Doping and de-doping of carbon nanotube transparent conducting films by dispersant and chemical treatment

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Single-walled carbon nanotubes (SWCNTs) dispersed with Nafion in a solvent mixture containing de-ionized water and 1-propanol (bisolvent) were sprayed on a poly(ethylene terephthalate) substrate to fabricate flexible transparent conducting films (TCFs). Different SWCNT-to-Nafion ratios were used to optimize the film performance of transparency and sheet resistance. The TCFs were then immersed in nitric acid. These steps resulted in p-type doping due to the presence of Nafion in the SWCNT network and de-doping (removal of doping effect) by the acid treatment. X-Ray photoelectron and Raman spectroscopy confirmed that the de-doping effect occurred with the partial removal of Nafion from the nanotube surface by the nitric acid treatment, which improved the film conductivity by a factor of ~4 with negligible change in transmittance.

Introduction

Carbon nanotube (CNT)-based flexible transparent conducting films (TCFs) have attracted considerable interest with the development of wearable displays in modern technology. The superb electrical conductivity, high elasticity and flexibility of CNTs, have allowed the CNT films to be applied as electrodes in wearable displays. Despite a considerable effort to improve the conductivity and transmittance of CNT films, the film performance strongly relies on the preparation of the film, the dispersion conditions, and the quality of the CNT types. Therefore, the reported results show considerable variations. Single-walled CNTs (SWCNTs) are mostly found in bundles as a result of van der Waals interactions that originate from SWCNTs of a few tens of micrometres in length. Therefore the SWCNTs show poor dispersibility in various solvents. This has been a bottleneck from scientific and technological points of view. One routine approach for fabricating TCFs with SWCNTs is to disperse the SWCNTs with sodium dodecyl sulfate (SDS) or sodium dodecylbenzene sulfonate as a dispersant, which can be used for solution casting through a variety of methods. Although this method can achieve nanodispersion to some extent, a loss of most of the SWCNTs during centrifugation to remove the large bundled SWCNTs is a major hindrance to their practical use in TCFs. Dispersants, such as designed thiophenones by 3-hexylthiophene, have been introduced to improve the dispersion of nanotubes. Although thiophene is a conducting polymer, the dispersants remaining on the CNT film still degrade the film performance but do achieve the nanodispersion without loss. It has been also suggested that a post-treatment of CNT bucky paper with acidic solution can improve the conductivity. The conductivity of the CNT–TCFs has been also improved by a SOCl2 treatment and acid treatment. Nevertheless, the underlying mechanism of these post-treatments and the effect on the film conductivity are still unclear.

Nafion is known to be a good electrolyte for ions. It is an ambipolar dispersant consisting of hydrophilic sulfonic acid-terminated perfluorovinyl ether pendants that are spaced regularly along the hydrophobic perfluoroalkyl backbone. Nafion is a highly stable dispersant for SWCNTs that are well dispersed in a bisolvent containing water and 1-propanol. In this report, Nafion was used as a dispersant of SWCNTs. TCFs were fabricated using Nafion-dispersed SWCNTs. The mixing ratio (1:1) of the SWCNTs to Nafion was optimized to achieve a sheet resistance of 400 Ω sq⁻¹ with a transmittance of 85% at 550 nm. Further post-treatment of these TCFs using a simple acid treatment enhanced the conductivity of the film by a factor of 3 ~ 4 with negligible change in transmittance. This enhanced conductivity was examined by X-ray photoelectron spectroscopy (XPS). The shift of the XPS C1s peak toward the lower binding energy indicated strong charge transfer from the SWCNTs to Nafion during the dispersion, i.e., p-type doping. On the other hand, this peak shift was partially recovered by the nitric acid treatment, i.e., a de-doping effect. The effects of the de-doping and the subsequent doping by chemical functionalization were confirmed by Raman spectroscopy. The typical film yielded a sheet resistance of 100 Ω sq⁻¹ at a transmittance of 80%. These films are expected to have a wide range of applications.

Experimental

Highly purified arc discharge SWCNTs (purity 96 wt %) were purchased from Iljin Nanotech Co., Ltd. Nafion was purchased...
from Aldrich as a 5 wt% solution in a mixture of lower aliphatic alcohols and 45 wt% water. The bisolvent was obtained by mixing 70 wt% de-ionized water and 30 wt% 1-propanol. This ratio provides better dispersion conditions for SWCNTs. To prepare the SWCNT solution, first, Nafion solution was dispersed in the bisolvent. The SWCNT powder was then added to the Nafion-dissolved bisolvent with different mixing ratios of SWCNTs to Nafion ranging from 1:10 to 1:0.5. The solution was ultrasonicated in a bath type ultrasonicator (Power sonic 505) at 400 W for 10 hours and further centrifuged at 10,000 g for 10 minutes in a centrifuge (MEGA 17R). The supernatant solution was decanted carefully for characterization. The absorbance of the SWCNT supernatant was recorded using an UV-Vis-NIR spectrophotometer (Varian Cary-5000). The SWCNT supernatant was sprayed directly onto the poly(ethylene terephthalate) (PET) substrate with an air brush pistol (GUNPIECE GP-1) to form the TCFs. During the spray process, the PET substrate was kept on the sample holder at 100 °C to accelerate the evaporation of the fine droplets on the surface. The CNT film was further immersed in acidic solution for some time and rinsed in de-ionized water. Nitric and sulfuric acids (12 M) were used separately for the test. The transmittance was reduced on a logarithmic scale, as expected from Beer's law. The inset in Fig. 1a shows the conductivity increased rapidly at low thickness and became saturated at approximately 60 nm, again demonstrating the strong dependence on the film thickness. The sheet resistance at a point of each curve, which is the closest point as a function of the mixing ratio.

Results and discussion

The degree of dispersion of the SWCNTs with Nafion was illustrated in the absorption spectra (Fig. 1a). The absorbance increased with increasing Nafion content at a given SWCNT concentration. The SWCNTs were dispersed better with a higher Nafion content so that more SWCNTs remained in the supernatant during centrifugation, and as a consequence the absorbance by the CNTs was increased. The degree of dispersion and the bundle size can be seen from FE-SEM images (Fig. 1b–d). The size distribution of the SWCNT bundles was quite uniform in case of a mixing ratio of 1:2 (Fig. 1b), which suggests that the SWCNTs were well dispersed in the Nafion matrix, even though the bundle size of the SWCNTs appeared to be enlarged due to the wrapping by Nafion. The wrapping of Nafion was realized by the hydrophobic tail interaction, as shown in the inset of Fig. 1a. The hydrophilic head groups of SO₃⁻, which are stretched outward, solubilized the SWCNTs well in water. The bundle size increased with decreasing Nafion content and their distribution was not uniform (Fig. 1c and d), even though most of the large bundles were precipitated during centrifugation.

Various amounts of the CNT solution were sprayed on the PET film to obtain TCFs with different thickness by varying the number of spray times. Fig. 2a shows the sheet resistance and transmittance as a function of the CNT film thickness, which was measured by AFM at the step edge and visualized in the line profile in Fig. 2b. Some of the SWCNTs were protruded at the step edge, after the removal of the shadow mask. The film roughness was approximately 10 nm, which is slightly larger than that (3 nm) of the indium tin oxide (ITO) film. The sheet resistance decreased with increasing film thickness. The sheet resistance was fitted well by the formula, $R_s = a(x - x_0)$, where $a$ is 12,000 $\Omega \cdot \text{sq}^{-1}$ and $x$ is the film thickness with $x_0 = 6.5$ nm. Here, $x_0$ can be regarded as the critical layer thickness for the percolation limit. On the other hand, the transmittance was reduced on a logarithmic scale, as expected from Beer’s law. The inset in Fig. 2a shows that the conductivity increased rapidly at low thickness and became saturated at approximately 60 nm, again demonstrating the strong dependence on the film thickness. The sheet resistance at a point of each curve, which is the...
closest point from an ideal condition (100% transmittance and zero resistance in Fig. 2c), decreased with increasing mixing ratio and increased slightly at a higher mixing ratio, as shown in Fig. 2d. As explained in the previous paragraph, the higher composition of Nafion improved the better dispersion of SWCNTs. Nevertheless, Nafion has a higher resistance than CNTs despite its conducting nature. The remaining Nafion in the film increases the contact resistance between the SWCNT networks. Too low Nafion composition yields a poor dispersion of the SWCNTs and high light absorption of the film from the large size bundles. On the other hand, high Nafion content improves the dispersion of CNTs and gives high film transmittance but the remaining Nafion content results in the increase of the sheet resistance. A SWCNT–Nafion mixing ratio of 1 : 1 was found to be an optimum for the minimum sheet resistance and maximum transmittance.

The TCF samples were further immersed in acidic solution to modify the film performance. Fig. 3a shows the sheet resistance as a function of transmittance before and after the nitric acid treatment for the SWCNT–Nafion mixing ratio of 1 : 2 and 1 : 1, respectively. The sheet resistance was reduced significantly, independently of the film thickness, while the change in transmittance was negligible after treatment, as shown in Fig. 3b with an optical image inset. For example, the acid-treated film with a 1 : 1 ratio yielded a sheet resistance of 100 Ω sq⁻¹ at a transmittance of 80%, which is competitive with conventional ITO films. It should be noted that the resistance decreased more significantly at a mixing ratio of 1 : 2 than at 1 : 1. This is related to the removal of more Nafion by the acid treatment, which will be discussed later. The resistance was reduced in a relatively short time, as shown in Fig. 3c. A longer treatment increased the resistance slightly. This might be due to defects developed on the SWCNT walls. The FE-SEM images showed that the roughness was not altered significantly but some of the Nafion aggregates had been removed by the acid treatment (Fig. 3d–e). Some protruded SWCNTs fell onto the film surface to reduce the roughness of the film. The film was stable in air without significant changes in conductivity (Fig. 3f). The film also showed strong adhesion to the PET substrate, and passed the tape test procedure (DIN 58196-K2).

The effect of the acid treatment was analyzed by XPS. The main C1s peak of the pristine SWCNTs after the pre-heat treatment at 200 °C appeared at 284.5 eV, which was identified as sp² carbon, with a side peak near 285.4 eV for sp³ carbon (Fig. 4a). The broad band at the higher binding energies, between 287.0 and 292 eV, corresponds to oxygen-related groups and a π–π* band.28–30 For the Nafion-dispersed SWCNT film, the main peak position was downshifted by 0.5 eV. A new peak at 291.3 eV was attributed to a carbon–fluorine species (F1s peak was observed at 689 eV, data not shown here) originating from Nafion.31 This downshift was related to a shift in the Fermi level originating from charge transfer from the adsorbates. The CF₂ group is an electron-acceptor, inducing p-type doping by depleting electrons from the SWCNT networks.32 The main C1s peak was not altered significantly by the sulfuric acid treatment. On the other hand, for the nitric acid-treated film, the main C1s peak was shifted back toward that of the pristine sample. This is in contrast to the previous report, which showed that a nitric acid-treatment of bucky paper caused a 0.2 eV downshift in the C1s peak.33 The presence of ambient oxygen on the SWCNT walls was identified by the O1s peak even in the pristine sample shown in Fig. 4b. In the case of the SWCNT–Nafion film, a CF–O–CF₂-related peak appeared near 535.2 eV.32 With the sulfuric acid treatment, the SO₂-related peak near 532.3 eV was increased slightly, indicating an additive effect of sulfur from the sulfuric acid. With the nitric acid treatment, the SO₂ and CF-related peak intensities were reduced, as shown in Fig. 4b and d. This
result was corroborated by the slight decrease in the sulfuric and fluorine atomic concentration (Table 1). Instead, more nitrogen atoms involving NO, NC, and NH groups near 398–403 eV and the NO$_3^-$ group near 406 eV (Fig. 4c) had developed with increasing acid-treatment time. This suggested a de-doping process$^{33}$ as a result of nitric acid treatment, where the Fermi level of the SWCNTs shifted back toward that of the pristine SWCNTs. This de-doping effect was realized by the partial removal of Nafion from the SWCNT surface, as indicated in Fig. 4b and d.

Charge transfer was confirmed by Raman spectroscopy. The typical Raman spectrum shows low frequency radial breathing mode (RBM), D-band, and high frequency tangential G-band.$^{34}$ The G-band in SWCNTs shifts substantially to lower frequencies (red shift) for electron-donor dopants (potassium and rubidium) and to higher frequencies (blue shift) for electron-acceptor (bromine) dopants.$^{35}$ These shifts provide evidence for charge transfer between the dopants and nanotubes. At a laser excitation energy of 514 nm (2.41 eV), the RBM showed a semiconducting peak (E$_{33}$) at approximately 180 cm$^{-1}$ in the pristine powder (Fig. 5a). With the SWCNT–Nafion film, the RBM peak was slightly depressed. The G-band was blueshifted by 3.0 cm$^{-1}$ due to functional groups from the adsorbed Nafion on the SWCNT walls. With one hour of sulfuric acid treatment, the G-band was blueshifted and the RBM intensity was depressed. In the case of one hour of nitric acid treatment, the G-band was blueshifted further and the RBM intensity was further suppressed.$^{36}$ This indicates that nitric acid is more effective in promoting charge transfer than sulfuric acid.

After 12 hours nitric acid treatment, the G-band was further blue-shifted to 1596 cm$^{-1}$. Since this shift is substantial, a deviation of the resonant condition is likely to have occurred, which suppresses the RBM intensity, as shown in Fig. 5a. Similar trends were observed at a laser excitation of 633 nm (1.96 eV) (Fig. 5b). In this case, the RBM exclusively shows the metallic SWCNTs near 170 cm$^{-1}$ (E$_{11}$). One intriguing difference in this case is that the Breit–Wigner–Fano (BWF) line representing the metalliclicity of SWCNTs$^{37}$ was greatly suppressed by Nafion. With further acid treatment, the change in the BWF line was negligible but the G-band was blueshifted in a similar manner to that observed at 514 nm. These blueshifts in the G-band simply indicate charge transfer from the SWCNTs to the adsorbates.

The effect of doping/de-doping and charge transfer has been discussed by XPS and Raman spectroscopy. Table 2 summarizes the peak shifts in the XPS and Raman spectra in comparison with other reports. The pristine arc discharge SWCNTs were taken as a reference for comparison to measure the shift. The nitric acid treatment of the pristine SWCNTs yielded a downshift of 0.5 eV in the C1s of XPS spectrum (Fig. 6a) and a blueshift of 17 cm$^{-1}$ in the G-band due to the presence of functional groups on the SWCNT walls (Fig. 6b). In case of the SWCNT–Nafion film, the shift in the C1s peak was similar to that of the nitric acid-treated pristine SWCNTs. The de-doping effect by the partial removal of Nafion should cause a G-band redshift towards the pristine SWCNTs in the Raman spectra. Because the G-band in the SWCNT–Nafion film reveals a much smaller shift (3.6 cm$^{-1}$) than the 17 cm$^{-1}$ in the acid-treated pristine SWCNTs, the total effect was still blueshifted. There was no significant change in the C1s peak for the sulfuric acid treatment, which concurs with the small G-band shift in the Raman spectra. The number of fluorine atoms in Nafion was reduced by 2 at.% and the nitrogen content was increased by 0.6 at.% by one hour of nitric acid treatment, while the sulfur level had decreased to 0.69 at.% from 0.95 at % (Table 1). The G-band was blueshifted.

Table 1 Atomic concentration (at. %) of the SWCNT–Nafion samples

<table>
<thead>
<tr>
<th>Treatment method</th>
<th>C1s</th>
<th>N1s</th>
<th>O1s</th>
<th>F1s</th>
<th>S2p</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWCNT–Nafion(1 : 1)</td>
<td>49.12</td>
<td>0.0</td>
<td>7.48</td>
<td>42.45</td>
<td>0.95</td>
</tr>
<tr>
<td>H$_2$SO$_4$ treatment 1 h</td>
<td>49.24</td>
<td>0.0</td>
<td>7.93</td>
<td>41.82</td>
<td>1.00</td>
</tr>
<tr>
<td>HNO$_3$ treatment 1 h</td>
<td>50.53</td>
<td>0.63</td>
<td>7.81</td>
<td>40.34</td>
<td>0.69</td>
</tr>
</tbody>
</table>

Table 2 Comparison of the XPS C1s and Raman G-peak shift

<table>
<thead>
<tr>
<th>Sample and treatment method</th>
<th>XPS C1s shift</th>
<th>Raman G-peak shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine arc SWCNT$^a$</td>
<td>(633 nm)</td>
<td>—0.5 eV +17 cm$^{-1}$</td>
</tr>
<tr>
<td>12 M HNO$_3$, 12 h</td>
<td>—0.5 eV +3.6 cm$^{-1}$</td>
<td>Our work</td>
</tr>
<tr>
<td>SWCNT/Nafion film</td>
<td>—0.5 eV +5.4 cm$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>As prepared film</td>
<td>—0.5 eV +8.0 cm$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>12 M H$_2$SO$_4$, 1 h</td>
<td>—0.4 eV +9.8 cm$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>12 M HNO$_3$, 12 h</td>
<td>—0.2 eV (514 nm)</td>
<td>+24 cm$^{-1}$</td>
</tr>
<tr>
<td>Laser SWCNT bundles</td>
<td>—0.2 eV —39 cm$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Br$_2$ doping</td>
<td>—0.2 eV +9.8 cm$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>K doping</td>
<td>—0.2 eV +9.8 cm$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Laser SWCNT paper</td>
<td>—0.2 eV</td>
<td>Graupner et al.$^{32}$</td>
</tr>
<tr>
<td>4 M H$_2$SO$_4$, 20 min</td>
<td>—0.2 eV</td>
<td>+20 cm$^{-1}$</td>
</tr>
<tr>
<td>4 M HNO$_3$, 15 min</td>
<td>—0.2 eV</td>
<td>Dettlaff-Weglikowska et al.$^{24}$</td>
</tr>
<tr>
<td>SOCl$_2$, 24 h</td>
<td>—0.4 eV (633 nm)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Pristine Arc SWCNTs were taken as a reference to measure the shift in this study.
further compared with that observed after the sulfuric acid treatment. A longer nitric acid treatment intensified these changes. The effect of de-doping on the SWCNT–Nafion film by the nitric acid treatment is quite intriguing. In the case of metallic SWCNT–Nafion, the BWF line was suppressed considerably, whereas the G-band shape was unaffected in the case of the semiconducting SWCNTs. This is closely related to the selective reactivity of Nafion to metallic SWCNTs over the semiconducting ones, which is in agreement with the previous reports for oxidants.38,39 In metallic tubes, electrons near the Fermi level are extracted to the adsorbates (Nafion), leaving a pseudo-gap opening in the nanotubes. On the other hand, hole carriers are generated by extracting electrons at the valence band from adsorbates for semiconducting nanotubes.

The sheet resistance of the CNT network film is governed by the sum of the series resistance of the CNT itself (\( R_{\text{CNT}} \)), the junction resistance between the CNTs (\( R_{\text{jun}} \)), and the resistance of the Nafion layer between the CNTs (\( R_{\text{Naf}} \)): \( R_{\text{film}} = R_{\text{CNT}} + R_{\text{jun}} + R_{\text{Naf}} \) (Fig. 7). The junction resistance is dominated by the metallic CNT–Nafion–metallic CNT, metallic CNT–Nafion–semi-conducting CNT, and semi-conducting CNT–Nafion–semi-conducting CNT junctions.40,41 In the case of Nafion doping, the resistance of the semiconducting tubes was reduced by a p-type doping effect, whereas the resistance of the metallic tubes was increased by pseudo-gap opening. Furthermore, the sheet resistance of the film was also overwhelmed by the high resistance of Nafion between the nanotubes. The Nafion layer was partially removed by the acid treatment. This reduces the contact resistance between the CNT networks due to the highly resistive Nafion compared with the SWCNT networks. The removal of Nafion recovers the metallicity of the metallic tubes, whereas the resistance of the semiconducting tubes is changed through a de-doping effect. As a consequence, the built-in potential reduced, and the thermionic emission current increased,42,43 as indicated in Fig. 7. Together with a decrease in the Nafion layer, the sheet resistance decreased compared with the as-prepared Nafion doping CNT films.

Conclusions

A new method for enhancing the film performance of TCFs was introduced using SWCNTs dispersed with Nafion in a bisolvent of de-ionized water and 1-propanol. Several important features were found while optimizing the film conductance: i) The SWCNTs dispersed better with a larger Nafion content; ii) the optimal SWCNT–Nafion ratio to give the highest film conductivity was of 1 : 1; iii) a p-type doping effect was observed with Nafion but the remaining Nafion increased the surface resistance of the CNT film; iv) the nitric acid treatment partially removed the Nafion layer from the SWCNT network and minimized the contact resistance and the de-doping effect, and a shift back of the Fermi level was also observed; and v) this de-doping effect increased the conductivity by a factor of 3–4. The acid-treated SWCNT–Nafion film is not so sensitive to the environment and showed high adhesion to the PET substrate. This simple process for improving the conductivity of the TCFs with reproducibility and reliability is expected to be useful in industrial applications for touch screens and flexible displays.

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