TRANSPARENT CONDUCTIVE CNT/POLYMER
NANOCOMPOSITES FOR ORGANIC SOLAR CELL APPLICATION

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1. Introduction

Current widely used transparent conductive films (TCFs) for various applications such as display, solar cell, optoelectronic devices are the indium tin oxides (ITO). ITOs have the high optical transmission about 80% in visible wavelength at low sheet resistance about 60 ~ 90 Ohm/sq. However, price of ITOs have been gradually increasing due to insufficient supply of indium, so development of alternating materials is required for TCFs.

Polymer nanocomposites using carbon nanotubes (CNTs) as a filler material have recently received much attention as new candidate materials for TCF applications. CNTs have low electrical percolation threshold at very small amounts of CNTs due to their one dimensional nanostructure and excellent electrical conductivity [1, 2]. It is believed that CNTs are the excellent filler materials in conductive polymer matrix for TCFs. However, CNTs show the high agglomeration states due to their large van der Walls force between each rope of CNTs. To solve this problem, functionalization of CNTs should be employed [3, 4]. Covalent functionalization of CNTs by chemical oxidation in strong acid is widely used to disperse CNTs in matrix. However, this method results in the lower electrical properties of CNTs due to the damage of CNTs during the covalent functionalization [5, 6].

In this study, we fabricated transparent conductive polymer nanocomposites from single walled carbon nanotubes (SWNTs) and poly (3, 4-ethylenedioxythiophene);poly (styrenesulfonate) (PEDOT:PSS). Covalent functionalization by strong acid treatment and non-covalent functionalization by π-π stacking were employed to functionalize the each of the SWNTs. SWNT/PEDOT:PSS solutions were spin coated on quartz substrates to obtain TCF. Incorporation of SWNTs in PEDOT:PSS matrix showed the enhancement of electrical conductivity without significant decrease of optical transmittance compared to raw PEDOT:PSS. Especially, non-covalently functionalized SWNT/PEDOT:PSS nanocomposites showed the higher electrical conductivity than covalently functionalized SWNT/PEDOT:PSS nanocomposites. FT-Raman and TEM results of covalently functionalized SWNTs revealed that collapsing the walls and shortening the length of SWNTs are critical to decrease the electrical property of nanocomposites. Furthermore, we applied non-covalently functionalized SWNT/PEDOT:PSS nanocomposites as a hole conducting layer in organic solar cell (OSC). Power conversion efficiency (PCE) of OSC using non-covalently functionalized SWNT/PEDOT:PSS nanocomposites showed 30% enhancement compared to OSC using raw PEDOT: PSS. This enhancement was mainly originated from effective charge collection of high conductive SWNTs in PEDOT: PSS matrix.

2. Experimental Procedures
SWNTs, supplied by Unidym, Inc, were sonicated for 1hr with a mixed solution of HNO₃/H₂SO₄ in a ratio of 1:3 for covalent functionalization. Covalently functionalized SWNTs were washed with H₂O by centrifugation and filtering several times. For non-covalent functionalization, SWNTs were sonicated for 12hr with a 1mM of 1-aminopyrene solution in DMF. Then, non-covalently functionalized SWNTs were washed with ethanol by centrifugation and filtering several times to remove the unattached 1-aminopyrene from SWNTs.

Functionalized SWNTs were dispersed in 2-propanol by sonication for 5hr to form stable SWNTs suspension. SWNTs suspension was mixed with high conductive grade PEDOT:PSS, purchased from sigmaaldrich, (volume ratio of SWNTs suspension: PEDOT:PSS = 2: 1) and then sonicated for 1hr to make homogeneous mixtures of SWNTs and PEDOT:PSS. This mixed solution was spin coated on the substrates at 1,000 rpm for 1min to fabricate the SWNT/PEDOT:PSS nanocomposites thin film, which was baked at 150°C for 10min.

Poly(3-hexylthiophene) (P3HT), supplied by Rieke Metals, and [6,6]-Phenyl C₆₁ butyric acid methyl ester (PCBM), supplied by sigmaaldrich were dissolved and stirred in 1ml chlorobenzene for 12hr, respectively. The blend of P3HT and PCBM was fabricated by mixing of two solutions for 12hr. The blend of P3HT and PCBM was spin coated on the raw PEDOT:PSS and SWNT/PEDOT:PSS thin film in glove box filled with N₂ gas. Al electrode was thermally evaporated in vacuum with a pressure of 10⁻⁵ torr. Finally, the organic solar cell device was directly placed on the digital hot plate at 150° for 5min.

3. Results and Discussion

Fig 1. shows schematics of non-covalent functionalization of CNTs by pyrene molecules in this work. Pyrene molecules have planar structures consisting of 4 benzene rings; it can be interated with sidewalls of SWNTs by π-π stacking. This non-covalent functionalization by pyrene molecules is non-destructive method to disperse SWNTs in matrix without the degradation of SWNTs compared to covalent functionalization.

Fig 1. Schematics of non-covalent functionalization of CNTs by pyrene molecules.

Fig 2. (a) Digital photograph of covalently functionalized SWNTs (left) and non-covalently functionalized SWNTs (right) dispersion after several days, (b) FT-IR results of covalently functionalized SWNTs, (c) absorption spectra of non-covalently functionalized SWNTs.

Fig 2. (a) shows the digital photographs of covalently and non-covalently functionalized SWNTs dispersed in 2-propanol after several days. Both of them show the higher dispersion stability and do not form the any aggregates even after prolonged standing (1 month). Fig 2. (b) is the FT-IR analysis results of covalently functionalized SWNTs. FT-IR spectrum of pristine SWNTs did not show any special peaks. However, after functionalization, C=O stretching in anionic carboxylates (v=1645 cm⁻¹) and carboxylate groups (v=1693 cm⁻¹, asymmetric), (v=1780 cm⁻¹, symmetric) is appeared in FT-IR analysis. These peaks are mainly related to carboxylate groups

![Image 1](image1.png)

![Image 2](image2.png)
which suggest that major functional groups of covalently functionalized SWNTs are carboxylate groups (carboxylate-SWNTs). Fig 2. (c) shows the UV-Vis absorption spectra of non-covalently functionalized SWNTs by 1-aminopyrene (AP-SWNTs). Pristine SWNTs show featureless spectrum within the whole wavelength, but AP-SWNTs show the additional peak at 285nm correspond to the peak of 1-aminopyrene. Furthermore, the peak of AP-SWNTs is much broader than 1-aminopyrene due to strong interaction between SWNTs and 1-aminopyrene via π-π stacking. It is the one evidence of non-covalent functionalization of SWNTs by pyrene molecules.

Fig 3. shows the optical transmission at 550nm versus sheet resistance of thin films fabricated from raw PEDOT:PSS and SWNT/PEDOT:PSS nanocomposites. Incorporation of SWNTs in PEDOT: PSS shows the decrease of sheet resistance without significant decrease of optical transmission. Especially, AP-SWNT/PEDOT:PSS nanocomposites show significant decrease of sheet resistance compared to raw PEDOT:PSS and carboxylate-SWNT/PEDOT: PSS at similar optical transmission. This difference was mainly originated from the decrease of length and crystallinity of SWNTs after covalent functionalization. From TEM analysis, it has been observed that pristine SWNTs show the much longer lengths over 1μm (Fig 4. (a)) compared to carboxylate SWNTs as shown in Fig 4. (b). Fig 5. is the FT-Raman analysis result of pristine SWNTs and carboxylate SWNTs. The ratio of graphene-like structure to diamond-like structure (G/D ratio) is decreased from 7.17 to 2.46 after covalently functionalization. It reflects that sp^2 structure of SWNTs is disrupted to sp^3 structure by covalent attachment of functional groups during covalent functionalization. From these results, we infer that shorter length and decrease of crystallinity of covalently functionalized SWNTs lower the electrical conductivity of nanocomposites compared to non-covalently functionalized SWNTs.

Fig 6. shows the SEM images of AP-SWNT/PEDOT:PSS nanocomposites. In order to better microstructures observation, AP-SWNT/PEDOT:PSS nanocomposites was spin coated on Si wafer and then Ar plasma treatment was conducted for 3min to etch out the polymer. We can clearly see the protruded AP-SWNTs in polymer matrix due to selective etching of PEDOT:PSS by Ar plasma treatment and confirm that AP-SWNTs are homogeneously dispersed in the PEDOT:PSS matrix as shown in Fig 6.
Fig. 6. SEM image of AP-SWNT/PEDOT:PSS nanocomposites after Ar plasma etching.

Fig. 7. (a) shows the schematic structures of OSC in this research. PEDOT:PSS layer works as a hole-conducting layer to transport holes from active layer to ITO. To achieve high PCE of OSC, PEDOT:PSS layer must be optically transparent and has high electrical conductivity to effectively collect the charges from active layer to ITO electrode. For this purpose, we used AP-SWNT/PEDOT:PSS nanocomposites as a hole conducting layer which have high electrical conductivity than raw PEDOT:PSS at similar optical transmission.

The I-V curves of OSC with raw PEDOT:PSS and AP-SWNT/PEDOT:PSS layer under 1 sun illumination are shown in Fig. 7. (b). OSC using SWNT/PEDOT:PSS nanocomposites shows the better photovoltaic properties than OPVC using raw PEDOT:PSS. PCE of OSC using AP-SWNT/PEDOT:PSS is enhanced from 2.3% to 3.0% compared to OSC using raw PEDOT:PSS. Enhancement of PCE is mainly originated from the large increase of short circuit current ($I_{sc}$). The enhancement of $I_{sc}$ is reflected in decrease of series resistance ($R_s$) of OSC using AP-SWNT/PEDOT:PSS ($R_s = 3.5 \, \Omega \cdot \text{cm}^2$) compared to $R_s$ of OSC using raw PEDOT:PSS ($R_s = 5.8 \, \Omega$). From the above results, we can conclude that the improvement of PCE and $I_{sc}$ of OSC is originated from the effective hole transport and collection by high conductive SWNT/PEDOT:PSS transparent thin films.

4. Conclusions

We fabricated the SWNT/PEDOT:PSS nanocomposites for TCFs. Non-covalently functionalized SWNT/PEDOT:PSS nanocomposites showed the higher electrical conductivity than raw PEDOT:PSS and covalently functionalized SWNT/PEDOT:PSS nanocomposites due to non-destructive functionalization of SWNTs. Furthermore, we applied non-covalently functionalized SWNT/PEDOT:PSS nanocomposites as a hole conducting layer in OSC. They showed 30% enhancement PCE compared to OSC using raw PEDOT:PSS. This clearly shows the big potential of non-covalently functionalized SWNT/PEDOT:PSS TCFs for organic solar cell applications.

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5. References


