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Seeing the Structure and Structural Evolution of Nano-crystallites in Soft Materials Using 4D Scanning Confocal Electron Diffraction

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Direct observation of organic molecular nanocrystals and their evolution using electron microscopy is extremely challenging, due to their radiation sensitivity and complex structure. Diffraction imaging, or 4D-STEM, using small convergence angles α (i.e., nano-beam diffraction, NBD) together with cryo-cooling to slow down beam damage has recently demonstrated its power to reveal the rich structural information in soft materials [1]. For crystallography-related studies, spot-like diffraction signals are preferred, not only due to the large unit cells (thus small diffraction angles) of typical molecular crystals, but also to increase the elastic diffraction signal to noise ratio (SNR) as well as signal to (inelastically scattered) background ratio (SBR). In standard NBD, the angular size of diffraction disks is coupled to the illumination convergence, resulting in conditions which are not optimized for SNR and SBR. Here, we introduce 4D-scanning confocal electron diffraction (4D-SCED) as a 4D-STEM modality which combines high dose-efficiency and high angular resolution. With 4D-SCED the complex (crystalline) structure of soft materials can be studied in detail, and we demonstrate that the technique even enables direct *in situ* observation of nanocrystal growth and coarsening in bulk heterojunction (BHJ) thin films [2].

4D-SCED applies defocused pencil beam illumination (Fig. 1b) on the sample and combines confocal electron optic setup with a pixelated detector to record focused spot-like diffraction patterns (Fig. 1c). The defocused illumination reduces the dose and generates a more homogenous electron beam sample interaction compared to 4D-NBD, even if the latter is performed with extremely small, customized condenser apertures. At the same time the confocal optics generates spot-like diffraction signals, boosting both SNR and SBR. The spatial and angular resolution can be estimated using geometric considerations (Fig. 1d), which is largely decoupled from illumination convergence. To balance spatial and angular resolution, small convergence (α~1 mrad) and large defocus ($z>>t$) is typically applied [2].

We first show the figure of merit of 4D-SCED compared to 4D-NBD (using standard apertures) with a single crystal thin film of organic semiconductor α,ω-DH6T bilayer [3], and compare 4D-NBD and 4D-SCED datasets subsequently acquired from identical region (Fig. 1e-h). The 4D-SCED dataset shows much stronger diffraction peaks with an order-of-magnitude higher SNR compared to 4D-NBD. Moreover, the focused diffraction spots result in high angular resolution thus the {110} diffraction spots from the two respective layers are clearly separated, whereas they strongly overlap and are hardly discernible in NBD. The in-plane rotation of 101.8° of the two stacked layers can be easily determined from a single frame SCED pattern without sophisticated noise reduction and disk detection typically

required for a similar analysis based on NBD disk patterns.

We then apply 4D-SCED to study an active layer in organic solar cells, namely DRCN5T:$PC_{71}BM$ BHJ thin films after solvent vapor annealing (Fig. 2a-c). With its high angular resolution, the patterns acquired via SCED enables mapping of the orientation of nano-crystallites not only in edge-on (large diffraction angles) but also in face-on orientation (small diffraction angles). Furthermore, the sharp diffraction spots in SCED can be used to locally analyze the crystallographic structure of individual nano-crystallites. The single indexed SCED patterns extracted from face-on domains, agrees well to that obtained from GIWAXS studies [4]. With careful balancing spatial and angular resolution for the given dose budget, structural details of DRCN5T nano-crystallites oriented both in- and out-of-plane are imaged at ~5 nm resolution and dose budget of ~5 $e^-/Å^2$ (the critical dose, after which almost complete structural damage of the π-stacking order is observed at RT). Finally, we use 4D-SCED to study the structural evolution of DRCN5T:$PC_{71}BM$ during thermal annealing by *in situ* heating the sample thin film in the vacuum of TEM (Fig. 2d). This allows us to directly reveal the evolution of crystallite size (coarsening) and texture, as well as the progressive enrichment of $PC_{71}BM$ at interfaces.

The unique combination of high dose-efficiency and high angular resolution makes 4D-SCED an ideal technique for studying beam sensitive soft materials. The new possibilities of the technique are currently employed for the investigation of further soft materials and corresponding results will be reported in the conference.[5]

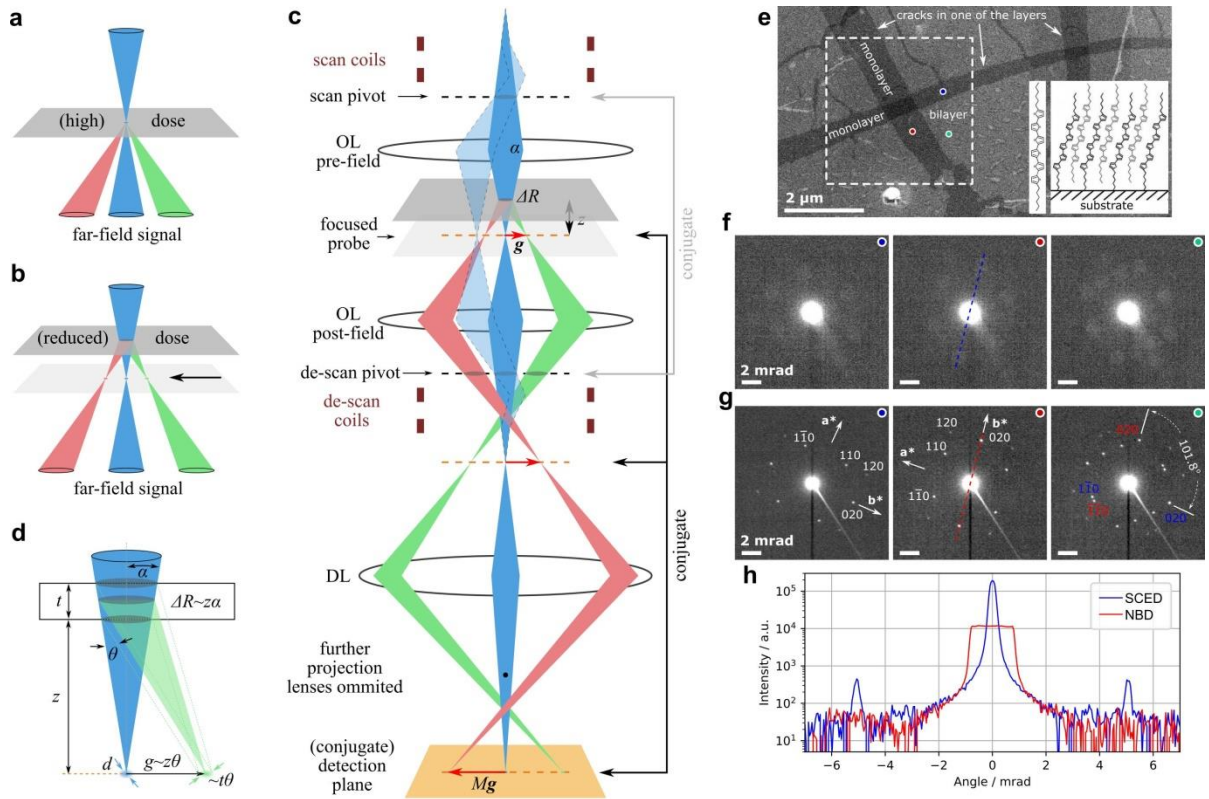

Figure 1. (a) Typical STEM setup where detector(s) is (are) located at far field. (b) Defocusing the probe mitigates limited dose budget for beam-sensitive samples. (c) A simplified optical path of scanning confocal electron diffraction. OL: objective lens, DL: diffraction lens. (d) A geometric scheme for considering spatial and angular resolution. (e-h) Comparison of NBD and SCED applied to a molecular

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2D single crystal film (α,ω-DH6T bilayer). (e) STEM-ADF image of the area of interest. Insets show the molecular structure and scheme of the assembled monolayer on the substrate. 4D-NBD and 4D-SCED data were acquired subsequently at the white box region. Representative raw patterns extracted from the positions marked with color dots are shown in (f) for NBD and in (g) for SCED. (h) Intensity profiles of the raw pattern comparing SNR/SBR of NBD and SCED.

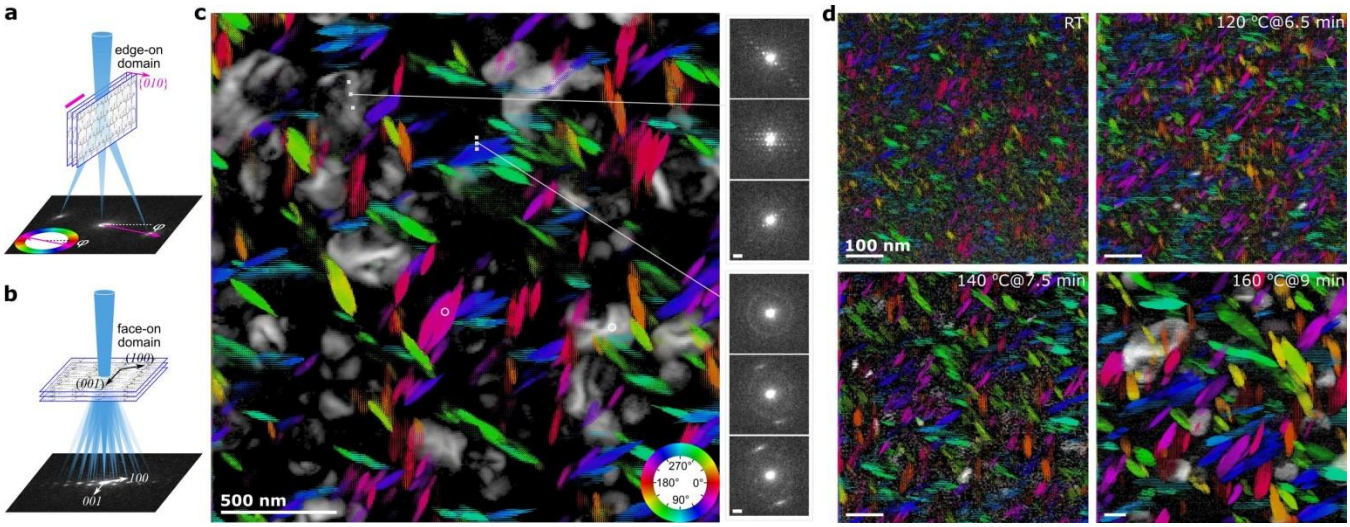

Figure 2. Visualization of the orientation of donor nano-crystallites of DRCN5T:PCBM blends. (a) scheme to illustrate color wheel method to encode the edge-on domain orientation at a probed location; (b) demonstrates our ability to determine the grain orientation of the face-on domains. Only gray scale pixels are superimposed in the maps to indicate the location of the face-on domains. (c) Nano-crystallites structure of the donor after solvent vapor annealed in CS_2 for 840 s. Insets on the right (scale bars: 2 mrad) are raw diffraction patterns extracted from the white dots. (d) The structural evolution of donor nano-crystallites during an *in situ* annealing experiment in the TEM.

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