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Solution-processable transparent conducting films by defunctionalization of amine functionalized carbon nanotubes

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Abstract. This paper presents a low temperature, solution-based processing method of highly transparent, sparse networks of carbon nanotubes via annealing process that dramatically improves the conductivity of thin films of octadecylamine functionalized highly soluble single-wall carbon nanotubes by up to five orders of magnitude. This increase in conductivity obtained at low temperatures allows for the creation of transparent conducting carbon nanotube (CNT) films via printed deposition of contacts for photovoltaic, light emitting, and display devices. An increase in films conductivity has been shown with process temperatures of 200°C at normal atmospheric pressure. The dependence between the sheet resistance of CNT layers and the annealing parameters is analyzed together with Raman and FTIR data, suggesting a relationship between the loss of octadecylamine functional groups along with the healing of CNT defects during the annealing process and the dramatic conductivity improvement of CNT layers. © 2018 Society of Photo-Optical Instrumentation Engineers (SPIE) [DOI: [10.1117/1.JPE.8.032221](https://doi.org/10.1117/1.JPE.8.032221)]

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1 Introduction

Carbon nanotubes (CNT) have been widely studied for the production of electronic devices due to their exceptional physical and electronic properties. The high conductivity, mechanical flexibility, and optical transparency of CNT mats make them excellent candidates for use in solar cell applications, light emitting devices, and flexible display. Currently, transparent conducting layers in such devices are mostly based on expensive rare metal oxides such as indium tin oxide (ITO). Many different materials have been suggested as replacements for ITO,¹ all of which strike a balance between transparency and conductivity. Some methods that use CNT for the replacement of ITO have been shown to have promise. A typical 200-nm-thick ITO film has an average transparency of 85% in the visible range and a sheet resistance of around 30 Ω /square.² Typical values for mixed semiconducting and metallic CNT conducting films are: 80% transparency 84 Ω /square sheet resistance (sodium dodecyl benzene sulfonate-treated SWCNT);³ and 90% transparency at 2×10^3 Ω /square sheet resistance (brush coating deposited single-wall CNT).⁴

One of the major roadblocks to using CNT for the production of solution processed, large area-printed electronic devices is the difficulty of dispersing them over larger areas during device fabrication without the degradation of their desirable electronic properties.⁵ The high van der Waals forces between pristine CNTs mean that they have a large clumping affinity and so are difficult to use in solution processes. The easiest way to solve this problem is the addition of

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polar side groups to the CNTs by processes, such as acid⁶ or amine⁷ functionalization. The addition of functional groups allows CNTs to interact with stronger polar solvents to create more evenly dispersed solutions, with lower interaction between the CNTs and significantly reduced aggregation. However, functionalization involves the use of covalent bonding, which disrupts the π bond overlapping along the CNT's long axis and so adversely affects their electronic properties.⁶ Another route to increase the solubility of CNT is the addition of surfactant materials. These are typically polymer or soap like materials that interact with CNTs by van der Waals and hydrogen bonding.⁸ Surfactants enhance solvent–tube interactions in the same manner as covalently bonded functional groups to allow the CNT to be dispersed. However, they have the disadvantage of being typically insulating materials that adversely affect the conducting properties of the deposited CNT films.

As well as the effects on the electronic properties of CNT by solubilization, pristine CNTs can also have lower than theoretically expected conductivities due to defects in their bonding structure. Previous studies have used high-temperature (>950°C) annealing,⁹ high-temperature ammonia washing,¹⁰ or disproportionation of carbon monoxide¹¹ for the healing of carbon structure defects in CNTs. Each of these techniques has some shortcomings. The first two techniques require high processing temperatures, which limits the materials that can be used for the rest of the device. The carbon monoxide disproportionation process relies on medium temperature reactions in a carbon monoxide atmosphere, which means the setting up of an additional step in any device production process with a high-pressure carbon monoxide chamber.

The process presented in this paper proposes to solve the problems stated above by the use of an octadecylamine (ODA) functional group on the CNTs. ODA functionalization of CNTs is a two-step process that first adds an acidic (COOH) group, which the ODA group is attached onto in the second step.¹² This preferentially happens at defect sites in the CNT structure due to the lower activation energies needed to bond at these positions (in the graphitic structure). An ODA functionalization on a defect site causes a reduction in the conducting properties of single-walled carbon nanotubes (SWCNT) in comparison with pristine CNT;¹³ however, using an annealing process can reverse this negative effect. This paper presents evidence of the improvement in conductivity after annealing and then uses infrared and Raman spectroscopy to suggest evidence for possible mechanisms of defect healing and the removal of the functional groups. The temperatures and pressures shown for the defunctionalization and defect healing by annealing are the lowest, which have been shown for such processes.

2 Experimental Section

2.1 Functionalized Carbon Nanotube Inks

Inks for the deposition of thin films were produced from a 1 g/L solution of octadecylamine functionalized SWCNT (ODA-CNT, Sigma-Aldrich) in toluene that was placed in a sonic bath at 100% power for 30 min. These solutions are stable for up to 2 weeks and can be redispersed after this time by sonication for 10 min. Initial Raman analysis of as supplied ODA-CNT revealed a mixture of semiconducting and metallic tubes with diameters between 0.7 and 1 nm, respectively. A D/G peak ratio in the Raman spectra of 0.13 ± 0.005 suggested a reasonably high concentration of CNT to amorphous carbon. More detailed discussion of the nature of D and G peaks is provided in Sec. 3 of the paper.

2.2 Deposition and Processing of Thin Films

Samples for electronic measurements were produced by spin coating ODA-CNT inks at 750 rpm for 60 s, with a slow acceleration, on glass slides. This was followed by heating of the samples to 60°C for 10 min to allow the evaporation of any remaining toluene. The thin layers of sparse ODA-CNTs were then annealed in a nitrogen atmosphere at temperatures between 150°C and 250°C for periods of time between 0 and 240 min. Contacts for conductivity measurements were produced by evaporating 70-nm thick aluminum strips onto the annealed films. These strips gave a series of contact separations between 3 and 12 mm in length.

Samples for Fourier transform infrared (FTIR) absorption and Raman measurements were produced by drop coating ODA-CNT inks at 60°C on semi-insulating gallium arsenide (GaAs) substrates. These substrates are transparent in the infrared and were polished to reduce losses in the substrate. Before spectrometry tests were performed, the samples were annealed under nitrogen at 200°C for periods of time between 0 and 240 min.

2.3 Characterization

Conductivity measurements were performed using a Keithley 4200 semiconductor parameter analyzer with a two probe set up in normal atmospheric conditions. The voltage was ramped between -5 and 5 V and the current was measured for several contact separations.

Thermogravimetric analysis measurements were performed using a TA Instruments Q500 thermogravimetric analyzer (TGA) scanning between 0°C and 800°C using 4.72 mg sample of dry ODA-CNT powder.

The IR transmittance of samples in the spectral range from 400 to 4000 cm^{-1} was measured using a Varian Cary 660 with a ceramic broadband source, a cesium iodide beam splitter, and a deuterated triglycine sulfate detector at room temperature. The GaAs semi-insulating substrate spectrum was obtained as a background for each measurement to remove any inherent artifacts. The resolution was chosen to be at 8 cm^{-1} and a scan size of 1000. The sample compartment was continuously purged with dry nitrogen to reduce absorptions due to atmospheric water vapor and carbon dioxide.

A UV-vis-NIR Varian Cary 5000 spectrometer was used to measure the transmittance of samples between 200 and 2300 nm.

Raman spectra were recorded using a Renishaw micro Raman-spectrometer with excitation from a green (514-nm) laser. This spectrometer was calibrated with a standard silicon reference sample and operated in continuous mode between 150 and 4000 cm^{-1} . Measurements were repeated at 15 sites across each sample and average values were calculated.

3 Results and Discussion

The conducting films presented in this paper have high transparencies above 90% between wavelengths of 400 and 2500 nm [Fig. 1(a)] and are entirely solution processed. These features demonstrate that the inks are good candidates for the printing of transparent CNT thin films. The CNT films display average film thickness of ~ 20 nm, and due to the sparse nature of CNT coverage of a substrate, a high degree of thickness variation, at a micron-scale, from 0 and 30 nm and a high number of crossing points between CNTs, as shown by AFM analysis [Fig. 1(b)].

A two contact current voltage (IV) plots of a thin film of ODA-CNT, with a 3-mm contact separation, before and after annealing at 250°C for 240 min are shown in Fig. 2(a). After annealing

Fig. 1 (a) UV-vis absorption and tapping mode AFM image (b) of a thin film of ODA-CNT spin coated onto glass substrates and annealed at 200°C for 240 min. For comparison, a UV-Vis absorption spectrum is shown for a 120-nm-thick film of indium tin oxide (Sigma-Aldrich; 703192) on glass substrate.

Fig. 2 (a) IV characteristics of an unannealed film of amine functionalized CNT and a film that was annealed for 240 min at 250°C. (b) Sheet resistance (R_s , Ω/square) and conductivity (σ , S/m) versus anneal time for amine functionalized CNT samples treated at temperatures of 150°C, 200°C, and 250°C under nitrogen. Experimental points are shown as dots, triangles, and squares, respectively. Lines are drawn to guide the eye. Average film thickness of the samples ~ 20 nm.

there is a large increase of approximately four orders of magnitude in the current obtained from the film. Resistance values were obtained from these plots and the total resistance was plotted against contact separation. The slopes of the contact separation versus resistance plots were used to find the samples sheet resistance for each annealing temperature and time. The change in sheet resistance as a function of annealing time for thin films annealed at 150°C, 200°C, and 250°C, with average film thickness of ~ 20 nm, is shown in Fig. 2(b). There is very little reduction in sheet resistance for the sample annealed at 150°C suggesting that this is below the activation temperature for the process that leads to an improvement in the sample conductivity.

Both the 200°C and 250°C samples display a large reduction in sheet resistance of almost five orders of magnitude between 0 and 180 min of annealing. The 200°C annealed sample shows a sharper decline in sheet resistance up to 180 min where it increases back to above the 250°C sample. This effect is nearly within the overlap of the error bars of these two sample sets, which suggests this low value is an outlier. The general trend of the 200°C and 250°C sample sets is of a sharp decline in sheet resistance followed by a steadier drop tending toward a maximum conductivity. This would be consistent with the loss of solubilizing side groups from the CNTs, as this loss of functional groups would be rapid at first, followed by a slower loss of material. The lowering of the rate of change in sheet resistance is also consistent with functional group loss as the groups that would survive for longer are likely to be bonded at more favorable bonding sites and so require more energy per bond to remove.

Despite the large improvement in the sheet resistance of CNT films by annealing, they still do not match the conductivity seen in pure indium tin oxide films.¹⁴ However, as shown in Fig. 1(a), they also have the advantage of being thinner films that are between 90 and 99% transparent. To provide a comparison with CNT samples, a 120-nm-thick film of indium tin oxide, ITO (Sigma-Aldrich; 703192) on a 1-mm-thick glass substrate was utilized. The ITO film shows consistently lower transparency than the ODA-CNT film across the entire optical range. There is also a steady decrease in the transparency of the ITO film in the lower wavelength ranges, which is not observed in CNT films. We note that with the use of isolated metallic CNT the conductivity could also be greatly improved by the reduction of contact resistance and the increase in the number of conduction pathways between the contacts.

Figure 3 shows TGA scans of a sample of ODA-CNT demonstrating both weight change and derivative weight loss with respect to temperature. The mass loss starts earlier than would be expected for nonfunctionalized CNT (typically around 500°C¹⁵) and has a small shoulder at 340°C. Further analysis of the derivative mass loss shows two main peaks, this suggests that there is an initial loss of material between 200°C and 340°C followed by a second loss from 340°C upward.

Fig. 3 TGA scan of amine functionalized CNT. The first peak of derivative weight loss (A) sits between 200°C and 340°C, close to the annealing temperatures of 200°C and 250°C suggesting the loss of functional groups. The mass loss then continues as expected¹⁵ for a functionalized CNT sample (B).

From the assay provided by the suppliers, the ODA-CNTs are known to contain 40% ODA by weight, which is equal to the weight loss within the bounds of the derivative weight peak. This agrees well with previous studies of ODA-CNT samples under heating.¹⁶ From this analysis of the TGA data, it can be inferred that the defunctionalization of CNT could be responsible for the loss of mass when ODA-CNTs were annealed within the temperature boundaries described above.

To better understand the chemical process of the loss of mass and decrease in sheet resistance, FTIR analysis was conducted for a series of samples annealed at 250°C. Figure 4(a) shows the measured spectra of these samples as a function of increasing anneal time. The general trend is for the reduction of peak height for all absorption peaks associated with the ODA functional group suggesting the loss of these functional groups from the ODA-CNT film. Figure 4(b) shows a normalized view of the characteristic amine carbonyl peak region.¹⁷ The amine NH bending peak seen in free ODA at 1585 cm^{-1} is vertically shifted to show several overlapping peaks in an unannealed ODA-CNT. There is also the addition of a small carbonyl C=O group stretch peak at 1651 cm^{-1} in the center of this overlapping region, which is associated with

Fig. 4 Baseline-corrected FTIR analysis of pure ODA compared with ODA-CNT films annealed for times between 0 and 240 min at 250°C. Spectra are shifted vertically to allow better comparison of the data. (a) The assignment of peaks for ODA in comparison with increasing annealing time. (b) Normalized view of the amine and carbonyl peak region showing the narrowing of the 1585 cm^{-1} (NH) peak and the reduction of the 1651 cm^{-1} (C=O) peak, which suggest a change in the bonding around the nitrogen and oxygen bonds.

the bonding of the ODA molecule to the CNT by an acid functionalization. The small changes observed in the C=O stretch (reduction in peak intensity) and NH bend (narrowing of peak width) peaks between different annealing times suggest that the CN bond is the site of the defunctionalization process, as the defunctionalization process reduces the amount of deformation in amine and carbonyl bonds.

The FTIR data suggest that there is bond breaking around the first CN bond in the functional group. This would leave the double-bonded carboxylic functionalization with a free bond at the defect site. This is a situation similar to that suggested in the disproportionation with carbon monoxide defect healing method¹¹ and so could lead to the healing of defects along the CNT.

To establish whether the CNT wall structure is improved by the annealing process, a Raman analysis was performed. In Raman spectroscopy of CNTs, the defect concentration in a particular sample can be inferred from the D/G peak ratio.¹⁸ The G^+ and G^- peaks are due to hexagonally bonded carbon atoms in a CNT structure with a dependence on the diameter and chirality of tubes. Conversely, the D peak is produced by nonhexagonally bonded carbon atoms and so gives a representation of the amount of non-CNT carbon in the sample.

The samples were analyzed with the use of Raman spectroscopy and the results are shown in Fig. 5. The change in D/G peak ratio was negligible between 0 and 120 min anneal at 250°C with all ratios sitting at 0.13 ± 0.01 . However, the samples display a sudden drop in D/G peak ratio to 0.07 ± 0.01 between 120 and 180 min. This is in line with a defect healing effect occurring between 2 and 3 h of annealing. This result fits well with the decrease in sheet resistance shown in Fig. 2 and the trend of changing FTIR peaks seen in Fig. 4.

The combination of data from the FTIR and Raman spectroscopy analysis shows that there is a removal of functional groups and defect healing as a consequence of sample heating in a nitrogen atmosphere. This explanation offers a possible picture of the chemistry along the ODA-CNT that is shown schematically in Fig. 6. This process predicts the loss of ODA groups by cleaving at the carbon-nitrogen bond leaving a carboxyl group on the nanotube surface. These carboxyl groups could then heal vacancy defects on the tube structure by the carbon monoxide disproportionation process detailed elsewhere.¹¹

Defunctionalization and defect healing processes such as the one described in Fig. 6 is normally performed at elevated temperatures ($>1000^\circ\text{C}$ ¹⁵) or pressures (2 MPa⁹). These parameters make it challenging to combine the use of defunctionalization methods with modern large area deposition techniques such as printed electronics. As such, the evidence of a defunctionalization and defect healing process displayed here at 200°C to 250°C and atmospheric pressure brings the solution-based, large area processing of ODA-CNTs on various temperature sensitive substrates, such as plastics, into the realm of possibility.

Fig. 5 Raman spectra of 250°C annealed samples for times between 0 and 240 min. (a) The D/G ratio sharply drops between 120 and 180 min annealing time suggesting an improvement in the graphitic structure of the CNT walls. (b) There is also a strong G^- shoulder which suggests the presence of semiconducting CNTs.¹⁸

Fig. 6 The carbon monoxide disproportionation defect healing process applied to ODA-CNTs. Atom colors: gray = carbon; red = oxygen; blue = nitrogen.

4 Conclusions

This paper has shown the evidence for a simple anneal process that improves the conduction properties of solution processed functionalized SWCNT layers by up to five orders of magnitude. We have suggested that the loss of functional groups as shown by TGA analysis leads to a drop in the sheet resistance of the CNT thin films. This effect is followed by a further improvement from defect healing along the tube axis, as shown by FTIR and Raman spectroscopy. The sheet resistance of annealed films is still high in comparison with theoretical values for metallic SWCNT; this is most likely due to the use of a mixed sample of metallic and semiconducting tubes for this research. The inclusion of semiconducting CNT in a layer has been shown to increase the resistance at the contact interface and so noticeably decreases the conductivity of the sample. If metallic SWCNT were isolated and functionalized with amide groups, then the thin film sheet resistance could potentially be reduced even further.

This method of low temperature annealing opens the way for in situ defect healing on CNTs, which would make it ideal as a part of printed electronic processes for transparent conductors deposition for energy harvesting applications, such as photovoltaics. In a roll to roll printing system, the anneal process could potentially be performed at a step after deposition. The substrate could be passed through a rapid heating system such as a laser sintering module, which could potentially dramatically speed up the defunctionalization process. This would allow for a quick and low-cost system for depositing electrodes, which have a transparency higher than that of ITO and (with isolated metallic CNT) also a comparable conductivity. These properties would be most desirable for photovoltaic and flexible display applications.

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