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Enhancement of hybrid solar cell performance by polythieno [3,4-b]thiophenebenzodithiophene and microplasma-induced surface engineering of silicon nanocrystals

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We have developed a room temperature fabrication technique for hybrid bulk heterojunction solar cells based on silicon nanocrystals (Si-ncs) embedded in polythieno[3,4-b]thiophenebenzodithiophene (PTB7) and that exhibit a high open-circuit voltage exceeding 1 V. This type of device outperforms the open-circuit voltage of analogous devices based on Si-ncs within poly(hexylthiophene) (P3HT).

We also demonstrate that three dimensional surface engineering of Si-ncs by microplasma processing in ethanol can be used to enhance the electronic interactions with PTB7, without using any surfactant, and increasing the power conversion efficiency. © 2012 American Institute of Physics.
dissociation efficiency and energy levels alignment. Our results show that PTB7 coupling with Si-ncs may be responsible for increased dissociation efficiency and increased $V_{OC}$ due to a matched band alignment. We also investigate the effects of two different optimization approaches, the first to increase the interface surface area (i.e., by sonication) and the second to improve Si-ncs surface passivation (i.e., by atmospheric pressure microplasma). In particular, the microplasma treatment allows for surface functionalization directly in liquid and may offer even greater opportunities for 3-dimensional (3D) surface engineering.

Surfactant-free Si-ncs were produced by an electrochemical etching procedure that used a boron-doped silicon wafer with a resistivity of $\sim 0.5 \, \Omega \, \text{cm}$ (p-type) and subsequent mechanical pulverization, as previously described. This technique produces a powder of single Si-ncs as well as Si-ncs aggregates of different sizes (up to micrometer range), which are referred to as “as-prepared” Si-ncs powder. The as-prepared powder was then dispersed in ethanol and the microplasma treatment was applied to engineer the Si-ncs/Si-ncs aggregates surface. A dc microplasma was generated between a Ni tubing (inner diameter 0.7 mm, outer 1 mm) and the surface of the ethanol/Si-ncs colloid. As a counter electrode, a carbon rod was immersed about 5 mm in the solution at a distance of about 3 cm from the nickel tubing. A positive voltage (0.8-2 kV) was applied to the carbon rod to sustain a current of 1.5 mA, while the nickel tubing was connected to ground through a 100 k$\Omega$ resistor. Pure argon was flown inside the Ni tubing at a rate of 25 sccm. The distance between the nickel tubing and the liquid dispersion surface was initially adjusted at 1 mm; however during 16 min processing, the distance was observed to increase to about 1.3–1.5 mm due to evaporation. A detailed analysis of the Si-ncs structural characteristics and the corresponding optical properties was carried out for both as-prepared and microplasma-treated Si-ncs. Si-ncs exhibited quantum confinement effects (energy band-gap $\sim 2$ eV) with diameters in the range 2–5 nm. Separate samples of the dried powder (in air for 1 day), of as-prepared Si-ncs and microplasma-treated Si-ncs, were mixed with commercially available P3HT (ALDRICH) or with PTB7 (1-material Chemistrytech, Inc., Canada) in 1:1 weight ratio and dissolved in chlorobenzene to produce different blends. The solar cells with thickness of about 100 nm were fabricated by spin coating the Si-ncs nanocomposites onto the PEDOT:PSS/ITO glass substrate. After spin-coating, in the case of P3HT, the deposited nanocomposite layer was dried at 130°C for 20 min and in the case of PTB7, the nanocomposites were dried at room temperature in a glove box filled with nitrogen. Finally, an aluminum electrode, 100 nm thick, was deposited by vacuum evaporation. The active area of the cell was 4 mm$^2$. For the photoconductivity measurements, AM 1.5 white light was used. The I-V characteristics of the solar cells were evaluated at room temperature in a N$_2$ atmosphere. In all cases, the irradiation intensities were calibrated by a standard a-Si solar cell.

The prototype hybrid solar cell architecture that we used for our investigation is shown in Figure 1 (inset). Figure 1 compares the current-voltage (I-V) characteristics in the dark (solid line) and under AM 1.5 irradiation of the cells fabricated from nanocomposites blends, Si-ncs/PTB7 (dashed line), and Si-ncs/P3HT (dotted line). All devices exhibited a diode-like behavior with non-linear current versus voltage with rather similar fill factor (FF; $\sim 20\%$, Figure 1). Since the slope at 0 V is non-zero, a small parallel resistance due to local shunts may be present. Due to the PTB7 host matrix, an increase in the $I_{SC}$ ($>0.1 \, mA \, cm^{-2}$) is observed compared with the $I_{SC}$ for the device with P3HT ($<0.01 \, mA \, cm^{-2}$). In the PTB7 matrix case, good rectification is accompanied with high $V_{OC}$ ($\sim 0.96 \, V$, Figure 1). The device based on the Si-ncs/PTB7 nanocomposite exhibit a clear enhancement for both $I_{SC}$ and $V_{OC}$. The current difference between the PTB7-hosted device and the P3HT-hosted device is considerable, when the same fabrication process is applied as in this case. However, the values of the short-circuit current for both devices are quite low if compared to other similar devices reported in the literature, which indicate that optimization of the blends characteristics is required to improve the overall efficiency. At the same time, the open-circuit voltage of the Si-ncs/PTB7 compares very favorably even with other devices and confirms that $V_{OC}$ strongly depends on the interface materials characteristics and transcend the device fabrication process. In fact, the $V_{OC}$ recorded here for the device with the Si-ncs/P3HT blend is $\sim 0.62 \, V$, similarly to the $V_{OC}$ recorded elsewhere (e.g., $V_{OC} = 0.6-0.8 \, V$, FF of $\sim 0.4$ and $I_{SC}$ of $\sim 3.8 \, mA \, cm^{-2}$). On the other hand, the combination of Si-ncs with PTB7 demonstrates the capability of high dissociation efficiency with a higher recorded $V_{OC}$ above 0.95 V.

The analysis of the external quantum efficiency (EQE) can provide further details on the characteristics of the two different devices (Figure 2). EQE for Si-ncs/PTB7 bulk heterojunction solar cells is reported in squares and Si-ncs/P3HT is in triangles (multiplied by a factor of 200 for better readability; circles will be discussed later in the manuscript). Devices based on PTB7 showed higher photon conversion efficiency (squares). Furthermore, the EQE range has also increased for PTB7-based devices possibly due to the lower band-gap of PTB7 ($\sim 1.8 \, eV$) compared to P3HT ($\sim 2.1 \, eV$). This can be observed in the energy diagram depicted in Figure 3.
In the case of P3HT, the highest occupied molecular orbital (HOMO) level is at 5.15 eV and the lowest unoccupied molecular orbital (LUMO) level is at 2.9 eV. The HOMO and LUMO energy levels for PTB7 were taken from the literature which reports values of -5.15 eV and -3.31 eV, respectively. The alignment of the energy levels confirms the feasibility of bulk heterojunction solar cells with quantum confined Si-ncs and PTB7. In this case, the Si-ncs that are interfaced with the polymer will serve as the electron transporting material. The improved performance of the Si-ncs/PTB7 may be attributed to a suitable alignment of the respective band-edge/LUMO levels, where the PTB7’s LUMO level might be better aligned with the maximum of the Si-ncs density of states, whereby P3HT may align with the low densities of the tail of the Si-ncs density of states. At the same time, the existence and effect of charge transfer states at the Si-ncs/polymer interface cannot be excluded.

The \( V_{OC} \) in organic solar cells is determined by charge transfer complexes and the alignment of their energy levels with corresponding HOMO and LUMO levels. Therefore, a combination of factors which include charge transfer states may also be responsible for the enhanced open circuit voltage.

As we have now compared the effect of using the two different polymers, PTB7 versus P3HT, we will now analyze different treatments of the Si-ncs/PTB7 blends. In particular prior to blending the Si-ncs with PTB7, we have processed the Si-ncs/ethanol colloid with a microplasma treatment directly in liquid as described elsewhere. Our previous work has shown that the microplasma process has improved the efficacy of the Si-ncs surface; effectively the H-terminations of Si-ncs and any surface defects are mostly replaced and passivated with short organic molecules of the type Si-O-R. The benefits of this surface treatment are clear from Figure 2 where the EQE of devices produced with as-prepared Si-ncs/PTB7 (squares) and microplasma treated Si-ncs/PTB7 are compared (circles). The efficiency has increased in the polymer-active spectral range indicating that the microplasma process has improved the efficacy of the Si-ncs surface to induce exciton dissociation at the polymer interface; importantly, this also corroborate that exciton dissociation is largely taking place at the Si-ncs/PTB7 interface because the improvements due to surface engineering are observed in this range.

In addition to the microplasma treatment, the effect of sonication prior to spin coating of the blends on the device substrate was also studied. Therefore, solar cell devices with sonicated blends of as-prepared Si-ncs/PTB7 and sonicated microplasma-treated Si-ncs/PTB7 are compared here below. Figures 4(a) and 4(b) correspond to the devices that used microplasma-treated Si-ncs/PTB7. All devices showed a diode-like behavior with non-linear current versus voltage. In both cases, the sonication process seems to be responsible for a further increase of the \( V_{OC} \) above 1 V compared to Figure 1. However, due to sonication, \( I_{SC} \) for the device with as-prepared Si-ncs has decreased to 0.08 mA cm\(^{-2}\) (Figure 4(a)) compared to \( I_{SC} \) for the device with microplasma-treated Si-ncs has remained to values above 0.1 mA cm\(^{-2}\) (Figure 4(b)) and with an improved rectification. In particular, the prototypical photovoltaic cells characteristics are shown in the respective Figures 4(a) and 4(b). The device with microplasma-treated Si-ncs presents overall better device performance.

**FIG. 2.** EQE under AM 1.5 illumination of the devices based on as-prepared Si-ncs/PTB7 (squares), as-prepared Si-ncs/P3HT (triangles), and microplasma-treated Si-ncs/PTB7 (circles). All results in these figures have been obtained with cells produced without sonication of the blends. Device based on P3HT/Si-ncs bulk heterojunction solar cell (triangles) are multiplied by 200.

**FIG. 3.** The energy levels of all the components of the solar cell structure: (a) Energy levels of P3HT, silicon nanocrystals (Si-ncs) with quantum confinement, Al, ITO, and PEDOT/PSS, and (b) shows corresponding energy level band diagram of Si-ncs blended with PTB7-conjugated polymer.
This has a direct effect on the overall performance by de-flocculation of the Si-ncs step may facilitate and increase the probability of Si-ncs is achieved without using any surfactant and the sonication (compared to Figure 2). It follows that microplasma-treated Si-ncs can preserve, even after sonication, efficient exciton dissociation and enhance charge transfer processes at the interface with PTB7. The increased open-circuit voltage for both devices may be also ascribed to an increased contribution of smaller sized Si-ncs, as these would present energy levels closer to the LUMO of PTB7. Both sonication and microplasma treatment can partly defragment Si-ncs aggregates, easily releasing in the solution small sized Si-ncs that can then interact with PTB7.

In conclusion, hybrid bulk heterojunction solar cells based on Si-ncs and PTB7 have been developed by a low-cost spin-coating technique onto an ITO substrate to form continuous thin films. The results indicate that Si-ncs are a viable, low-cost, and potential electron acceptor candidate in hybrid solar cell devices. The selection of materials, and, therefore, the combination of Si-ncs with PTB7 has resulted in a key finding to drastically improve the open-circuit voltage. Furthermore, our results suggest that microplasmainduced surface engineering represents a promising avenue to improve surface characteristics that are capable of efficient exciton dissociation. Atmospheric-pressure microplasmas can be efficiently used for 3D surface engineering of surfactant-free Si-ncs and potentially offer a range of other possibilities to include organic and inorganic terminations, directly in liquid media and with a significant impact in the overall solar cell performance. Overall, we have demonstrated that hybrid bulk heterojunction cells consisting of well-dispersed engineered Si-ncs show a rectification behavior, improved $I_{sc}$, and a relatively high $V_{oc}$ ($>$ 1 V). Finally, at this initial stage of our investigation, the fabrication steps and related control parameters did not undergo an optimization process and are, therefore, amenable to considerable improvements.

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FIG. 4. (a) and (b) I-V characteristics in the dark (solid line) and under AM 1.5 illumination of solar cells based on PTB7/Si-ncs (dashed line) where blends have been sonicated before spin-coating. (a) Devices produced with as-prepared Si-ncs and (b) devices produced with microplasma-treated Si-ncs (black squares) and PTB7/microplasma-treated Si-ncs (red circles). All results in these figures have been obtained with cells produced with sonication of the blends.


20See supplementary material at http://dx.doi.org/10.1063/1.4721437 for optical properties of the microplasma-treated Si-ncs and surface morphology of the blends.


