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## Disassembly of micelles to impart donor and acceptor gradation to enhance organic solar cell efficiency

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Arulraj Arulkashmir and Kothandam Krishnamoorthy\*

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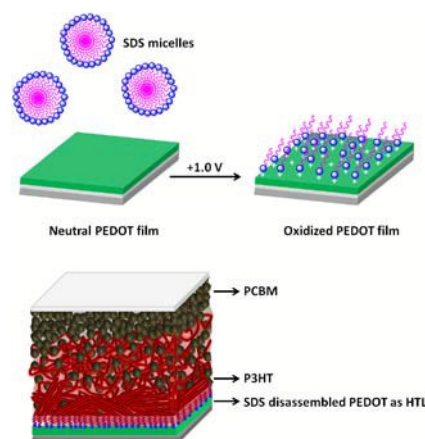
**Transparent, conducting and low surface energy surface was prepared by disassembly of anionic micelles, which altered the orientation of donor polymer and imparted gradation between the donor and acceptor. This configuration increased the solar cell device efficiency.**

Impressive efficiencies exceeding 10% have been reported using organic bulk hetero junction (BHJ) solar cells.<sup>1</sup> The power conversion efficiency (PCE) has been improved by increasing the short circuit current density ( $J_{sc}$ ) and open circuit voltage ( $V_{oc}$ ).<sup>2-5</sup> The other factor that impacts the PCE is fill factor (FF). The FF is affected by charge carrier mobility, charge recombination and microstructure of the active layer.<sup>6-9</sup> Bias and charge density dependent recombination dominate recombination losses in addition to Langevin and Schokley-Read-Hall type recombination.<sup>10,11</sup> The recombination can be reduced by improving the life time and mobility of charge carriers.<sup>12</sup> Thus, increase in these two parameters should increase the fill factor. We hypothesized that the charge carrier mobility and life time can be improved by properly crystallizing the donor polymer, which preferably leads to gradation of donor and acceptor materials. The microstructure emanates from the gradation is expected to increase the FF and PCE.

PEDOT-PSS has been the work horse of organic solar cells, although few other materials have also been explored.<sup>13-16</sup> The PEDOT-PSS film is prepared from water dispersion and the film is hydrophilic. The water drop contact angle, which is the measure of hydrophilicity, for PEDOT-PSS is 40° (Supporting Information Fig. S1). On the other hand, most active layers are hydrophobic due to the presence of long and branched alkyl chains. For example, the thoroughly studied Poly (3-hexyl thiophene)-PCBM film shows a water drop contact angle of 100°.<sup>17</sup> Thus, a very clear surface energy difference between the PEDOT-PSS and active layer exists.

Therefore, we hypothesized that a HTL that has surface energy close to the surface energy of active layer is essential for the formation of desired active layer morphology. However, preparing a transparent, conducting and low surface energy HTL is non trivial. Based on an approach reported by our group,<sup>18,19</sup> positive charge bearing PEDOT was used to disassemble SDS micelles and prepared low surface energy transparent conducting films. In these films, the sulfonate head group of SDS is attached with the PEDOT and the alkyl chain is protruding from the surface as shown in cartoon (Scheme 1). Thus, in this configuration, the methyl moiety at the end of the alkyl chain will interact with the active layer. The methyl moiety is known to interact with  $\pi$  cloud of a polymer via  $\pi$ -H interaction. H-S interaction is also possible if the polymer has sulfur atom. These interactions have been shown to enforce poly (3-hexyl thiophene) to align parallel to the substrate.<sup>20</sup> This is a desirable configuration for charge injection to the electrode. Considering all these factors, a well studied system P3HT-PCBM was chosen as active layer with SDS modified PEDOT (PEDOT-SDS) as HTL. The BHJ cells prepared using PEDOT-SDS exhibited PCE of 4.4% while using P3HT-PCBM (1:0.5 wt%) as active layer. Please note that this ratio of P3HT-PCBM exhibit less than 1% while using PEDOT-PSS as HTL. Thus, the approach described in this report renders a possibility to decrease the PCBM quantity in BHJ cells.

PEDOT was electrodeposited on top of ITO coated glass by applying a constant potential of 1.2 V vs Ag/Ag<sup>+</sup>. The polymerization



Scheme 1 Cartoon showing the envisioned gradation induced by PEDOT-SDS

CSIR-National Chemical Laboratory, CSIR-Networks of Institutes for Solar Energy,  
Dr Homi Bhabha Road, Pune 411008, India  
E-mail: k.krishnamoorthy@ncl.res.in

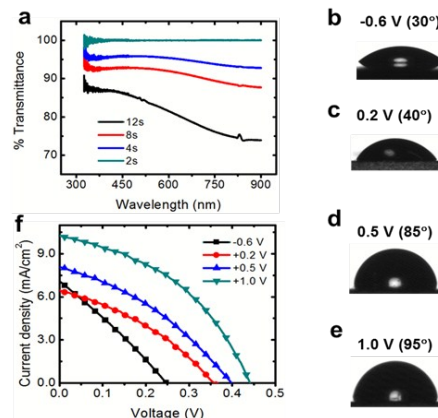
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potential was determined from the cyclic voltammogram (Supporting Information Fig. S2 and S3). The polymerization time was varied to obtain PEDOT with various thicknesses. We found that the polymerization of EDOT for 4 s resulted in a film with 95% transparency (Fig. 1a). Then, this film was reduced by applying a constant potential of -1 V, which resulted in opaque blue, neutral polymer film. To generate positive charges on the PEDOT, various oxidation potentials were applied with respect to Ag/Ag<sup>+</sup> in monomer free supporting electrolyte. The films were then exposed to 6 mM SDS solution. Please note that this concentration is slightly above the CMC of SDS in water. Water drop contact angle (CA) experiment was used to ascertain the hydrophobicity of the film. The PEDOT-SDS film prepared by applying -0.6 V showed CA of 30° (Fig. 1b). At this potential, the PEDOT doesn't have positive charges, hence the interaction between PEDOT and SDS micelles is unlikely. The CA increased to 40°, for a film prepared by applying a potential of 0.2 V to PEDOT and subsequent SDS treatment. The CA increased to 85° and 95° (1d and 1e) upon applying potential of 0.5 V and 1 V, respectively. From the transparency measurement (95%) and CA measurements (95°), PEDOT-SDS films prepared by applying a potential of 1 V seems suitable for fabrication of organic solar cells.

In order to test the suitability of PEDOT-SDS as HTL layer in BHJ solar cells, ITO substrates were coated with PEDOT-SDS prepared at various conditions. A P3HT:PCBM (1:1 wt%) photoactive layer was spun on top of the PEDOT-SDS HTL layer and aluminum was evaporated to complete the cell. The PCE was found to be 0.4 % (-0.6 V), 0.8 % (+0.2 V), 1.2 % (+0.5 V) and 2.3 % (+1 V) (Fig. 1f and Supporting Information Table S1). The potential mentioned in the parenthesis indicates the potential applied on the PEDOT film prior to SDS treatment. The other device metrics for these cells are provided in supporting information Table S1. From these experiments, it is clear that a HTL layer with 95% transparency and 95° CA provides best PCE. The next set of experiments was carried out by varying the ratio of P3HT and PCBM. We hypothesized that faster crystallization of P3HT would lead to gradation of P3HT and PCBM. Thus, we chose to decrease the concentration of PCBM compared to P3HT. BHJ solar cells were prepared by varying the PCBM weight percentage between 0.2 to 1% with respect to P3HT. The best PCE (4.4 %) was observed for cells fabricated using 0.5% PCBM (Fig. 2a). The corresponding IPCE spectra are shown in Fig. 2b. Interestingly, the PCE falls to 2.5% for cells fabricated with 1% PCBM. Thus, the PCE goes through a maximum. The  $V_{oc}$ ,  $J_{sc}$  and FF were poor for cells fabricated with PCBM wt% of 0.2% (Table 1). However, for BHJ cells fabricated with PCBM wt% of 0.5, the FF was 72% that is significantly higher than that observed for conventional



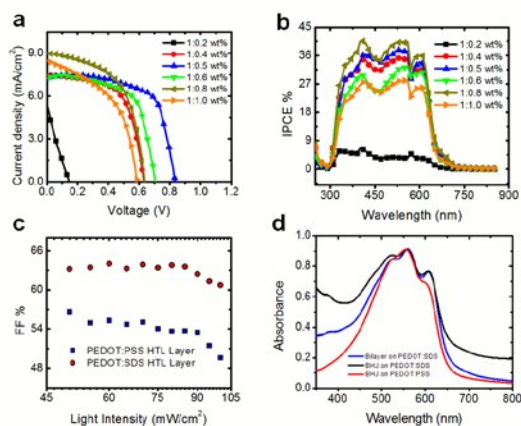
**Fig. 1** Plot showing the %T as a function of various duration of polymerization of EDOT (a). Contact angle of PEDOT after interaction with SDS micelles, as a function of applied potential, (b) -0.6 V, (c) 0.2 V, (d) 0.5 V and (e) 1V. IV curve of PEDOT-SDS HTL based P3HT:PCBM (1:1 wt%) solar cells. The potentials mentioned in the plot was the potential applied on PEDOT before SDS interaction (f).

P3HT:PCBM cells. The higher FF along with  $J_{sc}$  is attributed to the improved charge transport to respective electrodes (*vide infra*). It is interesting to note that the  $V_{oc}$  also increased in this case. Higher  $V_{oc}$  was observed for Schottky type cells made using very high quantities of acceptor.<sup>21</sup> In those cells, the  $V_{oc}$  is governed by the work function of anode and the LUMO of PCBM.<sup>22</sup> The higher  $V_{oc}$  in the cells fabricated using P3HT:PCBM (wt% 1:0.5) while using PEDOT-SDS as HTL layer is likely due to the formation of gradation that leads to a structure similar to Schottky type cells. However, the  $V_{oc}$  decreases upon increase in PCBM concentration because the P3HT:PCBM forms regular BHJ type cells instead of schottky type cells. The other probable reason is decreased recombination in the P3HT:PCBM (wt% 1:0.5) cells. Control experiments using PEDOT-PSS as HTL layer showed PCE of 0.9% while using P3HT:PCBM (wt % 1:0.5) (Supporting Information Fig. S5 and Table S2). This indicates that the morphology of P3HT:PCBM cells are different while using PEDOT-SDS as HTL layer.

This morphology facilitates better charge extraction, which results in increased FF. The increased FF in case of PEDOT-SDS HTL layer can be further studied by varying the intensity of illuminating light.<sup>23</sup> The light intensity was varied from 50 to 100 mW/cm<sup>2</sup> and the IV curves were recorded (Supporting Information Fig. S6). The plot of light intensity vs FF shows that the FF didn't vary significantly as a function of light intensity in case of PEDOT-SDS. The deviation was 4.7% (Fig. 2c). On the other hand the FF varied 14.7% as function of light intensity in case of PEDOT-PSS (Fig. 2c). The decreased variation of FF that was observed for PEDOT-SDS HTL layer is due to decreased bimolecular recombination.<sup>12</sup> The

**Table 1.** Device metrics for various P3HT-PCBM cells with PEDOT-SDS HTL

S. No	P3HT:PCBM wt% ratio	$V_{oc}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )	FF %	$R_s$ ( $\Omega$ )	$R_{sh}$ (k $\Omega$ )	IPCE %	$\eta$ %
1	1:0.2	0.14	5.3	20	356.9	0.2	4.80	0.2
2	1:0.4	0.61	7.6	67	74.9	6.6	34.6	4.1
3	1:0.5	0.81	7.2	72	47.9	3.3	38.4	4.4
4	1:0.6	0.70	7.1	65	49.2	6.4	33.1	3.1
5	1:0.8	0.62	9.0	62	84.4	13.8	39.7	2.9
6	1:1.0	0.58	8.8	53	141.6	13.3	27.8	2.4



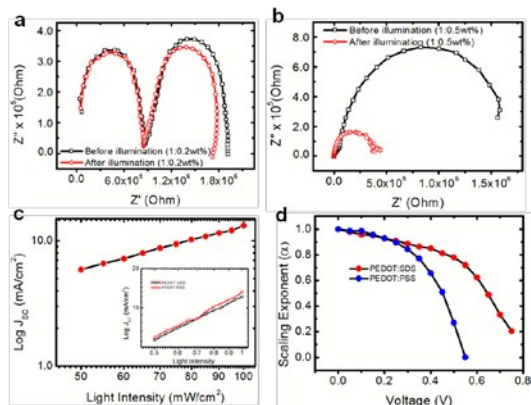
**Fig. 2** IV curve of P3HT-PCBM cells with various weight ratios of PCBM on PEDOT-SDS HTL (a) and the corresponding IPCE spectra (b). Plot of light intensity vs FF for cells prepared using PEDOT-SDS and PEDOT-PSS (c). UV-vis absorption spectra of P3HT-PCBM film on PEDOT-SDS and PEDOT:PSS HTL (d).

statistical analysis of the device data was carried out by following the reported procedure.<sup>24</sup> The detailed calculations are provided in supporting information (Fig. S16-S18). The Z value found to be 9.93, which results in a P value of  $\sim 0$ . This indicates that the device efficiency increase is significant. Please note that the analysis was carried out for P3HT:PCBM (wt% 1:0.5) prepared on PEDOT-SDS and P3HT:PCBM (wt% 1:1) prepared on PEDOT-PSS. It must be recalled that the  $\eta$  of P3HT:PCBM (wt% 1:0.5) prepared on PEDOT-PSS is 0.9%. Thus, the difference in  $\eta$  of same weight ratio of P3HT:PCBM on PEDOT-SDS and PEDOT-PSS is very significant.

We had envisioned that the SDS chains protruding from the PEDOT will preferentially crystallize P3HT. In case of P3HT, the crystallization can be easily identified by analyzing the UV-vis absorption spectra of the film. In addition to absorption maxima due to  $\pi$ - $\pi^*$ , a hump appears at higher wavelength, if the P3HT is crystallized well. Indeed, we were glad to notice a hump at 610 nm while the P3HT-PCBM film was prepared on PEDOT-SDS HTL layer (Fig. 2d). This is an indication that P3HT has crystallized well. We have used thin film XRD as well as X ray photoelectron spectroscopy to analyse the gradation of the donor and acceptor in the BHJ. The discussion is provided in ESI (supporting information Fig. S8). The protruding alkyl chain of SDS molecules is the key element in interacting with P3HT and facilitates gradation. This is similar to the alkyl chain containing silane modified  $\text{SiO}_2$  substrates used in field effect transistors (FET).  $\text{SiO}_2$  surface is hydrophilic, but the octadecyltrichlorosilane (OTS) modified  $\text{SiO}_2$  surface is hydrophobic. The  $-\text{CH}_3$  moiety at the end of alkyl chain induces the P3HT chains to pack parallel to the substrate due to H-S and  $\pi$ -H interactions. Due to this packing pattern, we envisioned the PCBM to move farther from the base substrate while a film is prepared using P3HT-PCBM blend. Two set of experiments were carried out using OTS modified and unmodified  $\text{SiO}_2$  dielectric based OFETs (Supporting Information Fig. S9 – S12). In case of unmodified substrate, we observed ambipolar charge transport ( $\mu_{\text{h}}$   $1.01 \times 10^{-3} \text{ cm}^2/\text{V}\cdot\text{s}$  and  $\mu_{\text{e}}$   $6.71 \times 10^{-4} \text{ cm}^2/\text{V}\cdot\text{s}$ ) due to the presence of P3HT as well as PCBM at the interface (supporting information S9 and S10). On the other hand, OTS modified substrate showed only p type mobility ( $\mu_{\text{h}}$   $1.39 \times 10^{-2} \text{ cm}^2/\text{V}\cdot\text{s}$ ) indicating the absence of PCBM at the interface (supporting information S11 and S12). This clearly proves our

hypothesis that the SDS modification of PEDOT, which is similar to silane modification on  $\text{SiO}_2$  results in alignment of P3HT parallel to the substrate. It also leads to the gradation of P3HT and PCBM.

Impedance spectroscopy is an effective and useful method to study the morphology of active materials in BHJ cells.<sup>25</sup> The nyquist plot of P3HT:PCBM cells prepared using PEDOT-PSS HTL layer resembled the reported data (Supporting Information Fig. S13 to S15). However, the nyquist plots of PEDOT-SDS based cells are very different, which indicate the morphology of P3HT-PCBM in these cells is different. For a cell fabricated using 0.2% PCBM, two large semicircles are observed (Fig. 3a). The high frequency semicircle is attributed to bulk resistance ( $R_1$ ) and capacitance ( $C_1$ ). The low frequency semicircle is attributed to recombination resistance ( $R_2$ ) and chemical capacitance ( $C_2$ ) associated with internal charge transfer between donor and acceptor.<sup>25</sup> The  $R_1$  and  $R_2$  for the cell fabricated with 0.2% PCBM was found to be  $8.3 \times 10^5 \Omega$  and  $9.8 \times 10^5 \Omega$ , respectively. The resistance change upon illumination is small. Upon increase in concentration of PCBM, the  $R_1$  starts decreasing. Indeed, for a cell fabricated using 0.5% PCBM, the high frequency semicircle is vanished upon illumination (Fig. 3b). This indicates that the resistance associated with transport through the bulk ( $R_1$ ) has become extremely small, which leads to lower bimolecular recombinations and better charge collection.<sup>26</sup> The lowest resistance ( $R_2$ ) calculated from the nyquist plot ( $3 \times 10^4 \Omega$ ) confirm this analysis. Further increase in PCBM concentration increases the resistance ( $R_2$ ). This is attributed to the distribution of PCBM throughout the film that is confirmed by XRD data as well (*vide supra*). Insights into the bimolecular recombinations can be gathered by  $J_{\text{sc}}$  vs light intensity measurements.<sup>1,27</sup> Towards this objective, the light intensity was varied between 0.5 to 1 sun and the IV curves were recorded. In organic solar cells,  $J_{\text{sc}}$  is proportional to  $I^{\alpha}$ . The  $\alpha$  is known as scaling exponent. The scaling exponent ( $\alpha$ ) can be calculated from the logarithmic plot of  $J_{\text{sc}}$  as a function of light intensity. The tangent line (slope 1) obtained from the plots were fitted with the power law (Fig. 3c). At maximum charge collection point  $J_{\text{sc}}$ , the linear dependents of  $J_{\text{sc}}$  with various light intensity was observed, which makes the  $\alpha$  close to unity. Insignificant change in  $\alpha$  was observed (at  $V = 0$ ) irrespective of HTL layers used can be attributed with the reduced bimolecular recombination at  $J_{\text{sc}}$  conditions as shown in Fig. 3c and inset of Fig. 3c. Scaling exponent close to one is an indication of reduced bimolecular recombination.<sup>27</sup> In case of PEDOT-SDS, the  $\alpha$  was found to be one at 0V and starts deviating upon increase in voltage towards maximum power (Fig. 3d). However, the deviation is significantly smaller compared to PEDOT-PSS based cells. Thus, we can conclude that the PEDOT-SDS layer provides gradation of P3HT and PCBM, which leads to reduced bimolecular recombination and increases the FF. The decreased series resistance ( $R_s$ ) and increased shunt resistance ( $R_{\text{sh}}$ ) calculated from the IV curves (Table 1). In an ideal cell, the series resistance is expected to be low. On the other hand, the shunt resistance is expected to be high, which is an indication of diminished charge losses. In case of P3HT-PCBM (1:0.5%), the  $R_s$  was lowest ( $47.9 \Omega$ ) and the  $R_{\text{sh}}$  increased to 3.3 k $\Omega$ . All these factors increase the efficiency of BHJ while using PEDOT-SDS as HTL layer.



**Fig. 3** Impedance spectra of P3HT-PCBM (1:0.2%) (a) and P3HT-PCBM (1:0.5%) (b) BHJ solar cells prepared using PEDOT-SDS HTL. Plot of light intensity vs  $\log J_{sc}$  (c) that was used to calculate  $\alpha$  and voltage vs scaling exponent (d).

## Conclusions

In summary, anionic micelles are disassembled on a transparent conducting polymer film. This amphiphile modified conducting polymer was found to exhibit low surface energy. Indeed, we were able to prepare a HTL with surface energy commensurate with that of photoactive layer. Furthermore, the methyl moiety of the amphiphile interacted with the  $\pi$  cloud of the donor polymer and facilitated the gradation of donor and acceptor towards the charge extraction electrodes. The gradation of donor and acceptor increased the FF to 72%, decreased the series resistance and increased the shunt resistance. Furthermore, the gradation also increased the  $V_{oc}$ . It is indeed essential to note that the gradation also decreased the bimolecular recombination and increased the charge transport to the electrodes. All these factors increased the amphiphile modified HTL based solar cell efficiency by 20%. One of the striking features of low surface energy HTL based organic solar cells is the use of low quantities of PCBM. The highest efficiency was obtained while using 0.5% PCBM with respect to the donor polymer. Thus, the low surface energy HTL renders the possibility of increasing the power conversion efficiency while decreasing the PCBM quantity.

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