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Closed-form expressions correlating exciton transport and interfacial charge carrier generation with the donor/acceptor morphology in organic bulk heterojunction solar cells

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ABSTRACT

Organic bulk heterojunction (BHJ) solar cells are frequently modeled with effective-medium device models; these models, however, do not resolve the relation between excitonic processes in the donor/acceptor (D/A) blend and the D/A morphology. In this context, we derive a simple analytical model to relate the interfacial exciton flux and the volumetric generation rate of interfacial electron–hole pairs with the morphological characteristics of a D/A blend. Our approach does not require explicit morphological information of the D/A blend, except for the specific interfacial area and the blending ratio between donor and acceptor materials, both of which can be assessed experimentally. The expressions are verified with numerical simulations based on randomly generated three-dimensional D/A morphologies – overall, good agreement is found. The analytical expressions developed in this paper can easily be integrated into existing effective-medium device models, allowing them to capture the effect of exciton transport and morphology on free charge carrier generation in more detail. These expressions potentially allow morphological features in a D/A blend to be optimized within a fast, 1D computational framework.

1. Introduction

Organic solar cells (OSCs) have the potential to become cheap and highly tailorable photovoltaic devices with a wide range of applications [1,2]. While OSC technologies have been developed for over three decades [3–5], their efficiency remained low (~1%) until the mid 1990s with the introduction of the bulk heterojunction (BHJ) device structure [6,7]. Before this invention, OSCs had suffered from a low exciton dissociation efficiency due to the short exciton lifetime in most organic semiconductors. The BHJ architecture overcomes this "excitonic bottleneck" by forming a bicontinuous network of electron donor and electron acceptor materials that contains large, dispersed donor/acceptor (D/A) interfaces, where excitons can dissociate efficiently into free charge carriers. The nanoscale intermixing between the donor and acceptor components ensures that excitons can reach D/A interfaces before exciton decay occurs, while still offering continuous pathways for charge carrier transport to the electrodes. Since then, the efficiency of BHJ-based OSCs has been improving continuously thanks to progress made in the synthesis of low band-gap and more conductive organic semiconductors [8–10], the design of more efficient solar-cell architectures [11,12], as well as the optimization of D/A morphologies [13–16]. The record efficiency for OSCs has exceeded 10% at a laboratory scale [17]. Due to the continued improvement of OSC efficiency, as well as the lower process energy associated with low-temperature roll-to-roll processing, OSCs are expected to demonstrate the shortest energy-payback time among major PV technologies in the near future [18].

The D/A blend of an organic BHJ solar cell is a multiscale system (see Fig. 1a), and the photovoltaic processes taking place in the blend (see Fig. 1b) are closely affected by its morphological features at different length scales. The first step of the energy conversion process, exciton generation, is dependent on the volume fraction of the donor material where the majority of photons are absorbed. The subsequent transport of excitons is not only limited by the exciton diffusion length, but also by the domain size of the donor material typically on the order of 10 nm [14,19–21]. If an exciton reaches a D/A interface before relaxing to the ground state, exciton dissociation occurs with a quantum efficiency close to unity [22], forming an interfacial electron–hole (e/h) pair. The interfacial e/h pair extends across the D/A interfaces over a distance on the order of 1 nm [23], and may separate

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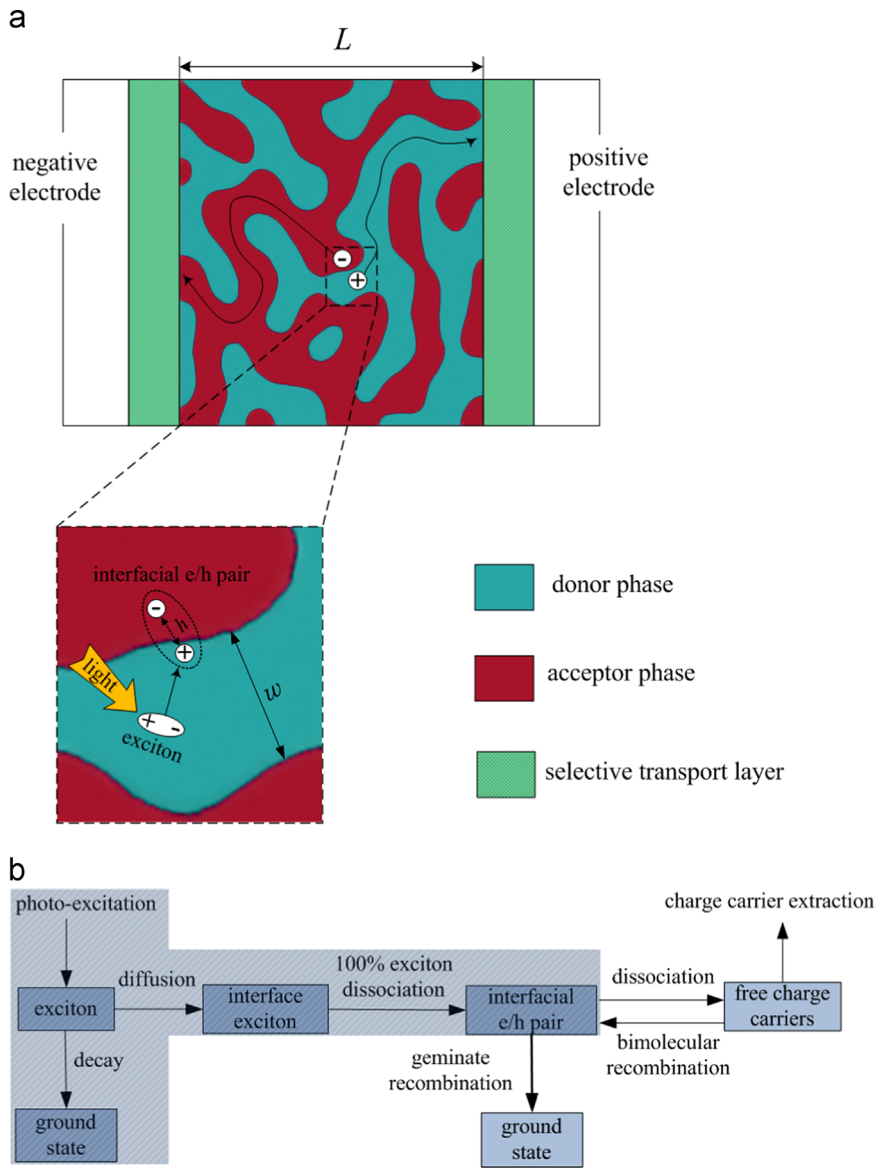

Fig. 1. Schematics for (a) a typical organic BHJ solar cell and (b) the major transport and conversion processes in a D/A blend. The shaded area represents the exciton generation, transport and decay processes considered in this paper. Excitons generated from light absorption travel within the donor material with characteristic length scale *w*, until reaching an D/A interface and dissociate into interfacial e/h pairs. The interfacial e/h pairs typically extend a distance *h* across the interface, and may separate into free charge carriers or decay to the ground state. The free holes and electrons are transported through the donor and acceptor phases over the D/A blend length scale *L* to be collected at electrodes.

further to produce free charge carriers or decay to the ground state through a process frequently called geminate recombination. The separation efficiency of e/h pairs is therefore likely to be influenced by the molecular-level interfacial structural details on the order of 1 nm [24]. Finally, the free holes and electrons need to travel across the D/A blend via continuous pathways in the donor and acceptor phases before it can be collected at the electrode contacts. The distance these free charge carriers are able to travel is limited by the bimolecular recombinations that take place at D/A interfaces, so that the thickness of the D/A blend is restricted to be on the order of 100 nm, which corresponds to the characteristic length scale for charge carrier transport. We note that illustrated morphology in Fig. 1 is an idealization of the real-world BHJ morphologies, which could contain impure domains, diffuse interfaces and hierarchical feature sizes [25–29].

The complex interplay between the transport of electrons, holes, and excitons and the multiscale morphology hampers the interpretation of experimental findings and the understanding of performance limiting factors – especially since precise control over the D/A morphology is not yet possible. In this context, device modeling and simulation can help to better understand and predict the photovoltaic behaviors of organic BHJ solar cells. Most of the continuum-level device models for organic BHJ solar cells employ either a two-phase [30–36] or an effective-medium [37–42] approach. The former captures the D/A morphology in the form of pure and contiguous donor and acceptor phases with smooth interfaces in-between (effects impurities and inhomogeneity of small donor and acceptor domains are not considered). These two-phase models consider electron and hole transport through their respective convoluted pathways at a lengthscale of O(100 nm) as well as exciton transport at the donor length scale of O(10 nm), but at the same time require not only significantly more computational resources than the effective-medium models, but also explicit information of the D/A morphology on the order of O(10 nm) that is not readily available. The effective-medium model, on the other hand, treats the D/A blend as one effective material