In-Situ Probing Nanostructural Evolution During Spin-Coating

A top-down understanding of the nanostructural evolution provides new insights and inspires alternative strategy for the morphology control of polymer solar cells produced by spin coating.

Polymer solar cells (PSCs) with a bulk heterojunction (BHJ) structure have been widely explored for their basic application as photovoltaic device because of their potential to become a low-cost renewable energy source that is also mechanically flexible. In solar cells of this type, the electron donor and acceptor are mixed together, forming a thin film of conjugated polymer/fullerene derivative blend. The morphology of the active layer of the BHJ thin film plays a key role in the device performance, which is formed by separation of the nanodomains of the conjugated polymer and fullerene phases.

The spatial intercalation of nanoscale phase-separated polymer crystal (as donor) and fullerene cluster domains (as acceptor) in BHJ thin films can constitute an interpenetrating network for effective separation and subsequent transport of charge carriers toward their respective electrodes. At the **TLS 23A1** endstation (**Fig.1**) the simultaneous measurements of the grazing incidence small-angle and wide-angle X-ray scattering (GISAXS/GIWAXS),[1] coupled further to time-resolved UV-vis reflectance techniques provides unique insights into the morphology of thin film layers used in polymer photovoltaic devices. GIWAXS can probe the molecular arrangement of the material, including the crystal structure and the orientation of the crystalline regions with respect to the electrodes. GISAXS can capture nanostructural features inside film, covering the length scale from subnanometer to several hundred nanometer. UV-vis reflectance further records the film thinning and layering process from several tens of micrometer down to a few nm. All relevant length scales of PSCs are detectable by combining time-resolved GISAXS/GIWAXS and UV-vis reflectance techniques at the **TLS 23A1** endstation. Although extensive studies and significant advances have been made in the understanding and manipulation of the morphology of the active layers in thin films, the film morphology of solution-processed polymer electronic devices, during spin-coating, have long-been speculated without concrete evidence due to a lack of appropriate methodology.

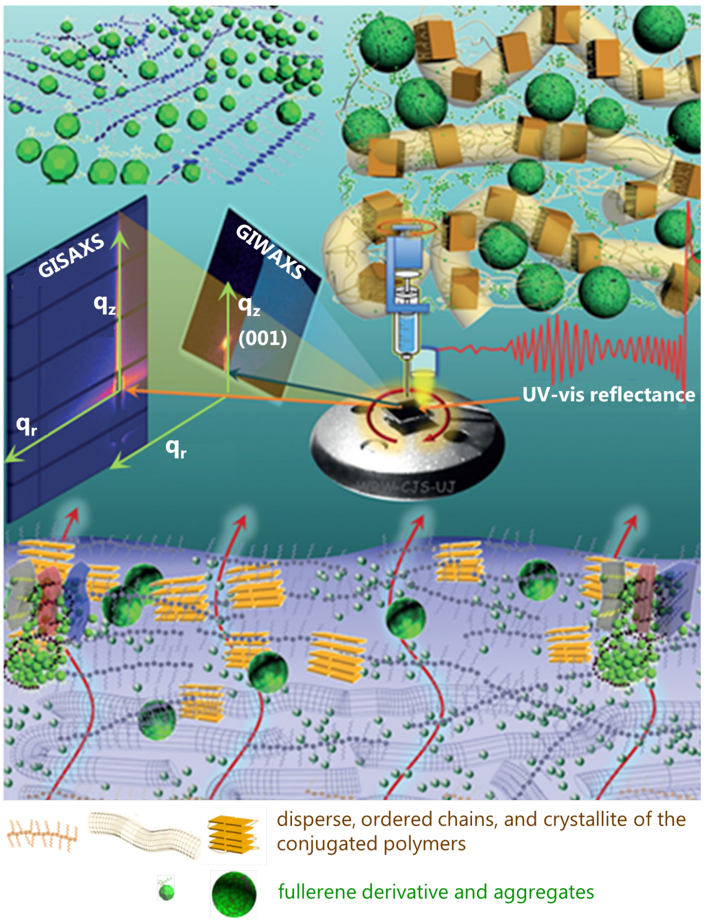

Fig. 1: Schematic representation of a spin-coating system for time-resolved and synchronized GISAXS/GIWAXS measurements, integrated further with UV-vis reflectance spectroscopy. [Reproduced from Ref. 1 and 2]

An international collaborative team led by Xinhui Lu (The Chinese University of Hong Kong) has reported a detailed GISAXS/GIWAXS analysis for solution-processed organic photovoltaic devices to obtain the morphology and structural information of the active layer.[2] Combining the fitting results of GIWAXS and GISAXS, GIWAXS provides detailed molecular level structural information of the active layer, such as lamellar spacing, π-π stacking spacing, crystallinity and molecular orientation, while GISAXS reveals the phase separation information of the binary and ternary films, including semicrystallites of conjugated polymers, fullerene cluster and intermixing domain. It is helpful to understand the phase separation and establish an overall picture of the nanoscale morphology in the films. Base on the result, the measurement technology was carried out to search for the reason of device improvement due to morphology differences. It would be interesting to try new ternary systems that can incorporate more high efficiency polymer to further improve the photoabsorption.

Chun-Jen Su, U-ser Jeng and their co-workers of NSRRC have reported a detailed study[3] of top-down nanostructural evolution during spin coating of thin film of conjugated polymer/fullerene derivative blend (poly(3-hexylthiophene)/[6,6]-phenyl-C_{61}-butyric acid methyl ester). In this work, the developed on-line spin-coating with simultaneous GISAXS/GIWAXS, integrated further with time-resolved UV-vis reflectance spectroscopy, finally can provide critical structural evidence for the long postulated mechanism on formation of the film structural features during spin-coating of solution-processed solar cell thin films. The results suggests that the PSC mixture undergoes vertical liquid-liquid phase separation over the transition from flow- to evaporation-dominance to generate a surface layering structure for mutually confined and intercalated nanodomains of aggregates of the fullerene derivative and surface-oriented crystallites of the conjugated polymers during the early stage of spin coating. The mechanistic understanding of coupled vertical phase separation and local nano-segregation starting from the solution surface, rather than from the bulk spin-coting solution commonly believed previously, provides insights and alternative strategy to the morphology control of spin-coated polymer solar cells in particular and various nano-films in general. The developed approach with time-resolved UV-vis reflectance spectra allows simultaneously observation of film thinning and formation of nanostructure and crystalline structures, covering a wide range of length scale from micrometer, nanometer, to atomic length scale. This work significantly enhances a new concept of surface nano-layering effect in influencing the final film morphology of polymer-solar-cell thin films, and would be valuable for general solution processed functional thin films. (Reported by Chun-Jen Su)

This report features the work of: (1) Chun-Jen Su, U-Ser Jeng and their colleagues published in ACS nano. ***5****, 6233 (2011) and Adv. Energy Mater.* ***7****, 1601842 (2017); (2) Xinhui Lu and her co-workers published in J. Mater. Chem.* A ***5****, 11739 (2017).*

TLS 23A1 IASW – Small/Wide Angle X-ray Scattering

- Grazing-incidence Small/Wide X-ray Scattering, UV-vis Reflectance Spectroscopy, Thin Film Characterization and Spin-coating
- Materials Science, Soft Matter, Polymer Science and Thin Film

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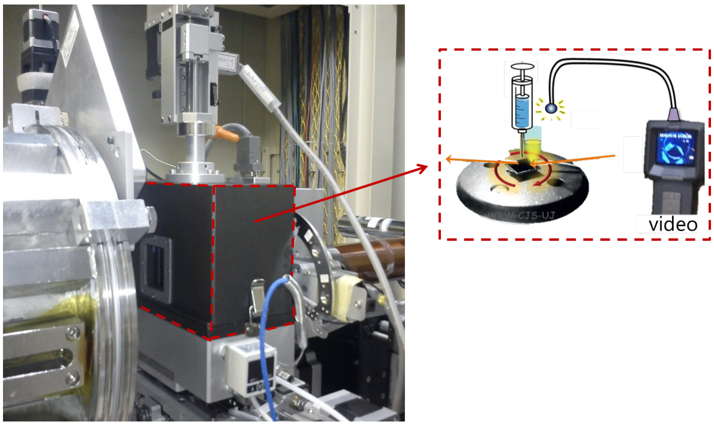
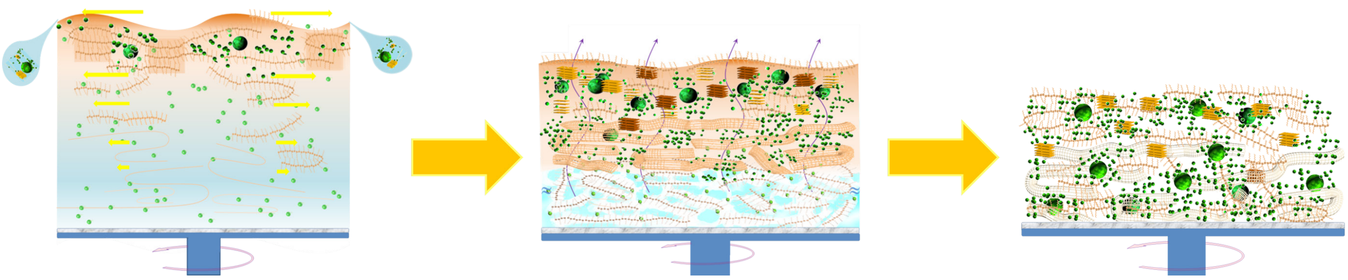


TLS 23A1 IASW – Small/Wide Angle X-ray Scattering



Proposed structural development during spin coating of a solution of P3HT/PCBM