

# Soluble carbon nanotubes/phthalocyanines transparent electrode and interconnection layers for flexible inverted polymer tandem solar cells



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## ABSTRACT

In this study, we focus on transparent electrodes for organic solar cells prepared from aqueous solutions consisting of single wall carbon nanotubes (SWCNTs) and a copper-phthalocyanine derivative (TSCuPc). We first investigated their electrical conductivity and optical properties. The high solubility level of the TSCuPc/SWCNTs enables the production of stable inks with high conductivity which allows obtaining flexible photovoltaic devices based TSCuPc/SWCNTs films with good performances. A power conversion efficiency of 3.2% was achieved in a device with a blend of poly (3-hexylthiophene-2,5-diyl):phenyl-C61-butyric acid methyl ester (P3HT:PCBM) as the active layer with a TSCuPc/SWCNTs sprayed electrode on a polyethylene terephthalate (PET) substrate. TSCuPc and TSCuPc/SWCNTs were also employed as the electron transport layer (ETL) and the interconnecting layer (ICL) in an inverted tandem organic solar cell based on front P3HT-ICBA and back [70]PCBM-PCDTBT active layers, achieving an efficiency of 7.40%.

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## 1. Introduction

Polymer bulk heterojunction solar cells are low-cost, lightweight, relatively easy to fabricate and have the potential for development/integration in flexible devices [1]. It is a good alternative to their inorganic counterparts due to the prospect of utilizing cheap printing processes. In this respect, solution deposition of transparent, highly conductive electrodes has become a major point of interest in both academic and industrial research activities.

The traditional material for transparent electrodes is indium tin oxide (ITO) with excellent conductivity and transparency. Unfortunately, ITO suffers from two considerable drawbacks. Firstly, the price of indium has soared over the last decade. Second, future display technology is likely to require flexible electrodes for applications such as touch screens, liquid crystal displays, organic light-emitting diodes and solar cells [2–5]. While, ITO is completely unsuited for such applications due to its brittleness. For instance ITO was shown to crack when used in the current generation of touch screen displays and consequently it is likely to do so in next-generation bendable displays and/or flexible solar cells [6,7]. Thus, it is clear that an ITO substitute is needed,

preferably a material whose conductivity is invariant under flexing and dispensed with the help of eco-friendly solvents. To meet minimum industry standards, such a material should have a sheet resistance,  $R_s \leq 100 \Omega/\square$  coupled to an optical transparency of  $T \geq 70\%$  ( $\lambda = 550 \text{ nm}$ ). This requires a material with relatively high conductivity and low optical absorbance as manifested by a large ratio of DC to optical conductivity,  $\sigma_{DC}/\sigma_{OP}$  (optical conductivity is related to the optical absorption coefficient) also referred as the figure of merit [8,9]. It can be shown that industry targets can only be met for a material with  $\sigma_{DC}/\sigma_{OP} \geq 35$ . Recently, more research efforts have developed higher efficiency solar cells using various strategies, such as morphological engineering [10], interface engineering [11], materials innovation and electrodes.

Today, SWCNTs embedded in a polymer matrix have emerged as promising candidates for transparent conducting thin films owing to the CNTs' high electrical/thermal conductivities, high aspect ratio and nanoscale diameter [12,13]. Commonly, the dispersion of SWCNTs in organic or aqueous media has been achieved by covalently or non-covalently modifying the nanotubes [14,15]. Recently many works [16–22] described developments and future outlooks for the use CNTs-polymers systems as potential alternative materials for various applications including printing flexible electrodes in organic electronics devices. Many approaches [23–25] used poly(-3-hexylthiophene) (P3HT), poly (3,4-ethylene dioxythiophene)-poly(styrene sulfonate) (PEDOT:PSS) and poly (-methyl methacrylate/acrylic acid), to disperse and deposit

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uniform carbon nanotube bundle networks for transparent conducting films (TCFs). The metallo-phthalocyanine complexes have attracted much attention due to their application in different areas such as in display devices, data storage and solar cells. In a recent work, we have shown that water-soluble copper metallo-phthalocyanines are promising materials as the electron transport layer in organic solar cells [26]. Moreover they can also be used as transparent conducting electrodes [27].

In this context, the primary objective of this work is to prepare transparent conducting electrodes on glass and plastic by spray-coating an aqueous dispersion of SWCNTs and tetrasulfonate copper phthalocyanine (TSCuPc). Besides, we used a neat TSCuPc film as an electron transport and interconnecting layer in tandem solar cells. This work demonstrates the use of TSCuPc films as an interlayer in single and tandem solar cells, as well as a conducting film for electrodes. In this report we obtained SWCNT/TSCuPc composite films with conductivity up to  $2 \times 10^5$  S/m and optical transmission higher than 70% at 550 nm. These characteristics made the film applicable as electrodes in P3HT:PCBM based solar cells, reaching an efficiency of 2.6% (glass substrate) and 3.12% (PET substrate). With the use of the TSCuPc/SWCNT film as an interlayer in tandem architecture [glass/ITO/TSCuPc/P3HT-ICBA/PEDOT/TSCuPc-SWCNT/TSCuPc/PC70BM-PCDTBT/MoO<sub>3</sub>/Ag] an efficiency of 7.4% was achieved.

## 2. Experimental details

Highly purified SWCNTs (ASP-100F), produced by arc discharge and purified by thermal and acid treatments, were purchased from Hanwha Nanotech Company and were used as received. We used deionized water soluble TSCuPc as a matrix to disperse the SWCNTs. First, we started by the optimization of the aqueous TSCuPc:SWCNT dispersion by varying the solute concentrations. The SWCNTs dispersions were ultrasonically treated by using a horn-type sonicator (ULS-700S) for 5 min and tip sonication by 30% of the maximum output power (700 W). Following a 90 min centrifugation at 5500 tr/min, the upper 80% solution in the containers was collected to obtain well dispersed SWCNTs free of large bundles and aggregates. Transparent SWCNTs/TSCuPc films were fabricated on polyethylene terephthalate (PET) and glass substrates by spray-coating. While spray-coating, the PET and glass substrates were heated at 110 °C to immediately dry the water. Washing was repeated twice, followed by drying on a hotplate at 110 °C. The sheet resistances of the films were measured using a four-point probe at room temperature. SWCNTs:TSCuPc (1:1) films were characterized by measuring both their sheet resistance and optical transmittance (*T*) on PET and glass substrates while comparing to the neat TSCuPc film. Optical transmissions were measured at a wavelength of 550 nm from UV–Vis–NIR absorption spectra of the SWCNTs films. Raman spectroscopy was used to investigate the interaction between SWCNTs and the polymer matrices with an incident argon laser excitation wavelength of 514 nm.

Solar cell devices based on P3HT/PCBM blends were fabricated by spin-coating a layer of TSCuPc/SWCNTs on PET (*t* = 20 nm) and glass substrates (*t* = 30 nm). After washing with water and drying at 110 °C for 10 min in the oven, the substrates were placed in a nitrogen-filled glove-box. P3HT (20 mg ml<sup>-1</sup>) and PCBM (20 mg ml<sup>-1</sup>), were dissolved in 1 ml of *o*-dichlorobenzene. Subsequently, the P3HT/PCBM blend was spin-coated on the TSCuPc/SWCNTs layer, forming a P3HT/PCBM active layer of 180 nm. Following solvent annealing, MoO<sub>3</sub> (10 nm) and Ag (80 nm) cathode were deposited on top of the P3HT/PCBM active layer by thermal evaporation at a pressure of approximately  $2 \times 10^{-6}$  Torr. The active area of the device, defined by a shadow mask, was 0.86 cm<sup>2</sup>.

## 3. Results and discussion

The sheet resistance of the TSCuPc/SWCNT film on glass is  $R_s \sim 88 \Omega/\text{sq}$  and the transmission at 550 nm  $T = 70\%$  ( $\sigma_{\text{DC}}/\sigma_{\text{Op}} \sim 11.06$ ). A higher  $\sigma_{\text{DC}}/\sigma_{\text{Op}}$  ratio implies a higher electrical conductivity of the SWCNT films at the same *T* (%) [28], where the  $\sigma_{\text{DC}}$  and  $\sigma_{\text{Op}}$  are the direct and optical conductivities respectively. The good conductivity and smooth surface of the TSCuPc/SWCNT films, which showed an absence of CNT bundles and low peak valley, make it a good candidate to be used as the transparent electrode in solar cell and OLED devices. Fig. 1 shows UV–Vis–NIR absorption spectra of the TSCuPc and SWCNTs/TSCuPc films prepared by spray-coating on glass. The copper (II) phthalocyanine-tetra-sulfonate (TSCuPc) exhibits a typical electronic spectrum with two strong absorption Q and B bands [29]. The Q band is in the visible region at about 600–700 nm, which is attributed to the  $\pi$ – $\pi^*$  transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the phthalocyanine ring. The B band is in the UV region at about 300–400 nm, arising from the deeper  $\pi$ -levels/LUMO transition.

Once the SWCNTs films were dispersed by TSCuPc, the absorption spectrum underwent a noticeable change. The UV–Vis–IR spectrum of the TSCuPc/SWCNT film shows the presence of the other two peaks which reflect the semiconducting nature of the SWCNTs. The *S*<sub>11</sub> (1.8 μm) and *S*<sub>22</sub> (1 μm) peaks are due to the inter-band transitions between the first and second pairs of van Hove singularities of the semiconducting tubes, respectively [30–32]. However, the small intensity of the *S*<sub>11</sub> peak may be attributed to the electrostatic charge interaction between the molecules of TSCuPc and SWCNTs. Herein, small ions such as Na<sup>+</sup> from the TSCuPc seem to play an important role in the electrostatic charge interaction [33–37]. Moreover, when the TSCuPc interacts with SWCNTs, the anion (SO<sub>3</sub><sup>-</sup>) bonds are expected to rotate and adjust to the shape of the SWCNTs to maximize the overlap of the  $\pi$ -orbitals between the Pc rings and the walls of the SWCNTs [30,31]. However these molecular adjustments do not prevent the charged sulfonated groups' interaction with water, thus facilitating the separation and stabilization of individual SWCNTs through electrostatic repulsion.

To understand the effect of the TSCuPc on SWCNTs we studied the films by Raman spectroscopy. Indeed, the Raman spectroscopic measurements provide further insight into the effects of doping with SWCNTs through the investigation of the G and G<sub>0</sub> bands which are often used to identify charge transfer in doped SWCNTs [38–42].

With chemical dopants, there is charge transfer from the SWCNTs'  $\pi$  system to the electron acceptors which stiffens the bonds and blue shifts the Raman peaks [39,40]. While, charge

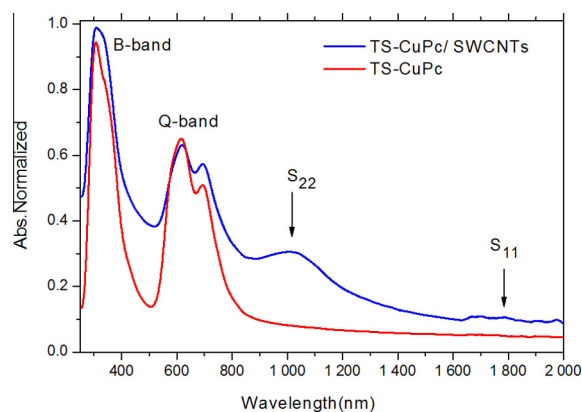


Fig. 1. Optical UV–Visible–NIR absorption spectra of TSCuPc/SWCNTs and TSCuPc.

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