Controlling organic polymer structure

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Dipolar solvents may improve the morphology of organic polymer junctions and increase the efficiency of low-cost photovoltaic materials.

Cost is the primary obstacle to widespread adoption of photovoltaic technology. Silicon-based solar cells are extremely efficient, but the energy they produce is more expensive than that provided by fossil fuel, wind, or nuclear sources. In order to bridge this price gap, researchers have begun studying organic photovoltaic (OPV) technology. These devices are produced from a mixture of a polymer and a fullerene, or carbon molecules that form into a spherical, ellipsoid, cylindrical, or planar shape. OPV technology offers significantly reduced production costs, since it can leverage mass-production printing techniques. In addition, the devices are becoming more efficient, with single-junction devices achieving efficiencies above 5%. 1

Currently, many basic questions about these polymers remain. For instance, researchers do not understand how their structure affects device function or what length scale is best for separating the polymer and fullerene components. Diffraction techniques cannot adequately characterize their structure, because the components form mostly amorphous layers with no large-scale ordering.

Past research showed that thermal treatment of the mixed layer increases both the device efficiency and the polymer crystallinity. In addition, other work has used nanoparticles or nanofibers that form in solution as a base conjugated unit to characterize OPV structure. 2, 3 This technique allows polymer components to be deposited in their crystalline form. The particles can then be studied in liquid suspensions.

Using both of these methods, we first quantified the percentage of the polymer in the aggregated, or crystalline, conformation. We employed ultraviolet-visible spectra of completely amorphous (dissolved) and completely aggregated (nanoparticle suspension) poly(3-hexylthiophene), or P3HT, to fit the percentages of the two phases present in the thin film. We measured the percentage of each before and after thermal treatment. The ratio of aggregated to amorphous P3HT increased from 2:3 to 3:1 after heating at 150°C for 10min. 4

Next, we developed two approaches to further improve the morphology of the polymer. One approach filtered out the P3HT nanofibers and then redeposited the preformed nanoparticles in a fully aggregated layer. 3 In the second technique, we added small quantities of a dipolar solvent additive to the casting mixture. The solvent forced the P3HT into the desired conformation during the drying process and yielded a 100% crystalline suspension. 4 As Figure 1 shows, this process increased efficiency relative to thermal treatment alone.

To determine what caused the efficiency increase, we imaged the device. Using mixtures of chlorobenzene and t-butanol, we spin-coated P3HT onto indium tin oxide substrates. The two solvents are miscible, but the P3HT is soluble only in the chloroben-
Figure 2. A scanning electron microscopy image of porous, aggregated P3HT reveals a continuous, spongy structure. The grainy background is the indium tin oxide substrate.

zene. Since the chlorobenzene dries faster, the P3HT aggregates as it is exposed to increasing concentrations of t-butanol.

We viewed the resulting polymer morphology with scanning electron microscopy (see Figure 2). The P3HT formed three-dimensional continuous, spongy structures, in which the nanoparticles were well connected. The ultraviolet-visible spectra revealed that the P3HT is all in aggregated form.

Three characteristics of the morphology improved the devices. First, the structures are about the size of one exciton diffusion length, which leads to efficient charge separation. Second, the three-dimensional morphology enables charges to be efficiently transported across the device layer. Finally, the P3HT is fully crystalline, indicating that it separates from the fullerene in these domains. This material separation provides for pure hole and electron conducting pathways.

Using polymer nanoparticles, we characterized the polymer crystalline content, then used dipolar solvent additives to increase aggregation. This technique enabled us to fabricate solar cells with improved efficiency. Future steps will focus on molecular models relating the observed phase changes to temperature and mole fraction. This approach will allow us to develop a general model for controlling structure in polymer mixtures.

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References