CNT/conducting polymer composite conductors impart high flexibility to textile electroluminescent devices†

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Received 23rd August 2011, Accepted 4th November 2011
DOI: 10.1039/c1jm14121j

Highly transparent polyethylene terephthalate (PET) mesh fabrics were dip coated with carbon nanotubes (CNT) followed by inkjet printing with poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) to develop textile-based CNT/PEDOT:PSS composite conductors. These coated fabrics show a combination of conductivity, transparency and flexibility suitable for use in flexible displays. Sequential CNT and PEDOT:PSS coating greatly enhances the conductivity at high tensile strains without reducing the optical transparency. Electroluminescent (EL) devices using such textile-based CNT/PEDOT:PSS composite conductors as the front electrodes exhibit superior flexibility and mechanical robustness over their ITO-coated PET film-based counterparts under stretching and tight bending.

Introduction

The development of new flexible optoelectronics such as liquid crystal displays (LCDs) and organic light emitting diodes (OLEDs) has led to a rapidly growing market of flexible transparent conductors. Normally, a transparent conducting oxide such as indium tin oxide (ITO)-coated glass or polymer substrate is used as a transparent conductor for its excellent optical transparency (≥80% at 550 nm) and low resistivity (15–200 Ω sq−1). However, ITO is brittle and cracks easily under stress or bending, limiting its application in flexible electronics. In addition, the indium materials and the sputtering process for depositing ITO are expensive.

An ideal candidate conductor that simultaneously meets transparency, conductivity, and flexibility is still not available. Conductive polymers such as poly-3,4-ethylenedioxythiophene: polystyrenesulfonate (PEDOT:PSS) are attractive for their good transparency and flexibility. The post-treated PEDOT:PSS film has a surface resistivity around 470 Ω sq−1 (15 nm) and can withstand strains above ten percent. Transparent films made from CNT have a sheet resistivity of 200 Ω sq−1 (transmittance ≥80–85%) and show small resistance changes up to strains as high as 25%. Surface roughness remains a problem especially when nanotubes are perpendicular to the film surface. Coatings of dispersed silver and copper nanowires can achieve an optical transmittance of 85%, a sheet resistivity of 10 Ω sq−1, and outstanding robustness upon being bent down 100 times to 5 mm. However, the poor adhesion of nanowires to the substrate and surface roughness also limit their applications to devices. Graphene is a promising candidate for transparent conductors with a resistivity ≤350 Ω sq−1 at 90% transmittance and a tensile strain up to 6%. The poor surface adhesion of graphene to substrate is still a major concern.

It has been reported that the conductivity of a conductive polymer can be greatly enhanced when incorporated with CNT. Blanchet et al., for example, found that the conductivity of dinonyl naphthalene sulfonic acid doped polyaniline (DNNSA-PANI) was increased from 10−4 S cm−1 to 2 S cm−1 with 3% of CNT dispersed in the polymer. By adding 0.01 wt% CNT, Moo reduced surface resistivity of the PEDOT film from 1182 to 249 Ω sq−1. The surface resistivity of an inkjet printed PEDOT:PSS film can be reduced from ~10 to ~1 kΩ sq−1 by adding carboxyl functionalized CNT. Presumably, PEDOT:PSS leads to the conductive bridging of some nanotube junctions, forming a composite with low resistivity. The addition of PEDOT:PSS is also effective in reducing the surface roughness of CNT. Ou et al. showed that the morphology of rough CNT surfaces is dramatically smoothed by coating with PEDOT:PSS.

In previous work we described electroluminescent (EL) devices based on a transparent textile mesh coated with a conducting polymer. The fine openings of the mesh imparted transparency to the electrodes, while the polymer-coated fibers provided the conductivity. The EL devices could be bent easily without any cracking. In this paper we describe composite electrodes of carbon nanotubes and conducting polymers which provide a much higher extensibility, flexibility and lower surface resistivity.
Here we describe the improved performance achieved with CNT/PEDOT:PSS composite conductors on transparent PET mesh, when compared to simple conducting polymer coated mesh electrodes described in previous work. The nanotubes do contribute somewhat to the unstrained conductivity but increase the tolerance of tensile strain. By using a second CNT/PEDOT coated nylon fabric conductor as the back electrode, the functions of the devices have been greatly improved under tight bending.

Experimental

Materials

Most of the materials used in this study have been reported elsewhere. Briefly, a phosphor powder, which consists of ZnS: Cu,Cl, was mixed with an organic binder (Conductive Compounds, Hudson, NH) at a weight ratio of 1:1 to form the phosphor paste. The BaTiO3 power with a particle size smaller than 3 μm was used to mix with the same organic binder at a weight ratio of 1:1 to form the dielectric paste.

The carbon nanotubes (CNT) used in this study are a mixture of single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs) obtained from NanoLab (Newton, MA). The CNT are produced by chemical vapor deposition (CVD) and their surfaces are functionalized with carboxyl (–COOH) at 2–7 wt% by a sulfuric/nitric acid oxidation process.

A type of highly transparent polyethylene terephthalate (PET) open-mesh fabric (Fig. 1b) was selected as the substrate for preparing transparent textile conductors. Such a PET fabric has a high light transmittance due to a low coverage factor (the ratio of the area covered by the yarns to that of the whole area of the fabric), with 58.7% open area (Table 1), and retains its optical transmittance after dip coating with CNT (Fig. 1c) and further inkjet printing with PEDOT:PSS (Fig. 1d). A nylon taffeta fabric (Table 1) was subjected to the same dip coating and inkjet printing process to become an opaque nylon conductor, which was used as the back conductor for assembling EL devices.

CNT ink formulation and dip coating

The CNT ink was formulated by dispersing acid treated CNT in de-ionized (DI) water (0.01 mg mL−1) with sodium dodecyl benzene sulfonate (0.1 mg mL−1) (Sigma Aldrich, ~80%) as the surfactant. A well-dispersed CNT ink was formed (Fig. 1a) after 30 min ultrasonic agitation at 200 W (CPX 750, Cole Parmer Instruments, IL). The ink remained stable for 2 weeks without noticeable precipitation. Both the PET and nylon fabrics were unidirectionally dip coated with the CNT ink and then dried in an oven at 120 °C for 10 min to remove water. The dried fabrics were then inkjet printed with PEDOT:PSS.

PEDOT ink preparation and inkjet printing

Inkjet printing of PEDOT ink on fabrics was performed by following the same process reported earlier, only that all the fabric samples used in this study were inkjet printed with a fixed number of 8 cycles. After printing, the CNT/PEDOT film coated PET and nylon textile conductors were annealed in an oven at 75 °C for 1 h and ready for further testing or assembling EL devices.

EL device fabrication

Preparation of the devices was described previously. The PET mesh fabric was dip coated with CNT and/or PEDOT:PSS by inkjet printing. Dielectric and phosphor layers were deposited by a nozzle extrusion system (EFD Ultra 2800, Providence, RI) on one back electrode and the top electrode was pressed and clamped on top.

Characterization

The transmittance spectra of the PET mesh fabric and the PET textile conductors with dip coated CNT and/or inkjet printed PEDOT ink were obtained using an Ocean Optics HR 4000 spectrometer (Dunedin, FL). The surface resistivity of the textile conductors was measured using a four point probe method. Atomic force microscopy (AFM) (XE100, Park systems Inc, CA) was employed to study the surface morphology of PET fibers before and after coating with CNT and inkjet printing with PEDOT ink. Scanning electron microscope (SEM) imaging was conducted using a JEOL JSM 5610 system or a JEOL 6335F Field Emission SEM (FESEM). The EL devices were driven by a DC power supply (EXTECH 382200) together with a JKL NDL-217 EL inverter. The EL light emission intensity and luminance were measured by a fluorescence spectrometer (Ocean Optics, Dunedin, FL). Various mechanical tests were carried out using an Instron 5569 system for both conductors (the textile conductors and ITO conductors) and the EL devices (the textile conductor based device and the ITO based devices).

Results and discussion

Morphology of PET textile conductors

The mesh fabrics (Fig. 1b) become conductive after a simple dip coating of CNT and a drying process. The color of fabrics
changes from white to light black due to adhesion of CNT onto the surface of polyester fibers (Fig. 1c). The mesh fabrics change to deep blue color after inkjet printing the PEDOT ink (Fig. 1d).

Shown in Fig. 2a and b are the SEM images of PET mesh fabric before and after coating with CNT. Localized dark spots can be observed on the surface of monofilament fibers (Fig. 2b, two representative dark spots are indicated by the white arrows), representing locally distributed CNT agglomerates as a result of dip coating. Adhesion of CNT to the fiber surfaces has converted the PET mesh fabric into a conductive substrate (Table 3), presumably due to the conductive paths formed by these CNT agglomerates interconnected with each other. On the other hand, CNT coating only results in limited conductivity (218 kΩ sq⁻¹, Table 3). Fig. 2c shows the CNT coated PET mesh fabric after further inkjet printing with PEDOT ink. A thin and conformal PEDOT:PSS film forms and covers the CNT coated fibers uniformly. The PET mesh fabric retains its texture and structure after inkjet printing with the polymer and has the same feel as the original.

AFM scans (Fig. 2d–f) show that the CNT coating increases the surface roughness of PET fibers from 8.0 nm to 29.0 nm, while the subsequent deposition of PEDOT ink offsets this increase to some extent (reduced from 29.0 nm to 15.9 nm) by forming a conformal film. Table 2 summarizes the surface roughness change after the CNT coating and PEDOT printing. It should be noted that after CNT coating, the fiber surface shows ridges oriented parallel to the dipping direction (Fig. 2e).

**Table 1** Specifications of the PET open-mesh fabric and the nylon fabric

<table>
<thead>
<tr>
<th>Fabric</th>
<th>Raw material</th>
<th>Yarn</th>
<th>Thread count</th>
<th>Weaving</th>
<th>Weight</th>
<th>Open area</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET mesh</td>
<td>PET</td>
<td>70 µm</td>
<td>32 ± 0.5 mesh cm⁻¹</td>
<td>Plain weave</td>
<td>37 g m⁻²</td>
<td>58.7%</td>
</tr>
<tr>
<td>Nylon Taffeta</td>
<td>Nylon 6,6</td>
<td>70 den</td>
<td>41 x 57 picks cm⁻¹</td>
<td>Plain weave</td>
<td>65 g m⁻²</td>
<td>5.1%</td>
</tr>
</tbody>
</table>

* Style no. is 83-70PW from Sefar Inc. * Style no. is 306A from Testfabrics Inc.

**Table 2** Surface roughness change of the PET mesh fabric before CNT coating, after CNT coating and after CNT coating and PEDOT:PSS printing

<table>
<thead>
<tr>
<th>Sample description</th>
<th>Roughness/µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>8.0</td>
</tr>
<tr>
<td>PET/CNT</td>
<td>29.0</td>
</tr>
<tr>
<td>PET/CNT/PEDOT</td>
<td>15.9</td>
</tr>
</tbody>
</table>

**Fig. 2** SEM and AFM images of PET mesh fabric (a and d) before coating; (b and e) after coating with CNT (7 dips); (c and f) after CNT coating and PEDOT inkjet printing (8 cycles).
with more dips. The surface resistivity of the CNT coated PET mesh fabric is high (about 165 MΩ sq⁻¹) after the first dip, but decreases dramatically after two more dips (about 1.26 MΩ sq⁻¹). The resistivity decreases much less rapidly after the third dip and reaches 230 kΩ sq⁻¹ after 7 dips. The CNT used in this study are a mixture of one-third of metallic and two-thirds of semi-conducting tubes. The high resistance may be due to the presence of a large number of CNT junctions.

Substantially enhanced conductivity is achieved by further inkjet printing a PEDOT:PSS layer on the CNT coated fabrics as shown in Table 3 and Fig. 4. Annealing does not help further increase the conductivity of the textiles coated with both CNT and PEDOT ink.

**Mechanical properties of PET textile conductors**

Fig. 5a shows the surface resistivity of PET mesh conductors and that of the ITO/PET sheet at different bending curvatures. The schematic representation of the two-point bending test is shown in the bottom left inset. The top right inset shows that the surface resistivity of both PET/PEDOT and PET/CNT/PEDOT decreases with decreasing bend radius. The origin of this decrease is not clear, although a similar decrease in resistance is seen for PEDOT-coated textiles on stretching. On the other hand, the surface resistivity of the ITO/PET sheet starts to increase dramatically as the bending curvature is smaller than 9 mm, presumably due to cracking of the ITO.

Cyclic bending tests were carried out to examine the mechanical reliability of PET mesh conductors (the inset in Fig. 5b). The change in surface resistivity as a function of the number of bending cycles at a fixed 6 mm bending curvature is monitored. The surface resistivity of both PET/PEDOT and PET/CNT/PEDOT is extremely stable during the 100 cycles of bending. On the other hand, the ITO/PET sheet starts to significantly increase its resistivity in the first 20 cycles of bending and levels off at a constant value of ~51 000 Ω sq⁻¹ after 100 cycles.

Since the PET mesh fabric is an orthotropic planar material with a very low shear modulus, it exhibits differences in tensile behavior depending on the direction of the applied external force. The fabric is much more compliant in the 45 degree direction than in the 0 degree direction because fibers move more freely in the diagonal direction than in the 0 degree direction under same levels of stress. Therefore, tensile tests were performed in both 0 (warp) and 45 (diagonal) degree directions, where the 0 degree direction is the CNT dip coating direction.

Fig. 6a shows that the ITO/PET sheet and PET/PEDOT mesh conductors both start to lose conductivity at a 3% tensile strain. The PET/PEDOT conductors fail at high tensile strains due to crack formation and delamination of the PEDOT:PSS coating. Fig. 7a and b show the SEM images of the PET/PEDOT conductors before and after the 0 degree tensile test. The PEDOT:PSS film cracks at the fiber junction and some films peel off from the fiber surface. The PET/CNT/PEDOT mesh conductor, on the other hand, has only slight change in surface resistivity from 152 Ω sq⁻¹ to 375 Ω sq⁻¹ as the strain rises up to 13% until catastrophic substrate failure occurs. One explanation is that the underlying CNT networks bridge cracks in the outer PEDOT:PSS shell and provide the conductive paths. This has been confirmed by the FESEM images of the cracks (Fig. 7c and d). The CNT layer can be seen below the cracked PEDOT film (Fig. 7c) and CNT fibers can be seen running up into the PEDOT layer near the crack (Fig. 7d).

In the 45 degree test (Fig. 6b) the PET mesh conductors can withstand 32% strain without a significant change in surface resistivity. The PEDOT:PSS coating on the fiber surface seems to retain its integrity under high strains except for some small flakes formed on the interlacing points of PET fibers (Fig. 7f, the representative flakes are indicated by the white arrows).
Optical and mechanical properties of textile-based EL devices

Textile-based EL devices were fabricated using the PET mesh conductor as the front electrode and aluminium foil (Al) or nylon conductors (Nylon/CNT/PEDOT) as the rear electrode. The two types of EL devices are coded as PET/CNT/PEDOT/Al and PET/CNT/PEDOT/Nylon, respectively. Both devices have a 4-layer structure with the same phosphor layer and the dielectric layer sandwiched by the two types of electrodes (Fig. 8a and d). The dielectric layer functions as an insulating layer against short circuit and arcing and also as a reflector by turning the light back to the front side of the device.

The average thickness of PET/CNT/PEDOT/Al is 248 ± 278 μm and 278 μm for PET/CNT/PEDOT/Nylon. In the two types of devices, the PET mesh conductors, which have an average thickness of 117 μm, are the thickest parts. The thicknesses of the phosphor layer and the dielectric layer are 80 μm and 35 μm, respectively.

<table>
<thead>
<tr>
<th>Sample description</th>
<th>After coating with CNT (7 dips)</th>
<th>After inkjet printing with PEDOT ink (8 cycles)</th>
<th>After annealing$^b$</th>
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</thead>
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<tr>
<td>PET/CNT</td>
<td>230 ± 25 kΩ sq$^{-1}$</td>
<td>245 ± 12 Ω sq$^{-1}$</td>
<td>215 ± 20 kΩ sq$^{-1}$</td>
</tr>
<tr>
<td>PET/PEDOT</td>
<td>230 ± 15 kΩ sq$^{-1}$</td>
<td>147 ± 10 Ω sq$^{-1}$</td>
<td>269 ± 15 Ω sq$^{-1}$</td>
</tr>
<tr>
<td>PET/CNT/PEDOT</td>
<td>31 ± 1 MΩ sq$^{-1}$</td>
<td>120 ± 15 Ω sq$^{-1}$</td>
<td>173 ± 9 Ω sq$^{-1}$</td>
</tr>
<tr>
<td>Nylon/CNT</td>
<td></td>
<td>31 ± 1 MΩ sq$^{-1}$</td>
<td>30 ± 1 MΩ sq$^{-1}$</td>
</tr>
<tr>
<td>Nylon/PEDOT</td>
<td></td>
<td>120 ± 15 Ω sq$^{-1}$</td>
<td>125 ± 20 Ω sq$^{-1}$</td>
</tr>
<tr>
<td>Nylon/CNT/PEDOT</td>
<td>31 ± 1 MΩ sq$^{-1}$</td>
<td>48 ± 10 Ω sq$^{-1}$</td>
<td>58 ± 10 Ω sq$^{-1}$</td>
</tr>
</tbody>
</table>

$^a$ Surface resistivity is the average surface resistivity. $^b$ Annealing was performed at 100 °C for 30 min.

Fig. 5 (a) Surface resistivity of PET mesh conductors and ITO/PET sheet as a function of bending curvature under the static bending test. Up right inset: surface resistivity of PET conductors at different bending radii. Bottom left inset: schematic representation of the two-point bending test. (b) Surface resistivity of PET mesh conductors and ITO/PET sheet under the cyclic bending test. The samples were subjected to 100 cycles of bending at a fixed 6 mm bending curvature and a 1 cycle per 16 seconds frequency. The inset shows the test setup.

Fig. 6 Surface resistivity changes of PET mesh conductors and ITO/PET sheet under 0 (a) and 45 (b) degree tensile strain. Insets are the SEM images of the PET mesh conductor to show tensile test directions.

Optical and mechanical properties of textile-based EL devices
The performance of textile-based EL devices is characterized and compared with an EL device of the same configuration but using an ITO-coated PET film as the front electrode and Al as the rear electrode, coded as ITO/PET/Al. The sheet resistivity of ITO/PET is approximately $60 \ \Omega \ \text{sq}^{-1}$, while that of the PET/PEDOT and PET/CNT/PEDOT conductors is $245 \ \Omega \ \text{sq}^{-1}$ and $147 \ \Omega \ \text{sq}^{-1}$, respectively. The lumiance of these EL devices as a function of applied AC voltages is shown in Fig. 9. Luminance of all the devices increases slowly as the voltage increases at the initial stage and a linear relationship develops when the voltage passes 125 V. The performance of PET/CNT/PEDOT/Al (green triangles) is slightly better than that of PET/PEDOT/Al (red circles), which is presumably due to the lower surface resistivity of the PET/CNT/PEDOT conductor (147 $\ \Omega \ \text{sq}^{-1}$) compared to the PET/PEDOT conductor (245 $\ \Omega \ \text{sq}^{-1}$). Since EL devices are high voltage driven but not high current driven electronics, their performance does not strictly depend on the conductivity of the conductors.

The inset in Fig. 9 shows the emitting spectra of the EL devices driven at a sinusoidal exciting signal of 100 V and 3.5 kHz. All the spectra have the same shape and peak centered at a wavelength of 493 nm which is located in the blue/green region.

Fig. 10a presents the luminance ($L$) of flexible textile based EL devices as a function of radius of curvature in the static bending test. The test was carried out by monitoring light output with an HR 4000 spectrometer at a constant AC bias voltage of 100 V and 3.5 kHz. ITO coated PET film-based EL devices start to exhibit a rapid degradation in performance as the radius reaches 6.25 mm, and completely lose the luminescent output at 5 mm radius. In contrast, the textile conductor-based EL devices only lose a small portion of their luminescent output over the entire radii tested. PET/CNT/PEDOT/Al loses about 10% of its initial lumiance at 1.25 mm radius, while PET/CNT/PEDOT/Nylon loses about 20% of the initial at the same radius. As shown in the inset of Fig. 10a, PET/CNT/PEDOT/Al fully functions by emitting uniform EL light even under the 1.25 mm maximum bending radius.

Some of the PET/CNT/PEDOT/Al devices exhibited local loss of luminescent output as the bending radius reaches 5 mm due to local failure and delamination of the Al foil (Fig. 10b). The PET/CNT/PEDOT/Nylon devices, on the other hand, remain robust even after being bent for 100 cycles.

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**Fig. 7** (a) and (b) are SEM images of the PET/PEDOT conductors before and after the 0 degree tensile test; (c) and (d) are FESEM images of cracks of the PEDOT film with nanotube networks embedded in it. The image was taken at a crack induced by tension; (e) and (f) are microscopy photographs of PET mesh conductors before and after the 45 degree tensile test.

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**Fig. 8** SEM images and photographs of textile-based EL devices. (a) Cross-sectional SEM image of the PET/CNT/PEDOT/Al device; (b) and (c) are photographs of the PET/CNT/PEDOT/Al device before and after applying 100 $V_{ac}$; (d) cross-sectional SEM image of the PET/CNT/PEDOT/Nylon device; and (e) and (f) are photographs of the PET/CNT/PEDOT/Nylon device before and after applying 100 $V_{ac}$. 

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*J. Mater. Chem.*, 2012, 22, 1598–1605 | 1603

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Conclusions

In summary, we have demonstrated that a dip coating of CNT ink combined with a subsequent inkjet printing of PEDOT ink can convert highly transparent PET mesh fabrics into textile-based CNT/PEDOT:PSS composite conductors with retained optical transparency and flexibility. The same process was applied to nylon taffeta for developing nylon conductors.

The mesh textile conductors demonstrated a surface resistivity of 173 $\Omega$ sq$^{-1}$ and 55.2% light transmittance after coating with CNT and PEDOT:PSS. The high transparency derives largely from light transmission through the open areas between the monofilaments. The CNT layer provides slight improvement in conductivity of the textile conductors compared to simple PEDOT:PSS coating but greatly improves the conductors' tolerance of tensile strain.

Further, EL devices assembled with textile-based CNT/PEDOT:PSS composite conductors exhibit superior flexibility and mechanical robustness over their ITO coated PET-based counterparts under stretching and tight bending. The textile-based EL devices only lost 10–20% luminance at a bending radius of 1.25 mm, while ITO-based devices lost all the luminescent output at a radius of 5 mm due to cracking of the ITO.

Fig. 9 Luminance versus applied forward bias for PET textile conductor- and ITO/PET-based EL devices.

Fig. 10 (a) Change in luminance of the PET textile conductor- and ITO coated PET film-based EL devices as a function of radius of curvature. Inset shows PET/CNT/PEDOT/Al under testing. (b) Delamination of Al foil results in the local failure of the textile based EL device during the bending test.
Acknowledgements

This work was supported by National Textile Center (NTC) under the project M08-MD07. The authors thank Global Tungsten & Powders Corp. for providing phosphor powders and Nanolab Inc. for providing carbon nanotubes. The authors also thank Mr Nandula Wanasekara and Dr Vijaya B. Chalivendra for the AFM measurements and the grant (CMS0618119) to acquire AFM from National Science Foundation. The authors also acknowledge Dr Chen-Lu Yang in Advanced Technology & Manufacturing Center for the SEM images.

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