Self-assembly of carbon nanotube films from room temperature ionic liquids

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ARTICLE INFO

ABSTRACT

A novel method for the assembly of thin, uniform transparent and conductive films of single-walled carbon nanotubes (SWCNTs) on glass substrates is described. This process involves the initial transfer of a temporary suspension of SWCNTs in room temperature ionic liquid to the surface of water and the subsequent transfer of the SWCNT film onto a glass substrate. The average sheet resistance of the films was determined by four point probe measurements to be 1.52 and 4.13 kΩ/sq, with an average optical transparency of 50% and 63%, respectively.

1. Introduction

Solution phase processing of carbon nanotubes has long been of interest to many researchers in various fields. There are significant challenges to suspending or dispersing and then depositing single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs), due to the strong van der Waals interactions of carbon nanotubes (CNTs) and a mismatch of their surface energy with most common solvents. The chemical functionalization of CNTs and the use of surfactants have been successfully used in creating useful CNT "inks" [1–5], but an ideal deposition of CNTs from solution should not require their chemical modification or the use of surfactant additives requiring subsequent removal. Numerous techniques exist for the deposition of CNT films including spraying [6], filtration and transfer [7], and Langmuir–Blodgett films [8]. Perhaps the most commonly used method is deposition from a spray nozzle such as an airbrush [6]. Moderately stable solutions of CNTs in organic solvents are typically employed for such applications, leaving little to no residual additives. The drawback of this method is that coverage of a surface with such a spray is inherently variable, requiring a great number of passes/layers to obtain a continuous film. Since these films have uniformity issues, thicker films must be deposited to obtain suitable film characteristics. This can pose a significant hurdle in preparing CNT films having the desirable characteristics of both high transparency and high conductivity.

The current study presents a facile deposition method from a water miscible, room temperature ionic liquid (RTIL)

solution of SWCNTs. The RTIL solvent is removed with water, forming a surface-film of SWCNTs on water that can be easily transferred to a variety of substrates.

2. Experimental section

2.1. Carbon nanotubes

Two forms of Elicarb brand SWCNTs (Swan Chemical, Lyndhurst, NJ, USA) were evaluated, a standard dry powder and also a 'wet cake' material that is approximately 90 wt.% water. The wet cake SWCNTs are produced by the same chemical vapor deposition (CVD) method as the dry SWCNTs, but after the purification steps the manufacturer does not dry the final SWCNT material. This prevents some of the bundling of the SWCNTs seen in the dry material.

2.2. Dispersion in room temperature ionic liquid

Shear mixing of SWCNTs in RTIL was achieved with a Cole Parmer Lab GEN7 set to 33,000 rpm for 2 h. The RTIL used in these experiments was 1-ethyl-3-methylimidazolium acetate or [EMIM][Ac] (97%, Aldrich, Milwaukee, WI, USA).

2.3. Optical characterization

2.3.1. UV–Vis
Transparency measurements of SWCNT films on glass were carried out with a Varian Cary 6000i UV–Vis spectrophotometer, over a spectral range of 375–750 nm. The background was collected with a blank glass slide in the sample chamber. Several runs were carried out to assure repeatability.

2.3.2. Raman
Raman spectroscopy was performed with SWCNT materials before and after processing and film deposition using a Renishaw Ramascope and a 785 nm laser source.

2.4. Electrical characterization

Resistance measurements were carried out in ambient conditions with a four point probe device. The probe spacing was 1.27 mm and the geometric correction factor used was 4.54. Resistance values are reported in Ohms (Ω) per square (sq), or Ω/sq. This common unit is exclusively used to express sheet resistance, and helps to differentiate sheet resistance from bulk resistance.

2.5. Scanning electron microscopy

Field emission scanning electron microscopy (FE-SEM) was performed to study the SWCNT films on the surface of glass substrates with a JEOL JSM-6332 FE-SEM (Tachikawa, Tokyo, Japan) equipped with a secondary electron detector at an accelerating voltage of 10 kV.

2.6. X-ray photoelectron spectroscopy

Analysis of the surface chemistry of the wet cake SWCNT material before and after processing and film deposition was performed with a Phi Versaprobe under UHV (ca. 10^{-10} - Torr). The results were interpreted with AAnalyzer Software (Version 1.0).

3. Results and discussion

One of the key challenges in preparing stable CNT dispersions in RTILs are difficulties in the physical mixing of these materials. RTILs are typically quite viscous (approx. 30–450 cP at 300 K) and, thus, require substantial agitation to mix. This high viscosity does however allow for the RTILs to have potential to disperse CNTs and at least temporarily reduce the bundling and agglomeration inherent to this class of materials. Sonication at power sufficiently low, so as not to impact CNT structure, requires extremely long periods of time to obtain even non-uniform RTIL dispersions of CNTs. Mechanical grinding of the materials in a traditional mortar and pestle affords moderate dispersions after 20 min, but this method also results in breakage of the CNTs and typically falls short of creating true CNT–RTIL dispersions. Mechanical grinding, favored by many researchers [9–11], often results in non-uniform dispersions containing large agglomerates of undispersed CNTs.

In the current study, shear mixing is used to obtain the uniform temporary CNT dispersions in RTIL required for forming superior films. Once a dispersion of SWCNTs in RTIL has been obtained by shear mixing, the formation of thin uniform films on a variety of substrates is relatively straightforward. Several milliliters of the SWCNT–RTIL dispersion are loaded as a 1–3 mm wide bead onto the edge of a glass slide. The glass slide is then slowly lowered into a vessel of water at approximately a 45° angle relative to the surface of the water, stopping as soon as the bead of SWCNT–RTIL dispersion has contacted the water. A film forms on the water surface very quickly, extending away from the edge of the glass slide covering approximately 15 × 30 mm area on the water's surface within a few seconds. The film is allowed to float on the surface of the water for several minutes as the remaining RTIL is extracted from the surface film into the water by diffusion. In fact these films could not be immediately removed intact, requiring several minutes for the films to set and develop sufficient cohesion to be removed intact onto clean glass substrate (Fig. 1).

An inline, four-probe resistance measurement determined the film sheet resistance (average of 5 measurements) to be 1.52 kΩ/sq for the dry SWCNT film (optical transparency of 51% at 550 nm), and 4.13 kΩ/sq for the wet cake SWCNT film (optical transparency of 63% at 550 nm) (Fig. 2). This is a significant improvement on previously reported values for spray deposited CVD SWCNTs, which were approximately 3.25 and 5.00 kΩ/sq for 51% and 63% transparency, respectively [12].

The wet cake SWCNTs produced superior films in regards to transparency, owing to the reduced bundling of the starting material relative to the dry SWCNTs. The increased sheet resistance associated with the improvement in transparency is expected, and is due to the reduced number of conductive pathways (i.e., SWCNTs) present in the film. The conductive networks of SWCNTs in these films are composed of SWCNTs randomly arranged and in contact with one another. The conduction occurs via percolation, and the resistance is a
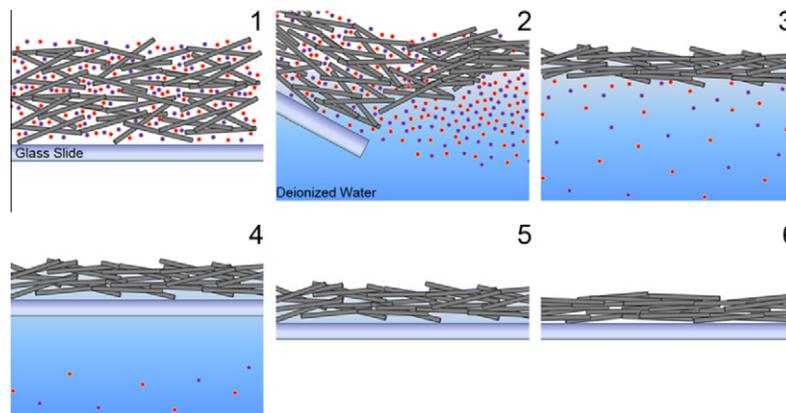
Fig. 1 – Schematic of film formation. Carbon nanotubes are represented by grey rods, RTIL by red and purple circles. (1) SWCNT in RTIL dispersion as a bead on the edge of a glass slide is (2) added at angle of approximately 45° to deionized water rapidly forming a SWCNT film on the water's surface, (3) the RTIL is extracted from the film into the bulk water over the course of several minutes. The cured surface-bound film is (4) collected on clean glass substrate and (5–6) allowed to dry *in vacuo* at 60 °C.
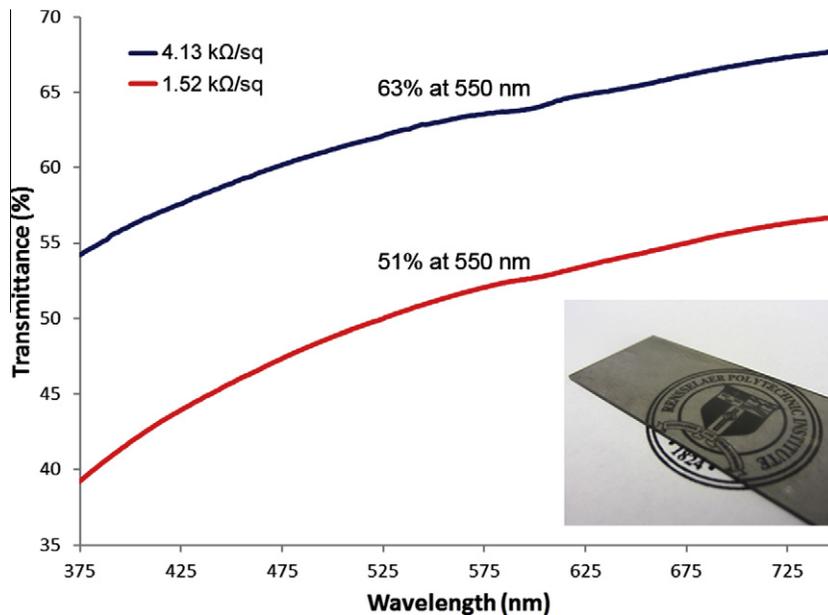

Fig. 2 – Spectrophotometric analysis of SWCNT film transparency, showing between 40–60% transmittance over the visible range. Photograph of SWCNT film on glass microscope slide formed by deposition from RTIL, shown inset.

function of both the number of tube–tube contacts and the number of conduction pathways. Conductivity of these films can be improved by delivering the longest SWCNTs possible to the surface of the glass (or other substrate), and increasing the number of SWCNTs. Increasing the density of such films improves the conductivity but also reduces transparency.

Field-emission scanning electron microscopy confirmed the higher uniformity of the films produced by this shear mixing method that was apparent to the unaided eye. The non-uniformity of the film prepared with mechanically ground dry SWCNTs–RTIL mixture shows large agglomerates seen at low magnification (Fig. 3A). The films studied appeared increasingly similar at higher magnifications, although the network of SWCNTs is better distributed in the shear mixed samples (Fig. 3B and C). The wet cake SWCNTs produced

the most distributed and uniform films, resulting in the highest optical transparency.

Inhomogeneity can be observed in all three samples, with considerably less in the shear mixed samples. Increasing the shear mixing time from 1 to 2 h resulted in an improved homogeneity, and it is assumed that further increasing the shear mixing time will continue to improve the homogeneity of these films. It should be noted that increased shear mixing times may result in shortening of the SWCNTs and this would in turn result in higher sheet resistance values.

Raman spectroscopy was used to evaluate the effect of the prolonged shear mixing on the SWCNT structure. The most prominent peak in the spectra (Fig. 4) is found about 1590 cm^{-1}, which is the so-called G-peak that corresponds to the ordered graphitic lattice of the SWCNTs [13]. There is
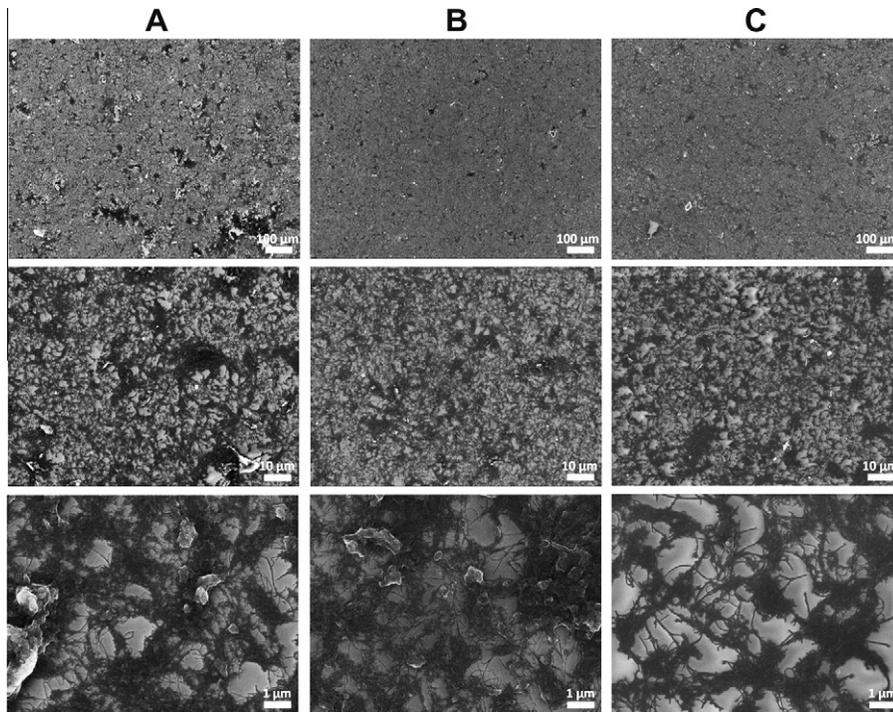
Fig. 3 – Electron micrograph at various magnifications of films formed from dispersions of mechanically ground (A) dry SWCNTs and shear mixed (B) dry SWCNTs and (C) wet cake SWCNTs in RTIL.

also a neighboring peak at about 1300 cm^{-1} for the wet cake SWCNTs and at 1350 cm^{-1} for the dry SWCNTs, known as the D-peak, which corresponds to disorder in the graphitic lattice of the SWCNTs. The ratio of these two peaks is commonly used to assess the relative level of damage to CNTs. This G/D ratio decreased from 3.06 to 2.24 for dry SWCNTs and from 5.62 to 2.09 for wet cake SWCNTs after 2 h of shear mixing. This represents an increase in disorder of approxi-

mately 40% for the dry SWCNTs and 170% for the wet cake SWCNTs.

Despite the fact that the wet cake SWCNTs exhibited a significantly larger decrease in the G/D ratio, both films showed a similar G/D ratio. The difference in this change between dry and wet cake SWCNTs may be caused by the larger number of agglomerations in the dry SWCNTs protecting the SWCNTs within them from the shear forces in the RTIL solution. The
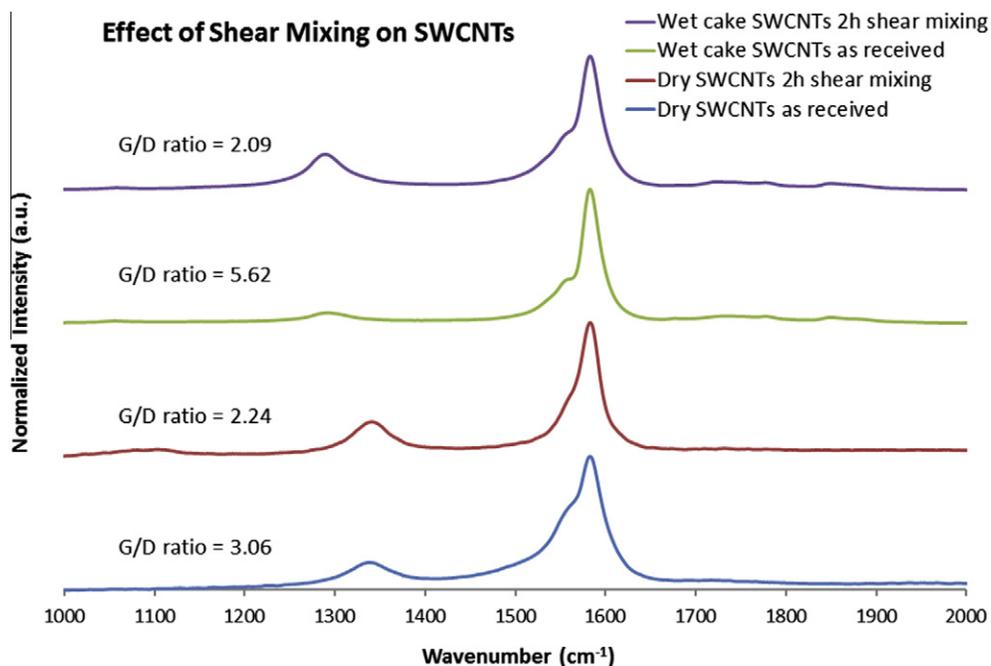

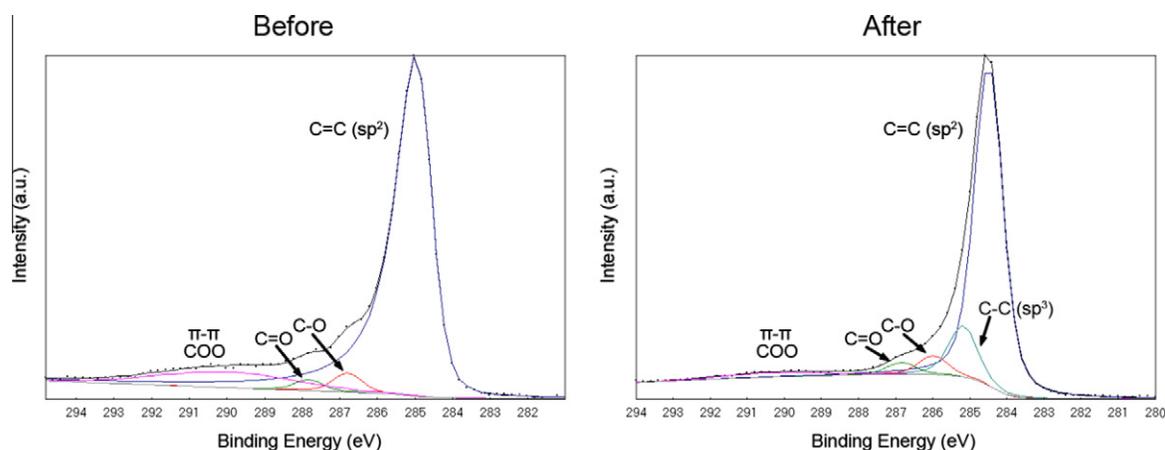**Fig. 4 – Raman spectra of SWCNT as-received (lower) and after 2 h shear mixing in RTIL (upper).**

Fig. 5 – XPS spectra of wet cake SWCNTs before and after 2 h shear mixing. Peaks for C=C sp² bonding (284.8 eV), C–O bonding (286.5–286.7 eV), C=O bonding (287.3–287.9 eV), O–C=O bonding and π–π interaction (289.9–290 eV) are observed in both samples. A peak for C–C sp³ bonding (285.7 eV) was only observed after the 2 h shear mixing.

radial breathing mode (RBM) was not observed for the SWCNTs due to the fact that the average diameter was determined by the manufacturer to be approximately 2 nm. The RBM is typically only observable for SWCNTs with diameters less than 2 nm [13].

X-ray photoelectron spectroscopy (XPS) was performed to evaluate changes in the surface chemistry of the SWCNTs as a result of the shear mixing in RTIL. Fig. 5 shows that the surface chemistry of the SWCNTs essentially remains the same before and after shear mixing except for the appearance of a significant peak at 285.7 eV. This peak corresponds to sp³-hybridized carbon–carbon single bonds, and is the result of bond breaking during the shear mixing. This agrees with the Raman data (Fig. 4), which shows a greater degree of disorder after shear mixing. The broad peak centered about 290 eV is attributed to both carboxylic functionalities on the SWCNTs and π–π interactions. The apparent reduction in this peak after shear mixing and film deposition suggest de-bundling of the SWCNTs relative to the as-received sample. It is possible that the imidazolium component of the RTIL is able to interfere with the π–π interaction of SWCNTs and that this partially explains the mechanism of dispersion.

4. Conclusions

The shear mixing SWCNTs in RTIL for the formation of thin films of CNTs holds great promise for application in high-throughput roll to roll manufacturing of transparent conductive materials. Films of CVD synthesized SWCNTs with average optical transparencies of 50% and 63% were obtained with sheet resistance values of 1.52 and 4.13 kΩ/sq respectively. Surface chemistry characterization with XPS and Raman spectroscopy showed a relatively small amount of damage to the SWCNT structure during processing. Further optimization of this process is currently underway and will be extended to a variety of potential RTILs and CNTs to afford a broad knowledgebase to enable a multiplicity of manufacturing needs.

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