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Transparent carbon nanotube sheets as 3-D charge collectors in organic solar cells

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Abstract

Strong transparent multiwall carbon nanotube (t-CNT) sheets [M. Zhang, S. Fang, A.A. Zakhidov, S.B. Lee, A.E. Aliev, C.D. Williams, K.R. Atkinson, R.H. Baughman, Science 309 (2005) 1215] can be used as effective anodes in organic photovoltaic cells (OPV) [A.D. Pasquier, H.E. Unalan, A. Kanwal, S. Miller, M. Chhiwalla, Appl. Phys. Lett. 87 (2005) 203511]. We prove here that t-CNT plays an essential role as three-dimensional (3-D) hole-collecting network with extended interface connectivity to photoactive layer of bulk heterojunction OPV. Although, the sheet resistance of as-prepared t-CNT is higher than that of ITO, we demonstrate that combining 3-D t-CNT network with planar ITO leads to twice increased photocurrent. So even in unoptimized OPV, a short circuit current density of 11 mA/cm^2 is obtained, which is a significant increase, compared to only ~5.5 mA/cm^2 of photocurrent in sole ITO device, and in sole t-CNT case, increasing the overall efficiency to ~2%. This enhancement is due to a combined effect of an enhanced hole collection by 3-D t-CNT and improved transport via planar ITO part. Flexible OPVs on plastic substrates also show enhanced performance with hybrid t-CNT–ITO anodes.
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Keywords: Organic photovoltaics; Carbon nanotubes; Transparent electrode

1. Introduction

There is a critical need for development of new types of flexible transparent conductive electrodes for solar cells. Considerable academic and industrial research activity involving applications of carbon nanotubes (CNTs) lead to development of several types of transparent conductive coating and films based on CNTs [3]. All previous methods are able to produce transparent single-wall CNT-based electrodes, with good optical transparency (⩾80%) and flexibility, but these electrodes are not strong mechanically, and therefore, cannot be in the form of self-supporting freestanding films, which would be easy to coat without the use of the liquid phase (as in previous methods, which are limited to use only in small-area devices).

Our new process allows creating multiwall CNT-based sheets and yarns, that are strong freestanding materials [1] with exceptional mechanical strength, and can be produced with practically unlimited length and widths of 5–10 cm or more.

Recently, transparent films of CNT have been used in solar cells [2]. In our previous work [4], we have demonstrated that P3HT/PCBM solar cells with bottom t-CNT electrode on glass shows surprisingly high efficiency of 1.1% for the very high sheet resistance of t-CNT, which is ~600 Ω/sq, 30 times higher than in ITO. This indicated that some other photo processes occurring in t-CNT are much more efficient than in planar ITO-based bulk OPV heterojunctions. We suggested that t-CNT is a much more efficient 3-D charge collector, due to its network topology (shown in Fig. 1) of a 3-D nano-mesh, which has large pores for infiltration of P3HT/PCBM nanocomposite layers. The motivation of the present paper is to check this hypothesis of a 3-D CNT hole collector and to create a better electrode for OPV device.

With this goal in mind, we have created three types of solar cells for comparison: same type P3HT/PCBM

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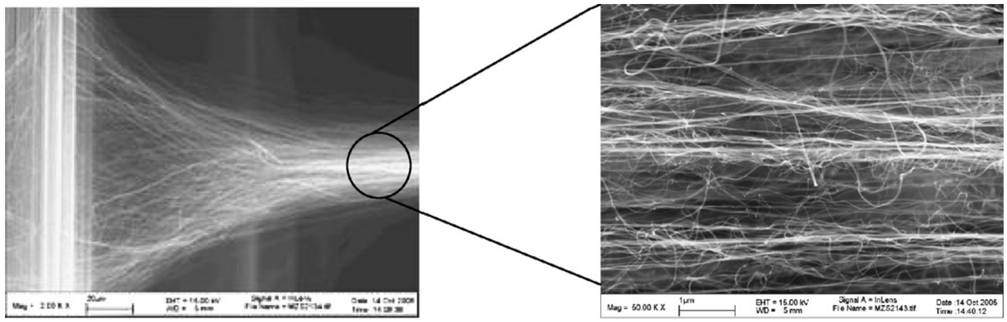

Fig. 1. SEM micrograph of freestanding strong multiwall CNT sheet: (a) the drawing of oriented sheet from a CVD grown forest and (b) structure of undensified CNT sheet in its aerogel, low density state.

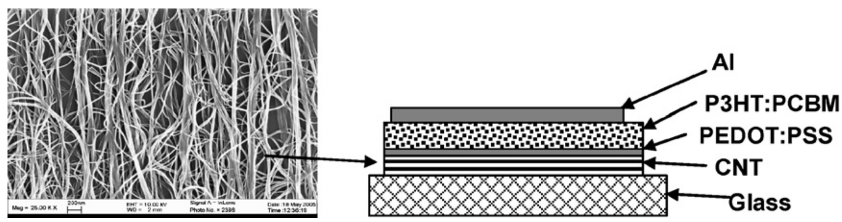

Fig. 2. The schematics of OPV device of type 2, having multiwall t-CNT layer on glass as an anode. SEM of densified t-CNT clearly shows large porosity, which remains, even after deposition of thin layer of PEDOT–PSS (shown at inset).

nanocomposite with three types of anodes: (1) ITO on glass, (2) t-CNT on glass, and (3) a hybrid anode with t-CNT on the top of ITO on glass. Similar three types of OPVs are built on flexible substrates. It is found that the last type of OPV with hybrid anode: "t-CNT–ITO" shows twice higher short circuit photocurrent, compared to OPVs with only ITO or only t-CNT anodes. We also clarify the role of thin PEDOT–PSS coating on t-CNT for planarizing CNT network and avoiding shorts and for blocking electrons from recombination on t-CNTs.

2. Experimental

A freestanding CNT sheet is drawn laterally from the side of a CNT forest (as shown in Fig. 1). It is then placed on a clean substrate of Corning 1737 display glass or flexible plastic (PET or PEN). The CNT sheet was then densified using surface tension effects of an imbibed liquid (for example, methanol). The rapid evaporation of the solvent absorbed in the sheet causes compression of CNT sheet by surface tension forces leading to densification. After densification, the t-CNT is converted from its aerogel state (shown in Fig. 1, which is 20 μm thick), to a state of a thin porous film (shown in Fig. 2, left), which is only 50–100 nm thick due to a factor of 400 shrinkage. A layer of PEDOT:PSS was then spin-coated onto the substrate at 6100 rpm creating a 50–55 nm layer, and then dried by being heated at ~120 °C for 45 min in a glove box. The photoactive material solution was then spin-coated onto the sample.

An aluminum cathode was then deposited under high vacuum ($<10^{-6}$ Torr) and the finalized device was then annealed on a hot plate in a glove box for 5 min at 100 °C. Fig. 2 shows the schematic structure of OPV solar cell of type 2) formed on a glass or plastic substrate (more details on preparation and measurements can be found in our Refs. [1,4]). The device of type 1 had only ITO as the bottom electrode, while device of type 3 had a hybrid electrode: t-CNT on ITO. We fabricated multiple sets of four devices of each type on a substrate, each having an area of ~9 mm^2, and obtained consistent behavior for each type of OPVs, although devices with CNT electrodes had a larger statistical scatter due to accidental shorting.

3. Results and discussions

Fig. 3 shows transmission spectra of a pure single layer of CNT sheet on quartz substrate and the same CNT sheet after layers of PEDOT:PSS have been spin-coated on top of it. The single CNT sheet has a flat transmission better than 80% over a very broad spectral range from visible to infrared (Fig. 3, solid curve). Extended transmission up to 10 μm was shown in our previous paper [1]. Transmission spectrum of pure single layer of PEDOT:PSS (50–55 nm in thickness) is shown for comparison (dot–dash curve). Multiple PEDOT:PSS spin-coatings reduce significantly transmission of electrode to 65%, 60%, and 50%. At the same time, the sheet resistance of CNT sheet in parallel direction is slightly decreased from 717 to 605, 603, and 588 Ω/sq. Usually, resistivity of CNT network increases by 5–10 times after mixing with conducting polymers because of the deteriorating intertube contacts. In contrary, spin-coating of PEDOT:PSS on top of the CNT sheet improves densification and, probably, the intertube contacts. It is important that PEDOT coating leaves the t-CNT film porous, (Fig. 3(b)), leaving enough space for filling up the

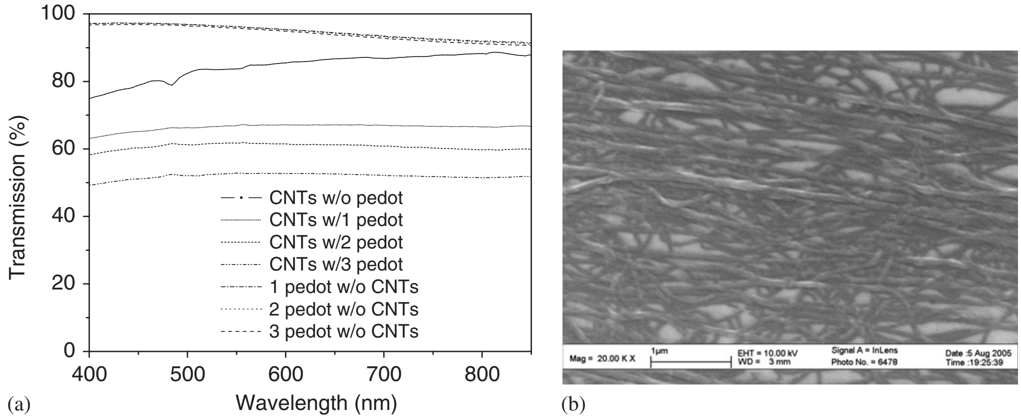

Fig. 3. (a) Optical transmission spectra of t-CNT film on glass and PEDOT–PSS coated CNT with different number of coatings, and several layers of pure PEDOT–PSS on glass (all showing nearly same transmission) and (b) SEM of CNT film coated by three layers of PEDOT–PSS.

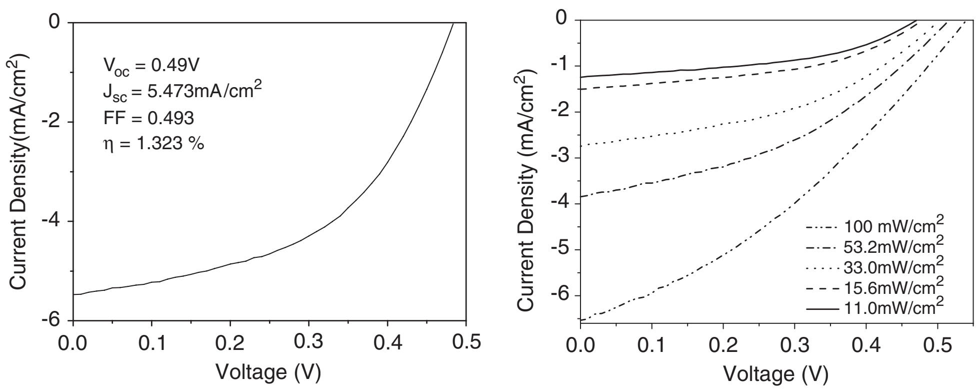

Fig. 4. (a) *I–V* curves under AM 1.5 photoexcitation (light intensity 100 mW/cm^2) for best device of type 2 with t-CNT on glass anode and (b) typical light intensity dependence of *I–V* curves for similar device, showing systematic lowering of V_{oc} and FF change with lowering light intensity.

photoactive layer of P3HT–PCBM. Fig. 4 shows current–voltage characteristics of the best t-CNT/PEDOT:PSS/PCBM + RR-P3HT/Al device under simulated solar light AM 1.5 100 mW/cm^2 (Fig. 4a). Good diode characteristics and, surprisingly high photovoltaic parameters were obtained after annealing at 90 °C for 3 min: an open circuit voltage $V_{oc} = 0.49$ V, a short-circuit current $J_{sc} = 5.47$ mA/cm^2, a fill factor FF = 0.49, and efficiency $\eta = 1.32\%$. The intensity dependences of *I–V* at Fig. 4b were measured under white light from a solar simulator using neutral density filters. The J_{sc} increases linearly with intensity. The V_{oc} decreases with decreasing intensity. The efficiency reached a maximum of $\eta = 1.43\%$ at 23 mW/cm^2 and then decreased to $\eta = 1.15\%$ at AM1.5 84 mW/cm^2. The reduction in efficiency is because of high serial resistance of the solar cell.

Fig. 5 shows the most important result of present study, comparing the performance of OPVs with two distinct types of anodes: sole ITO anode with a hybrid anode: t-CNT-on-ITO both on glass and on plastic substrates. It is clear, that while the sole ITO-anode OPV shows $J_{sc} = 5.6$ mA/cm^2, (nearly same as J_{sc} of sole t-CNT anode of Fig. 4), the hybrid anode shows more than twice increased J_{sc}. Taking into account the dramatically decreased transparency for OPV with t-CNT coated with optimal PEDOT–PSS layer (which is about 50%), and also the rather high sheet resistance of t-CNT part, the actual increase of photocurrent, if normalized to the absorbed light intensity should be even higher in a hybrid device. Let us now try to explain this dramatic photocurrent increase by a less optically transmissive and more resistive device. It is clear that only the actual collection of an additional large number of photo-generated carriers (holes avoiding recombination with electrons) can explain the increase in J_{sc} and η. For clarity, let us start with the opposite case, i.e. consider a hypothetical case of planar, not porous t-CNT. So if the t-CNT would be a planar, continuous film (like ITO, just with higher sheet resistance), it would be like collecting the same amount of photocurrent of holes, arriving to it from P3HT polymeric chains. Since this planar t-CNT would stay on the top of ITO, blocking it from direct contact with photoactive P3HT, no additional current can be collected by ITO. Therefore, the hybrid anode would not show any photocurrent increase (as compared to the case of the sole ITO device of type 1), but just would provide better transport of photocarriers via

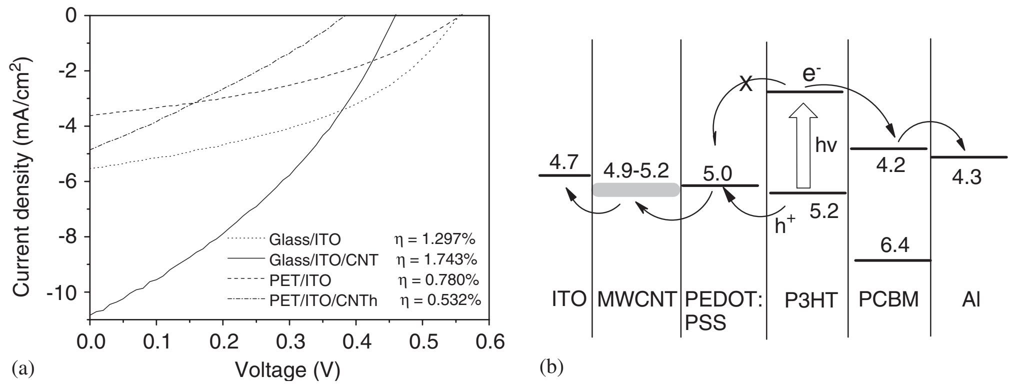

Fig. 5. (a) Comparison of I–V curves for OPVs of type 1: only ITO electrode (dotted curve) and type 3: hybrid "t-CNT-on-ITO" anode (solid curve), both on glass. Twice J_{sc} increase results in efficiency increase from $\eta = 1.29\%$ to 1.74%. Comparison of similar devices on plastic substrate: only ITO anode OPV (dash curve) with hybrid "CNT–ITO" anode (dash-dot). In both cases, V_{oc} and FF decreased for the hybrid device, while I_{sc} increased, (b) the electronic energy diagram of the (t-CNT–ITO)/PEDOT/P3HT:PCBM/Al device, and photo processes in it. Arrows show electron transitions.

lower sheet resistance of a hybrid (due to the planar ITO part), which would only increase the filling factor, and slightly increase the η. Now, if one considers the actual case of a highly porous t-CNT, sitting on the top of ITO, than clearly the upper porous part of hybrid, namely t-CNT 3-D network (shown in Figs. 1–3), which retains even after coating it with PEDOT–PSS, allows the contact of photoactive P3HT in pores with ITO (although at possibly somehow smaller area). The extended surface area of 3-D network in this case collects holes, which reaches its "vertical side-walls" within the holes diffusion length ($L = \sqrt{D\tau}$) from the point of photo-induced charge separation inside a pore, between CNT nanowires. This part of the photocurrent collected by t-CNT network, can be roughly estimated as a current of the type 2 OPV, with only t-CNT anode on glass, which (according to Fig. 4) is $J_{sc} = 5.5\,\mathrm{mA/cm^2}$. The other part of the photocurrent, collected directly on the ITO part of a hybrid anode, corresponds to photo-generated carriers in pores, which reach a "horizontal" bottom ITO part of the anode, and it is roughly $5.6\,\mathrm{mA/cm^2}$, from Fig. 5 (dotted curve). The total J_{sc} is roughly a sum of two photocurrents, estimated above and is should be about $11\,\mathrm{mA/cm^2}$, which actually coincides with the observed J_{sc} (red curve at Fig. 5). The decreased V_{oc} of hybrid anode OPV can be explained in terms of lower light intensity in it, since same trend of V_{oc} decrease is observed upon decrease of light intensity, as discussed above (Fig. 4(b)), due to only 50% transmission in type 3 OPV. The same trend of increased total J_{sc}, and decreased V_{oc} is observed also in plastic substrate case, although less pronounced.

4. Conclusion

To prove the enhanced role in charge collection, we have deposited t-CNT on ITO, and found that the performance is further improved in such a hybrid anode device, in which the part of the t-CNTs collects more charges from the bulk of the OPV and transports carriers to the ITO, while part of the PEDOT:PSS-coated ITO, in contact with P3HT in the pores further collects and transports charges to the current leads. This type of hybrid anode can increase the efficiency of OPVs and allows thicker OPV architectures, and is important for large area OPVs. In fact, a hybrid anode can be viewed as a hole-collecting analog of mesoporous TiO_2 on FTO, which is a well-known electron-collecting network in Graetzel cells. In summary, we have demonstrated that an oriented MWCNT sheet can be used as a hole-collecting electrode in polymer solar cells with P3HT/PCBM. Relatively high photovoltaic characteristics have been obtained even with a non-optimized OPV for a hybrid t-CNT/ITO anode: a short circuit current of $11\,\mathrm{mA/cm^2}$, a fill factor of 0.49, and an efficiency of 1.74%. If optimized P3HT/PCBM OPV is used, even more dramatic enhancement of η can be expected with a hybrid t-CNT/ITO anode.

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