Optimal Morphology of a Bulk Heterojunction Layer: Toward Highly Efficient Solar Cells

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Efficient and renewable energy sources are desired for a "green" life. Polymer solar cells have drawn promise as candidates due to their advantages of low cost, small mass and adequate flexibility for sustainable conversion of solar energy. Great progress is being made to develop bulk heterojunction (BHJ) thin-film solar cells, in which one conjugated polymer as electron donor and one fullerene derivative as electron acceptor are closely intermixed, yielding a three-dimensional interpenetrating network of conjugated polymers blended with soluble fullerene derivatives. BHJ solar cells of this type account for the absorption of light leading to strongly bound electron-hole pairs, excitons, in the conjugated polymer. These excitons can diffuse only small distances (ca. 10 ~ 20 nm) before their recombination. As the fullerene derivative is within this range, the exciton can dissociate into a polaron pair, which is a precursor of free charges. These free charges eventually generate the photocurrent.

Manipulating the nanostructure of the active layer of BHJ thin-film solar cells is, therefore, a primary factor in improving device performance. In general, the polymer-rich domains require fullerene units in a fine dispersion in the polymer to provide large interfaces because of the small length of exciton diffusion, whereas the fullerene-rich domains require a suitable feature size to form paths to inhibit a recombination of electrons and holes. To probe the nanostructures of the active layer, simultaneous 2D grazing-incidence small-angle and wide-angle X-ray scattering (GISAXS and GIWAXS) at the TLS end station **BL23A1** provide a scattering angle over a wide range ($q = 0.3$ ~10 nm^{-1}) to capture the kinetics of fullerene aggregation and conjugated polymer crystallization in the corresponding BHJ thin films. Understanding the kinetics of the fullerene aggregation and polymer crystallization and their correlation in the morphological development of conjugated polymer/fullerene composite films

would hence provide information about the optimal processing of future BHJ solar cells with varied components of fullerene derivatives or other conjugated polymers.

Kung-Hwa Wei (National Chiao Tung University, Taiwan) investigated structure-property relations of BHJ polymer solar cells with varied solvent processes. An appropriate solvent can induce improved crystallinity and an optimized size of fullerene domains and their distribution, resulting in the best device performances. The molecular structures of a conjugated polymer (PBTC$_{12}$TPD) and two fullerenes (PC$_{61}$BM and ThC$_{61}$BM) used to prepare the active layers in the devices are illustrated in Fig. 1(a). To obtain an optimal morphology of the active layer for high efficiency, three solvents (trichloromethane (CF), chlorobenzene (CB), and dichlorobenzene (DCB)) were tested to dissolve two blends of PBTC$_{12}$TPD/PC$_{61}$BM and PBTC$_{12}$TPD/ ThC$_{61}$BM to prepare the thin-film layers. The device efficiency was found to be strongly affected by the three processing solvents. The efficiency of power conversion of the device incorporating the CF-processed PBTC$_{12}$TPD/ThC$_{61}$BM layer (6.2 %) was 46 % greater than that (4.2 %) of the devices incorporating the DCB-processed PBTC$_{12}$TPD/ ThC$_{61}$BM layer.

Kung-Hwa Wei and coworkers used synchrotron-based GISAXS and GIWAXS to elucidate the PBTC$_{12}$TPD crystallinity and domain sizes of the fullerenes in the active layers. As a result of GIWAXS for PBTC$_{12}$TPD/PC$_{61}$BM and PBTC$_{12}$TPD/ThC$_{61}$BM (Figs. 1(b) and 1(c)), both the crystallinity and crystal size of the PBTC$_{12}$TPD lamellae in the CF-processed film were much larger than those in the CB- or DCB-processed films. The domain size of fullerene aggregates is determined on fitting the GISAXS profiles, as shown in Fig. 1(d). The fitted results of SAXS based on an appropriate fractal model revealed that the ful-
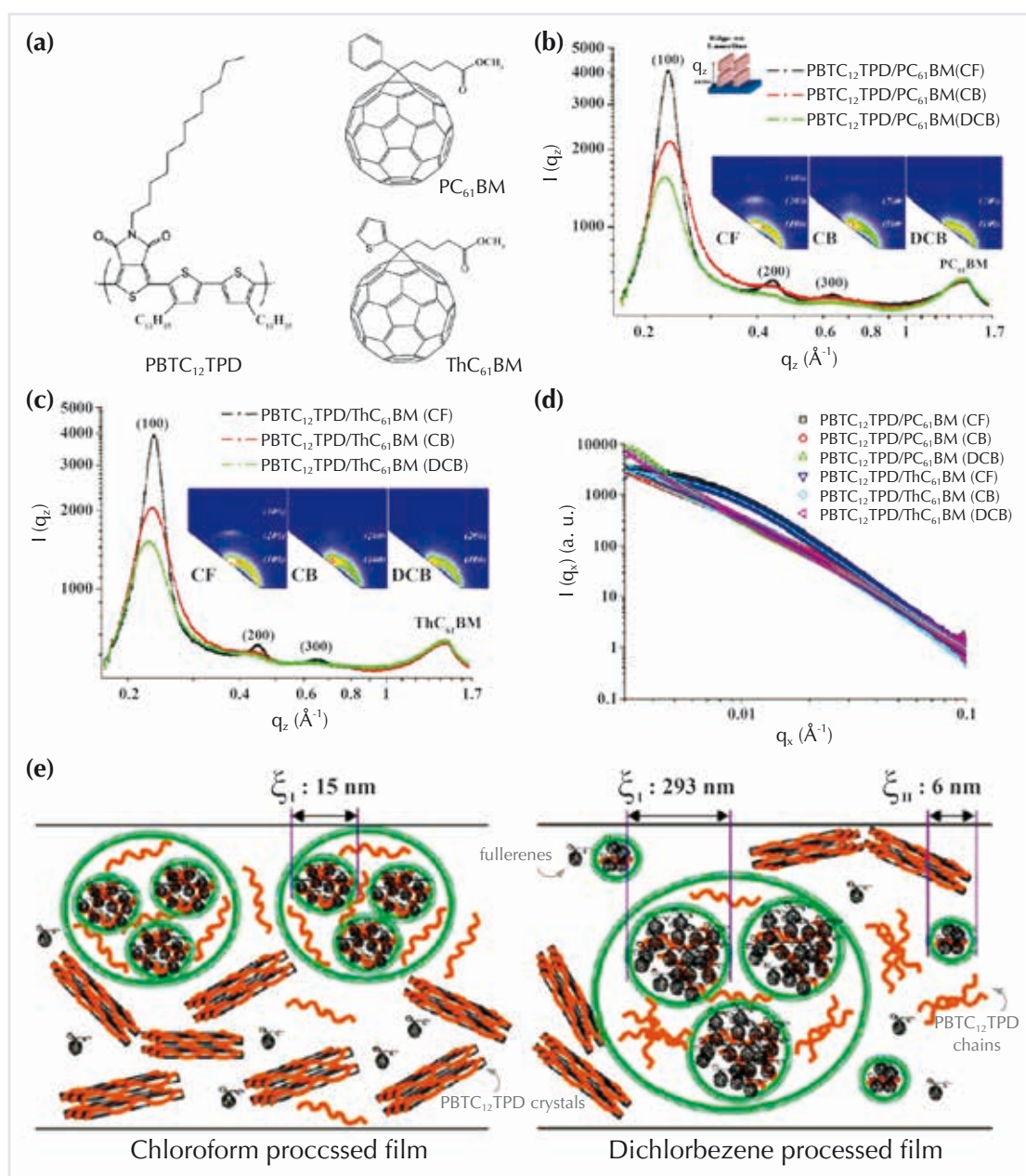
Fig. 1: (a) Molecular structures of PBTC$_{12}$TPD, PC$_{61}$BM, and ThC$_{61}$BM; out-of-plane GIWAX profiles of (b) PBTC$_{12}$TPD/PC$_{61}$BM films and (c) PBTC$_{12}$TPD/ThC$_{61}$BM films for the CF, CB, and DCB processes; (d) in-plane GISAXS profiles of PBTC$_{12}$TPD/PC$_{61}$BM and PBTC$_{12}$TPD/ThC$_{61}$BM films for the same processing solvents; (e) cartoons of cross-sectional views of films processed from CF (left) and DCB (right). (Reproduced from Ref. 1)

lerene aggregates of the CF-processed film showed a single fractal structure of characteristic length 15 nm, whereas that of the CB- and DCB-processed films displayed a hierarchical bi-fractal structure of two characteristic lengths 293 nm and 6 nm (as illustrated in Fig. 1(e)).

In summary, these scientists demonstrated that morphologies of the conjugated polymer and fullerene aggregates were affected by the nature of the processing solvents. The optimal device performance obtained from the CF-processed active layer is attributed to the greater polymer crystallinity, fullerene-rich domains of finer and more uniform size, and nano-scale interpenetrating networks with a gradient distribution.

Reference

1. C. M. Liu, M. S. Su, J. M. Jiang, Y. W. Su, C. J. Su, C. Y. Chen, C. S. Tsao, and K. H. Wei, ACS Appl. Mater. Interfaces **5**, 5413 (2013).