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Improvement of photovoltaic performance of inverted hybrid solar cells by adding single-wall carbon nanotubes in poly (3-hexylthiophene)

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ABSTRACT

Solution prepared hybrid solar cells show promising low cost technology for electricity generation from sun light, although their power conversion efficiency has to be improved. One of the approaches is to increase the absorbance or charge carrier mobility of organic semiconductors. In this work, pristine single walled carbon nanotubes (SWCNT) were added into poly(3-hexylthiophene) (P3HT) solution to form P3HT:SWCNT composite films with different weight percent (wt%) of SWCNT. It is observed that optical absorbance spectra as well as the morphology of the composite films were modified by the addition of SWCNTs. This phenomenon could be explained by the π-π interaction between the conjugated polymer and carbon nanotubes. Most importantly, the electrical conductivities of the composite films increased with the SWCNT wt%. When these films were used as hole conductor layers in inverted planar hybrid solar cell, with CdS thin films as electron acceptor layers, the fill factor (FF) and open-circuit voltage (Voc) of the corresponding cells were decreased with the increase of the wt% of SWCNT. However, the short-circuit current density (Jsc) and the power conversion efficiency (PCE) showed a maximum value at about 0.4 wt% of SWCNT in P3HT. The transient photovoltage measurements (TPV) revealed that the presence of SWNCT promoted the charge recombination process at P3HT/CdS interface, and as a result, reduced the Voc. The photovoltaic performance of the hybrid solar cells could be optimized by choosing an adequate weight percentage of SWCNT in P3HT to balance the charge carrier transport and charge recombination processes at the donor-acceptor interface.

1. Introduction

Organic or hybrid solar cells are heterojunction based electronic devices in which electron acceptor (n-type) and electron donor (p-type) are solution prepared organic or inorganic semiconductors. The easy processability, low fabrication cost, and flexibility [1,2] are principal premises of solution prepared solar cells. In particular, the active layers of hybrid solar cells are consisted of one solution prepared inorganic semiconductor (II-IV compounds, for example), and one organic semiconductor that could be soluble poly(3-alkylthiophenes) (P3AT). The inorganic electron acceptor offers a better stability of the cell in comparison with a 100% organic one. However, it is still a challenge to obtain high power conversion efficiency (PCE) in hybrid solar cells because of the mismatch of the optoelectronic properties of two components in the active layers of the cells. In recent years, there are several attempts on the incorporation of one-dimensional (1-D) nanostructures like carbon nanotubes in P3AT for solar cell applications. Kymakis et al. reported an increase of the hole mobility in single-wall carbon nanotubes (SWCNT) doped poly(3-octylthiophene) (P3OT) [3]. They explained that the SWCNT acted as conducting bridges connecting polymeric chains, leading to a decrease in localized states of P3OT matrix. The authors probed various SWCNTs weight percentage ratios and the optimal concentration was found as 1 wt%. For concentrations higher than 1% a decrease in hole mobility was attributed to the formation of shallow hole traps in polymer, or to the surfactant used for the dispersion of SWCNT [3]. The same group of authors also studied noncovalent functionalization of SWCNT by a dye and

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incorporated to P3OT. But of all the reported works, the photovoltaic parameters of the best solar cells were Jsc=0.25 mA/cm^2, Voc=0.75 V, FF=0.48, and a PCE of 0.1% [4].

More recently, regioregular poly(3-hexylthiophene) (P3HT) have been used as hole conductor with different electron acceptors: with C_{60} fullerenes in organic bulk heterojunction [5,6], with inorganic semiconductor nanoparticles in hybrid solar cells [7–11], as well as with carbon nanotubes (CNT) [12–20] as electron acceptors. Specifically, P3HT/CdS heterojunctions have showed a very large Voc, around 0.9 V [11] and 1.0 eV [10], and a maximum PCE of about 4% [10]. It seems that the interaction between polythiophenes and carbon nanotubes occur via π-π stacking, allowing overcome the Van Der Waals forces between CNT, so obtaining good dispersion of CNT by P3HT in common solvents [21]. The electronic properties and stability of CNT allow that exciton dissociation occur at the interface between the two materials and quenches the radiative recombination [12]. Also, the presence of defects on nanotubes surface, caused by chemical and physical treatment, disrupt the effective interaction between SWCNT and P3HT [13]. Various authors have studied the photoinduced charge transfer between SWCNT and P3HT, Ferguson et al. measured transient microwave conductivity and transient photoconductance of the P3HT:SWCNT films and reported a long-lived free carriers in the composite materials [16]. They also probed the influence of either enriched metallic or semiconductor SWCNT. The experimental results showed that charge separation was enhanced when the nanotubes metallic species was decreased in the SWCNT mixture [17,18]. On the other hand, E.Lioudakis, et al. found that the electron-phonon interactions at the vibronic sidebands quench the radiative emission by introducing nonradiative relaxation channels. They observed shorter exciton lifetimes as the amount of SWCNT is increased [22].

CNT have also been incorporated into P3HT:CdSe/ZnS hybrid solar cells with and without [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) [23,24]. In these cases the presence of CNT improved the photovoltaic performance of the cells. However, the correlation between the photocurrent density at short-circuit (Jsc) and photovoltage at open-circuit (Voc) with the incorporation of CNT in P3HT was not well explained. In this work, SWCNT was added at different weight percent into P3HT polymer and the P3HT:SWCNT composite films were used as electron donors, together with cadmium sulfide (CdS) thin films as electron acceptor in inversed hybrid solar cells. Optical and electrical properties of the P3HT:SWCNT films were studied. The CdS/P3HT:SWCNT solar cells were studied by transient photovoltage experiments to understand the charge recombination phenomena at the interfaces of CdS and P3HT:SWCNT. It is observed that Voc value of the cells decreases with the weight percentage of SWCNT, which was consistent with the decreased charge carrier recombination times under open circuit conditions. The Jsc, on the other hand, showed an optimal value as the concentration of SWCNT in P3HT was about 0.4 wt%. The power conversion efficiency (PCE) of hybrid solar cells could be enhanced by 46.3% with respect to that without SWCNTs due to an enhanced molecular order and electrical conductivity by the presence of SWCNTs in P3HT.

2. Experimental

Commercially available SWCNTs with 80% purity and 1–2 nm of external diameter were used as received. To get a good dispersion of the SWCNT product in regioregular P3HT (Aldrich, 97%) solution, carbon nanotubes were firstly dispersed in 1,2-dichlorobenzene (DCB) under stirring (ultrasonic bath) for one hour until the agglomerates were not visible in the solution. Then P3HT was added into SWCNT solution and the composite solution was vigorous stirred for one hour at room temperature before use. In all P3HT-SWCNT composite solutions, the concentration of the P3HT was kept at 2.5 mg/ml in accordance to a previous report [25], varying only the SWCNT mass. The weight percentage (wt%) of the SWCNTs in the composite solutions was varied from 0.2, 0.4, 0.8, 1.6–5 wt%, the last one beyond the percolation threshold (about 2 wt%). As the amount of SWCNT increased in the P3HT solutions, these turned to slightly dark. It is observed that if stirring solution was stopped, some dark material was deposited on the walls of the vial glass like precipitate after a short time, which could be probably amorphous carbon [26,27] or carbon nanotubes not well dispersed, since the untreated SWCNT product could contain amorphous carbon and catalytic particles. Therefore, to avoid the precipitation of SWCNT or amorphous carbon, the P3HT:SWCNT composite solutions were drop-cast onto the glass or CdS surface immediately after their preparation to form thin films of the composite materials.

Absorbance spectra of thin films of P3HT:SWCNT, deposited on glass substrates by drop casting, were measured using a SHIMADZU UV-3101PC UV–VIS–NIR Spectrophotometer . The thickness of the films was about 200 nm, measured with an AMBIOS XP-100 profilometer. For photoconductivity measurements, two silver electrodes were painted on P3HT:composite films and the data were recorded by 10 s in dark and 10 s under illumination at room temperature with 1 V of applied potential.

Hybrid solar cells were prepared by first the deposition of thin films of CdS on ITO coated glass substrates (Delta Technologies, sheet resistance of 8–12 Ω) with chemical bath deposition [28]. The composition of the solution consisted of 1.25 ml of cadmium nitrate (1 M), 7.5 ml of sodium citrate (1 M), 1 ml of concentrated ammonium hydroxide, 2.5 ml of thiourea (1 M), and finally 26.5 ml of distilled water. The thickness of CdS depended on the deposition time, measured as 33–96 nm for a deposition time from 1.5 to 2.5 h. The composite solution of P3HT:SWCNT were drop-cast on top of CdS films to ensure that the amount of carbon nanotubes inside the polymer was remained unchanged as much as possible after deposition. The freshly prepared composite films were dried and annealed in air at 190 °C for 10 min. Then conductive carbon paint (CP,SPI Chem) was deposited on top of polymer films in an area of 0.1 cm^2 through aluminum shadow mask to improve the ohmic contact between P3HT and the top metal contact [29]. Finally, Au electrode with 40 nm of thickness was deposited by evaporation in vacuum. A second annealing at 110 °C for 10 min was made for the whole devices. The device configuration had an inversed solar cell structure ITO/CdS/P3HT:SWNT/CP/Au, in which electrons were extracted from ITO and holes from Au.

An irradiance of 70 mW/cm^2 of a solar simulator (Oriel) was used to illuminate the ITO side of the cell samples, and the current density (J) – applied voltage (V) curves were recorded in dark and under illumination in air at room temperature. For transient photovoltage (TPV) measurements, the cell samples were kept under illuminating by a white lamp under open circuit voltage conditions. A laser pulse of 4–6 ns with a wavelength of 532 nm, 150 mW power average (Continuum, Minilite I Nd:YAG laser) was incident on the ITO side, and the photovoltage decays were recorded on an oscilloscope (Agilent Infiniium model 54833A DSO, 1 GHz) [25].

3. Results and discussion

Normalized optical absorbance spectra of the P3HT:SWCNT thin films with different SWCNT concentrations are shown in Fig. 1. The absorption spectrum of SWCNT was in the inset in Fig. 1. It is observed that the spectra of all the composite films have the