Advancing spray deposition for low-cost solar cell production

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Organic active-layer and contact depositions using an ultrasonic spray process show that spray-deposited organic thin films may be comparable to spin-coated films.

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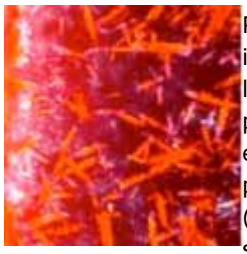

Polymeric solar cells may be the least expensive means to convert solar irradiation to electricity.[1] This cost reduction is based on soluble organic active layers coupled with ultralow-cost deposition technologies. However, profitable production and sales of these devices require improvements in device stability, efficiency, and processing. Material and processing developments of organic photovoltaics (OPVs) in the past few years have resulted in certified small-area (< 1cm^2) device efficiencies of approximately 6% with multiple-material systems.[2] The ability to approach competitive power-conversion efficiency has thus heightened commercial interest in product development.

Together with improved device performance, it is important to develop process technology matched to the needs of organic devices. To succeed as a useful manufacturing technique, the specific deposition approach must be highly scalable while still producing films with the quality of laboratory deposition methods, e.g., spin coating. Some scalable organic thin-film deposition techniques that show promise are inkjet printing, airbrush spray, ultrasonic spray, evaporative spray, slot coating, and screen printing. Among these, spray deposition is historically scalable to large areas, and may also be applicable to a range of organic electronic devices such as tailored photodiodes and LEDs. Independent studies of low-cost spray depositions using a handheld airbrush to deposit the active layer in an OPV device show power-conversion efficiencies of 2.83 and 2.35%.[3,4] The active layer in these studies was composed of poly(3-hexylthiophene) (P3HT) and [6,6]phenyl-C61 butyric-methyl ester (PCBM), which typically result in 4% efficient OPV devices when spin coating is used.

We have evaluated ultrasonic spray deposition for reducing the cost of functional thin-film fabrication (see Figure 1). In addition to scalability, an advantage of this approach is uniform coverage using picoliter drop volumes. A tri-phase pump delivers solution to the ultrasonic nozzle, which creates droplets with mean diameters of 18μm. An inert carrier gas focuses the droplets onto the substrate. Film thickness is built up layer by layer, by scanning the substrate under the spray. We showed that the poly(3,4-ethylenedioxythiophene)-polystyrene sulfonate (PEDOT:PSS) electrode used in an OPV prototype device may be spray deposited without significant losses to film quality or device performance.[5] In a recent article, we discussed a case study that tested solvent effects on active layers, showing that the morphology and device performance of ultrasonically-sprayed organic layers rely heavily on the choice of solvent.[6]

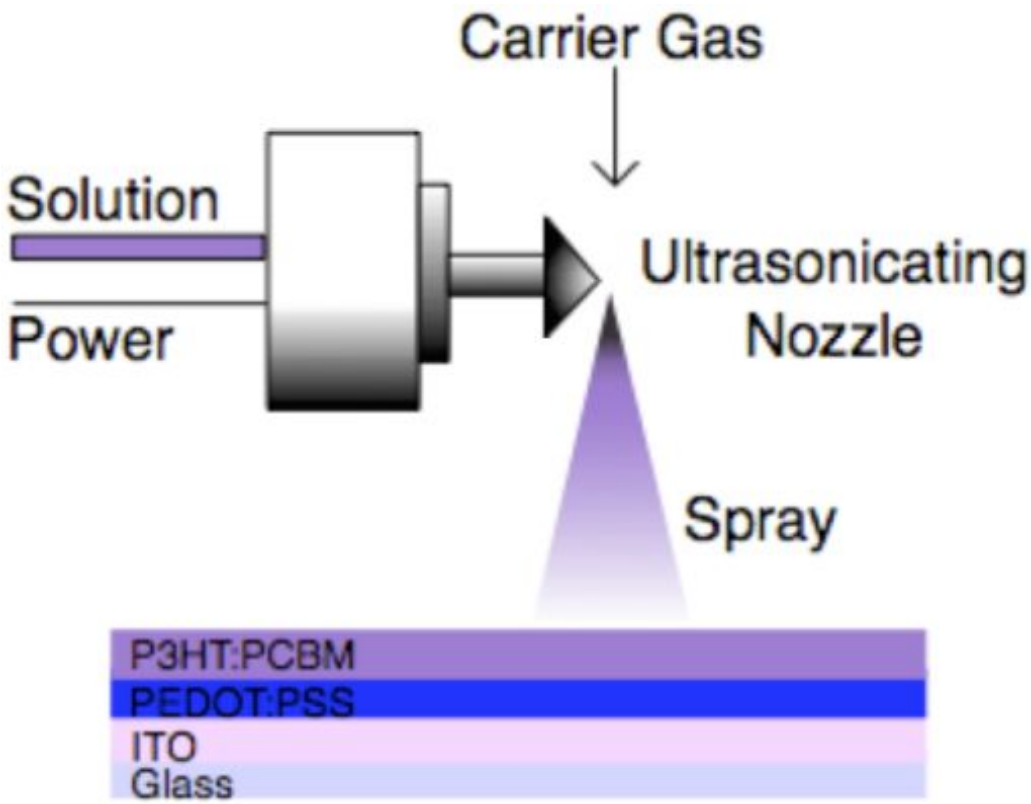

Figure 1. *Ultrasonic spray deposition. Solution is delivered to the ultrasonic nozzle, creating a spray with uniform-diameter droplets. The spray is focused onto the substrate using nitrogen as the carrier gas. Thick films for this study were built up layer by layer. P3HT:PCBM: Poly(3-hexylthiophene):[6,6]phenyl-C61 butyric-methyl ester. PEDOT:PSS: poly(3,4-ethylenedioxythiophene):polystyrene sulfonate. ITO: Indium-tin oxide.*

We investigated the structural and optical properties of bulk-heterojunction P3HT:PCBM thin films that are ultrasonically sprayed with either chlorobenzene or p-xylene as solvent. The solvents were chosen on the basis of their similar boiling points and bulk properties. The largest variant in our case study is the solvent's dipole moment. Sprayed bulk-heterostructure films were tested using UV-visible absorption spectrometry, optical microscopy, x-ray diffraction, and stylus profilometry. Films using chlorobenzene as solvent resulted in x-ray diffraction patterns identical to drop-cast films, indicating similar morphology. When p-xylene is used as solvent, the diffraction data shows variations in the planar stacking of the polymer phase. Visible absorption spectra also indicate a marked decrease in short-wavelength photon absorption. Profilometry and optical-micrograph studies also show a high degree of separation between the P3HT and PCBM phases compared to chlorobenzene-sprayed films (see Figure 2).

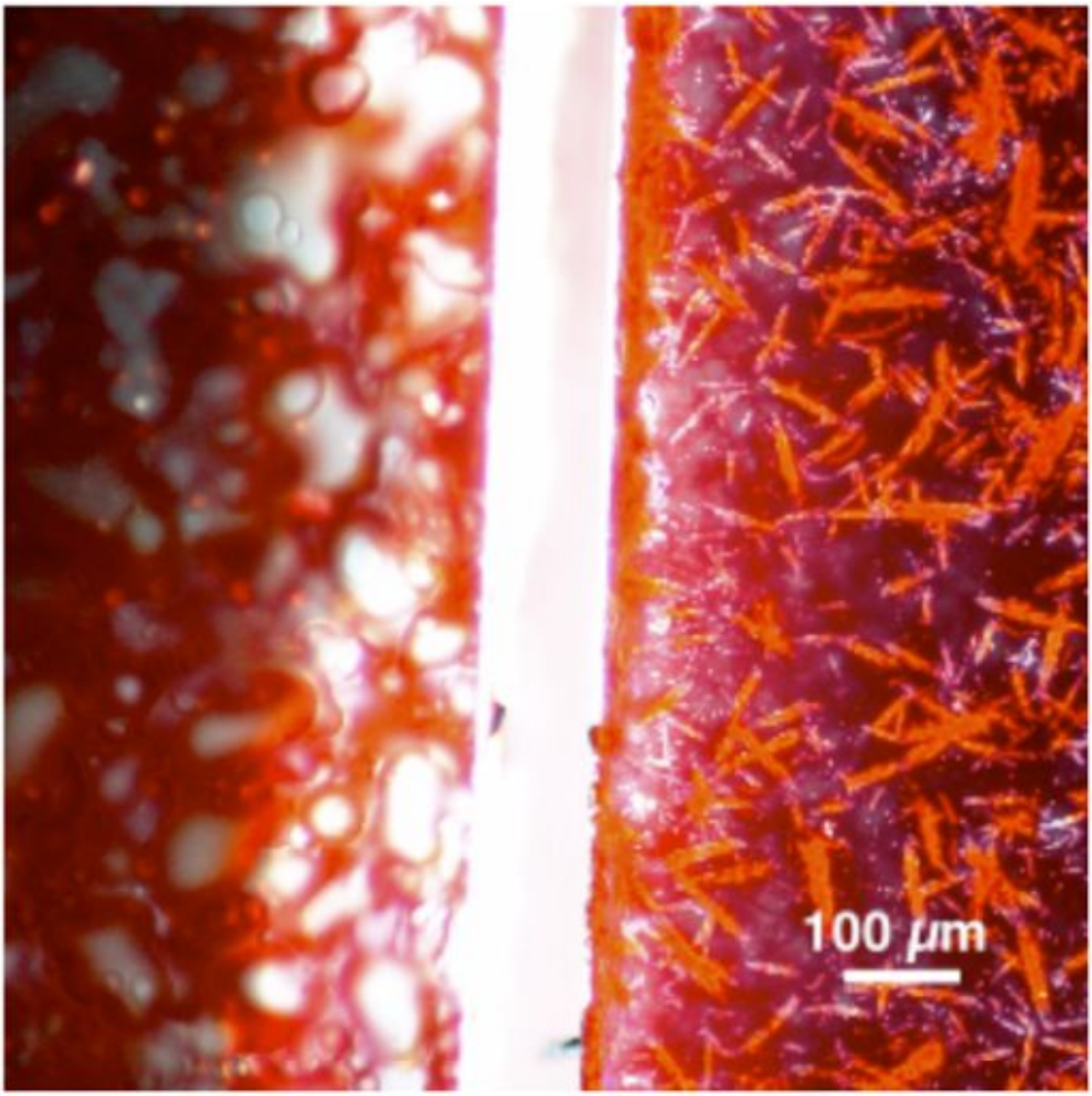

Figure 2. *Dark-field optical micrograph of two separately deposited bulk-heterojunction P3HT:PCBM films sprayed using chlorobenzene (left) and p-xylene (right) as solvents.*

To test the morphological implications for photovoltaic conversion, devices were fabricated in a nitrogen-filled glove box using the active layers sprayed using chlorobenzene or p-xylene solvents. Testing of devices illuminated under one-sun conditions provide typical current-voltage curves (see Figure 3). The power-conversion efficiencies of chlorobenzene-sprayed devices were 3.0%. Two final flood layers, where the spray rate was doubled, were then deposited onto the active layer of chlorobenzene-sprayed devices. This gave the desired result of smoothing the film surface and increasing efficiency to 3.2%. Devices sprayed using p-xylene gave efficiencies of 0.1%. The efficiency loss compared to the chlorobenzene-sprayed devices was primarily due to extreme phase separation in the p-xylene system. Flooding the active layer did not significantly affect the p-xylene-sprayed films, and a higher deposition temperature was used to arrest the large grain growth (see Figure 2). Increased substrate temperature for active-layer deposition resulted in a similar morphology to that of the chlorobenzene-sprayed films, although with enhanced coffee-stain effects, and an increase of device efficiency to 1.2%.[6] Carrier-recombination characteristics were then determined by measuring short-circuit, current-density dependence on illumination intensity. Devices using active layers sprayed using p-xylene solvent exhibited the highest degree of current loss from second-order recombination resulting from the high degree of phase separation.[6]

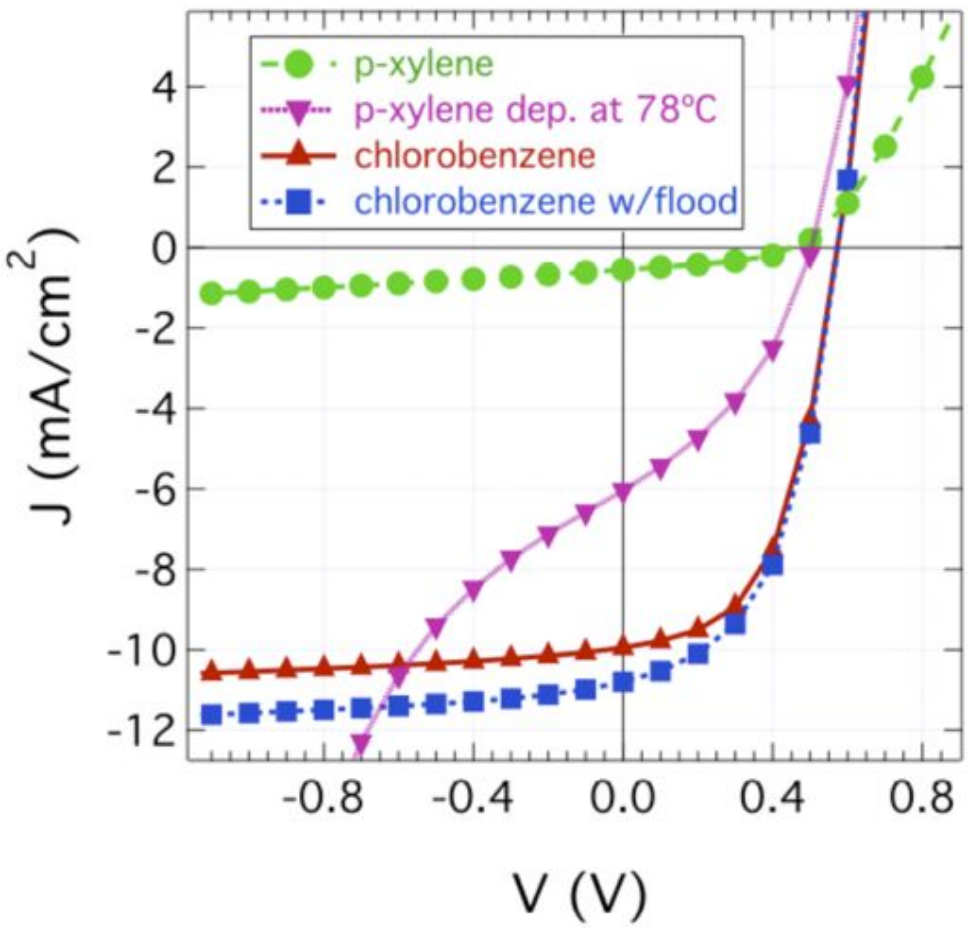

Figure 3. *Measured illuminated (AM1.5 standard, i.e., at an air mass of 1.5) current density versus voltage curves for chlorobenzene-sprayed devices with and without an additional flood layer and p-xylene-sprayed devices at room temperature (25°C) and 78°C.*

These results indicate that ultrasonic-sprayed organic thin-film morphology strongly depends on solvent choice and processing conditions. With optimized processing parameters, sprayed active layers can produce OPV devices with high efficiency. Spray deposition may, therefore, play an important role in developing scalable processing techniques for large-area organic thin-film depositions. Future development of spray processing could include the use of surface modifiers for reducing film roughness or solvent blends for finetuning microstructures.

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References:

1. M. A. Green, *Physica* E 14, no. 1-2, pp. 65, 2002.

2. Personal communication with Keith Emery of NREL's Characterization and Measurement group.

3. D. Vak, S. Kim, J. Jo, S. Oh, S. Na, J. Kim, D. Kim, Fabrication of organic bulk heterojunction solar cells by a spray deposition method for low-cost power generation, *Appl. Phys. Lett.* 91, pp. 081102, 2007.

4. R. Green, A. Morpha, A. J. Ferguson, N. Kopidakis, G. Rumbles, S. E. Shaheen, Performance of bulk heterojunction photovoltaic devices prepared by airbrush spray deposition, *Appl. Phys. Lett*. 92, pp. 33301, 2008.

5. K. X. Steirer, J. J. Berry, M. O. Reese, M. F. A. M. van Hest, A. Miedaner, M. W. Liberatore, R. T. Collins, D. S. Ginley, Ultrasonically sprayed and inkjet printed thin film electrodes for organic solar cells, *Thin Solid Films* 517, pp. 2781-2786, 2008.

6. K. X. Steirer, M. O. Reese, B. L. Rupert, N. Kopidakis, D. C. Olson, R. T. Collins, D. S. Ginley, Ultrasonic spray deposition for production of organic solar cells, *Sol. Energy Mater. Sol. Cells* 93, pp. 447-453, 2009.