



ELSEVIER

Contents lists available at ScienceDirect

# Solar Energy Materials & Solar Cells

journal homepage: [www.elsevier.com/locate/solmat](http://www.elsevier.com/locate/solmat)

## Multi-wall carbon nanotube coating of fluorine-doped tin oxide as an electrode surface modifier for polymer solar cells

A. Capasso<sup>a,\*</sup>, L. Salamandra<sup>b</sup>, A. Chou<sup>a</sup>, A. Di Carlo<sup>b</sup>, N. Motta<sup>a</sup><sup>a</sup> School of Chemistry Physics and Mechanical Engineering, Queensland University of Technology, 2 George St, Brisbane, QLD 4000, Australia<sup>b</sup> CHOSE (Centre for Hybrid and Organic Solar Energy), Department of Electronic Engineering, University of Rome Tor Vergata, Via del Politecnico 1, 00133 Rome, Italy

### ARTICLE INFO

#### Article history:

Received 2 September 2013

Received in revised form

14 October 2013

Accepted 21 October 2013

Available online 12 November 2013

#### Keywords:

Carbon nanotubes

Organic photovoltaics

Polymer solar cells

Transparent conductive oxide

Chemical vapor deposition

Surface modifier

### ABSTRACT

A controlled layer of multi-wall carbon nanotubes (MWCNT) was grown directly on top of fluorine-doped tin oxide (FTO) glass electrodes as a surface modifier for improving the performance of polymer solar cells. By using low-temperature chemical vapor deposition with short synthesis times, very short MWCNTs were grown, these uniformly decorating the FTO surface. The chemical vapor deposition parameters were carefully refined to balance the tube size and density, while minimizing the decrease in conductivity and light harvesting of the electrode. As created FTO/CNT electrodes were applied to bulk-heterojunction polymer solar cells, both in direct and inverted architecture. Thanks to the inclusion of MWCNT and the consequent nano-structuring of the electrode surface, we observe an increase in external quantum efficiency in the wavelength range from 550 to 650 nm. Overall, polymer solar cells realized with these FTO/CNT electrodes attain power conversion efficiency higher than 2%, outclassing reference cells based on standard FTO electrodes.

© 2013 Elsevier B.V. All rights reserved.

### 1. Introduction

Organic photovoltaics has been gaining momentum in recent years and is now one of the fastest-developing technologies in the field of green energy. Its success largely hinges upon the low manufacturing and material costs, simple fabrication via printing techniques [1], which also opened to the creation of flexible devices by roll-to-roll processing [2,3], providing the access of organic solar cells to market areas generally closed to silicon-based solar cells [4]. Thanks to a strong research interest, polymer solar cells have undergone a steady increase in power conversion efficiency (PCE) [5,6], becoming a mature technology able to compete in the market [7–9].

Indium tin oxide (ITO) is a transparent conductive oxide commonly used as a standard electrode in thin film and organic photovoltaics [10]. However, its electrical/optical properties require further optimization to achieve maximum device's performance. In the past, several research groups proposed carbon nanotubes (CNT) in the cell architecture to take advantage of their superior electrical and morphological properties [11]. As for electrodes, CNT layers have been deposited on glass to replace ITO as electrode material, yet failing to attain a ratio between sheet

resistance and transparency that would promote an effective replacement of ITO [12]. Hybrid configurations combining ITO and CNT proved to be a more effective strategy, albeit with a large room for improvement. Freestanding CNT sheets have been placed on top of ITO reaching 1.7% of PCE [13]. In order to exploit further such promising results, CNTs have been embedded in the cell architecture by growing them directly on the ITO surface by chemical vapor deposition (CVD), in an attempt of improving the charge collection at the electrode [14,15]. However, the high temperature required for the CVD process (500–600 °C) is extremely detrimental to the conductivity and optical transmittance of ITO [16], and thus represents a major hindrance to this approach's application. Therefore, although the direct synthesis of CNT on ITO have successfully demonstrated the possibility of using a transparent conductive oxide as CVD substrate, the overall PCE of as-built solar cells never reached values as high as the references due to the inherent incompatibility in material processing, so putting an end to this line of research.

In order to overcome such an impasse, in this article we explore for the first time the direct synthesis of CNT on fluorine-doped tin oxide (FTO). Differently from ITO, FTO can sustain a prolonged sintering at temperatures higher than 500 °C without changing its properties [17]; remarkably, it has been reported even a drop in FTO's resistivity by 1 Ω/sq after a thermal treatment in air at 600 °C [18]. By analyzing the synthesized materials by electron microscopy and Raman spectroscopy, we investigated the impact of a wide range of CVD parameters and ultimately found the

\* Corresponding author. Tel.: +393397057135.

E-mail address: [a.capasso@qut.edu.au](mailto:a.capasso@qut.edu.au) (A. Capasso).

process conditions providing the best combination of conductivity and transparency for FTO/CNT electrodes. We developed polymer solar cells by using these modified FTO/CNT electrodes, finding an increased efficiency compared to the conventional architectures.

## 2. Experimental methods

### 2.1. MWCNT synthesis on FTO electrodes

MWCNT were synthesized on FTO electrodes. The glass/FTO substrates (Pilkington,  $8 \Omega/\text{sq}$ , 3 mm/700 nm thick) were cleaned by ultrasonic baths in acetone and isopropyl alcohol. A 3 nm layer of Ni was deposited in high-vacuum by thermal evaporation at  $10^{-6}$  mbar. The substrates were loaded face-down on top of a Si stage in a CVD system, where the set temperature on the stage is reached by Joule effect. The CNT synthesis was performed at 600 °C for the desired time with an Ar/C<sub>2</sub>H<sub>2</sub> flow (300/30 sccm). When the synthesis was complete, the samples were quickly cooled down to room temperature (fast extraction).

After CVD, the substrates were analyzed by FE-SEM (JEOL JSM-7001F) and TEM (Jeol 1011 TEM). Raman spectra were collected using an inVia Renishaw Micro-Raman system. The 632.8 nm line of a He–Ne laser at room temperature were focused on an area of the samples about 1 μm wide, choosing a low laser power to prevent heat accumulation. On each sample, several areas were probed and the spectra were averaged to rule out possible discrepancies in the surface. The transmittance spectra of the electrodes were acquired with a UV–vis spectrophotometer (Shimadzu UV-2550). The sheet-resistance of FTO/CNT electrodes were measured with a Keithley 2410 source-meter in four-probe configuration

### 2.2. Solar cell assembly and testing

Bulk-heterojunction (BHJ) solar cells were built in a glove-box filled with nitrogen by using standard glass/FTO and glass/FTO/CNT electrodes. A film of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) was deposited by spin coating as hole transport layer between FTO and photoactive blend. This is a standard step in the polymer solar cell assembly, required to flatten the ITO surface, improve the charge collection, align the energy level and increase the  $V_{OC}$  [11], but it is unfeasible on FTO/CNT because of the high hydrophobicity of the CNT layer. Therefore, alternate transport layers with equal performance were used to adapt the work function energy of the electrodes to the HOMO-LUMO levels of the donor/acceptor blend. Two specular configurations of polymer solar cells were implemented: inverted (electrode/Cs<sub>2</sub>CO<sub>3</sub>/P3HT:PCBM/MoO<sub>3</sub>/Ag) and direct (electrode/MoO<sub>3</sub>/P3HT:PCBM/Ca/Al). In the inverted cell, a Cs<sub>2</sub>CO<sub>3</sub> electron transport layer, deposited via liquid phase processing [19,20], allows the energy level alignment between cathode and active layer; similarly, an evaporated MoO<sub>3</sub> [21,22] hole transport layer promotes the charge transfer between the active layer and the metal anode. In the direct cell, the MoO<sub>3</sub> is at the interface with transparent conductive oxide anode [23].

For the inverted cell, the 2 nm layer of Cs<sub>2</sub>CO<sub>3</sub> was spin-coated on glass/FTO/(CNT) cathode from a solution of 0.2 wt% in 2EE (2-ethoxyethanol) at 5000 rpm for 60 s. A 2 wt% solution (1:0.7) of regio-regular P3HT (Sigma-Aldrich) and PCBM (Solenne BV) was diluted in DCB (dichlorobenzene) and spin-coated at 400 rpm for 60 s (~100 nm), as active layer. At last, 5 nm of MoO<sub>3</sub> and 100 nm of Ag were deposited via thermal evaporation at  $10^{-6}$  mbar, respectively as hole transport layer and top metal anode. For the direct structure, both MoO<sub>3</sub> and P3HT:PCBM layers were deposited as before. Finally, 20 nm of Ca and 80 nm of Al were deposited via

thermal evaporation ( $10^{-6}$  mbar) as top metal cathode. For the two architectures, 8 devices were realized. All the 16 cells have an active area of 16.6 mm<sup>2</sup> and were not encapsulated.

The current–voltage ( $J$ – $V$ ) characteristics of the cells were measured with a Keithley 2410 source-meter under AM1.5G (100 mW/cm<sup>2</sup>) illumination of a Sun 2000 Class A ABET solar simulator. To measure the external quantum efficiency (EQE), the devices were illuminated by monochromatic light and the photocurrent was recorded by a Keithley 2612B source-meter. A Lot-Oriel IPCE system, comprising a Xe-arc lamp as white light source and a monochromator, was used to generate monochromatic light, whose intensity was measured using a Thorlabs UV-Enhanced FDS1010 calibrated Si photo-detector. Sample transmittance was obtained with a Shimadzu UV2020 spectrophotometer with integrated sphere.

## 3. Results and discussion

### 3.1. Electrode characterization

After the CVD synthesis, the electrode was less transparent, with a greyish layer covering the FTO area. Upon FE-SEM inspection, the FTO surface appears coated by a layer of multi-wall carbon nanotubes (MWCNTs), which are uniformly distributed all over the oxide crystals (Fig. 1a). Low CVD temperature (600 °C) combined with short time (3 min) gave rise to the growth of CNT with small radius of curvature. The CNT length in this case could be controlled to a large extent, the nucleation rate on the tin oxide substrate being rather slow (as compared for instance to Si or SiO<sub>2</sub>) [13]. As seen in the SEM micrograph, we managed to obtain short MWCNTs, which in some cases appeared to be solely nucleated. On average, the tubes had a diameter around 30 nm and are shorter than 100 nm, as confirmed by TEM analysis (Fig. 1b). The low synthesis temperature led to the growth of defective MWCNTs, whose walls were in some cases partially covered by residual amorphous carbon.

The Raman spectra taken on the FTO/CNT samples show features in the typical bands of graphitic materials as CNT (Fig. 2): D (~1350 cm<sup>-1</sup>), G (~1580 cm<sup>-1</sup>), and 2D (~2700 cm<sup>-1</sup>). In carbon-based materials, the D band is usually attributed to defective graphitic structures (as carbonaceous impurities with  $sp^3$  bonding, broken  $sp^2$  bonds in the sidewalls, etc.), bending or finite-size effects [24,25]. The G band arises from the zone center  $E_{2g}$  mode and corresponds to ordered  $sp^2$  bonded carbon; it is enhanced in the case of carbon atoms vibrating along a nanotube axis (LO phonon mode) [26]. The 2D band is related to the iTO (in-plane transversal optical) branch in the phonon dispersion of  $sp^2$  carbon materials [27,28], and may represent an accurate indication of the CNT quality or purity [29].

For all the samples, the G peak (centered at ~1600 cm<sup>-1</sup> with FWHM of 70–92 cm<sup>-1</sup>) is the most intense feature but is not very sharp as in the case of single wall carbon nanotubes (SWCNT) and graphene, thus confirming the presence of MWCNTs. The peak is also shifted from 1580 to 1600 cm<sup>-1</sup>, indicating the presence of graphitic layers with small crystallite sizes or abundant edges. The broad D peak (centered at ~1330 cm<sup>-1</sup>) is also typical of multi-wall carbon nanotubes, which may possess defects between the various walls. The D peak shape is also coherent with the low-temperature synthesis process used (< 700 °C), where the available energy can usually allow only the formation of MWCNTs of large diameter (i.e. many walls), most likely with imperfect levels of graphitization and more abundant defects [30]. This inference is also supported by the presence of a weak and broad 2D mode (the mesa-like component centered at 2780 cm<sup>-1</sup>). Besides, no radial breathing modes are visible in the spectra, further proving that

متن کامل مقاله

دریافت فوری ←

**ISI**Articles

مرجع مقالات تخصصی ایران

- ✓ امکان دانلود نسخه تمام متن مقالات انگلیسی
- ✓ امکان دانلود نسخه ترجمه شده مقالات
- ✓ پذیرش سفارش ترجمه تخصصی
- ✓ امکان جستجو در آرشیو جامعی از صدها موضوع و هزاران مقاله
- ✓ امکان دانلود رایگان ۲ صفحه اول هر مقاله
- ✓ امکان پرداخت اینترنتی با کلیه کارت های عضو شتاب
- ✓ دانلود فوری مقاله پس از پرداخت آنلاین
- ✓ پشتیبانی کامل خرید با بهره مندی از سیستم هوشمند رهگیری سفارشات