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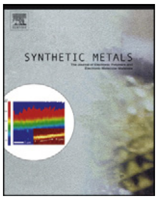

Carbon nanotube-based flexible transparent electrode films hybridized with self-assembling PEDOT

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ABSTRACT

SWCNT-based flexible electrode films with improved conductivity were prepared by hybridization with self-assembling poly(3,4-ethylenedioxy thiophene):*p*-toluene sulfonate (PEDOT:PTS). The conducting PEDOT chains were interconnected between the SWCNT networks, which resulted in a threefold increase in conductivity compared to the SWCNT network alone. The optimized hybrid films showed a sheet resistance as low as 280 Ω/sq. at 80% transparency, which is in stark contrast to the conductivity of the SWCNTs themselves, 1250 Ω/sq. On the other hand, compared to the traditional composite technique and film-forming procedures of CNTs, this process can increase the carrier mobility for electrical conductivity due to the conducting bridge connecting PEDOT:PTS, increased conductor density, and simultaneously improved surface uniformity.

1. Introduction

Flexible organic electronic devices, such as organic light-emitting diodes (OLED) and organic photovoltaics (OPVs), have attracted increasing interest [1–5]. These devices require the use of a transparent electrode to allow photons to enter or exit the devices efficiently and allow the simultaneous extraction or injection of charge carriers. Conventionally, indium tin oxide (ITO)-sputtered plastic films are used widely as a highly transparent and conducting material for flexible display devices, owing to its relatively low resistivity ($\sim 10^{-4}\,\Omega\,\mathrm{cm}$), and work function that is compatible with the injection and collection of charge carriers in organic semiconductors. On the other hand, ITO films are quite brittle and broken down easily by externally applied bending forces, i.e. lacking mechanical flexibility [6,7]. Therefore, flexible electrode materials of a different type are needed to further improve the flexibility of devices. One of the aims of research in this field is high-performance, fully plastic electronic devices. Before such technology can be realized, organic electrode materials with conductivities and stabilities comparable to those of ITO are required.

Single-walled carbon nanotube (SWCNT) films are a class of special organic conductors with excellent electrical properties. Therefore, they can replace electrical conductors and even semiconductors in a range of applications requiring electronic materials due to the strong carbon–carbon bonding between the atoms in the tube, and the near perfection of the lattice. In particular, SWCNTs possess the mobility in the order of $10^4\,\mathrm{cm^2/Vs}$ and conductivity up to $10^4\,\mathrm{S/cm}$ [7]. The semiconducting tubes have a band gap of 0.7 eV for a 1 nm diameter [8] and the intrinsic work function in the range of 4.7–5.1 eV [9], which is in the range of ITO (4.4–4.9 eV). Recent reports have also shown that SWCNT films can be produced with a sheet resistance as low as 160 Ω/sq. and a transmittance of 87% [10]. Furthermore, continued advancements in the processing of SWCNT films have shown progress in reducing the sheet resistance, thereby, reducing the gap in sheet resistance compared to ITO (100 Ω/sq.). This higher sheet resistance of SWCNT films can be attributed largely to the fact that a 2-dimensional CNT network, forming a “film” on a surface, has high contact resistant for randomly oriented CNTs. Therefore, the bulk conductivity can be enhanced considerably through the efficiently arrangement in the CNT-network to decrease the contact resistant or increasing the carrier mobility by effective percolation. On the other hand, a network can be made to cover arbitrarily large areas, limited only by the deposition process. The deposition process is an important factor in film fabrication, and the dispersion of CNTs is always a key issue when attempting to achieve highly conducting CNT films [11–14]. On the other hand, poly(3,4-ethylenedioxythiophene) (PEDOT) [15,16] as a type of conducting polymer with a conjugated π-electron bond system, can be a good material for optoelectronic devices owing to its high conductivity up to 500–2000 S/cm [17–20] and electrochemical stability with moderate transparency and good film forming properties.

A hybridized SWCNT network structure interconnecting self-assembling PEDOT chains between the SWCNT networks was examined to produce SWCNT films with better electrical performance and light transmittance (see chemical structure of network,

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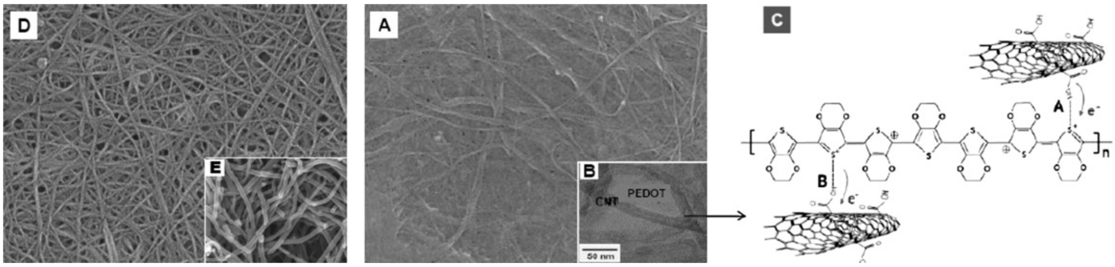

Fig. 1. Network images of SWCNT interconnected with self-assembling PEDOT chains. (A) SEM and (B) TEM morphology, (C) schematic structure and charge transfer mechanism (electron transfer from CNT to polymer chain, and subsequently from polymer chain to CNT) (D) SEM and (E) TEM morphology of a conventional SWCNT film network after spray coating and water rinsing.

as shown in Fig. 1). Therefore, the highly conducting pure PEDOT chains were assembled directly between the CNT networks by self-organization of the 3,4-ethylenedioxythiophene (EDOT) monomer on the substrate film. Their surface characteristics were also extremely uniform and exhibited a compact and tight morphology. These hybrid CNT films exhibited high conductivity and optical transmittance as low as 100 Ω/sq. and up to 80%, respectively, when the SWCNT were hybridized to 1:1 with self-assembling PEDOT. Consequently, these hybrid network films might have up to twofold higher conductivity than SWCNT alone as well as the higher carrier mobility due to the effective percolation for electrical conductivity.

Recently, a range of methods for producing composites from a combination of CNTs with conducting polymers has been reported [21–25]. The goal was to achieve a synergistic effect in terms of the properties of the two components. Han et al. [23] synthesized composite films of PPy–CNT using the electrochemical deposition method. Karim et al. [24] demonstrated the complexity of the nanotubes coated with PANi. These complex nanotubes had higher conductivity and thermal stability than PANi but lower than CNT. More recently, for the organic electrode of solar cell, CNT–PEDOT nanostructures composed of CNT cores and PEDOT shells synthesized by chemical oxidative polymerization are reported [26], which the resulting CNT–PEDOT core/shell nanostructures showed the enhanced thermal stability and increased electrical conductivity relative to pure PEDOT and CNT itself. Valentini et al. [27] also demonstrated the casting film composited of SWCNT and PEDOT:PSS in liquid phase under a magnetic field. These composite films prepared from solution casting had high conductivity (<100 Ω/sq.) and high optical transmittance (>80%) for transparent electrode of flexible devices.

This study evaluated a new fabrication approach for SWCNT electrode films hybridized with self-assembling PEDOT chains via gas-phase deposited polymerization. The highly conducting poly(3,4-ethylenedioxythiophene):*p*-toluene sulfonate (PEDOT:PTS) was interconnected between the CNT networks by self-organization of the EDOT monomer. The highly conducting and uniform CNT–PEDOT:PTS matrix films were assembled directly on the substrate. Compared to the traditional composite technique and film-coating procedures, this process increased the carrier mobility through effective percolation for electrical conductivity, and increased the conductivity up to threefold.

2. Experimental

SWCNTs synthesized by arc discharge (Hanwha nanotech) were used to fabricate 2-D films using a wet method. A hydrothermal treatment was carried out with concentrated HNO_3 in a closed stainless bomb equipped with a Teflon tube to dissolve any impurities and modify the surface of the CNTs. The hydrothermally treated CNTs were dispersed ultrasonically in water with a dispersant (polyvinylpyrrolidone, PVP, Mw; 40,000) for 40 min at room temperature. A 0.05% (w/w) SWCNT dispersed solution was then coated using a wet coating method on PET films followed by rinsing several times in water to remove the remaining PVP. SWCNT film samples 1 (high purity SWCNT) and 2 (60% SWCNT) were prepared using the above mentioned method. Fig. 1(D) shows a SEM image after rinsing. In the second step, the porous structured SWCNT networks film were immersed an oxidant solution of 20 wt% Fe(III) *p*-toluene sulfonate (FTS) (Aldrich, GR) in n-butyl alcohol, and the CNT film immersed with the oxidant was exposed to EDOT vapor for 10 min in a vapor deposition chamber for PEDOT:PTS assembling. The electrically conducting PEDOT:PTS matrices were assembled directly or interconnected between the SWCNT networks by polymerizing the EDOT monomer in the vapor-phase (their SEM image is shown in Fig. 1(A)). The thickness of the assembled PEDOT layer and the SWCNT content were controlled freely by the thickness of the oxidant layer immersed with CNTs and the oxidant/SWCNT mixing ratio. Finally, the PEDOT:PTS matrix films assembled between the CNT networks were finished by alcohol washing/drying after polymerization. The molecular structure of the resulting PEDOT–CNT hybrid films was characterized by SEM, as well as ultraviolet (UV), Fourier transform infrared (FT-IR) and 514.5 nm excited (Ar laser) Raman spectroscopy. The conductivity was measured using the standard four-probe technique and the thermal stability was examined by thermogravimetric analysis (TGA).

3. Results and discussion

Fig. 2 shows SEM images of the PEDOT–SWCNT hybrid film. Fig. 2(a) presents an SEM image of the dispersed CNT film networks (sample 1) formed by spray coating and water rinsing. Fig. 2(b)–(d) shows the images of the SWCNT layer hybridized with the PEDOT chains at a ratio of 0.4, 0.6 and 0.8, respectively. PEDOT was deposited only between the CNT networks, as shown in (b), which grew with increasing deposition time. Finally, the surface morphology of the composite films was more uniform and compact than those obtained by the CNT matrix only. Moreover, the PEDOT content was increased up to a value of 80% (w/w) with no aggregation. The thickness of the composite films was changed by varying the synthesis conditions. The CNT content was also changed freely by varying the mixing ratio in the first step of the deposition process. On the other hand, the conducting pure PEDOT chains were assembled directly between the CNT networks by the EDOT monomer on the substrate film. As a result, hybridized network films with a higher roughness and dense structures were formed, as shown in Fig. 2(d). Furthermore, the hybrid network films consistently exhibited much higher sheet conductance than the pure SWCNT itself by more than twice the magnitude at similar optical transparency with respect to the film thickness, as shown in Fig. 2(e). Fig. 3 shows the relative sheet