Probing a Correlation Between Morphology and Performance in Bulk Heterojunction Solar Cells

This report features the work of Wei-Fang Su, Cheng-Si Tsao and their co-workers published in Energy Environ. Sci. ***6****, 1938 (2013).*

Polymer-based bulk heterojunction (BHJ) solar cells have attracted increased research because of their promising advantages in light weight, mechanical flexibility and inexpensive fabrication, relative to silicon-based solar cells. In BHJ solar cells, a conjugated polymer blended with a fullerene electron acceptor can form a nanoscale morphology in a thin-film active layer with a large area of donor–acceptor (D–A) interface for efficient photo-induced charge separation, and with a bi-continuous interpenetrating network of phase-separated fullerene (acceptor) and polymer (donor) domains for charge transport to the electrodes. As the active layer of BHJ solar cells largely determines the device performance, a thorough and quantitative structural characterization of BHJ films with regard to polymer crystallization, fullerene aggregation and their mutual influence on multiple length scales and a correlation with opto-electronic properties is necessary. Grazing-incidence small-angle and wide-angle X-ray scattering (GISAXS and GIWAXS) at the TLS end stations **BL23A1**[1] and **BL17A1** provide in combination 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, respectively.

BHJ solar cells based on poly(3-hexylthiophene) (P3HT) have shown a high performance with thermal annealing or solvent-vapor annealing to optimize the blended film morphology, but the large optical band gap of P3HT limits the absorption of near infrared light and decreases light harvesting and the efficiency of devices. Developing a polymer with a small band gap is suggested to be required to achieve BHJ polymer solar cells with efficiency 10 % or greater. BHJ solar cells adopting new D–A conjugated copolymers with a small band gap have achieved a large efficiency of power conversion (PCE) toward commercial validity. Moreover, solvent-additive processing has become the most effective strategy to refine the nanostructure of copolymer/fullerene BHJ solar cells of D–A type to improve the efficiency of power conversion, but the effect of solvent additives is still unclear, based on the discrepant reported results of various polymer/fullerene BHJ.

Wei-Fang Su (National Taiwan University, Taiwan) and Cheng-Si Tsao (Institute of Nuclear Energy Research, Taiwan) investigated cooperatively a copolymer/fullerene BHJ solar cell of D–A type, consisting of [2,6-(4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-*b*;3,4-*b*′]-dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)]/[6,6]-phenyl-C_{71}-butanoic acid methyl ester (PCPDTBT/PCBM) (as shown in Fig. 1(a).[2] They employed GISAXS and GIWAXS to investigate systematically that additive solvent 1,8-diiodooctane (DIO) in varied amounts influenced the morphologies of pristine PCPDTBT films and PCPDTBT/PCBM blend films, and their correlation between morphology and performance of the copolymer/fullerene BHJ solar cell of D–A type. Because the GISAXS characterizations of the PCPDTBT/PCBM system are distinct from past investigations of P3HT/PCBM systems[3] of which only nanoscale PCBM clusters contributed to the GISAXS intensities relative to large-scale amorphous polymer domains, they established a quantitative multi-length-scale GISAXS model analysis to resolve the bi-hierarchical nanostructures to which two aggregations of crystalline polymer PCPDTBT and PCBM contribute, relative to the surrounding matrix of amorphous polymer/PCBM molecules.

GISAXS in plane and GIWAXS out of plane of PCPDTBT/PCBM blend films processed without and with 0.5 %, 3 %, 5 % and 10 % of DIO are shown in Figs. 1(b) and 1(c), respectively. The GISAXS profiles are fitted well with a proposed SAXS model analysis. Figure 1(d) shows the curves of photocurrent vs voltage of photovoltaic devices based on varied BHJ. The PCE were increased from 3.2 % to 5.2 % with the DIO processes. From the SAXS analysis based on the form factor of particles and a fractal structure factor, the bi-hierarchical structural evolution of both fractal-network-aggregated polymer crystals and the fractal structure of fullerene clusters without and with DIO was schematically proposed in the PCPDTBT/PCBM BHJ solar cell (Fig. 1(e)). The PCBM phase has a line-like fractal network with fractal dimension D_{PCBM} ~ 1.5 when the content of DIO is less than 0.5 %. This structure of a network is able to disrupt effectively the nucleation of PCPDTBT crystals or to inhibit the crystallization. Upon increasing the DIO to more than 3 %, the sufficient additive would selectively dissolve the PCBM to form a dense aggregation with D_{PCBM} ~ 3 surrounding the polymer networks, which remains in a dispersed solution phase longer than PCPDTBT because the DIO has a boiling point higher than that of the host solvent. PCPDTBT crystalline networks can thus naturally develop with rapid kinetic growth analogous to the pristine polymers. The BHJ processed DIO revealed bi-continuous routes of a dense fractal-aggregated PCPDTBT network formed of PCPDTBT primary particles ($2R_{\mathrm{PCPDTBT}}$ ~ 20 nm) and surrounded with PCBM fractal aggregations ($R_{\mathrm{g\text{-}PCBM}}$ ~ 15 nm). These continuous paths enable the dissociated free electrons and holes to escape efficiently from geminate recombination and to move apart.

In summary, the present work clarified significantly the interplay among bi-hierarchical nanostructures, the effects of solvent additive and fullerene content, the mechanism of film forming and the nanostructural evolution of D–A copolymer/ fullerene BHJ solar cells. They demonstrated that the bi-continuous phase of PCPDTBT and PCBM formed with the respective hierarchical nanostructures tuned

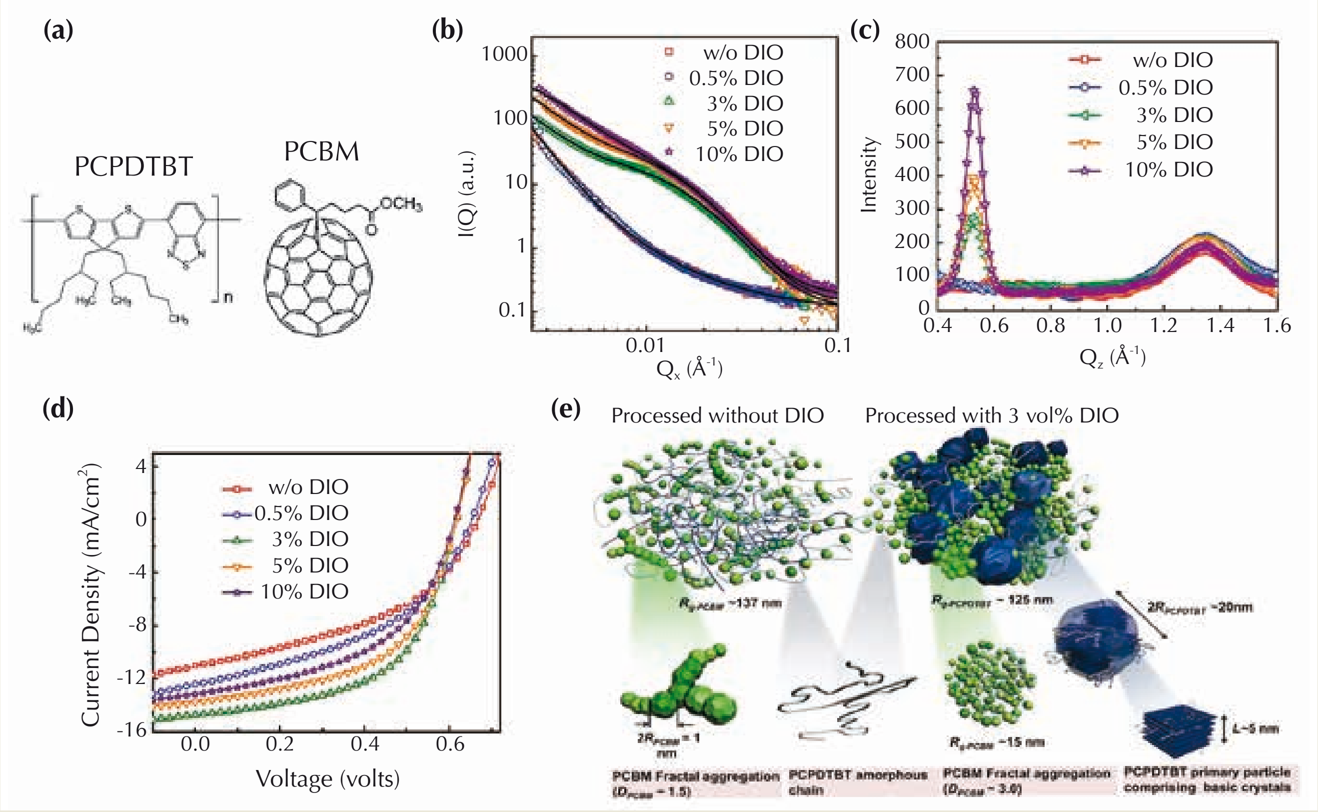

Fig. 1: (a) Molecular structures of PCPDTBT and PCBM; (b) GISAXS and (c) GIWAXS profiles of PCPDTBT thin films processed without and with 0.5 %, 3 %, 5 %, 10 % DIO; (d) photocurrent density-voltage curves of PCPDTBT/PCBM solar cells processed without and with 0.5 %, 3 %, 5 % 10 % DIO; (e) schematic diagrams of 3-D nanostructures of PCPDTBT/PCBM blend films processed without DIO and with 3 % DIO. (Reproduced from Ref. 2)

by the DIO additives is the most important factor to achieve both highly efficient exciton dissociation and carrier transport.

References

1. U. Jeng, C.-H. Su, C.-J. Su, K.-F. Liao, W.-T. Chuang, Y.-H. Lai, Y.-J. Chang, Y.-J. Chen, Y.-S. Huang, M.-T. Lee, K.-L. Yu, J.-M. Lin, D.-G. Liu, C.-F. Chang, C.-Y. Liu, C.-H. Chang, and K.-S. Liang, J. Appl. Crystallogr. **43**, 110 (2010).
2. H. C. Liao, C. S. Tsao, Y. T. Shao, S. Y. Chang, Y. C. Huang, C. M. Chuang, T. H. Lin, C. Y. Chen, C. J. Su, U. S. Jeng, Y. F. Chen, and W. F. Su, Energy Environ. Sci. **6**, 1938 (2013)
3. H.-C. Liao, C.-S. Tsao, T.-H. Lin, M.-H. Jao, C.-M. Chuang, S.-Y. Chang, Y.-C. Huang, Y.-T. Shao, C.-Y. Chen, C.-J. Su, U.-S. Jeng, Y.-F. Chen, and W.-F. Su, ACS Nano **6**, 1657 (2012).

3D Ordered Macroporous Inverse-Opal Electrodes Enable High Energy Storage

This report features the works of Ming-Jay Deng, Jin-Ming Chen, Kueih-Tzu Lu and their co-workers published in Energy Environ. Sci. ***6****, 2178 (2013).*

Facing predicaments – a limited availability of fossil fuels but their insatiable demand, climate change and atmospheric pollution, human society actively seeks renewable and clean energy for sustainable living. Although many productions of clean energy from sun and wind have been developed, a great problem is that those natural resources cannot be formed anytime and anywhere. The development of systems to store energy thus becomes an important subject for the efficient storage of solar and wind energy. Supercapacitors are an electrochemical energy storage device but with characteristics different from those of a battery. Whereas existing supercapacitors have energy densities that are approximately one tenth those of a conventional battery, their power density can be thousands of times greater. This greater power density results in much shorter charge/discharge cycles of which the battery is capable, and a greater tolerance for numerous charge/discharge cycles. Supercapacitors have thus attracted intense attention because of their great advantages to meet the demand of both great energy density and power density in many advanced technologies, such as consumer electronics, energy management, memory back-up systems, industrial power and mobile electrical systems.

The current performance of supercapacitors hinges on the design of electrode materials. Three-dimensionally ordered macroporous (3DOM) materials are an active topic for supercapacitors, because they not only create structural interconnectivities with a large surface area,[1-3] but also possess an increased electrical conductivity and maintain improved structural mechanical stability to offer significantly enhanced properties for large energy storage. Direct growth of 3DOM on conductive substrates can facilitate the diffusion of active species and transport of electrons, and hence might broaden further their applications in supercapacitors. Ming-Jay Deng, Jin-Ming Chen and Kueih-Tzu Lu *et al*. from NSRRC, Taiwan, developed a nanoarchitecture comprising a 3DOM metal core–metal oxide shell inverse-opal structure using electrodeposition of a metal within a polystyrene (PS) bead template, which was subsequently anodized in aqueous solution with varied anodization courses to construct a nanoarchitectured pseudocapacitive electrode.[1, 2] The 3DOM metal/metal oxide core–shell structure is expected to produce an electrical conductivity more easily than a conventional chaotic metal-oxide electrode. The periodic pore structure inherent in ordered inverse opals is expected to provide an ionic conduction in the electrolyte-filled pores greater than in the circuitous pore structure in chaotic metal-oxide electrodes. The synthesis strategy is briefly illustrated in Fig. 1(a). The 3D structure of the electrodeposited porous films is particularly dependent on the arrangement of the PS spheres on the substrate; in general, closely packed arrays of PS sphere yield highly ordered porous films. These scientists also compared the capacitive behavior of 3DOM manganese (Mn)/manganese oxide