Chapter 5

Enhancing Quantum Dot Solar Cells stability with Semiconducting Single-Walled Carbon Nanotubes interlayer

Semiconducting Single-Walled Carbon Nanotubes (s-SWNT) are used as a protective layer between the active layer and the anode of lead sulfide colloidal quantum dot (PbS CQD) solar cells (SCs). The introduction of the carbon nanotubes increases the stability of the device, with 85% of the initial performance retained after 100-hour exposure to simulated solar light in ambient condition. This is in sharp contrast with the behavior of the device without s-SWNTs, for which the photoconversion efficiency, the open circuit voltage, the short-circuit current and the fill factor all experience a sharp decrease. Therefore, the inclusion of s-SWNT in CQDs solar cells does not affect the initial photoconversion efficiency of the devices (efficiency of 8.8%) and prevents their performance degradation under harsh conditions.

This chapter is based on the article:

5.1 Introduction

Colloidal quantum dots (CQDs), have shown to be a promising material for the fabrication of solar cells (SCs) from solution with a power conversion efficiency exceeding 13%.\(^1\) Lead sulfide (PbS) has been one of the most studied materials for CQD SCs, and recently power conversion efficiencies above 11% have been demonstrated.\(^2\) Besides the impressive efficiency reached in fewer than eight years from the first certification, the interest in PbS CQD solar cells is also determined by their stability in ambient conditions, which make them superior to several other emerging materials.\(^3,4\)

One of the peculiarities of PbS CQDs is their electronic tunability obtained with the use of different ligands. Due to their high surface to volume ratio, the ligands are not only important to improve the conductivity, by decreasing the interdot distance, but are also fundamental for the passivation of surface traps.\(^5,6\) Moreover, it was recently demonstrated that PbS CQDs allow for tuning the energy levels,\(^7–9\) and for controlling doping concentrations.\(^10–12\)

The state-of-the-art architecture for PbS CQD solar cells utilizes a junction between an n-type layer of PbS, treated with tetrabutylammonium iodide (TBAI), and a p-type layer of PbS, which is treated with ethanedithiol (EDT).\(^13–15\) The PbS-TBAI/PbS-EDT structure not only results in the highest PCE,\(^14\) but it has also shown a stable performance over a period of 110 days when stored in dark and air.\(^16–18\) However, there are only a few studies where PbS CQD SCs were tested in an environment closer to real working conditions.\(^19\) In a recent work, Konstantatos et al. showed CQD SCs with a PbS-TBAI/PbS-EDT active layer stable under illumination in nitrogen atmosphere, which, however, degraded fast under concurrent exposure to ambient conditions and illumination.\(^20\)

Semiconducting single-walled carbon nanotubes (s-SWNTs) are an appealing building block for the fabrication of SCs, due to their outstanding properties, which include high chemical stability and remarkable charge mobility along the tube axis.\(^21\) SWNTs have already been successfully incorporated in perovskite SCs to fulfill the double function of hole transporting layer and protecting layer to improve the stability of devices.\(^22–25\) This has been explained with the hydrophobicity of these nanocarbon materials which result in the protection of the active layer from the atmospheric humidity, which is highly harmful for hybrid perovskites.\(^23\)

Besides a recent report of An et al., who showed that using a conductive carbon paste instead of Au improves the stability of CQDs SCs,\(^4\) there is no data in the literature on the compatibility of CQD SCs with SWNTs.
Here we report the performance of PbS CQD solar cells using semiconducting SWNTs as an interlayer towards the Au top anode. The power conversion efficiency (8.1 ± 0.6 %) remained unaffected compared to the devices without interlayer. The stability of both devices stored in dark and ambient condition was constant during the 78 days of the testing. Importantly, under more demanding conditions, such as solar illumination in ambient condition, the SCs with the s-SWNT interlayer are profoundly more stable, with minimal performance reduction (15%) after more than 100 h of testing. This is in sharp contrast with the behavior of the device without SWNTs, which degraded to 20% of the initial efficiency during the same time.

5.2 Results and discussion

The bilayer PbS CQDs SCs are prepared as reported previously by several groups.\cite{14,26} The device structure is depicted in Figure 5.1a. A compact film of TiO$_2$ is deposited as an electron transporting layer on top of a pre-patterned fluorine-doped tin oxide layer deposited on a glass substrate. The PbS CQD active layer is fabricated via layer by layer spin casting and is composed of two regions. In the first one, which is in contact with the TiO$_2$ layer, PbS is treated with TBAI and the charge carrier transport is n-type dominated.\cite{7,27,28} The second region is treated with EDT, which results in a p-type character.\cite{7,29} The device structure is finished with the evaporation of the Au anode (see Figure 5.1a).

This device structure gives rise to PbS CQDs SCs with power conversion efficiencies above 8.5%.\cite{2,13,14,26} It has been proposed that the PbS-EDT layer act as an electron-blocking/hole-extraction layer between the PbS-TBAI layer and the anode.\cite{14} Moreover, that the different doping of the TBAI and the EDT layers controls the depletion width, which improves the charge carrier dissociation and allows for the implementation of thicker active layers that absorb more light.\cite{15} The insufficient hole concentration in the EDT treated layer was in this context identified as a limiting factor in the device efficiency.\cite{15,26}

To obtain high-quality s-SWNT for the interlayer, we used the polymer wrapping technique to separate the semiconducting species from the metallic species in the initial SWNT sample. The s-SWNT inks were prepared using poly-(3-dodecylthiophene) (P3DDT) to select HiPCO (high-pressure CO method) nanotubes following the procedure described in the experimental section and reported earlier by Gomulya et al.\cite{30}.

The resulting s-SWNT:polymer ink was used to prepare the device structure depicted in Figure 5.1b. The atomic force microscopy (AFM) measurements reported in Figure 5.2 confirm the presence of the SWNTs on top of the active layer. Unfortunately, the s-SWNT network density cannot be determined from this measurements, as the active layer has a
more significant roughness than the average diameter of the carbon nanotubes (about 1 nm).

Figure 5.1. Device structure of the PbS CQD reference SC (a), and with a s-SWNT interlayer (b). (c) JV characteristics of SC devices with (black curve) and without (red curve) s-SWNTs under simulated AM1.5G solar illumination. The inset shows JV measurements of the same devices in the dark. (d) EQE spectra of the two type of devices.

The JV characteristics of the best SCs with and without the s-SWNT under simulated AM1.5G solar illumination are reported in Figure 5.1c. The two device types exhibit similar performances with minor differences only in the $J_{SC}$ and in the fill factor. The figure of merit of the two devices are reported in Table 5.1.

Table 5.1. Summary of best solar cell figures of merit. These measurements were performed after 12 days when the solar cells reached a stable value.

<table>
<thead>
<tr>
<th>Device</th>
<th>$J_{SC}$ [mA/cm$^2$]</th>
<th>$V_{oc}$ [V]</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>With s-SWNT</td>
<td>26.2</td>
<td>0.56</td>
<td>0.61</td>
<td>8.92</td>
</tr>
<tr>
<td>Without s-SWNT</td>
<td>26.7</td>
<td>0.56</td>
<td>0.59</td>
<td>8.82</td>
</tr>
</tbody>
</table>
The external quantum efficiency (EQE) spectra of the two devices are reported in Figure 5.1d, also in this case the performance is virtually identical. We estimated that the thickness of the SWNTs interlayer is lower than 10 nm. Therefore, the light absorbed by the interlayer is negligible and their influence on the EQE is not detectable.

As mentioned above, another important characteristic of SCs besides their efficiency is their stability under working conditions. We thus first examined the long-term stability of the two types of SCs when stored in ambient conditions and darkness. Figure 5.3 reports the figures of merit of the two devices measured in a N$_2$-filled glove box for 78 days. After each measurement, the devices were stored back outside the glove box. The PCE of both devices increases within the first 12 days, from around 7% to almost 9%. This is mainly due to the increase in FF and $V_{OC}$ and can be attributed to a further p-doping in the active layer. After 12 days, both devices reach a stable PCE, $J_{SC}$, and $V_{OC}$. These results are consistent with previous reports where similar devices were studied.\[14\]

However, more realistic device stability tests involve the constant exposure to solar light. We, therefore, studied the performance when exposed to concentrated illumination of 7 times AM1.5G in a nitrogen atmosphere. Figure 5.4, reports the JV characteristics of the devices at time zero (initial conditions), after 20 h of continuous illumination, and after the devices had been stored in the dark for 4 days. The devices reached approximately 340 K during the prolonged illumination of the SCs. All the figures of merit are summarized in Table 5.2.
Figure 5.3. Device parameters over time of SCs with s-SWNT interlayer (black curve) and without interlayer (red curve). Both devices were stored in ambient conditions and in dark over a period of 78 days, and measured in N₂-filled glove box.

Table 5.2. Summary of solar cells figures of merit in different conditions, the 20 h illumination was performed under 7 times AM1.5G solar illumination.

<table>
<thead>
<tr>
<th>Device</th>
<th>$J_{sc}$ [mA/cm$^2$]</th>
<th>$V_{oc}$ [V]</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>With s-SWNT</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1) initial conditions</td>
<td>26.3</td>
<td>0.58</td>
<td>0.59</td>
<td>8.83</td>
</tr>
<tr>
<td>(2) 20 h illumination</td>
<td>23.77</td>
<td>0.512</td>
<td>0.47</td>
<td>5.74</td>
</tr>
<tr>
<td>(3) Stored 4 days in dark</td>
<td>26.16</td>
<td>0.541</td>
<td>0.54</td>
<td>7.67</td>
</tr>
<tr>
<td>Without s-SWNT</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1) initial conditions</td>
<td>26.42</td>
<td>0.57</td>
<td>0.57</td>
<td>8.64</td>
</tr>
<tr>
<td>(2) 20 h illumination</td>
<td>23.67</td>
<td>0.506</td>
<td>0.45</td>
<td>5.36</td>
</tr>
<tr>
<td>(3) Stored 4 days in dark</td>
<td>25.8</td>
<td>0.526</td>
<td>0.53</td>
<td>7.16</td>
</tr>
</tbody>
</table>

Both devices show a degradation of the main device parameters, namely $V_{oc}$ and $J_{sc}$ after 20 h of illumination. Therefore, in a nitrogen atmosphere, the s-SWNT interlayer does not appear to have any beneficial effect on the SCs. Interestingly, the degradation is partially
reversible, and the SCs recover a large portion of their initial performance after a few days of storage in the dark.

Figure 5.4. JV characteristics of the PbS CQD SCs (a) with and (b) without the s-SWNTs interlayer after extreme illumination in nitrogen. The devices were measured at three point in time: 1) initial JV curves, 2) after 20 h of illumination (7 times AM1.5), 3) after 20 h of illumination plus 4 days of storage in dark. The two inset show the dark JV characteristics.

At this point, it is important to investigate our solar cells at AM1.5G constant illumination and in ambient conditions. Figure 5.5a reports the JV characteristics of the two solar cell types continuously illuminated with AM1.5G for 105 hours. The electrical parameters are shown in Figure 5.5b.

The SCs without the s-SWNT layer showed a continuous degradation over a period of 105h. This is evident from the JV curve gradually developing an s-shape. A closer look at the figures of merit shows that the \( J_{SC} \) and the FF decrease immediately after the beginning of the illumination, while the \( V_{OC} \) remains constant for the first 60 h. Consecutively, rapid degradation of the \( V_{OC} \) results in 50% of the initial value after 105 h. The overall corruption of the figure of merits results in the decrease of the PCE of more than 75% after 105 h. We speculate that this is due to the chemical reaction of the active layer with oxygen and water. Degradation of PbS CQD SCs after illumination in air has also been observed previously, where the degradation is due to oxidation of the active material which drastically reduced the PCE of SCs that were photostable in \( N_2 \) atmosphere. Those SCs were photostable in \( N_2 \) atmosphere after the passivation of hydroxide species on the surface.\(^{20}\)
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Figure 5.5. Stability of the JV characteristics of PbS CQD SCs with (black curves) and without (red curves) s-SWNTs interlayer tested for 105 h under AM1.5G illumination in ambient conditions (a) the JV-curves at different times and (b) the figure of merit (PCE, FF, V_{OC} and J_{SC}) of the two devices at different testing times.

Interestingly, the PbS CQD SCs with the s-SWNT interlayer show much better performance under prolonged illumination. The JV characteristics remain more stable, and the figures of merit decrease only marginally. In case of the PCE, it decreased by 15% after the 105 hours illumination. The results indicate that the presence of the s-SWNT interlayer successfully stabilized the PbS CQD SCs. We speculate, that the increased stability might be caused by the hydrophobicity of the carbon nanotube layer that prevents the interaction of water with the active layer. Another possibility is that the presence of the chemically stable s-SWNT interlayer avoids the interaction of photo-generated electrons with molecular oxygen, which can be harmful for the stability of SCs.
5.3 **Conclusion**

In conclusion, we have demonstrated that PbS QD SCs including a thin layer of s-SWNT wrapped by P3DDT, can withstand harsher stability tests under constant solar illumination in ambient condition for more than 100 hours losing only 15% of their initial power conversion efficiency. The interlayer of SWNTs has an impressive role in protecting the active layer, which without SWNTs degrades after 100 hours of illumination losing about 80% of the starting power conversion efficiency.

5.4 **Experimental section**

**PbS CQD synthesis:** Lead sulfide Colloidal quantum dots (PbS CQDs) capped with Oleate ligands were synthesized by the hot injection method. As a Lead precursor 1.516 g of Lead(II) acetate trihydrate (PbAc2·3H2O) were used. PbAc2·3H2O powder was dissolved in the mixture of 50 ml Octadecene (ODE) and 4.5 ml Oleic acid (OA). Then Lead precursor solution was dried for 2 hours under vacuum at 120 °C in a three-neck reaction flask, using a Schlenk line. As a Sulfur precursor Bis(trimethylsilyl)sulfide (TMS2S) was used, 0.420 ml of TMS2S were dissolved in 10 ml of ODE in the nitrogen-filled glovebox. The reaction was carried out under the nitrogen atmosphere. The lead precursor solution was heated to 145 °C, and when the temperature reaches this point, the sulfur precursor solution was quickly injected to the lead precursor solution. At the end, the heating mantle was removed, and the reaction was quenched by cooling the reaction flask down to room temperature, using a cold water bath. To isolate the nanocrystals hexane and ethanol were added, followed by centrifugation. CQD were re-dispersed in hexane and precipitation by ethanol two more times (All of the washing steps were carried out in air). Finally, PbS CQDs were re-dispersed in hexane. Solutions concentrations were determined by the measurement of the absorption of diluted solutions at 400 nm, as well as by drying and weighing the small portion of the PbS CQD solution. For the following building of the devices the solution of PbS QDs with a first excitonic peak in absorption spectrum at 851 nm was used. Thus the band gap value is 1.46 eV, and the size of each nanocrystal is around 2.72 nm.

**Polymer Synthesis:** The homopolymer P3DDT were synthesized as described previously and the molecular weights were measured using gel permeation chromatography (GPC). P3DDT was obtained after Soxhlet extraction with methanol, acetone, ethyl acetate and hexane. For the experiments reported herein, the hexane fraction with $M_n = 19.200$ g/mol and $M_w = 22.300$ g/mol was used.

**Preparation and characterization of semiconducting SWNT dispersion:** HiPCO SWNTs (diameters between 0.8-1.2 nm) were purchased from Unidym Inc. The polymers were solubilized in toluene using a high power ultrasonicator (Misonix 3000) with cup horn bath (output power 69 W) for 10 minutes, followed by overnight stirring at 60 °C. Subsequently, SWNTs were added to form the SWNT:polymer dispersions with a weight
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to 1:2 (3mg of SWNTs, 6mg of polymer, 15 ml of toluene). These solutions were then sonicated for 2 h at 69 W and 16 °C.

After ultrasonication, the dispersions were centrifuged at 30 000 rpm (109 000g) for 1 h in an ultracentrifuge (Beckman Coulter Optima XE-90; rotor: SW55Ti) to remove all the remaining bundles and heavy-weight impurities. After the centrifugation, the highest density components precipitate at the bottom of the centrifugation tube, while the low-density components, including small bundles and individualized SWNTs wrapped by the polymer, and free polymer chains, remain in the upper part (the supernatant).

One extra step of ultracentrifugation was implemented to decrease the amount of free polymer in solution (enrichment). For this purpose, the supernatant obtained after the first ultracentrifugation is centrifuged for 5 h at 55 000 rpm (367 000 g), where the individualized s-SWNTs precipitates to form a pellet, and the free polymer remains in the supernatant. Finally, the pellet is re-dispersed by sonication in the solvent of choice.

Optical characterization of the semiconducting SWNT dispersion: Optical measurements were performed to check the concentration of the carbon nanotubes selected by the polymers. Absorption spectra were recorded by a UV–Vis–NIR spectrophotometer (Shimadzu UV-3600).

Device fabrication: Pre-patterned with Fluorine doped Tin oxide SnO\textsubscript{2}:F (FTO) glass substrates (13 Ω sq-1), purchased from Visiontek Systems Ltd, were cleaned with detergent and then subsequently sonicated in acetone and isopropanol and dried in oven at 120°C for at least 20 min. Then, FTO substrates were treated with O\textsubscript{3} to remove any possible organic residues and to improve wettability of the substrates. Titanium oxide (TiO\textsubscript{2}) sol was prepared by mixing ethanol, titanium(IV) butoxide and HCl (37%) in the ratio 20:2:1, then sol was spin cast onto FTO substrates and annealed at 450 °C for 30 min.

PbS CQDs films were made in the nitrogen filled glove box. For the preparation of PbS CQDs layer-by-layer spin-casting method was used. Capped by Oleate ligands, PbS QDs were spin cast from hexane solutions (10 mg ml\textsuperscript{−1}) onto the prepared earlier TiO\textsubscript{2} films. Ligand exchange was performed by subjecting the films of PbS capped by Oleate ligands to the 15 mg ml\textsuperscript{−1} methanol solution of Tetrabutylammonium iodide (TBAI) or acetonitrile solution of Ethanedithiol (EDT), prepared in concentration of 0.01% by volume for 30 s. Spin-drying removed the residuals of the ligands solutions. In order to get rid of the products of ligand exchange and the excess of unreacted ligands after the ligand exchange the films were washed twice with methanol or once with acetonitrile for the TBAI and EDT treated films respectively. The cycles of deposition of the hexane solution of PbS QDs, ligand exchange and washing were repeated 12 times for TBAI treated layers and four times for EDT treated layers in order to rich the total thickness of the QD solids about 260 nm. The PbS CQDs films were subjected to air for 20 min to make layer of PbS NCs treated by EDT more oxidized and though more p-doped.
For the devices with s-SWNTs the toluene dispersion of the polymer-wrapped carbon nanotubes was spin cast on top of the PbS CQD film after air exposure. S-SWNT dispersion was sonicated before deposition.

The devices were finalized by thermal evaporation of 80 nm gold under the pressure of $5 \cdot 10^{-8}$ mBar at a rate of $0.5 - 2$ Å s$^{-1}$. The device area defined by the overlap of FTO and Au electrodes is $0.16$ cm$^2$. After Au deposition JV-characteristics of the devices were measured for the first time and after that, the devices were kept on air in darkness.

**Current-voltage characterization:** JV measurements were carried out in the nitrogen filled glove box under simulated AM1.5 G solar illumination, using a Steunagel Solar constant 1200 metal halide lamp set to 100 mW cm$^{-2}$ intensity and a Keithley 2400 source-meter. Light intensity was calibrated using a monocrystalline silicon solar cell (WRVS reference cell, Fraunhofer ISE) and corrected for the spectral mismatch. For efficiency calculations, the illuminated area was confined by the shadow mask (0.10 cm$^2$) to avoid any edge effects. The temperature was set to 295 K and controlled by a nitrogen gas flow through a liquid nitrogen bath.

For the stability test performed in air J−V curves were measured under AM1.5 G solar illumination with a solar simulator (SF150 class A, Sciecnetech) and a SP-200 Bio-Logic potentiostat. The light intensity was adjusted in a way to get the same initial values of Jsc, which were obtained using 100 mW cm$^{-2}$ AM1.5 G solar light in the measurements in nitrogen atmosphere.

The External Quantum efficiency measurements The External Quantum efficiency (EQE) was measured under monochromatic light at short circuit conditions. For the source of white light a 250 W quartz tungsten halogen lamp (6334NS, Newport) with lamp housing (67009, Newport) was used. Narrow bandpass filters (Thorlabs) with a full width half maximum (FWHM) of $10 \pm 2$ nm from 400 nm to 1300 nm and a FWHM of $12 \pm 2.4$ nm from 1300 nm to 1400 nm had been used for monochromatic light. The light intensity is determined by calibrated PD300 and PD300IR photodiodes for visible and infrared parts of the spectrum respectively (Ophir Optics).

**Measurement of the light intensity for the stability test carried out in the glovebox:** Light intensity was measured using a thermal power/energy laser measurement sensor (OPHIR 30A-P-SH-V1) and NOVA II Laser Power/Energy Meter on the height where devices were subjected to illumination.

**Morphology and thickness characterization:** AFM measurements were obtained under ambient conditions. The AFM images were taken with a Bruker microscope (MultiMode 8 with ScanAsyst) in ScanAsyst Peak Force Tapping mode with SCANASYST-AIR probes having elastic constant $k = 0.4$ N/m, resonance frequency of 70 kHz, and tip radius less than 12 nm (nominal 2 nm).
5.5 References


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