date, and attributed to both the high quality of the CNT material and the exfoliation/doping by the superacid. This work demonstrates that CNT transparent films have not reached the conductivity limit; continued improvements will enable these films to be used as the transparent electrode for applications in solid state lighting, LCD displays, touch panels, and photovoltaics.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Carbon nanotube (CNT) thin films are quickly developing as a transparent conductive material [1, 2] that can potentially replace the traditionally used indium tin oxide (ITO) for many device applications including touch panels [3], LCD displays [4], transparent FETs [5], solid state lighting [6], and photovoltaics [7]. CNT based transparent conductive films have several advantages over ITO including mechanical flexibility, durability [8], neutral color, lower reflection, compatibility with roll-to-roll coating processes such as gravure and slot die, and lower cost [3, 9]. Currently, the major limiting factor from a technical perspective for wide adoption of CNT films is the DC conductivity (σ_{dc}), which must continue to improve in order to make CNT films competitive with ITO from a sheet resistance (R_s)/optical transmission (T) standpoint.

The σ_{dc} of CNT films is determined by various factors, including CNT purity, length [10], diameter, number of walls [11, 12], side wall perfection, bundle diameter [10], metallic tube fraction, residual dispersing agent in film, and degree of doping [13, 14]. An ideal high conductivity film would consist of pure, long, highly de-bundled, highly doped,

defect free CNTs, with a minimal number of walls. The difficulty in obtaining such a film is that de-bundling and dispersing CNTs without destroying the electrical properties remains challenging.

There have been several dispersion schemes proposed in the literature. Covalent dispersion schemes can lead to highly concentrated solutions of individualized tubes; however, the introduction of covalent functionalization disrupts the π -binding and causes sp³ carbon bonds that significantly decrease the CNT conductivity. Several non-covalent dispersion schemes have been successfully demonstrated, including the use of a surfactant or polymer to wrap around the CNTs and pull them into solution. Typically this is done with the assistance of high power sonication that helps overcome the 0.5 eV nm⁻¹ attractive Van der Waals interaction between adjacent tubes within a bundle and allows the dispersant material to penetrate the interstitial spaces. Although these non-covalent solvation schemes can lead to stable CNT dispersions, they have several disadvantages. The necessity of aggressive sonication has been shown to introduce defects along CNT walls, and dramatically shorten CNT length, leading to decreased electrical conductivity. Also, these methods can leave behind dispersant residue, which is difficult to completely remove after tube deposition. This residual dispersant can diminish the overall conductivity by creating

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insulating transport barriers between tubes [15].

In this paper, a unique CNT deposition scheme for superacid dispersions is demonstrated, leading to films that are uniform, cohesive, and of superior electrical conductivity. Superacids have previously been shown to be effective at dissolving CNTs at high concentration [16], forming true thermodynamic solutions at weight concentrations up to 0.5 wt% in chlorosulfonic acid [17] (CSA).

We use the superacid CSA to create highly de-bundled CNT dispersions that can be deposited onto various surfaces. Washing with a proper organic 'non-solvent' to remove excess superacid and coagulate the film results in a continuous, uniform, and cohesive film consisting of largely de-bundled and doped CNTs. The use of the superacid in place of a polymer/surfactant to disperse the tubes has several benefits including (1) high efficiency of dispersion of CNTs into individual tubes without sonication, (2) high degree of de-bundling in the solid state films, (3) absence of residual surfactant/polymer in final film, and (4) high level of p-type doping in final film. Films deposited using this method were transferred to a poly(ethylene terephthalate) (PET) substrate so that the sheet resistance and transmission could be measured. These films have the highest conductivity reported to date for CNT transparent films, up to $12\,825\text{ S cm}^{-1}$. This level of conductivity would open doors for applications in touch panels, LCDs, solid state lighting, and possibly photovoltaics.

2. Experimental details

Two different grades of CNT were used in this paper. The first are p-grade HiPco tubes made by Unidym and the second are Unidym's 'OE' CNT-grade, which were grown by Unidym by a chemical vapor deposition process, followed by air oxidation and acid purification to remove residual catalyst and amorphous carbon. The OE CNTs are predominantly single-walled and double-walled tubes, and have greater than 95% purity. OE tubes have an average length of 2–3 μm and an average diameter of 1.5–2 nm as measured via AFM and TEM imaging.

The CNTs were dispersed in the superacid chlorosulfonic acid (CSA) as follows. 10 mg of CNTs were added to 50 ml of CSA and stirred in a closed vessel at room temperature for 12 h. Various volumes of dispersion (some further diluted with CSA) were passed through a 0.2 μm anodisc filtration membrane with vacuum assistance to form CNT networks of the desired thickness on top of the membrane. Films were then rinsed with 50–100 ml of diethyl ether, to remove excess superacid and allow the CNT film structure to form. This washing process caused a color change from yellow-brown to black. The films were then transferred from the coated membrane filter into a water bath, causing the film to float on the water surface, allowing them to be transferred to a PET surface. Once on the PET surface, the optical transmission at 550 nm was measured using a Cary 5000 UV–vis spectrometer, and the 4-pt sheet resistance was measured using a Jandel 4-point probe. 5 points over the films surface were measured and average results reported; typically, film sheet resistance was relatively uniform over the entire film surface, leading to about

a 10% standard deviation in sheet resistance values. Raman measurements were made using a LabRAM Aramis Raman spectrometer with a laser excitation wavelength of 785 nm.

3. Results and discussion

From the measured R_s and T of the CNT films, the σ_{dc} of the film can be calculated using the following equation [1]:

$$T = \left(1 + \frac{1}{2R_s} \sqrt{\frac{\mu_0 \sigma_{op}}{\epsilon_0 \sigma_{dc}}}\right)^{-2} = \left(1 + \frac{188(\Omega) 200(\text{S cm}^{-1})}{R_s \sigma_{dc}}\right)^{-2} \quad (1)$$

As this equation has become quite widespread in the literature, a word should be said here regarding its use. This equation is an approximation that relates the R_s , σ_{dc} , T , and optical conductivity (σ_{op}) for thin conductive films. The equation is valid assuming that (1) the film is much thinner than the wavelength of light being measured and (2) the reflection is much less than the absorption. The thickness of these transparent thin CNT films is between 5 and 50 nm. Analysis of the films by vis–NIR spectroscopy using an integrating sphere attachment confirms that the reflectance is $>1\%$. Thus, both of these conditions hold for transparent CNT films on PET. Typically a value of 200 S cm^{-1} is used for the optical conductivity, which was measured by Ruzicka *et al* on potassium doped single-walled CNT films [18]. One should keep in mind that the optical conductivity for films made from various tubes can be quite different; for example, one might expect that the optical conductivity of films made from single-walled CNTs would be different from those made with multi-walled CNTs. Therefore, the σ_{dc} as 'calculated' using this equation should not be taken as the true value (σ_{dc} is difficult to define regardless for porous films with a surface roughness on the order of the film thickness). However, this equation is a good way to parameterize the R_s and T results for films made by various groups at different thicknesses into a single value (σ_{dc}) which can then be easily compared. Certainly, the ratio of σ_{dc} to σ_{op} should be a good parameter to use when comparing various films with different R_s/T relationships.

HiPco CNT films of various thicknesses were prepared using CSA dispersions; these films were characterized by Raman spectroscopy at 785 nm excitation and the results shown in figure 1. Raman spectroscopy has been shown to be useful for characterizing the aggregation state of CNTs both in solution and in the solid state [19]. For HiPco SWNTs, the radial breathing mode (RBM) at 267 cm^{-1} observed at 785 nm excitation can be attributed to the presence of bundled CNTs. Typically, films prepared from surfactant assisted dispersions show the presence of this mode at 267 cm^{-1} , indicating that the samples are composed of bundles. The samples prepared from CSA show only a minor peak at 267 cm^{-1} , indicating that the samples are primarily de-bundled. The difference in morphology suggested by the Raman results indicates that aqueous surfactant is insufficient in preventing coagulation and/or coalescence of the SWNTs during film formation. CSA disperses the CNTs by protonation or oxidation of the CNTs, resulting in positively charged CNT molecules. Electrostatic repulsion is sufficient to prevent re-aggregation during the

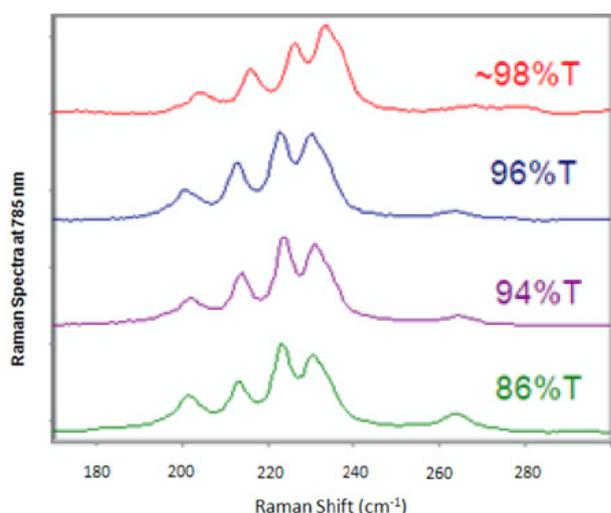


Figure 1. Raman spectra for HiPco CNT films made from CSA for films of various thickness.

deposition and coagulation steps, when diethyl ether is used as the coagulating solvent. The morphology obtained using this process is quite different than the alewife structures produced upon coagulation with water [16].

A second set of films were prepared using HiPco CNTs dispersed in CSA as described, and the sheet resistance and transmission were measured. Using this data and equation (1), the σ_{dc} was calculated and plotted versus transmission in figure 2. The σ_{dc} varies from 1500 S cm⁻¹ for films at 95% transmission up to a peak value of 2934 S cm⁻¹ for a film transmission of 86.75%. These values are 2–3 times higher than are typically obtained in the literature for surfactant assisted dispersions of HiPco CNTs [20]. The ability of CSA to exfoliate and dope the CNTs leads to highly conductive films as a result. This will be discussed in more detail below.

Unidym's OE-grade CNTs were made into films using the CSA dispersion method and the opto-electronic properties characterized. Figure 3(a) shows the R_s/T values obtained for films measured in this paper, and compared to the best results that the authors could find in the literature on CNT transparent films. The values from figure 3(a) were then converted to a σ_{dc}/σ_{op} ratio using equations (1) and plotted versus film transmission. It is evident that the OE-grade CNT films shown here have the highest σ_{dc} (12 825 S cm⁻¹ @ 90.5%) reported to date. Figure 3(b) plots the σ_{dc}/σ_{op} ratio as a function of transmission because it is known that the σ_{dc} of CNT films (and films made of any material) decreases with decreasing film thickness (below a critical thickness, which is about 10–40 nm for CNT films). Therefore, to compare the performance between films made from various groups, it is imperative to compare films at similar thickness values. Since we do not measure the film thickness directly, we use the indirect measurement of the film transmission as a proxy. Therefore, a fair comparison can be made when comparing the σ_{dc}/σ_{op} ratio for films at the same transmission. Figure 3(b) shows the R_s/T data from figure 3(a) plotted as a function of the σ_{dc}/σ_{op} ratio. In this manner, it is easy to compare the 'quality' factor of various CNT films. It has been demonstrated that the σ_{dc}/σ_{op}

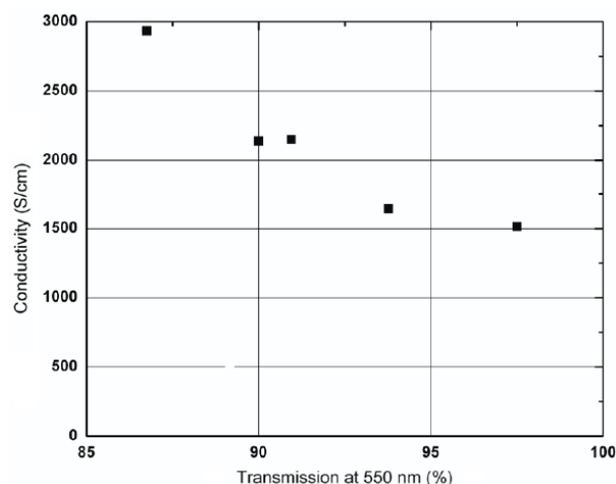


Figure 2. σ_{dc} as calculated using equation (1) for HpCo CNT films deposited from a CSA solution for films of various thickness (transmission).

ratio will begin to decrease for very thin films (above 90–95% transmission); certainly it must approach zero for films falling below the percolation threshold, where the σ_{op} remains finite but the σ_{dc} is 0. Here it is clear that the films reported in this work have over a 25% higher performance quality than previously reported films.

The ultrahigh conductivity measured for OE-grade CNT films prepared from CSA arise due to: (1) high conductivity of starting CNT material stemming from high CNT purity and suitable CNT geometry (2) small bundle size in the final film due to dispersion scheme (3) p-type doping from superacid traces residual in final film. The effects of doping should not be underestimated, as almost all the literature data referenced in figures 3(a) and (b) come from films that are explicitly doped, typically either through strongly oxidizing acids such as nitric acid or through electron withdrawing inorganic materials such as thionyl chloride.

One of the most critical issues with chemical doping agents on CNTs is that, to date, there has been limited evidence for long-term stability of the conductivity enhancement effect. In the transparent conductor industry, typical stability tests are done at 85 °C/85% relative humidity for 1000 h, as well as at 150 °C for several hours. The sheet resistance cannot change by more than 10–20% as a result of these stability tests. The majority of doping reports on CNT films in the literature are not subjected to these types of stability tests, which are important for real world applications. Those that are reported typically are not stable [21].

The doping enabled by the superacid reported in this work is likewise not stable at room temperature; a 15% increase in sheet resistance is observed over the first two days after making the film and a more significant increase after long-term storage in air. This instability can be accelerated under high temperature/humidity. After 24 h at 85% relative humidity and 85 °C, the film sheet resistance increases by 220% (from 38 OPS to 121.6 OPS). More research effort remains to find stable p-type dopants that can withstand industry accepted accelerated ageing tests.

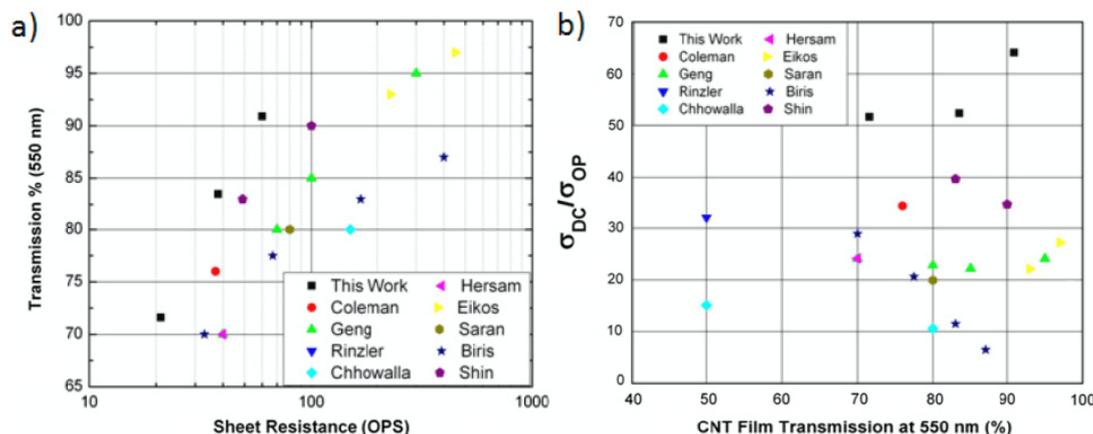


Figure 3. (a) CNT film transmission at 550 nm versus 4-pt sheet resistance for data measured in this paper compared to the best data found in the literature. (b) Ratio of DC to optical conductivity as calculated by formula 1 for data presented in this work, as compared to the best data presented in the literature to date. Referenced in the figure [2, 11, 13, 22].

The high σ_{dc} to σ_{op} ratio exhibited by these films is due to both the high quality of the CNT starting material and the debundling/doping of the superacid solvent/deposition process. To characterize the CNT material, Raman spectroscopy was performed with a 514 nm laser, resulting in a G/D band ratio of 64. This shows that the OE-grade CNTs have high relative amounts of graphitic CNTs to amorphous carbon impurities. This coupled with their long length and relatively large diameter makes them a highly conductive grade of CNT.

4. Conclusion

In this paper, we compare the opto-electronic properties of two different CNT grades (HiPco and OE, Unidym) deposited from CSA. We note that the conductivity of films made from OE tubes and CSA dispersions lead to the highest conductivities for CNTs yet reported. Increasing the film conductivity is one of the remaining challenges for use of CNT materials for electronic applications, especially for transparent electrodes [23]. Use of a superacid such as CSA, though here demonstrated on a laboratory scale, has been used before in industrial scales on products such as Kevlar (manufactured by Dupont) [24], and so has the potential to be useful from a commercial perspective as well.

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