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1 Introduction

Flexible organic photovoltaic cells on elastomeric substrates need a transparent electrode, which is different from traditional ITO. The problem with ITO is that it has poor mechanical properties and is brittle. Creating a substitute for ITO or fluorinated tin oxide (FTO), is one important challenge not only for organic photovoltaics (OPV), but also for dye solar cells (DSC) and many other types of flexible devices.

After the discovery of carbon nanotubes (CNT), it has been realized that carbon nanotubes can be a perfect material for transparent flexible electrodes for optoelectronic devices [1].

Recently, three groups [2–4] reported on the fabrication and characterization of thin films of carbon nanotubes. All groups have achieved good optical transparency (≥80%) and flexibility, but the transmission was limited to the visible spectral range and the minimum sheet resistance was only ~100 Ohm/sq in the best samples. A. G. Rinzler first noticed high transmittance of a SWNT film in the near infrared (IR) range (3–5 μm). Many transparent conducting coatings (TCC) are transparent in the visible part of the spectrum, but only a few materials retain good transparency in the infrared (IR) while maintaining good electrical conductivity. All three methods are able to produce transparent electrodes, but these electrodes are not strong mechanically, and therefore cannot be in the form of self-supporting, self sustaining and free standing films, which would be easy to coat without the use of the liquid phase. All three methods used a liquid phase and therefore are strongly limited to use in small area devices.

A new, dry and simple process has been developed [1] which allows one to create CNT-based fibers, yarns, and sheets that are incredibly strong free-standing materials. CNT sheets described herein have exceptional mechanical strength, and can be produced with practically unlimited length and widths of 5–10 cm or more.

Carbon nanotube sheets thus self-assembled [1] have the following unique properties and combinations of such properties are particularly useful for solar cells: (1) high optical transparency in very broad spectral range from UV to MIR, (2) low electrical sheet resistance, (3) three-dimensional topology of the

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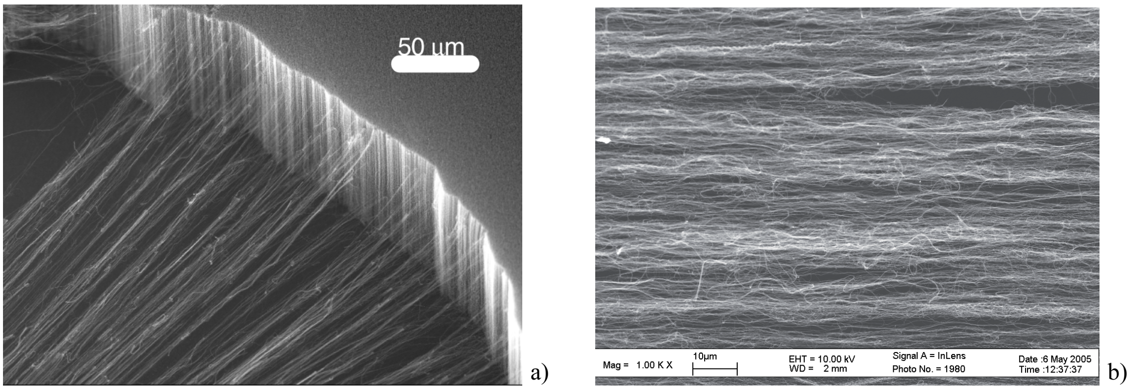

Fig. 1 a) SEM of the CNT sheet being dry drawn from a CNT forest into a self-assembled sheet. b) Undensified, dry-drawn single layer sheet of free standing CNT.

mesh-like CNT network, which allows charge collection from a large surface area, and not only from a planar interface, like from usual ITO electrodes, (4) extended interface of the three-dimensional network, which enhances charge separation and collection, (5) high thermal conductivities and thermal diffusivities, which provide heat dissipation, (6) high work function required for collection of holes, (7) high flexibility as opposed to brittle ITO and other inorganic TCCs, (8) very high resistance to creep, (9) interpenetrating continuous morphology of the nanofiber network, as opposed to the nonpercollated morphology of nanoparticle electrodes, which is favorable for the collection of charge carriers from bulk heterojunction type architectures, (10) retention of strength even when heated in air at 450 °C for one hour, and (11) very high radiation and UV resistance, even when irradiated in air.

The goal of our work is to create flexible plastic solar cells (SC), using nanoscale composites of conjugated polymers with inorganic components (fullerenes, nanotubes, titania nanofibers) on the load bearing carbon nanotube transparent electrodes in bulk heterojunction solar cell architecture, which we have optimized earlier at ~4% efficiency [5]. Figure 2 depicts an organic solar cell based on carbon nanotube ribbons as a front-surface transparent conducting electrode, formed on a glass or plastic substrate.

2 Experimental

A free-standing carbon nanotube (CNT) sheet is drawn laterally from the side of a CNT forest (Fig. 1a). It is then placed on a clean substrate of Corning 1737 display glass or flexible plastic (PET or PEN) (Fig. 1b). The CNT sheet was densified using surface tension effects of an imbibed liquid (for example, methanol). The rapid evaporation of the solvent absorbed in the sheet causes shrinkage leading to densification. Four devices were fabricated on each substrate, each having an area of ~3 mm^2 (Fig. 2). A layer

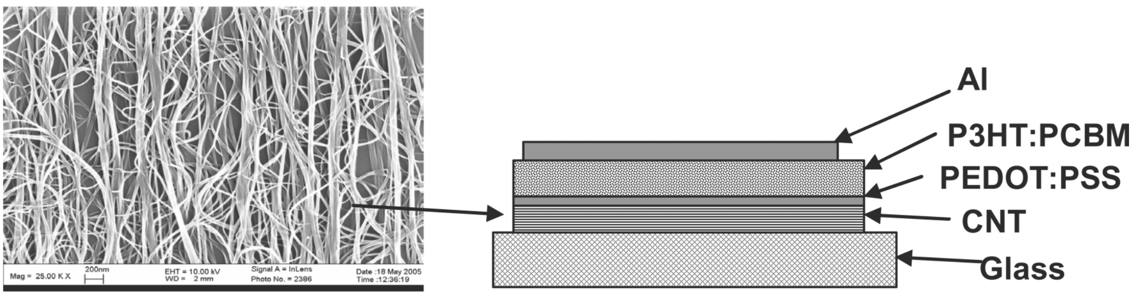

Fig. 2 Illustrates a solar cell or photodetector based on liquid densified carbon nanotube ribbons as a bottom transparent conducting electrode.

of PEDOT:PSS was then spin-coated onto the substrate at 6100 rpm creating a 50–55 nm layer. The sample was then dried by being heated at ~120 °C for 45 minutes in a glove box. The photoactive material solution was then spin-coated onto the sample at 700 rpm creating a 175–225 nm layer using a toluene solution consisting of roughly 9:10 weight ratios of PCBM and RR-P3HT, respectively. An aluminum cathode was then deposited under high vacuum ($<10^{-6}$ torr) at an initial deposition rate of 0.4 Å/s and gradually increasing to 1.0 Å/s with a 450 sec ramp time to create a final thickness of 1000 Å. A surface profiler (AMBIOS XP-1) was used to measure film thickness. EL-grade PEDOT-PSS was purchased from Bayer AG. RR-P3HT and PCBM were purchased from American Dye Source. All materials were used as received without further purification.

The absorption spectra were measured on a Perkin–Elmer Lambda 900 UV-VIS-NIR Spectrophotometer. The current–voltage characteristics were recorded with a Keithley 236 source-measure unit. A solar simulator (ORIEL 300 W) with light intensity calibrated at 100 mW/cm^2, was used as the light source for solar cell efficiency measurements. The reported efficiency measurement was not corrected for spectral mismatch. Photovoltaic measurements were done in a nitrogen-filled glove box.

3 Results and discussion

Bulk heterojunction device architecture of regioregular P3HT and PCBM was created with a CNT anode using extended homogenization by steering followed by heat treatment at the optimal temperature and time [5]. The nanocomposites of home synthesized fresh P3HT with PCBM spin coated on an ITO coted glass substrate at optimal concentration is demonstrated to give a record >4% power efficiency [5]. Our AFM studies showed the formation of a fine three-dimensional interpenetrating network.

For the key task of creating a flexible, mechanical load bearing and transparent charge collection network to substitute for ITO, we have developed several new methods to create multifunctional structures by a simple method of dry spinning self-assembly, as recently described [1]. These structures are based on very thin free-standing sheets of multiwall carbon nanotubes starting from a forest of MWCNTs home-synthesized by CVD.

This method allows one to obtain freestanding, strong ribbons of multiwall CNTs, which are highly oriented, have high optical transparency and can be easily transferred on various flexible substrates or even on ready to use photogeneration layers as effective hole collecting electrodes.

A single layer CNT sheet has a flat transmission better than 80% over a very broad spectral range from visible (0.4 μm) to infrared (2 μm) (extended transmission up to 10 μm was shown in [1]). The resistivity of the CNT sheet parallel to the direction of orientation decreases from 717 Ohm/sq to 605,

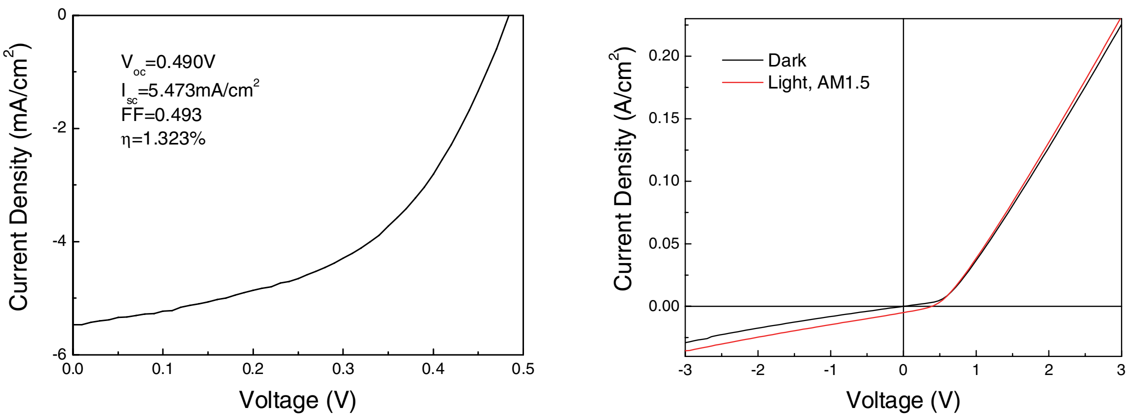

Fig. 3 (online colour at: www.pss-b.com) Current–voltage characteristics of the best ITO/PEDOT:PSS/PCBM + RR-P3HT/Al device in dark and under simulated solar light AM 1.5 100 mW/cm^2.

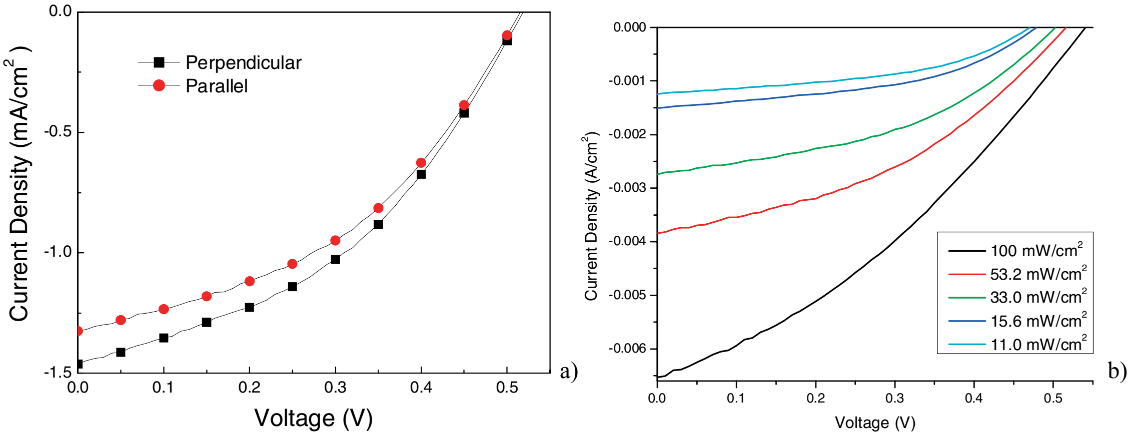

Fig. 4 (online colour at: www.pss-b.com) a) Current–voltage characteristics of the CNT/PEDOT:PSS/PCBM + RR-P3HT/Al device under simulated solar light AM 1.5 100 mW/cm^2 for two orthogonal polarizations of incident light. b) Dependence of $I-V$ curves on light intensity: filling factor increases at low power, so at 10 mW/cm^2 efficiency increases to 2.4%.

603 and 588 Ohm/sq and in the perpendicular direction from 3.96 kOhm/sq to 3.59, 3.54 and 3.47 kOhm/sq with the addition of 1, 2 and 3 layers of PEDOT:PSS respectively. Usually, resistivity of a carbon nanotube network increases 5–10 times after it is mixed with conducting polymers because of deteriorating intertube contacts. In contrary, spin-coating PEDOT:PSS on top of the carbon nanotube sheet decreases the resistance due to improved densification and, probably, intertube contacts.

Figure 3 shows current–voltage characteristics of the best ITO/PEDOT:PSS/PCBM + RR-P3HT/Al device in dark and under simulated solar light AM 1.5 100 mW/cm^2. Good diode characteristics and, surprisingly high photovoltaic parameters were obtained after annealing at 155 °C for 5 min: an open circuit voltage $U_{oc} = 0.49$ V, a short circuit current $J_{sc} = 5.47$ mA/cm^2, a fill factor FF = 0.49, and efficiency $\eta = 1.32\%$.

The efficiency of our preliminary created OPV SCs with transparent CNT collecting networks is slightly above 1% at AM 1.5 while at smaller incident photon power of 10 mW/cm^2 it increased to 2.4% (Fig. 4b), which is significantly higher than earlier reported 0.081% efficiency of MEH-PPV based SCs with non-transparent and thick MWCNT hole collectors [3]. Not only were the previous MWCNTs not mechanically strong structures, but also they were not oriented and transparent.

The CNT sheet electrode shows a polarization effect as seen in Fig. 4a. Current–voltage characteristics of the CNT/PEDOT:PSS/PCBM + RR-P3HT/Al device under simulated solar light AM 1.5 100 mW/cm^2 for two orthogonal polarization of incident light differ by 4.6%. The aligned carbon nanotube sheet can be used in polarization sensitive photodetectors.

4 Conclusions

In summary, we have demonstrated that an oriented multiwall carbon nanotube sheet can be used as the hole collecting electrode in polymer solar cells with RR-P3HT as the donor material and PCBM as the acceptor material. Relatively high photovoltaic characteristics have been obtained even with a non-optimized carbon nanotube sheet electrode: an open circuit voltage of 0.49 V, a short circuit current of 5.47 mA/cm^2. The next major task is creating SWCNT sheets by a method similar to [1]. This can be solved since forrests of SWCNT, a precursor for transparent sheets, have recently been grown [7] successfully, and we are now testing suitable forests for making strong sheets.

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