

Carbon nanotube–polybithiophene photovoltaic devices with high open-circuit voltage

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We report the preparation of photovoltaic devices using modified single wall carbon nanotubes, SWNTs. Devices are produced stacking on top of fluorine-doped tin-oxide, an electrochemically deposited polybithiophene layer, a layer of SWNT blended with poly(3-octylthiophene) and an evaporated

top metal contact, Ca/Al or Al. Ca/Al-top-electrode devices achieve open-circuit voltages of 1.81 V and average power conversion efficiency of 1.48% at irradiance of 15.5 W m⁻², spectrally distributed following AM1.5.

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1 Introduction Organic photovoltaics have received increasing attention in the last years, since the demonstration of photovoltaic devices based on copper phthalocyanine and perylene tetracarboxylic derivatives by Tang [1]. Several different materials and combinations were investigated using both, small molecular weight materials and conjugated polymers [2], aiming at the production of efficient, flexible and cheap large active area devices.

Carbon nanotubes are being seriously considered for photovoltaic applications, mainly composing blends formed with conjugated polymers [3–13]. The use of carbon nanotubes allows the formation of devices with high interfacial area between nanotube and conjugated polymer, potentially creating large pair dissociation regions, which in case of existing electric potential differences, may still benefit from the enhanced potential gradients at nanotube terminations.

Quite recently, the application potential of carbon nanotubes for hole-collecting electrodes in photovoltaic devices was also emphasized [11, 12]. The substitution of ITO (indium-tin oxide) electrodes is attractive considering that indium prices recently achieved the highest level of the last decades [14]. Electrode/substrate substitution may be relevant for device cost reduction strategies.

The SWNT-based photovoltaic devices reported until now, however, have a common characteristic, its low open-circuit voltage V_{oc} , typically below 1 V [3, 4, 6, 9–12]. This is one important factor imposing power conversion efficiency η limitations, since there is a direct proportionality between η and V_{oc} , quantitatively expressed by

$$\eta = \frac{V_{oc} \cdot J_{sc} \cdot FF}{\Phi}, \quad (1)$$

where Φ is the total irradiance, J_{sc} is the short-circuit current density and FF, the fill-factor, which is given by

$$FF = \frac{V_p \cdot I_p}{V_{oc} \cdot I_{sc}}, \quad (2)$$

where V_p and I_p represent the maximum-power-rectangle of $I \cdot V$ values and I_{sc} is the short-circuit current.

Leguenza et al. [15] have quite recently reported the production of single-layer polybithiophene-based devices showing $\eta = 0.44\%$ at $\Phi_{AM1.5} = 6.6 \text{ W m}^{-2}$ (irradiance distributed following AM1.5), with the remarkable characteristic of $V_{oc} = 2 \text{ V}$. Their device electrodes (fluorine doped tin oxide and Al) have almost similar work functions, so that the built-in electric field originated by the electrode

work function difference cannot be responsible for the high-observed V_{oc} , which was attributed to polarization of the polybithiophene layer.

In SWNT-poly(3-octylthiophene) (POT) based devices V_{oc} is weakly dependent on the difference between electrode work functions [4], so that the strategy of using electrodes with work function difference as large as possible has only a poor efficacy in V_{oc} improvement. For this reason it is worth trying the strategy of insertion of a polarized layer to improve V_{oc} in SWNT-based devices, helping again to avoid shorts produced by a small, but existing fraction of metallic SWNTs. If a continuous polymer layer is inserted between one electrode and the layer containing SWNTs, this layer is expected to hinder the occurrence of too low shunt resistance [16].

In this letter we report the preparation of photovoltaic devices using modified SWNTs. Devices are produced by stacking on top of fluorine-doped tin-oxide (FTO), an electrochemically deposited polybithiophene (PBT) layer, a SWNT + POT blend layer and an evaporated top metal contact. In these devices electrons are collected and carried by the nanotubes to the top metal contact, whereas the holes are transported by the PBT, which also avoids nanotube contact with the FTO, to the FTO. FTO is cheaper than the most usual indium-tin oxide (ITO), but as recently demonstrated, is also suitable for highly efficient organic solar cell production [17].

POT was chemically synthesized following a procedure reported elsewhere [18]. Carbon nanotube soot (Carboxlex Inc.) was produced by arc-discharge method using ~4 at% Ni–Y loaded carbon electrodes. The samples were purified by dry oxidation in air at 350 °C during 1 h to remove amorphous carbon, followed by a reflux in 3 mol l⁻¹ of HNO₃ during 8 h to remove metallic particles. This purification protocol is known to add carboxylic groups to the nanotube edges and defects [19].

For additional SWNT functionalization, 15 mg SWNT-COOH and 3 ml SOCl₂ were stirred at 80 °C during 24 h. The SOCl₂ was then evaporated, 2 ml 2-(2-tienyl)ethanol were added, and the resulting solution was stirred during 72 h at 80 °C, resulting in 2(2-tienyl)ethanol modified SWNTs, SWNT-TIOPH, like shown in Fig. 1. POT + SWNT-TIOPH blends were prepared adding a 10 mg ml⁻¹

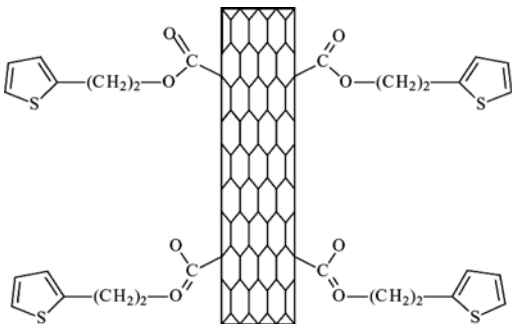


Figure 1 Schematic representation of the SWNT-TIOPH structure.

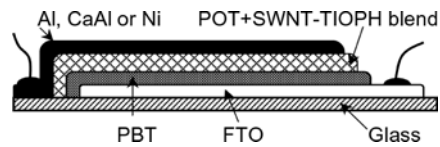


Figure 2 Scheme of the FTO/PBT/POT + SWNT-TIOPH/Ca/Al device structure.

POT solution (stirred during 24 h) to a SWNT-TIOPH dispersion in toluene with Polywell 3900 (dispersion agent) at 1% w/w in respect of the final POT weight. The proportion of the solutions was selected to achieve the final desired 5% SWNT-TIOPH:POT w/w proportion. POT, SWNT, SWNT-COOH, SWNT-TIOPH and the POT + SWNT-TIOPH blend materials were fully characterized and their characterization will be fully reported in due course.

The heterojunction devices were prepared by electrochemically depositing a 160 nm PBT layer on top of FTO covered glass substrate (10–15 Ω/sq., supplied by Vidcon Ltda), following exactly the same deposition conditions as reported elsewhere [15]. This PBT thickness was selected because it corresponds to the highest observed V_{oc} in FTO/PBT/Al devices [15], i.e., ~2 V. On top of the PBT, a 200 nm thick 5% w/w SWNT-TIOPH:POT layer was deposited by spin coating 10 mg/ml SWNT-TIOPH:POT suspension in toluene, followed by top metal contact (Al or Ca/Al) evaporation at 10⁻⁶ Torr (see Fig. 2).

Device photovoltaic characterization was performed measuring the current vs. voltage $I(V)$ characteristics in the dark and under AM1.5 spectral distribution using a 150 W Oriol solar simulator plus filters. The samples were illuminated through the glass substrate and the irradiance was controlled using neutral filters. The irradiance was determined using a calibrated silicon photodiode.

Absorption spectra of POT and POT + SWNT-TIOPH present a broad band centered at ~510 nm, with a full width at half maximum (FWHM) of ~180 nm and ~210 nm, respectively. PBT absorption band is centered at 470 nm, with a FWHM of ~200 nm. The photon to collected electron conversion efficiency, quantitatively described by

$$IPCE = \frac{1.24 \times 10^{-6} J_{sc}}{\lambda \Phi_{\lambda}}, \quad (3)$$

where λ is the wavelength and Φ_{λ} is the irradiance at wavelength λ , presents pronounced peaks at ~350 nm and ~600 nm and a less intense peak at ~470 nm, suggesting a charge-transfer interaction between the PBT and POT + SWNT-TIOPH blend layers.

In Fig. 3 we present the $I(V)$ curve of an FTO/PBT (160 nm)/POT + SWNT-TIOPH (200 nm)/Ca/Al device, which demonstrates the high achieved open-circuit voltage. The most relevant data are summarized in Table 1, which also includes the data of FTO/PBT(160 nm)/POT+SWNT-TIOPH(200 nm)/Al devices, for comparison. Devices with

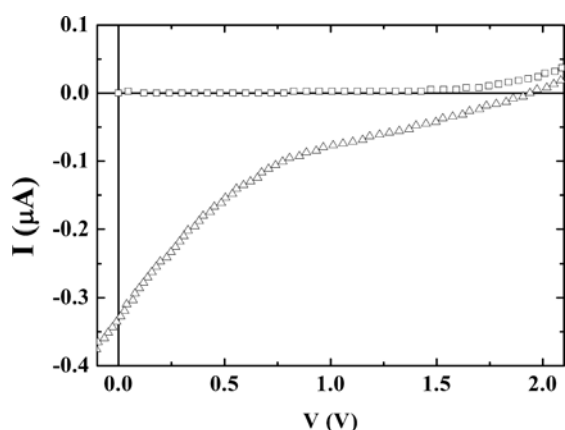


Figure 3 $I(V)$ curve of an FTO/PBT (160 nm)/POT + SWNT-TIOPH (200 nm)/Ca/Al device in the dark (squares) and at $\Phi_{AM1.5} = 15.5 \text{ W m}^{-2}$ (triangles).

Ca/Al top electrodes show a broad dispersion of J_{sc} and as a consequence, also of η . We observed that even different devices, i.e., different top contacts, prepared on the same sample usually show different η , which achieved values up to 3%. This dispersion of values constitutes a problem but the high observed values justify a stronger research effort aiming at the control of reproducible high power conversion efficiency.

The work functions of Ca ($\sim 2.9 \text{ eV}$) and Al ($\sim 4.3 \text{ eV}$) differ considerably, but the substitution of Al by Ca/Al as top contact produces a change in V_{oc} , which is lower than the work function difference, as previously observed in case of Au, Cu, Cr and Al [4]. Additionally, it demonstrates that strategies based on the insertion of polarized layers are promising for V_{oc} improvement in heterojunction devices. Using such layers for V_{oc} increase and taking advantage of the good charge dissociation/collection properties of carbon nanotube blends interfaces with conjugated polymer homolayers, allows envisaging significant future improvements in organic photovoltaic devices.

An important point regards the PBT layer. Our results demonstrate the feasibility of devices with polarized organic semiconductors forming interfaces with SWNT-based blends. It must be emphasized, however, that this was the first material that we identified as suitable for this purpose. Considering that electrets were widely investigated during a long period, it is reasonable to expect that more appropriate materials, conjugated molecules or polymers showing high permanent polarizability can be found for photovoltaics. This enterprise, however, will request addressing other issues, like long-term thermal- and photo-stability, which are out of the scope of this letter.

Table 1 Comparison of average values of device parameters for Ca/Al and Al top electrodes, at $\Phi_{AM1.5} = 15.5 \text{ W m}^{-2}$ and $\Phi_{AM1.5} = 12.5 \text{ W m}^{-2}$, respectively.

device	V_{oc} [V]	η [%]
FTO/PBT/POT + SWNT-TIOPH/Ca/Al	1.81	1.48
FTO/PBT/POT + SWNT-TIOPH/Al	1.02	0.38

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