Mapping nanoscale efficiency variations in plastic solar cells

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Time-resolved electrostatic force microscopy reveals efficiency variations in plastic solar cells with ~100nm resolution.

In the pressing drive to develop economical solar cells, blends of conjugated polymers with fullerenes, polymers, and nanocrystals show a great deal of promise as building materials. These materials can be chemically synthesized and processed from solution into low-cost devices. So if an efficient and long-lived solar cell based on such materials could be realized, then solar power might become a more economically competitive energy resource. Thus, the efficiency and stability of organic solar cells are areas of active research.

In a typical organic solar cell, light absorption creates strongly bound excitons that must be dissociated into free charges at donor/acceptor interfaces. To create these interfaces throughout an optically thick film, donor and acceptor materials are often blended together in a bulk heterojunction cell. While this donor/acceptor structure is necessary for good charge generation, the exact structure influences charge recombination and transport to the electrodes. Slight changes in the material ratios (see Figure 1) or processing conditions can cause large changes in the nanostructured film morphology, thereby causing significant performance variation in resulting devices.

The question of how film morphology governs device performance is inherently a nanoscale problem. The exciton diffusion length, or the distance an average photoexcited electron hole pair travels before it decays, is on the order of ~10 nm in most organic semiconductors. Although domain sizes this small may or may not be optimal for solar cells, depending on the balance of charge generation and extraction, conventional methods of optical spectroscopy can only probe the optical and electronic properties of these blends on much larger (~250–500nm) scales. On the other hand, high-resolution microscopy techniques like atomic force microscopy (AFM) do not provide information about the relevant electronic properties of these heterogeneous organic films. Indeed, AFM cannot tell us which regions are efficient at generating charge, which regions suffer high charge-recombination rates, nor which regions suffer poor charge mobility.

In response to this problem, our group has developed a new, high-resolution characterization technique. With time-resolved electrostatic force microscopy (trEFM), we measure charge creation in organic thin films with better than 100nm spatial resolution and 100µs temporal resolution using an experimental setup that includes an AFM probe and LED illumination (see Figure 2). Electrostatic force microscopy (EFM) is a version of AFM and measures the long-range coulombic force between a metal-coated AFM tip and a substrate, and can be used for sensitive potentiometry of organic semiconductor films. In a standard steady-state EFM experiment the tip is positioned 5–50nm above a surface while vibrating with an amplitude of 10–20nm. In this configuration, the EFM tip can be approximated as a classic harmonic oscillator driven at its resonant frequency. Electrostatic force gradients between the tip and the sample change the effective spring constant of the system, thus inducing a shift in the resonance frequency of the cantilever. In trEFM, we record this frequency shift as a function of time after the sample is illuminated in order to monitor how fast charge builds up in various locations of a thin film (see Figure 3).

We first applied this technique to image many polymer/polymer (PFB/F8BT) blend films. While the PFB/F8BT sys-
Figure 2. Schematic diagram of a polymer blend film illuminated with a pulsed LED through a transparent electrode. Charge accumulation in the film is measured with a biased electrostatic force microscope tip using frequency shift feedback.

Figure 3. Cantilever frequency shift versus time for a F8BT/PFB film. At time equal to zero, the LED illuminates the film, which generates free charge. The biased tip collects this charge, and the resulting capacitor charging data can be fit well by an exponential function, giving a charging rate.

Figure 4. (Left) AFM height image of an F8BT/PFB film. The recessed domains are enriched in PFB. (Right) The corresponding electrostatic force microscopy photoinduced charging rate map generated by plotting the inverse exponential time constant for photoinduced charging at each point in the left-hand panel. The dark rings indicate regions of slower charging.

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even higher resolutions than are presently achievable would be desirable (for instance, to probe processes with resolution better than the exciton diffusion length), we believe that trEFM specifically, as well as optical and electrically sensitive scanning-probe methods in general, has shown it has much to teach us about the fundamentals of charge generation, recombination, trapping, and transport in nanostructured optoelectronic devices.

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References