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Optimum Morphology and Performance Gains of Organic Solar Cells

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ABSTRACT

Morphology of light absorbing layer is known to dictate the power conversion efficiency of organic photovoltaic (OPV) cell. The innovation of bulk heterojunction (BH) led to significant improvement for exciton harvesting, but carrier recombination at the distributed interfaces and variability of performance have been persistent concerns . *The purpose of this paper is to theoretically explore the efficiency- space of OPV as a function of the degree of randomness of its morphology and to optimize the BHJ morphology for the maximum efficiency*. We use systematic numerical simulation of exciton/electron/hole transport to predict the efficiency and variability associated with various OPV morphologies. We find that while (1) the efficiency of random BHJ morphology can be close to optimal, (2) the significant variability associated with cells suggests reduced efficiency in a series-connected configuration. (3) We also find that a simple fully ordered structure may also not be optimum; instead a fin like geometry (Fig. 4) may improve efficiency. (4) We also analyze the effect of each transport parameters on the cell efficiency and show that under certain configuration of transport parameters, the long-abandoned PHJ structure may re-emerge as optimal geometry.

INTRODUCTION AND BACKGROUND

Research in the area of organic photovoltaic (OPV) cell started with a very simple two layer device structure [1] of donor (D) and acceptor (A) materials (called planar heterojunction (PHJ) OPV). The poor efficiency of PHJ OPV was attributed to small short circuit current (J_{SC}), mainly caused by poor exciton collection. Photo-generated excitons in the organic material dissociate into charge carriers only at the D-A heterojunction, otherwise they are lost due to self recombination. Thus in PHJ OPV exciton collection is limited by small exciton diffusion length ($L_{ex}\sim 10\ nm$) from the center junction of the cell (see fig. 1(a)). This problem of poor exciton collection (or low J_{SC}) is later solved by the elegant idea of bulk heterojunction [2] (BHJ), where the junction between the donor and acceptor material is distributed randomly throughout the volume of the cell. This distributed D/A junction enables to harvest exciton irrespective of its point of generation, but unfortunately this device structure suffers from higher recombination due to increased interfacial area. Thus even though BHJ solar cell has achieved almost 100% internal quantum efficiency [3], its open circuit voltage (V_{oc}) and fill factor (FF) remains poor.

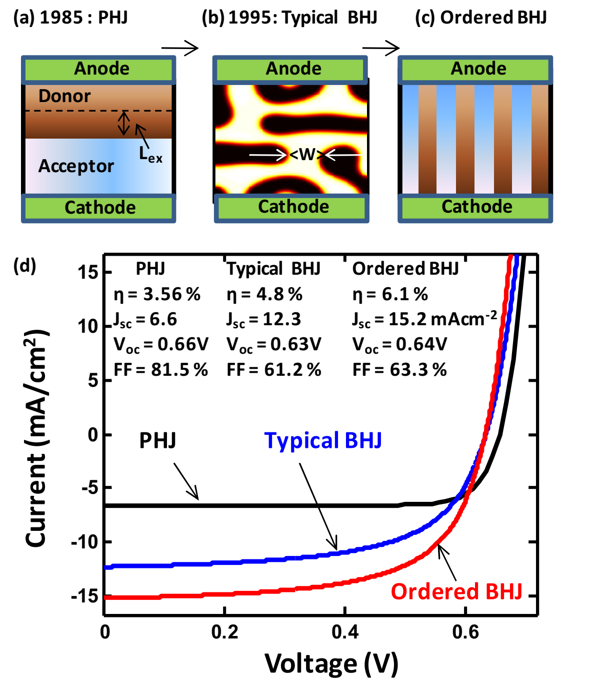

Fig. 1: Structure of the (a) PHJ, (b) typical BHJ and (c) ordered BHJ (OHJ) solar cell in the chronological order of development. (d) Comparison of I-V characteristics for various OPV geometry. The assumed model parameters are: $L_{ex} = 20\ nm$, $\mu_e = \mu_h = 10^{-3} cm^2V^{-1}s^{-1}$, $\gamma = 10^{-9} cm^3/s$, $G_o = 10^{22} cm^{-3}/s$ (uniform), $T_{film} = 100\ nm$.

There have been several efforts [4-6] in the recent years to improve the transport property of BHJ OPV by regularizing its morphology. Fabricating ordered morphology has a lot of technological challenges and questions of economic viability. *However, regardless these technical and economic challenges, the fundamental theoretical question of optimum geometry of polymer-based OPV and the limits of the efficiency improvement with such optimum morphology remain an unanswered question.* Several recent simulation based comparative studies on the ordered and disordered structures [7-9] has already described the relevance of the problem but (1) systematic study of statistical distribution of OPV efficiency as a function of random morphology is yet to be explored. Moreover, (2) there is no clear guideline for the design of the ordered/optimum morphology as a function of the transport/recombination parameters, making it difficult to predict the circumstances for which engineering ordered

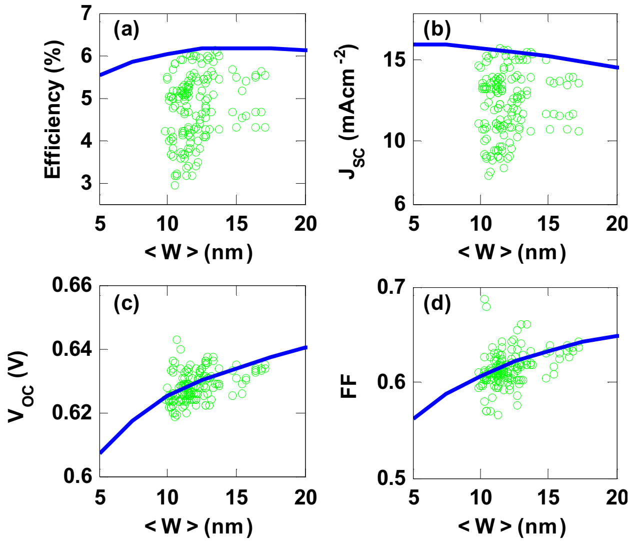

Fig. 2: Performance comparison of ordered and disordered BHJ solar cell. The performance matrices are (a) efficiency (η), (b) short circuit current (J_{SC}), (c) open circuit voltage (V_{OC}), and (d) fill factor (FF). Each scattered symbol corresponds to a particular random morphology with an average domain size <W> (x-axis). Solid line represents the performance of ordered geometry with domain width in x-axis.

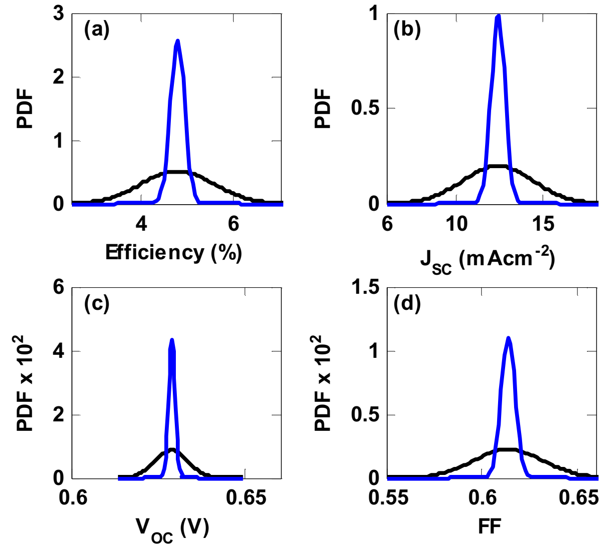

Fig. 3: Probability density function (PDF) of the solar cell performance matrices ((a) efficiency (η), (b) short circuit current (J_{SC}), (c) open circuit voltage (V_{OC}), and (d) fill factor (FF)). Variation in the performance arises from the structural randomness. Black solid curves are for devices with smaller active area (100nm x 100nm) and blue lines are for larger active area.

morphology may be appropriate. Finally, (3) it is not clear which transport parameter (e.g., electron/hole mobility, exciton diffusion length, recombination strength etc) has the highest impact to boost the efficiency for a given randomness of morphology.

In this paper, we address the above mentioned problems through systematic numerical simulation of exciton/ electron/hole transport. We find that (i) efficiency of the classical BHJ solar cell fluctuates in a wide range ($<\eta_{BHJ}> \sim 4.8\%,\ SD = 0.8\%$) for typical transport and optical properties (values are given in caption of Fig 1). (ii) Regularization eliminates this fluctuation and improves the efficiency up to 6.5%. (iii) However, optimal morphology is not the trivial fully ordered structure (Fig.1c), but a fin like geometry (Fig. 2) with dimensions given by transport parameters. (iv) Finally, we analyze the effect of each transport parameters on the cell efficiency and show that an order of magnitude improvement in carrier mobility will saturate the efficiency of BHJ cell at 8% while with the improvement in exciton diffusion length $(L_{ex} \sim T_{film}/2)$, long-abandoned PHJ structure will re-emerge as optimal geometry.

PROCESS-DEVICE CO-MODELING OF BH-OPV

The random bulk heterojunction morphology is simulated for various process conditions by phase field approach with Flory-Huggins Cahn-Hilliard model [10]. The details of the free energy function and the model parameters are described in the literature [7],[11],[12]. Once the morphology is simulated, we characterize the structure by average domain size as shown in Fig. 1. The current-voltage characteristic of OPV corresponding to a given morphology is calculated by self-consistent solution of Poisson and Continuity equations for the potential and carrier densities. The transport of charge carriers is described by drift-diffusion formalism [7]. The generation of charge carriers is obtained from the solution of the steady state exciton diffusion equation. The recombination term of the charge carriers is implemented by the bi-molecular recombination: $R = \gamma(np - n_{int}^2)$ where n_{int} is the intrinsic carrier concentration at the cross-gap of D/A interface and γ is the recombination strength which captures the quality of interfacial region between the donor and acceptor materials. The generation and the recombination terms are non-zero only at the D/A interfacial nodes. Detailed description of the transport equations are given in the literature [7].

RESULTS AND DISCUSSION

With the model system described in the previous section, we now explore the effect of active layer geometry on the cell efficiency. It should be noted that we do not limit our analysis to a particular polymeric system, but we choose typical values for the model parameters (see Fig. 1 caption) to capture the general properties applicable for the broad class of BHJ OPV. The optical absorption and the energy band profile is taken similar to P3HT: PCBM system.

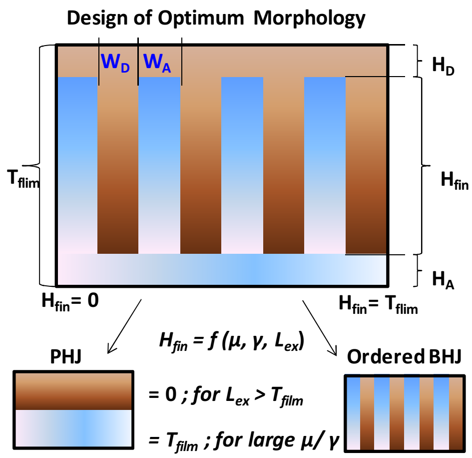

Fig 4. Design rules for fabricating the optimum morphology. The optimum fin width (W_{fin}) and the fin height (H_{fin}) height are determined as a function of the transport parameters.

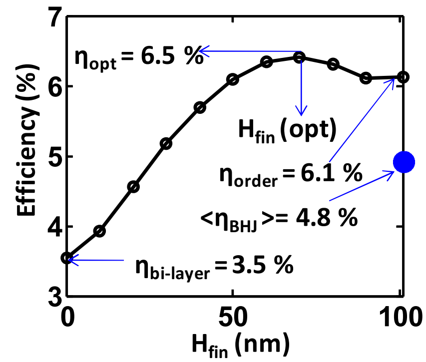

Fig. 5. Efficiency variation of FIN-OPV (Fig. 4) is plotted for the various fin heights. The fin width is kept fixed to the value of $W_{fin} = 1.5L_{ex}$. We find optimum fin height to be $H_{fin}(opt) \sim T_{flim} - \xi L_{ex}$, where ξ is a number in the range ($1 < \xi < 2$).

Ordered Vs Disordered BHJ cell

We first analyze how the randomness in the OPV morphology affects the key device parameters like J_{sc}, V_{oc} and *FF*. For this, we first generate a series of BHJ structures with an initial random configuration (details of process simulation is described in Ref. [7],[11]). Figure 1(b) shows one of such simulated structures. For each simulated random structure, we calculate its average cluster size $< W >$ (the x-axis in all the subplots of Fig. 2). The solution of transport equations on these random structures generates the current-voltage characteristics, from which we calculate efficiency and the other solar cell parameters. We plot these performance matrices as green open circles in Fig. 2(a-d) for many sets of simulated structures corresponding to various process conditions. We also compare the performance of ordered morphology with the same domain width ($< W >$) in all those subplots (solid lines). The probability density function (PDF) for the performance variation is also plotted in Fig. 3(a-d). The figure shows that there is a significant variation in efficiency (mean efficiency $< \eta_{BHJ} > \sim 4.8\,\%$; standard deviation $SD = 0.8\%$) due to the inherent randomness in the classical BHJ structures. We attribute this unexpectedly large variation to the finite size of the simulated structure. However, with larger active area (blue lines in Fig. 3) we expect this performance variation will reduce and only the mean efficiency will be measured.

We now summarize the important findings of this randomness analysis of disordered BHJ morphology. First, we find that among all the solar cell parameters the variation in open circuit voltage with morphology is the smallest. This proves the fact that V_{OC} is a weak function of morphology and mainly determined by the material constants. Second, the fill-factors for both ordered and disordered morphologies vary in the range of 0.55-0.65, which is much lower than that of PHJ cell ($FF^{PHJ} \sim .8$). This indicates that FF of PHJ cell is optimal. Finally, we observe from Fig. 2(a) that there are few disordered BHJ structures whose efficiency is as high as that of ordered structure ($\eta_{order} \sim 6.1\%$ for $< W >= 15\,nm$). Thus, performance of a random BHJ morphology can be close to optimal, but for a larger area cell the average efficiency ($< \eta_{BHJ} > \sim 4.8\,\%$) will be obtained. On the other hand, ordered BHJ structure shows significantly reduced variability (solid line in Fig. 2a) and sensitivity to structural variation (W~10-25nm). Such robust behavior of ordered cell arises from the fact that the ordered morphology operates above percolation threshold for all domain width ($< W >$) and mixing ratios. *Therefore, the key advantage of regularization is not dramatic increase in efficiency (slight improvement can be traced to lower interface recombination that increase* V_{oc} and FF, see Fig. 2) *but rather in reduction in fluctuation and insensitivity to details of process conditions.*

Design rules for Optimum Morphology

Remarkably, efficiency analysis shows that neither PHJ, nor the fully ordered BHJ cell is the optimum. There is an opportunity for further improvement in efficiency by proper designing of the active layer morphology. We show that instead of fully ordered structure (Fig. 1c), partial ordering defined as the interpenetrating Fin like morphology (Fig. 4), provides better efficiency. In this work, we address this optimization problem by our transport simulation framework and calculate the optimum morphology as a function of the transport parameters. For simplicity, we assume the structure is symmetric with equal volume of donor and acceptor material, so that $W_A = W_D = W_{fin}$ and $H_A = H_D = (T_{flim} - H_{fin})/2$, with two independent variables of fin height (H_{fin}) and fin width (W_{fin}) available for optimization. The more general problem of optimizing partially ordered OPV with unequal volume fraction is easily addressed in our methodology.

The proposed fin-like morphology unifies both the PHJ ($H_{fin} = 0$) and the fully ordered ($H_{fin} = T_{flim}$) structure within a common geometrical construct. The reason for the existence of an optimum fin height is as follows: PHJ structure is excellent for charge carrier transport to the contact, but has a very poor efficiency for exciton collection. On the other hand ordered BHJ collects almost all the excitons but the structure is non-optimal for the charge transport. The fin-like morphology essentially balances the excellent carrier transport property of PHJ cell and the exciton collection property of ordered cell. Indeed, our systematic and extensive transport simulation of the FIN-OPV detects an optimum fin height which lies between the two extreme geometries (PHJ and ordered BHJ). In Fig. 5, we plot this efficiency variation as a function of fin height. The figure clearly shows that the maximum efficiency is close to $\eta_{max}\sim$ 6.5% corresponding to $H_{fin}(opt)\sim 75nm$. The efficiency numbers and the values of optimal fin dimensions depend on the choice of material system. However, in general, $H_{fin}(opt)\sim T_{flim} - \xi L_{ex}$ where ξ is a number in the range $(1 < \xi < 2)$ depending on the values of the transport parameters like L_{ex}, μ and γ. The width optimization mainly depends on the efficient exciton collection, which is guaranteed if $W_{fin}\sim 1.5L_{ex}$, consistent with results in Fig. 2a. Given the transport parameters, PHJ OPVs (η~ 3.5%) are far from optimal, a well known result for traditional material systems.

Efficiency Limits

In this work we have shown that OPV efficiency critically depends on the underlying active layer morphology. Based on the detailed simulation study on numerous random BHJ morphologies, we now define the efficiency limit of OPV for a given material system. We have shown by numerical simulation that the open circuit voltage and the fill factor of PHJ based devices are optimal. In contrast, the short circuit current of ordered BHJ (OHJ) is the maximum. Thus, for a given material system, the efficiency limit can be given by $\eta_{max} = J_{SC}^{OHJ} V_{OC}^{PHJ} FF^{PHJ}$.

In the previous section we have discussed the design rules for the optimum morphology based on typical transport parameters (L_{ex}, μ and γ). We now extend our analysis by exploring the impact of each transport parameters on the cell efficiency. In fig. 6(a) we study the effect of mobility improvement on the various OPV morphologies (other transport parameters are kept same at typical values). We find that improvement in mobility has significant effect on the efficiency of BHJ structure, where as it has very little effect on the PHJ geometry. In Fig. 6(c) we plot the efficiency variation of both PHJ and ordered BHJ with respect to mobility. Remarkably we find that mobility improvement more than $10^{-2} cm^2 V^{-1} s^{-1}$ will not have any significant effect on the efficiency. Fig. 6(c)

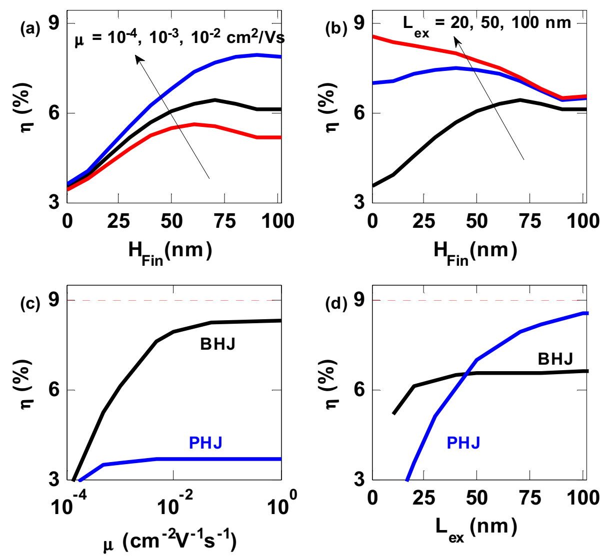

Fig. 6. Efficiency variation with improved transport parameters. (a) Effect of carrier mobility and (b) L_{ex} on the FIN-OPV cell is shown. Efficiency improvement of both PHJ and ordered BHJ with respect to (c) mobility and (d) exciton diffusion length is plotted.

shows that efficiency of BHJ cell remains saturated at 8% value with the improvement in mobility. However, the typical mobility value for the present material systems is close to $10^{-3} cm^2 V^{-1} s^{-1}$, for which the efficiency is close to 6%. Thus, with respect to current materials, mobility improvement will significantly improve the OPV efficiency. Indeed, many recent works report this improvement in carrier mobility by increased polymer crystallinity [13] or by insertion of carbon nano-tubes [14]. We also study the effect of excition diffusion length on the efficiency in Fig. 6(b), which shows that L_{ex} affects PHJ cell efficiency significantly, while it has very little effect on the ordered BHJ structure. Fig. 6(d) shows that for $L_{ex}\sim T_{flim}/2$, PHJ geometry will be the optimal among all the possible OPV morphology.

CONCLUSION

In this paper, we have demonstrated through detailed exciton/electron/hole transport simulation that even with the classical material system, there remain opportunities to improve the performance of OPV by optimum ordering of cell morphology. Classical BHJ structures suffer from the statistical variation in performance due to the inherent randomness in the device geometry. Regularization of morphology eliminates this variability problem and reduces the carrier recombination. Regularization also improves the cell efficiency by improving V_{oc} and FF of the cell. However, we find that even if the OPV morphology is perfectly regular, still it is not necessarily the optimal. The optimal morphology resembles to the interpenetrating fin-like architecture with the exact dimensions given by the transport parameters. We also show that with the improvement in exciton transport, structures similar to PHJ OPV could re-emerge as the optimum morphology of organic solar cells.

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