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High Efficiency Panchromatic Hybrid Schottky Solar Cells

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Photovoltaics based on inorganic materials (for example, the Cd chalcogenides) show high efficiencies due to their excellent charge carrier mobility and carrier collection capability.¹⁻⁷ However, their constituent materials are generally more expensive, and their fabrication is more complex ⁸⁻⁹ than in organic photovoltaics.¹⁰⁻¹² Organics, however, tend towards lower charge carrier mobility and short exciton diffusion lengths leading to low short circuit currents and increased carrier recombination, often resulting in lower efficiencies.¹³⁻¹⁴ Fabricated judiciously, hybrid photovoltaics combining inorganic and organic materials may avoid one or more of these drawbacks.¹⁵ Inorganic semiconductors (CdSe, CdS, n-Si, n-CdTe, TiO₂, ZnO, etc) are often used as electron acceptors due to their large carrier mobility, long exciton diffusion length and effective light absorption.¹⁵⁻²³ And, organic semiconductors, which have large absorption coefficients, are commonly used in hybrid solar cells as electron-
donors, making use of their significant hole mobility which often exceeds their electron mobility.\cite{24}

Bulk heterojunction (BHJ) hybrid solar cells, first demonstrated by Alivisatos, employ semiconductor nanocrystals dispersed in conducting polymer.\cite{15} In BHJ solar cells, the separation of excitons occurs efficiently due to the short distances the carriers need to traverse and large interface between the conducting polymer and the inorganic semiconductor. On the other hand, charge carrier collection is limited by the poor charge transport that occurs via electron hopping among the poorly connected semiconductor nanocrystals. Highly ordered inorganic semiconductor nanorods grown vertically from the substrate up, can remedy the poor conductance of materials comprised of compacted nanocrystals, resulting in better transfer of electrons from the p-n junctions to the external circuit.\cite{3, 16, 25}

Recently we described such a hybrid photovoltaic comprised of ordered CdSe nanorods embedded in a conductive polymer (poly 3-hexylthiophene (P3HT)).\cite{16} We noted that deep in the red, where only the CdSe absorbed light the internal quantum efficiency of the cell was very high; yet the overall external efficiency of the device was only slightly above 1%, due to the fact that the P3HT absorbed over a substantial portion of the visible spectrum, but was inefficient in transferring holes to the external circuit on account of this material’s small recombination length. In essence, the P3HT absorbed a large portion of the incoming photons whose energies it subsequently wasted. We reasoned that if we were to replace the P3HT with a p-type polymer with very low light absorbance, making the CdSe essentially the sole light-harvesting material, the external efficiency of the device would improve significantly. A good candidate for such a material is PEDOT:PSS, a conductive polymer mixture of two ionomers: a sulfonated polystyrene carrying a negative charge, and PEDOT which carries a positive charge. Apart from its excellent stability and solution processability, the main advantage of PEDOT:PSS in this rather unusual application is its optical transparency in its conducting
state. Indeed, highly conductive PEDOT:PSS is considered to be a synthetic metal and the most suitable polymeric substitute for transparent conducting oxides. Furthermore, the PSS-enriched surface, which blocks electrons and functions as an efficient hole transport layer, has been successfully used in organic solar cells as either as transparent bottom or top electrode.\textsuperscript{[11, 12]}

Here we describe a hybrid photovoltaic consisting of an array of aligned CdSe nanopillars embedded in PEDOT:PSS, which acts as a hole filter that is almost wholly transparent to light. Devices with external efficiencies exceeding 3\% were routinely produced using this strategy. Moreover, we estimate that devices with efficiencies exceeding 4.5\% could be produced in this way with CdSe, and even higher efficiencies with other combinations of materials. This approach can potentially be the basis of a new strategy for inorganic/organic hybrid solar cells in which only the inorganic phase – in which the electron-hole recombination length is sufficiently long so that the majority of electrons produced are collected – absorbs photons.

The photovoltaic (PV) devices were fabricated on an ITO substrate coated with TiO\textsubscript{2} which served as a hole-blocking layer (see Experimental for more details). CdSe nanorods were electrochemically grown on the TiO\textsubscript{2}/ITO substrate in the nanopores of porous aluminum oxide (PAO) prepared by Al anodization. The nanogaps between the CdSe nanorods were infiltrated with the conducting polymer following the removal of the PAO. Gold electrodes were thermally evaporated onto the conducting polymers as top contacts, while the ITO/Au served as the back contact (Figure 1A). For comparison, two conducting polymers: P3HT (Plexcore OS2100) and PEDOT:PSS (Clevios PH500), were alternately used in fabricating these PV devices. In the CdSe-P3HT PV devices, CdSe served as the electron-acceptor (n-type) whereas P3HT served as hole-acceptor (p-type) (Figure 1B). Unlike the HOMO and LUMO states for P3HT which are separated by a band gap, the filled and unfilled electronic states of PEDOT:PSS form a continuum with the highest occupied state defining its
Fermi-level, as in a metal (Figure 1C). PEDOT:PSS in contact with n-CdSe therefore forms a Schottky rather than a p-n junction with the depletion region resident exclusively in the inorganic semiconductor (in the present case n-CdSe) as the PEDOT is unlikely to support a space charge.\cite{26,27} Schottky junction photovoltaics (some with significant efficiencies) are, of course, well-studied devices.\cite{28-34} Most are based on bulk interfaces as with the most common p-n photovoltaics in which one of the semiconductor layers is replaced with a material that behaves as a metal, often ITO, which also has the beneficial property of being transparent to light. Additionally, a device that foreshadows what we report here, consisting of GaAs rods produced by dry etching a GaAs single crystal through a “mask” formed by close-packed silica microspheres, which are pressed against PEDOT:PSS has also been reported.\cite{35}

The CdSe nanorods used in this study were ~466 ± 56 nm long, with diameters ~ 115 ± 14 nm and with inter-rod gaps ~24 ± 5 nm (Figure 2A). The overall thickness of layers consisting of CdSe nanorods embedded in the conducting polymer was ~ 744 ± 100 nm (Figure 2B). The device was fabricated in such a manner that the overall cell thickness (inorganic + organic phases) for both CdSe/P3HT and CdSe/PEDOT: PSS devices were similar. The absorptances of CdSe, embedded alternately in P3HT and PEDOT:PSS are shown in Figure 2C. The red absorption edge of CdSe is ~750nm, while that P3HT occurs at ~ 650nm. Both CdSe and P3HT absorb strongly in the visible region of the spectrum. By contrast, the absorptance of PEDOT:PSS is negligible throughout the UV/Visible range.

The current-voltage (J-V) curves of typical cells in the dark and under simulated Air Mass 1.5 Global (AM1.5G) full sun illumination are presented in Figure 3. Both the devices fabricated with P3HT and PEDOT:PSS showed diode behavior with good rectification (Figure 3A and 3B). The open circuit potential ($V_{oc}$) of a typical PV device fabricated with P3HT was 0.57 V, with a short circuit current density ($J_{sc}$) of 4.12 mA cm$^{-2}$, a fill factor (FF) of 0.35, and a maximum conversion efficiency ($\eta$) of 0.83 % at 0.35 V. By contrast the results...
of analogous measurements carried out on a device based on PEDOT:PSS were $V_{oc} = 0.27 \text{ V}$, $J_{sc} = 38.71 \text{ mA cm}^{-2}$, $FF = 0.30$, and $\eta = 3.22\%$ at 0.15 V. Notably, the short circuit current density of PEDOT:PSS-based device was overall an order of magnitude higher than for the device with P3HT (Figure 3C), and one of the largest reported for a nanostructured hybrid solar cell.\cite{15-23} Our device fabrication methodology is very reproducible, with measured device to device performance variability below 10\% (Fig. S1). The data presented are for the best performing cells.

The somewhat lower open circuit potential obtained for the Schottky barrier n-CdSe-PEDOT:PSS solar cell in comparison to n-CdSe-P3HT (p-n junction) solar cell is not surprising; considering the increased saturation current density ($J_0$) obtained in a Schottky diode caused by the recombination of majority carriers at the anode. In fact, the calculated $J_0$ values for CdSe-P3HT ($3.82 \times 10^{-4} \text{ mA cm}^{-2}$) and CdSe-PEDOT:PSS (0.94 mA cm$^{-2}$) showed a three orders of magnitude difference (See Experimental Section for more details on the calculations). The maximum $V_{OC}$ for, respectively, a CdSe-P3HT and a CdSe-PEDOT:PSS solar cells are 0.76 V and 0.59 V (calculated from the fitted dark and light J-V curves using the Richardson equation). The latter is in close agreement with the 0.6 eV energy barrier height obtained from ideal Mott-Schottky limit as given by:

$$\Phi_b = \Phi_m - \chi$$

where $\Phi_m$ is the metal work function, and $\chi$ is the semiconductor electron affinity.

Although the open circuit voltages obtainable for a Schottky type hybrid solar cell are somewhat lower than for a p-n junction cell, the strategy of using an inorganic phase in the form of nanorods with a transparent organic anode (PEDOT:PSS), produced considerably increased values of $J_{sc}$, leading to a corresponding 4-fold increase in the solar conversion efficiency as compared to what was achieved with p-n junction CdSe-P3HT solar cells. These results are consistent with the measured action spectra of the cells.
The measured external quantum efficiency (EQE) and the internal quantum efficiency (IQE) of the devices fabricated with P3HT and PEDOT:PSS are plotted in Figure 4 along with the absorptance of each device. Since PEDOT:PSS absorbs very little in the visible spectrum, the absorptance of PEDOT:PSS solar cell tracks the absorptance of the CdSe nanorods alone (Figure 2C). By contrast, the absorptance of the P3HT solar cell reflects the combined absorptances of the CdSe nanorods and the P3HT. Notwithstanding the stronger absorption of the CdSe-P3HT (Figure 4A), the EQE of this device is significantly lower in the region where P3HT is strongly absorbing (Figure 4B). As previously suggested, this is due to the parasitic role of P3HT in cells in which carrier recombination in P3HT prevents electrons from reaching the electrodes, while simultaneously absorbing photons that would otherwise have successfully produced excitons in the inorganic phase.[16]

Taking only the absorbed photons into account, the internal quantum efficiency (IQE) of the P3HT solar cell was decreased by approximately 50% in the P3HT absorbing region (Figure 4C, red trace). The EQE spectrum of the photovoltaic cell which used PEDOT: PSS tracked the device’s overall absorptance rather faithfully from ~750 nm, where the CdSe begins to absorb, to ~350 nm where absorption by the TiO$_2$/ITO substrate limits light absorption by the device at shorter wavelengths. The IQE spectrum (Figure 4C, blue trace) for the PEDOT: PSS solar cell reaches approximately 65 % and is approximately constant over the active spectral region of the device. This level of internal quantum efficiency is somewhat lower than what we had previously achieved for the CdSe/P3HT cell in the red portion of the spectrum where the P3HT does not absorb. This indicates that the current series of devices have not yet been optimized; and when they are, their external efficiencies will exceed 4.5 %.

In Summary, an almost 4-fold increase in solar conversion efficiency was achieved (to $\eta > 3 \%$) in a CdSe-based (inorganic-organic) hybrid solar cell by replacing the absorbing P3HT with a transparent PEDOT:PSS, thereby permitting the inorganic phase to function as the sole
electron transporting medium, thereby avoiding carrier losses due to the very short recombination distances in the polymeric phase. By so doing, the polymer was used essentially as a hole filter with quasi metallic electrical properties. Formally, these cells are Schottky rather than p-n junction photovoltaics. With appropriate choice of materials – including earth-abundant materials – hybrid photovoltaics with external quantum efficiencies exceeding 10 % are possible based on this strategy.

**Experimental**

**Device Fabrication:** ITO glasses were sequentially cleaned under sonication in acetone, IPA and water followed by ozone cleaning for 20 minutes. A layer of TiO$_2$ in thickness of 20 nm was e-beam evaporated on ITO glasses followed by annealing at 500 $^\circ$C in air. Aluminum was e-beam evaporated on the TiO$_2$ layer in rate of 1 Å s$^{-1}$ in the first 5 nm, 2 Å s$^{-1}$ until 50 nm and 5 Å s$^{-1}$ until the thickness reached 850 nm. The anodization of Al film was carried out in oxalic acid (0.3 M) with applied voltage of 60 V at 0 $^\circ$C. The as-made porous aluminum oxide (PAO) was then placed in phosphoric acid (5 wt%) for 65 minutes to widen the pores and remove the barrier layer in the bottom of the pores. CdSe was electrodeposited in an electrolyte consisted of sulfuric acid (0.3 M), cadmium sulfate (0.3 M), selenium oxide (7 mM) and triton x-100 (5 v/v%). The voltage was swept from -0.4 to -0.8 V vs SCE in cycle for 4000 counts at rate of 750 mV s$^{-1}$, which corresponds to the nanorod length of ~450 nm. As-deposited CdSe nanorods were annealed in Ar environment at 500 $^\circ$C for 1 hr to improve the crystallinity of CdSe. Later, the PAO template was dissolved in NaOH (0.1 M) for 30 minutes. Native oxide layers on CdSe nanorods were removed by HF (0.1 wt%) for 10 seconds. Immediately after oxide removal, P3HT dissolved in chlorobenzene (30 mg ml$^{-1}$) was spin-casted on CdSe nanorods at 1100 rpm for 1 minute in a N$_2$-filled glove box. The device was annealed in the glovebox at 230 $^\circ$C for 1 hr. Dimethyl sulfoxide (DMSO) (5 v/v%) was added to PEDOT: PSS to improve its conductivity and wettability. PEDOT:PSS
was drop-cast on the CdSe nanorods (25 μl per 1 cm²) immediately after the removal of the oxide layer. Drop casting was preferred over spin casting in order to better control the overall cell thickness of the CdSe/PEDOT:PSS device and make it comparable to that of the CdSe/P3HT devices. “Cell thickness” refers to the total thickness of the active layer (CdSe + Polymer), and the volume of PEDOT: PSS used in drop casting was selected accordingly. The CdSe nanorod lengths for both the devices were ~ 466 nm and the overall cell thickness was ~ 750 nm. The device was then immediately annealed in air at 120 °C for 10 minutes to drive off the water in the polymer. The device was then immediately annealed in air at 120 °C for 10 minutes to evaporate the water molecules in the polymer. The top and bottom Au contact was thermally evaporated on the polymer and on the ITO glass through a patterned mask in thickness of 100 nm (rate 1 Å s⁻¹ in the first 5 nm, and slowly increased to 5 Å s⁻¹ in the next 10 nm).

Characterization: The absorptance was measured on UV-Vis-NIR spectrophotometer equipped with integrating sphere (Shimatzu UV3600, ISR3100). The photovoltaic J-V characteristics were measured using a Keithley 236 Source Measure Unit with Newport Air Mass 1.5 Global full spectrum solar simulator (100 mW cm⁻²). EQE spectra were measured using a QEW7 Solar Cell QE measurement system.

Analysis of J-V curves: The $V_{OC}$ of CdSe-P3HT was calculated using the diode equation:

$$V_{OC} = \frac{n k T}{q} \ln \left( \frac{J_{sc}}{J_0} \right)$$

where, $n$ is the ideality factor, $k$ is the Boltzmann constant, $T$ is the temperature, $q$ is the charge of electrons, $J_{sc}$ is the short-circuit current density and $J_0$ is the saturation current density.

The Schottky barrier height of CdSe-PEDOT:PSS was deduced from the Richardson equation:
\[ \phi_b = -\frac{kT}{q} \ln\left( \frac{J_0}{A^* T^2} \right) \]

where, \( A^* \) is the effective Richardson constant.

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Figure 1. (A) Schematic representation of the device: n-CdSe nanorods are grown over a TiO$_2$ layer (20 nm) deposited on an ITO film (140 nm). Conducting polymer is spin-cast over the nanorods. Separate gold electrodes were thermally evaporated on the conducting polymer and on the ITO. (B) and (C) Energy level diagrams for the CdSe nanorods, with P3HT and PEDOT:PSS.
**Figure 2.** (A) Scanning electron micrographic (SEM) image of electrochemically grown CdSe nanorods on TiO$_2$/ITO substrate taken at 15° from normal (scale bar: 500 nm). (B) Cross-sectional SEM image of CdSe nanorods embedded in the conducting polymer. The device was tilted 52° for imaging (scale bar: 500 nm). (C) Absorptance characteristics of P3HT, PEDOT:PSS and vertically-standing CdSe nanorods.
Figure 3. Representative J-V curves of PV devices fabricated with (A) P3HT and (B) PEDOT:PSS in the dark and under AM 1.5G illumination at intensity of 100 mW cm$^{-2}$. (C) Combined J-V curves of CdSe-P3HT and CdSe-PEDOT:PSS devices under 1 sun illumination. Note the log scale on the left hand side, which indicates at least an order of magnitude increase in short circuit current density for CdSe-PEDOT:PSS device over that of CdSe-P3HT.
Figure 4. (A) The absorptance spectra; (B) the external quantum efficiency (EQE); and, (C) internal quantum efficiency (IQE) of PV devices fabricated with CdSe nanorods as the inorganic phase and alternately P3HT (red), or PEDOT:PSS (blue) conducting polymer.
Nanostructured Schottky inorganic-organic solar cell in which an aligned array of CdSe nanorods (sole absorbing phase) infiltrated with a synthetic metal PEDOT:PSS (transparent Schottky contact) provides an overall power conversion efficiencies exceeding 3%; with extremely large short circuit photocurrents. The device’s EQE tracks faithfully the absorptance of the CdSe nanorods, and the IQE is approximately constant over the entire visible spectrum as opposed to a p-n junction hybrid solar cell fabricated with a highly absorbing organic polymer.

Keywords: Hybrid solar cell, cadmium selenide, PEDOT:PSS, Schottky barrier, internal quantum efficiency.