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Effect of purity on the electro-optical properties of single wall nanotube-based transparent conductive electrodes ☆

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ABSTRACT

We present a detailed assessment of centrifugation technique for purification of single wall carbon nanotubes (SWCNTs) for application as transparent conductive electrodes. As-grown and highly-purified SWCNTs were dispersed in surfactants by ultrasonication, and then centrifuged to selectively remove carbonaceous and metal impurities. The centrifuged supernatant suspensions were made into thin films by transferring filtrated nanotube coatings onto glass slides. The absorbance and resistance of nanotube coatings were measured, and their optical purity level estimated from a comparison of the area of the near-infrared S_{22} SWCNT optical absorption band relative to the area of the background. The single-step centrifugation process is shown to purify laser-vaporization grown SWCNTs from an initial optical purity of 0.10 to an averaged purity of 0.23, with an 8.8% yield, which is comparable to other purification techniques. The quality of transparent conductive electrodes estimated as a ratio of visible-spectrum absorbance to sheet conductivity is improved by a factor of 12 upon purification.

1. Introduction

The solution processability and high conductivity of carbon nanotubes make them ideal candidates to replace brittle and expensive indium tin oxide (ITO) electrodes currently used in applications such as organic light emitting diodes and organic photovoltaics. However, SWCNT grown by high-temperature plasma processes such as laser vaporization or arc production include large quantities of impurities, including metal catalyst nanoparticles and non-nanotube carbon. Unfortunately, these impurities inhibit achieving the stated goal of high transparency, high conductivity films, and methods of removing impurities can be both costly and time-consuming. A simple, low-cost method to remove impurities and undispersable aggregates from SWCNT suspensions is therefore crucial to further the development of flexible, transparent, and conductive nanotube electrodes.

Most nanotube purification techniques are multi-step procedures, which include a combination of acid reflux, oxidation, microfiltration, or centrifugation [1–14]. After purification, SWCNTs are heavily bundled as a result of strong Van der Waals interactions, and hard to disperse without additional surface functionalization. Attempting chemical functionalization or sonication to increase dispersibility results in degradation of the SWCNT optical and electronic properties to well below that of the starting material [15–18]. For this reason, it is important to do an assessment of purity after the nanotubes are formed into a film, in order to assess the true film quality. In these studies, however, nanotube purity assessment has been done prior to deposition as a film,

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which intrinsically ignores any changes in purity during the deposition process.

Also, after purification, the amount of material remaining is low, from 3% to 50%, depending on the method used [14,19,20]. The SWCNT purity in these solutions is typically assessed using NIR spectroscopy, where the relative areas of the S_{22} interband transition, *A*, is compared to the total area (*A* + *B*) under this same region (see Fig. 2). This ratio, or the "optical purity", has been assessed from 0.134 to 0.319, depending on the method of purification used [14,21–23].

It should be emphasized that while many studies report the purification yield or the optical purity, very few report both [14,20], so correlations between purity and yield are difficult to compile. Many publications report the use of simple centrifugation treatments to purify as-produced SWCNTs, [14,19,20,22,24,25] but all lack assessments of carbonaceous purity using NIR absorption spectroscopy. Moreover, centrifugation has also been used to improve the electrical properties of SWCNT films, but without rigorous characterization of any improvements to optical absorption [26,27].

Here we report on the effectiveness of a simple, single step purification procedure for producing SWCNT thin films, as compared to films produced from a multi-step acid purification and oxidation procedure. The improvement in SWCNT purity is correlated to electrical and optical properties of the resultant SWCNT film. The ratio of optical absorbance to sheet conductivity (the figure of merit), and the weight yield for this single-step process are shown to be comparable to films produced by more complex multi-step methods.

2. Experimental methods

As-produced, laser-grown SWCNTs were dispersed in 1 wt.% SDS/H_2O to form a 5 μg/g concentration. SWCNT dispersion was carried out in an ultrasonic bath (Blackstone~NEY Multisonik 2) operating at 360 W, 40 kHz, until no aggregates were visible to the eye, approximately 90 min. A film was made with 1.5 ml of this solution, and the remaining 19 ml was centrifuged at 9000 rpm (8800*g*) (Fisher Marathon 21000 with a fixed angle rotor) for 2 h. No further improvement of the SWCNT film quality was observed for solutions, which were centrifuged longer than 2 h.

A sample of chemically purified (pre-purified) laser SWCNTs was subjected to the same sonication and centrifugation procedure to test if further improvements in film quality can be made. The chemically-purified SWCNTs were

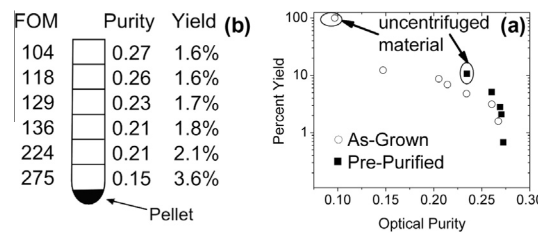

Fig. 1 – (a) Weight yield of filtered material from different aliquots in the centrifuge tube vs. optical purity from corresponding thin films, for two different qualities of starting surfactant suspensions. As-grown SWCNT material are open circles, and oxidatively pre-purified SWCNTs are closed squares, for which the yield of the pre-purification process was 10.7%. (b) Summary diagram for as-grown SWCNT suspension shows the weight percentage of material collected from corresponding aliquots in the centrifuge tube, and the optical purity and figure of merit (FOM) of the corresponding transparent conductive thin films.

purified by HNO_3 reflux, filtration, multiple HCl treatment, oxidative burns, and oven dryings before undergoing the dispersion and centrifugation process. The chemical purification process yielded 10.7 wt.% of the as-grown material.

Six films were made from each of the centrifuged solutions, starting with the top 3 ml of the centrifuge tube, and continuing in 3 ml increments until no solution was remaining. The films were made by vacuum-filtration of the solution onto 25 mm diameter cellulose nitrate filters (Millipore, 1 μm pore size). The surfactant was removed by pumping large amounts of deionized water through the filter. The washed filter was inverted onto a glass substrate, and the filter dissolved with acetone [28]. The quality and electro-optical properties of each SWCNT film was evaluated by Raman and absorbance spectroscopy, SEM and TEM imaging, and four-probe resistance measurements.

Absorbance measurements from 300 to 2800 nm were made with a Cary 5000 UV–vis–NIR spectrophotometer, and used to assess the carbonaceous purity and transparency of the films. We used the procedure proposed by Itkis to determine the relative carbonaceous purity of the SWCNTs [29] The carbonaceous purity (optical purity) is defined as a relative area of S_{22} interband transition of SWCNTs corrected for the contribution of π-plasmon of carbonaceous impurities.

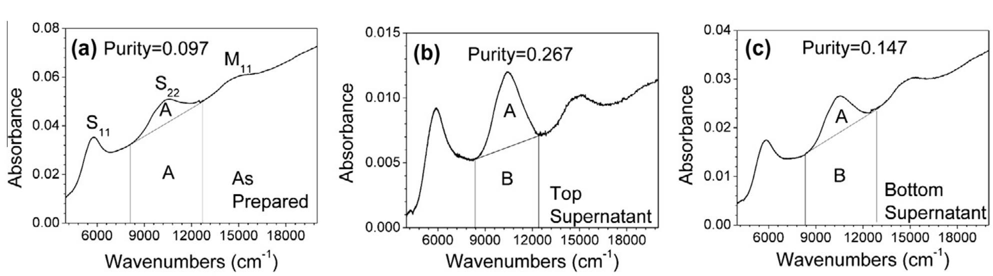

Fig. 2 – Absorbance spectra of SWCNT films with different amount of carbonaceous impurities prepared from: (a) from as-grown nanotubes (b) purified SWCNTs from the topmost portion of the centrifuge tube, (c) bottommost supernatant of the centrifuged material. Optical purity is calculated as a relative area of S_{22} inter band transition: *A*/(*A* + *B*) where *A* is the area of S_{22} peak integrated to the baseline and *B* is the integrated area under the baseline.

Table 1 – Optical transmittances (at 550 nm) and sheet resistances of nanotube films prepared from starting material and after centrifugation based purification.

Dispersant/SWCNT type	kΩ/Sq	%T	Optical purity	G/D	FOM (abs/σ)
Nanotube films without centrifugation					
SDS/as-grown	19.7	86	0.1	3.1	1280
SDS/pre-purified	2.4	84	0.23	8.7	188
Sodium cholate/as-grown	8.0	70	0.09	2.5	1239
After single step centrifugation					
SDS/as-grown	7.6	97	0.26	7.1	104
SDS/pre-purified	2.2	86	0.27	8.7	144
Sodium cholate/as-grown	8.0	96	0.18	4.6	142

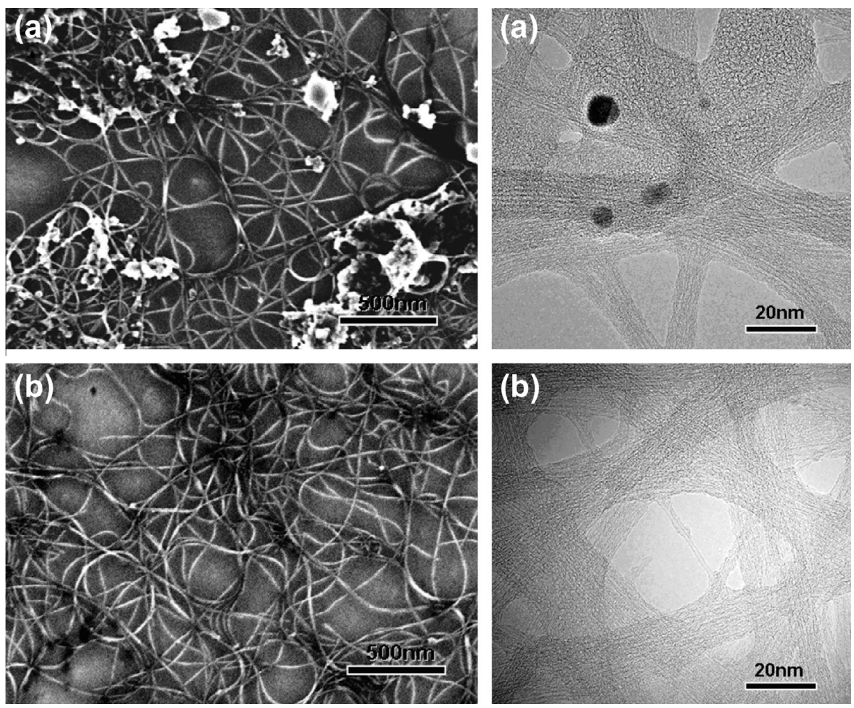

Fig. 3 – SEM (left) and TEM (right) images of (a) as-produced SWCNTs showing nanotube bundles, large nanotube aggregates, catalyst nanoparticles, and carbonaceous impurities. (b) SWCNT purified by centrifugation (8800*g* for 2 h) showing SWCNT bundles free from catalyst nanoparticles and large aggregates.

The resistances of all films were measures by a Jandel four-point-probe with a Keithley 6430 source-ohm-meter. Each sample was analyzed under scanning electron microscope (SEM) for the presence of SNWT aggregation, and non-nanotube material. A Renishaw 1000 confocal Raman microscope, using 633 nm laser for excitation, was used to measure the level of defects and carbonaceous impurities in each SNWT film, by comparing heights of *G* and *D* bands [30].

3. Results and discussion

The quality of each film was determined by defining a figure of merit (FOM) as a ratio of the optical absorbance at 550 nm to the electrical sheet conductivity (square/Ω) [31], with a lower FOM indicating a higher-quality film. Nanotube carbon purity was also assessed with absorbance spectroscopy by the method of Itkis et al. [29], and by Raman spectroscopy, as a ratio of G-band to defect band intensities (*G*/*D* ratio) [30].

For as-grown material, centrifugation improved the FOM over 12-fold, decreasing from 1280 for films made directly from as-grown SWCNTs to 104 for films prepared from centrifuged solution. For pre-purified SWCNTs, the FOM decreased from 188 to 144 with centrifugation. The same procedure carried out with as-grown SWCNT dispersed in 1% sodium cholate solution improves the FOM by a factor of 8.7, confirming that this method of purification is applicable to surfactants other than just SDS.

It should be noted that one of the major drawbacks for assessing film quality via FOM is the dependence of FOM on film thickness, a topic that has been addressed repeatedly in the literature [32]. Thicker films made from the same material will have a lower FOM, therefore making them appear to be of higher quality. Indeed, our experiments show that a 5% increase in transmittance in a nanotube film can increase the FOM by as much as 40%. However, since the films prepared by centrifugal purification demonstrate higher transmittance than the control samples, the FOM actually underestimates the improvements to film quality from this procedure.

For the solution of as-grown material, the figure of merit and purity of the resulting films was highest for films made with material from the topmost aliquot taken from the centrifuge tube, and lowest for the bottommost material, as shown in Fig. 1(a). Interestingly, despite being the lowest purity films made with centrifuged solution, the SWCNT films made from bottommost aliquot of solution was still of higher purity than the original solution. This is because most of the carbonaceous impurities were concentrated in the pellet at the bottom, such that all of the supernatant was at least somewhat purified. At the same time, the series of films made from pre-purified material still showed an improvement in the FOM, only without the large increase in optical purity and Raman *G/D* ratio (Table 1).

From basic percolation theory and previous SWCNT studies, it is known that higher-aspect ratio nanotubes form more conductive pathways at lower loadings [33]. Therefore, as chemical purification is known to shorten SWCNTs [17,18], the better FOM for as-grown, centrifuged SWCNTs, compared to pre-purified centrifuged SWCNTs, is likely due to the longer, higher-aspect-ratio nanotubes. On the other hand, for centrifugation of pre-purified material, the FOM improvements can be attributed to the removal of poorly dispersed nanotube aggregates, which, despite having high nanotube content, make little contribution to the film conductivity, while detracting from the visible-spectrum transmittance. This is explained by the constant *G/D* ratio and the barely-changed optical purity in these films, in combination to the noticeable decrease in the number of aggregates that is visible after centrifugation. For as-grown nanotubes, centrifugation removes not only nanotube-containing aggregates, but also non-nanotube carbon, as evidenced by the change in *G/D* band ratios and optical purity (Fig. 2).

SEM images confirm this, showing a more uniform, less aggregated film for the samples that are made from centrifuged solution, while TEM shows a sample freer from catalyst particles and non-nanotube carbon (Fig. 3).

One of the most important quantities for any purification procedure is yield. A useful purification procedure will recover the largest amount of SWCNTs possible from the original material. By using a Beer's law linear dependence of the visible-spectrum absorbance on the amount of SWCNTs per square area of a film, the percent yield of pure nanotubes was calculated from the purification procedure as follows: The weight per unit volume of nanotubes in the prepared solution is known. Since the films we prepared are all of the same surface area, with only thickness varying, then the ratio of the weight of this starting material to the weight of the centrifuged material will be equal to the ratio of the absorbance of the starting material to the absorbance of the centrifuged material. So from the known volumes of solution that comprise each sample, the total yield of nanotubes in each aliquot can be calculated, and is shown in Fig. 1(b).

At a purity of 0.26, 3% of the as-produced material remains after centrifugation, and 48% of the pre-purified SWCNTs remain after centrifugation. At a purity of 0.23, 8.8% of the as-produced material remains after centrifugation, which is the top 80% of the supernatant (Fig. 1). However, considering that the chemical purification process yielded 10.7% of the starting material, this means that upon chemical purification and subsequent centrifugation, only 5% of the as-grown material remains after the complete pre-purification and subsequent centrifugation process. Hence, the overall yields of both purification procedures are comparable.

4. Conclusions

We have shown that single-step centrifugation is a simple, feasible method of creating purified SWCNT transparent conducting films, and that incorporating chemical purification into the purification process is an unnecessary added step. The centrifugation purification procedure produces SWCNTs with optical purity and yield comparable to that produced by extensive acid-oxidation purification methods. Thus, centrifugation purification eliminates re-dispersion step, which is required for SWCNT purified using acid-oxidative methods. When applied to as-grown SWCNTs, this method can increase film conductivity by a factor of 2.5, and decrease visible-spectrum (550 nm) absorbance by a factor of five. The pure SWCNT can be produced with 8.8 wt.% yield comparing to 10.7 wt.% yield for the more time-consuming chemical purification method for the same optical purity of 0.23. The proposed method of film quality and nanotube purity assessment allows one to determine the purification yield for a desired FOM or for a desired optical purity, important for cost analysis and potential industrial applications.

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