Reversible Structural Transformation and Enhanced Performance of PEDOT:PSS-Based Hybrid Solar Cells Driven by Light Intensity

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Supporting Information

ABSTRACT: Hybrid solar cells made of poly(3,4-ethylendioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) and appropriate amounts of a cosolvent and a fluorosurfactant on planar n-type silicon substrates showed a photoconversion efficiency (PCE) of above 13%. These cells also exhibited stable, reproducible, and high external quantum efficiency (EQE) that was not sensitive to light-bias intensity (LBI). In contrast, solar cells made of pristine PEDOT:PSS showed low PCE and high EQE only under certain measurement conditions. The EQE was found to degrade with increasing LBI. Here we report that the LBI-sensitive variation of EQE of the low-PCE cells is related to a reversible structural transformation from a quinoid to a benzoid structure of PEDOT.

KEYWORDS: PEDOT:PSS, hybrid solar cell, external quantum efficiency, light-bias intensity, structure stabilization

Contemporary solar cells comprised of organic or organic–inorganic hybrid materials have attracted a lot of interest in the area of green energy because they offer low-cost fabrication of high-efficiency solar cells.1–4 Typically, these cells contain a p-type transparent conducting polymer layer, poly(3,4-ethylendioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), as either an active layer or an electrode.1–4 Hybrid solar cells made of PEDOT:PSS and n-type silicon substrates have attracted much recent attention because of their simple fabrication processes for low-cost device applications and their high photoconversion efficiencies (PCE) of 10–13%.3,4,7–17 However, there exists a large discrepancy in the PCE values for these types of solar cells in the literature,9–17 which is mainly caused by unoptimized PEDOT:PSS properties12 or interface effects.14

The PCE of a solar cell is typically estimated from its current versus voltage (I−V) spectrum measured with light illumination under standard one-sun conditions (AM 1.5G, 100 mW/cm²).18,19 In addition to I−V data, external quantum efficiency (EQE) measurement has also been used as an important tool to quantify the efficiency of conversion of light to charge carriers as a function of the wavelength of the incident light.1,2,19–22 The variation of EQE under external light-bias intensity (LBI) in organic solar cells has been discussed in the literature.3,19–22 More importantly, EQE measurements as a function of LBI have been used to characterize the nature of cell recombination.19 It is a common belief that the EQE for a good cell should be stable under different LBI conditions. In most solar cell studies reported to date, it is however not a common practice to validate the EQE data against the I−V data. It is therefore not surprising that the EQE performance of the PEDOT:PSS/Si hybrid solar cells under different LBI conditions has yet to be reported. We demonstrate here that EQE measurement under different LBI conditions is an important integral part of ascertaining the robustness of the cell performance because LBI dependence corresponds to an important indicator of underlying structural changes in PEDOT:PSS. Because PEDOT:PSS has been a technologically important conducting polymer, studies of LBI-dependent effects for solar cells made of PEDOT:PSS and silicon could give insight into the structural stability of PEDOT:PSS with different LBI, which might have important implications in optimizing its properties and further improving the performance of PEDOT:PSS-based electronic devices.

Here, we report that, under no LBI, very high EQE can be obtained for both the high- and low-PCE hybrid solar cells made respectively with and without the addition of ethylene glycol (EG) in PEDOT:PSS. However, the high short-circuit current density estimated from the EQE of the low-PCE cell is contradictory to the value obtained from its J−V data measured under one-sun conditions. Our experiments further reveal a decrease in the EQE with increasing LBI for the low-PCE cells, which is in marked contrast to the extremely stable EQE found for the high-PCE cells. We attribute the latter LBI-insensitive, stable EQE performance of the high-PCE cells to their cosolvent-stabilized quinoid structural changes in PEDOT:PSS.

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The experimental methods are discussed in detail in the Supporting Information (SI). Briefly, PEDOT:PSS (PH1000) was mixed with optimized 7 wt% EG to achieve a highly conducting form. To enhance the wettability of PEDOT:PSS, 0.25 wt% fluorosurfactant (FS) was added. Prior to spin coating of the PEDOT:PSS layer, precleaned n-type silicon substrates were kept in ambient atmosphere for 1.5 h after a hydrofluoric acid dip and bottom aluminum metal electrode deposition. Silver metal deposited in the form of a comb on the PEDOT:PSS/SiO$_2$ hybrid solar cells with side scale bars of 0–8 nm.

![Figure 1](image)

**Figure 1.** (a) Current density versus voltage, (b) EQE, (c) Raman spectra, and (d) reflectance spectra of high-efficiency (H) and low-efficiency (L) PEDOT:PSS/SiO$_2$/silicon cells. The high-efficiency cell was made of EG7–PEDOT:PSS, and the low-efficiency cell was made of pristine PEDOT:PSS, both after the addition of 0.25 wt% FS on silicon substrates. AFM images (500 × 500 nm) of (e) high-efficiency and (f) low-efficiency hybrid solar cells with side scale bars of 0–8 nm.

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**Table 1. Solar Cell Properties of High-Efficiency (Cell H) and Low-Efficiency (Cell L) PEDOT:PSS/SiO$_2$/Silicon Hybrid Solar Cells**

<table>
<thead>
<tr>
<th>sample</th>
<th>$V_{OC}$ (mV)</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cell H</td>
<td>558 (560 ± 5)</td>
<td>31.7 (31.1 ± 1.1)</td>
<td>76 (71 ± 6)</td>
<td>13.4 (13.1 ± 0.3)</td>
</tr>
<tr>
<td>cell L</td>
<td>524 (520 ± 7)</td>
<td>15.5 (14.1 ± 1.4)</td>
<td>34 (32 ± 6)</td>
<td>2.8 (2.5 ± 0.3)</td>
</tr>
</tbody>
</table>

*The values in parentheses correspond to the average values along with their estimated standard deviations obtained from seven similar cells.*

The EQE corresponds to the ratio of the number of generated outgoing electrons to the number of photons incident on the device. Our measurements show a maximum EQE (EQE$_{max}$) of above 85% at 500 nm for cell H and of above 82% at 560 nm for cell L (Figure 1b). The high EQE near the blue-wavelength region suggests a good front surface carrier collection efficiency for cell $H$, which is improved by the addition of EG to PEDOT:PSS. However, the high EQE for cell L (made of pristine PEDOT:PSS) does not correlate with its estimated $J_{SC}$ values from the EQE ($\sim$26 mA/cm$^2$) and $J$–$V$ data ($\sim$15 mA/cm$^2$). It should be noted that EQE measurement is normally carried out with a light intensity of about 1

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 conditions. It should be noted that calibration of LBI to be assigned to C for cell L (Figure 2b). This EQE reduction is particularly significant for cell H (Figure 2a). In contrast, a rearrangement of the PEDOT chains, from the coil-like structure, which increases the size and facilitates closer packing of the PEDOT grains.12,25,26 The corresponding reflection spectra of the PEDOT:PSS films on silicon (Figure 1d) show that the PEDOT:PSS layer acts as an antireflection coating on the silicon substrate. For comparison, the reflectance spectrum of the silicon substrate is also included in the figure. A slight blue shift in the reflectance minima for the EG-added sample (cell H) relative to the pristine PEDOT:PSS sample (cell L) is observed, which indicates that the cosolvent addition does not significantly affect the optical properties of these films. This structural rearrangement is also supported by our surface morphological studies. The respective atomic force microscopy (AFM) images show larger ellipsoidal, closely packed grains in EG7-PEDOT:PSS (Figure 1e), in marked contrast to the smaller elongated grains in pristine PEDOT:PSS (Figure 1f). The addition of EG in PEDOT:PSS (cell H) enhances the formation of extended linear quinoid structures, which are believed to give rise to the observed large PEDOT grains.12

To determine the origin of low-J–V and high-EQE properties of the cell made of pristine PEDOT:PSS (cell L), EQE measurement is carried out under different LBI conditions. It should be noted that calibration of LBI to match the illumination condition between 1 and 100 mW/cm² is difficult because of the complexities in performing such a measurement in situ during EQE measurement. For EQE measurement, the monochromatic beam is incident normal to the sample surface (between the electrodes as shown in the inset in Figure 2a).20,21 To replicate a LBI similar to that used in J–V measurement, i.e., conducted with LBI normal to the sample surface, is therefore not physically possible. Thus, the LBI is delivered at an angle (approximately 45° from normal) to completely flood the total sample area (Figure 2a, inset). Using a power meter to measure the light intensity, we then adjust the illumination appropriately to reach a maximum intensity of 100 mW/cm² (one sun or an appropriately chosen LBI). Figure 2 compares the EQE spectra of cells H and L under different LBI conditions. Evidently, a minute blue shift and an extremely minor increase in the EQEmax with increasing LBI are observed for cell H (Figure 2a). In contrast, a significant reduction in the EQE with increasing LBI is found for cell L (Figure 2b). This EQE reduction is particularly apparent with LBI above 40 mW/cm². In addition, we observe a series of spectral features between 800 and 1000 nm with increasing LBI, the origin of which is not clear. It is possible that structural changes could produce such changes in the EQE spectrum when exposed to different LBI conditions.

To further investigate the cause of the LBI-induced variation in the EQE found for the low-PCE cell (cell L), we also perform in situ Raman spectroscopy measurement under one-sun LBI conditions (100 mW/cm²) but do not find any difference in the Raman data. We then subject these cells to one-sun LBI for a prolonged period of time (2 and 5 h) and subsequently measure the Raman spectra (Figure 3a,b). The Raman spectrum of the high-PCE cell (cell H) does not exhibit any changes after exposure to LBI for 2–5 h (Figure 3a). However, the corresponding Raman spectra for the low-PCE cell (cell L) indicate a discernible transformation from a quinoid to a benzoid structure after 2 h of LBI exposure (Figure 3b). The quinoid and benzoid peak positions are marked with vertical lines in the figure. The structural transformation trend becomes more apparent after exposure of cell L to LBI for 5 h.

To summarize these results, we show schematic models of the two cells in Figure 4. For cell H with the EG7-PEDOT:PSS/SiO₂/silicon structure (Figure 4a), EG addition induces the formation of larger PEDOT grains and more orderly compacting of these grains while excess PSS is stabilized at the grain boundaries.12,26 Such a grain likely consists of linear quinoid chains (Figure 4c). The formation of large grains indicates that EG acts as a boundary layer between PEDOT and PSS chains and helps to extend the linearity of the quinoid structure by converting the coil-like benzoid structures near the grain boundaries. For cell L with a PEDOT:PSS/SiO₂/silicon structure (Figure 4b), smaller grains are arranged more randomly in the film with the coexistence of both linear quinoid and coil-like benzoid structures of PEDOT (Figure 4d). For clarity, we have not depicted micropore defects at the

![Image](https://example.com/image.png)
interface between PEDOT:PSS and SiO\textsubscript{x}/silicon in these cells, the formation of which has been discussed in our earlier work.\textsuperscript{4} The presence of the coil-like benzoid structure could account for the smaller grain size, and their aggregation near the grain boundaries would reduce the charge-transport efficiency. We propose that a high LBI exposure causes considerable structural changes in the PEDOT grains, with reduction in the quinoid chain length and extension of the benzoid chains (Figure 4e). The structural changes are found to be reversible under short LBI exposure, which is confirmed by our observation that high-EQE spectra after exposure of cell L to LBI for a few minutes can be obtained repeatedly. Conversely, the EQE of cell L exposed to LBI for 5 h measured again without LBI (Figure S2 in the SI) indicates a partial structural reversibility. The large EQE variation in organic solar cells subjected to LBI reported in the literature\textsuperscript{2,20} may therefore be attributed to reversible structural changes in the PEDOT:PSS layer. Our results do not, however, rule out the earlier suggestions that space-charge buildup\textsuperscript{7} and increased recombination are the major causes of the observed EQE variation.\textsuperscript{20} It is possible that the structural changes in PEDOT:PSS under LBI exposure could lead to different space-charge generation processes. For pristine PEDOT:PSS (cell L), the structural transformation from quinoid to benzoid limits the hole transport and results in slower charge-carrier dynamics and significant recombination under high LBI. These results indicate that the addition of cosolvent, EG, is beneficial to producing a stable and linear quinoid structure of PEDOT chains, the improved electronic properties of which are better suited for high-performance organic electronic device fabrication. Moreover, the performance of devices made with PEDOT:PSS could be further improved with the introduction of plasmonic nanoparticles or cells made of surface-structured silicon substrates.

In summary, we report highly stable solar cell properties of a high-efficiency PEDOT:PSS/planar silicon hybrid solar cell that is insensitive to light intensity. This is achieved by stabilization of the quinoid structures in PEDOT:PSS with an optimized amount of cosolvent (EG) addition. While LBI-dependent EQE measurement on the low-efficiency cell revealing its high EQE obtained under normal measurement conditions could be misconstrued as a technical problem, LBI-dependent structural changes in pristine PEDOT:PSS are the real culprit to such a phenomenon. Indeed, solar cells made with pristine PEDOT:PSS (without EG) are found to be highly light-intensity-sensitive, which is attributed to the structural switching from quinoid to benzoid in the PEDOT grains. The structural switching increases the charge-carrier concentration and high recombination rate under intense light, which results in the poor performance of these solar cells. These results provide new insight into the positive effect introduced by the addition of an optimized amount of cosolvent in stabilizing the PEDOT structure, which is important to achieving a stable performance from PEDOT:PSS-based organic and organic–inorganic electronic devices.
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AUTHOR INFORMATION

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