Morphology optimization in excitonic photovoltaics

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We investigate the role of morphology in excitonic photovoltaics through simulation. In particular, we attempt to find general trends in the behavior of morphologies as their interfacial surface is varied and under simulated damage. We find that all classes of morphologies in our study obey the same general trend of efficiency versus the average number of neighbors of the same type. The damage can thus be optimized to improve the efficiency of oversegregated morphologies. We also find that within our model, there is only a small gain from very ordered structures over some disordered structures with an optimal segregation.

Direct conversion of solar radiation into electricity has the potential to be an important part of the future clean energy strategy. Currently, most solar cells are made from silicon, which offers long lifetimes and potentially high efficiencies, however at high cost compared to traditional sources of energy such as coal and oil. Since the sun irradiates the earth with approximately 1300 W/m^2[1], solar energy has a unique ability to be scaled up to provide large amounts of energy. However, to do so, the cost of a solar cell must be reduced significantly. One possibility for reducing the cost of light to electricity conversion is to use different types of devices than those based on the traditional P-N junction. Of particular interest is the excitonic cell arranged in a bulk heterojunction morphology. An excitonic cell works by arranging two materials in close contact with each other to form a type II heterojunction. The materials, organic (discussed well in reviews[2–4]) or not[5], have large exciton binding energy and are ideally inexpensive to manufacture. When light is absorbed, the resulting exciton must diffuse to the interface between the two materials to separate into an electron and hole. The charge carriers must then diffuse to the anode and cathode to produce current.

There are thus two somewhat conflicting design parameters to consider when designing an excitonic device. The first is that the exciton must be able to find an interface before it decays, and the second is that the electron and hole must be transported out of the device efficiently. The optimal morphology for the former is a homogenous mixture of the two materials, and for the latter a completely separated bilayer. The optimal morphology is somewhere between these two extremes. It has been shown experimentally[6–9] that processing such as annealing can improve the efficiency of excitonic devices dramatically. However, as a function of material parameters such as the exciton lifetime and charge transport characteristics, the optimal morphology is not currently known. It has been proposed[10] that highly ordered columnar morphologies are optimal. However, these morphologies are difficult to produce experimentally with inexpensive solution-based methods, obviating one of the largest advantages of excitonic materials.

In this article, we attempt to find not only highly ordered and high efficiency structures, but also to examine less ordered structures that also offer high efficiency. The aim is that some of these disordered structures could offer a guide to experimentalists for creating high efficiency morphologies while still retaining inexpensive fabrication methods.

We follow a similar strategy to Refs [10, 11]. Our model was a lattice of 'molecules' that could be either D (for donor in the type II interface) or A (for acceptor). Excitons, electrons, and holes then could move on the lattice according to a kinetic Monte Carlo model. Excitons are created according to the light intensity incident on the material. They can then either diffuse within the class of material in which they were created, decay and be destroyed, or, if they are at an interface, dissociate into an electron and hole. The charge carriers (electrons or holes) then can diffuse within the donor or acceptor. If an electron and hole are adjacent, they can recombine with some rate. If they are near the anode (electron) or cathode (hole), they will be removed from the simulation and counted as current.

Our model is meant to capture the general features of the physics, rather than accurately model a particular system. It thus should be indicative of general trends that will aid in the design of bulk heterojunction devices. We standardized on 10 unit thick cells, with a converged lateral size. The results did not change significantly with thicker cells.

One difficulty in modeling the performance of bulk heterojunctions is that often the mobilities of the constituent materials are not known. Instead physical intuition and experimentation are typically used to find an optimal morphology. There are several drawbacks to this approach however. The optimal morphology is one which not only maximizes the efficiency at the time of manufacture, under careful lab preparation, but is also robust to industrial preparation and damage over time. It is also an interesting question of which types of morphologies have the broadest maximum in the phase space of physical parameters. These morphologies would be extremely valuable in evaluating materials whose parameters are not known.

We scanned several types of trial morphologies. Our space consisted of a bilayer device consisting of equal layers of D and A type material, checkered A and D

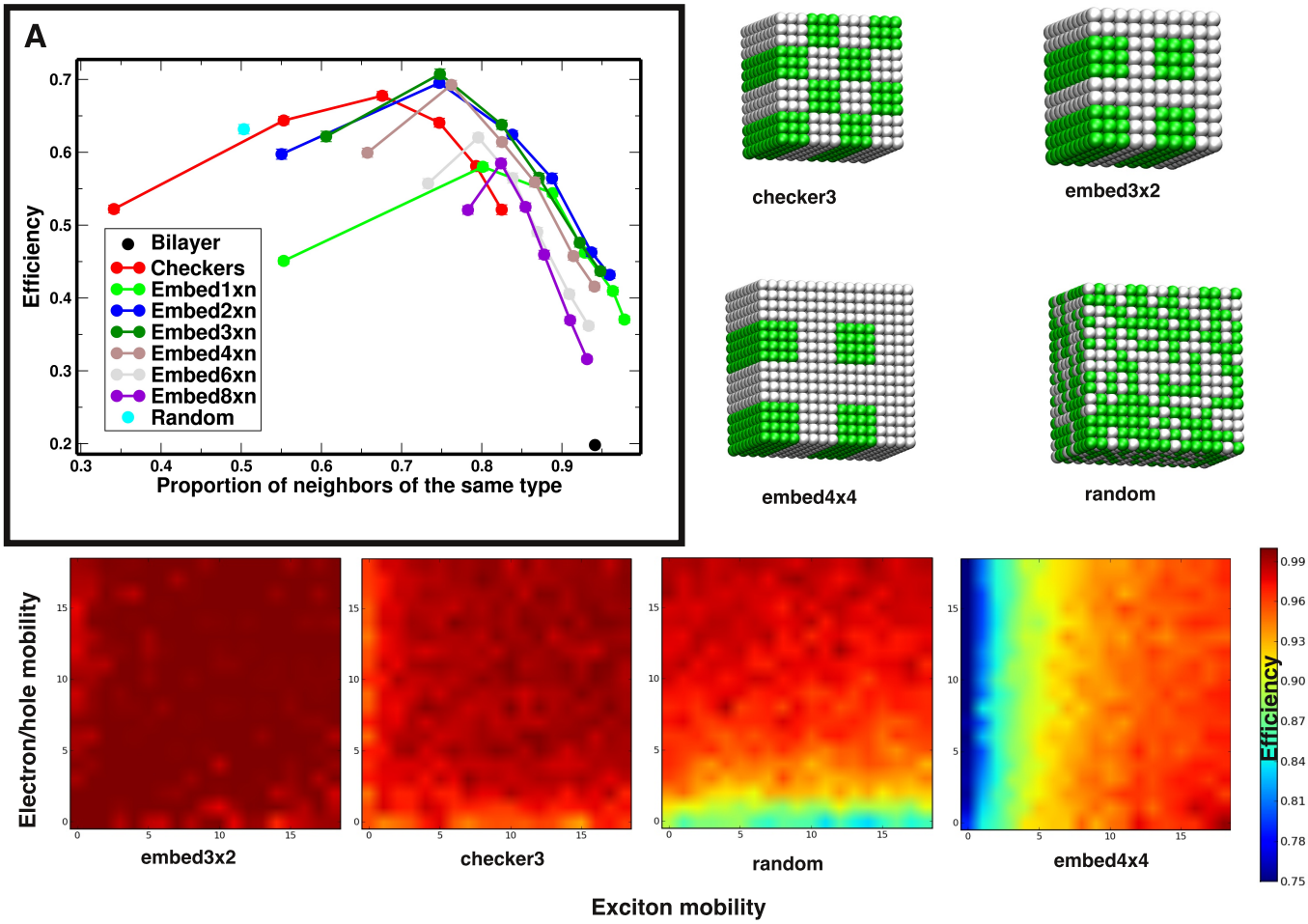

FIG. 1: A few representative pictures of the morphologies generated using different strategies. The percentage shown is the percentage of the highest efficiency morphology shown for that set of parameters.

columns with adjustable width, columns of A embedded in a medium of D, and a completely randomized structure, with each element decided as D or A with probability equal to 0.5. The checkers morphology has one adjustable parameter, and the embedded column morphology has two adjustable parameters, the thickness of the column and the spacing between the columns.

We found a universal behavior of the efficiency of morphology types with respect to a single parameter, the average proportion of neighbors of the same type(α) (Fig 1A). The peak for each type of morphology varied, although they were all in the range between 0.65 and 0.8. Qualitatively, this is easy to understand. If α is large, then an exciton will have to travel on average a long distance to reach an interface, and for $\alpha \to 1$, the efficiency must go to zero. As α becomes small, excitons almost always find an interface to separate, but electrons and holes begin to find each other more frequently and annihilate. There thus is a maximum for intermediate α.

To understand the behavior of these various morphologies with different physical parameters, we scanned the exciton and the electron/hole mobilities for many different morphologies. These two mobilities are the first-order parameters that differentiate the morphologies. We give representative examples in Fig 1. One can observe some expected results; for example, for low charge carrier mobility, a random morphology is very poor, but its performance is more or less independent of the exciton mobility. On the other hand, a morphology with large feature sizes is mostly dependent on the exciton mobility.

For the parameter range that we scanned, it is clear that there is an optimal feature size, in this case roughly three units. However, different morphologies have very different optimal ranges. In our calculations, the checkers morphology is less effective than the embedded columns morphology over the entire range, and for low exciton or charge carrier mobilities, it is about 10% lower in efficiency. It is instructive to consider why this is. For low exciton mobility, the checkers morphology contains a center point within each checker, which needs to diffuse

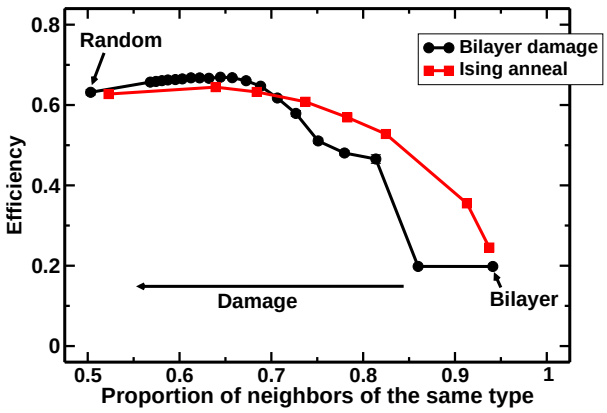

FIG. 2: A damaged bilayer device (averaged over 36 damage runs) versus annealing an Ising model (averaged over 16 configurations per point).

to the edge to dissociate. This gives an extra opportunity to lose an absorbed photon, which the embedded columns lacks for one type of absorber. For low charge carrier mobility, there are larger channels in the embedded columns for a charge to wander far away from the initial exciton dissociation site, and thus not recombine.

One question we can address with the simulation framework was whether or not one could have a better than random morphology by preparing an ordered but suboptimal morphology and then damaging it. In experiment, this might be done by heating or otherwise roughening the surfaces. The "damage" has the effect of making a multi-scale morphology.

We simulated the damage as a flip event, as follows. We choose a lattice point at random. If it has neighbors of an opposite type, we accept the choice, otherwise, another point is chosen. One of the neighbors of an opposite type is chosen at random, and the types are flipped. After a sufficient number of these flips, the morphology is completely randomized, so one would expect an efficiency equal to the random morphology with the D/A proportion of the original morphology. For comparison, we generated cells using an Ising model in a similar way to Ref [10]. Compared to their results, our peak is less extreme, due to somewhat different choices for the model parameters.

We found that the efficiency as a function of damage is not necessarily monotonic. As an example, we show the bilayer morphology (Fig 2). At first, there is a quick improvement in the efficiency, peaking, and then descending to the random limit. The peak is significant, around midway between the random morphology and the optimal columnar morphology we found for this parameter set. At the peak, the distribution of acceptor and donor particles is uniform in the z-direction, but the parameter α is in the peak range of Fig 1A. By damaging the bilayer, we are thus following the curve shown in that graph until we reach the full random morphology. Compared to the Ising anneal curve, the peak is higher, so it may be a way to obtain higher efficiency devices than through annealing.

In summary, we have performed calculations for a wide range of mobility parameters, an embedded columns morphology with a 3-2 ratio between the column width and the embedding material width is near optimal. All morphologies studied, whether columnar or not, had a very similar trend in the efficiency with respect to the average number of neighbors with the same type α. This can be easily understood by considering the dynamics of single excitons and pairs of electrons and holes.

By beginning with ordered but inefficient morphologies such as a bilayer and partially randomizing them, one can obtain morphologies that are quite efficient by lowering α. These morphologies may not be as efficient as perfectly ordered morphologies that are precisely tuned, but may be more easy to produce than perfectly ordered systems. These semi-randomized morphologies are complementary to annealed morphologies that are typically used in producing organic solar cells, in which one starts with a random morphology and imposes order through annealing.

Finally, we note that the maximum efficiency obtained by damaging the bilayer is similar to the maximum efficiency found for perfectly ordered columns (~ 0.69 vs ~ 0.71). This seems to indicate that within our model, highly ordered columns may not be worth the extra effort to manufacture them, if the proper type segregation is available with an easier method such as damaging a bilayer. In order for columnar morphologies to have large gains above less-ordered morphologies, other physics must come into play, such as the existence of crystalline rods[12].

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