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Scanning confocal electron diffraction (SCED): high angular resolution diffraction imaging with order-of-magnitude improved dose efficiency

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Diffraction imaging, or 4D-STEM, using small convergence angle α (i.e., nano-beam diffraction, NBD) has demonstrated its power to reveal structural information, including strain state, crystallography, electro-magnetic properties etc., at nanoscale and flexible field of view in very wide range of material samples [1]. Mapping the orientation of π-stacking in organic semiconductors molecular crystals was recently shown possible [2], opening a new application field in beam sensitive soft materials. Despite the radical developments pushing the limit of detection, the NBD setup is intrinsically poor in dose efficiency. This is because a focused probe is interacting with a small sample region (high dose rate) and, as signal, far field diffraction disks are detected spreading over many pixels of the camera (Fig. 1a), resulting in lowered signal to noise ratio (SNR) and limited angular resolution. Certain strategies can be applied to enhance dose effeciency, including defocusing beam probe (at cost of spatial resolution, Fig. 1b), using tiny convergence, $\alpha < 1$ mrad (e.g., condenser zoom and/or customize probe-defining aperture) and smaller camera length. For the study of molecular crystals the limited angular resolution due to the disk nature of NBD is particularly critical since relatively large unit cell parameters result in small diffraction angles (see Fig. 2c) leading to disc overlap under standard NBD conditions (Fig. 1f). In this work, we propose an alternative 4D-STEM scheme based on confocal optics settings [3-4], albeit differing to scanning confocal electron microscopy (SCEM) such that very small α and a large sample defocus *z* are utilized, which we call scanning confocal electron diffraction (SCED). We demonstrate that this 4D-STEM modality is capable to improve dose efficiency by an order of magnitude, deliver high angular resolution for study of molecular crystals and maintain sub-5 nm (instrumental) spatial resolution at identical dose budget compared to similar NBD setup.

In case of defocused probe/sample in STEM (Fig. 1b), there exist a plane with cross-over of the (transmission and diffracted) beams, which contains focused diffraction information, between the sample and the disk-like far-field pattern. Detection of this plane can be realized using a confocal optics setting, Fig. 1c. In this setup, the plane is magnified onto the detector (camera) which is set to a conjugate plane by operating the intermediate lens in image mode. The sample is physically raised by a distance z to reach the desired defocus, thus integrated diffraction information is formed at the stable confocal plane located at eucentric height. Lowering the sample ($z < 0$) is also possible and results in a similar spot pattern, however with a 180^0 rotation. Careful alignment of de-scan is necessary to stabilize the image of the probe, which is typical in SCEM [3]. We use a simple geometry (Fig. 1d) to examine the experimental parameters that govern the achievable (instrumental) spatial and angular resolution. To suppress the z-dependence, $z >> t$ (sample thickness) is required. For typical TEM specimen with $t < 100$ nm, a defocus $z > 2$ µm can result in well-defined spot patterns. Under such condition, α is desired as small as possible to maintain good spatial resolution. Using a double Cs corrected, monochromated TFS Titan Themis TEM operated at 300kV, and the smallest possible $\alpha = 0.7$ mrad with standard 50 µm C2 aperture (with convergence zoom), a spatial resolution of ~2 nm at 2 µm defocus ($\Delta R \approx$ (2 µm * 0.7 mrad + residual aberration)/0.61, where 0.61 account for Rayleigh criteria) is expected and obtained

using an ADF detector at confocal plane (Fig. 2e). Higher defocus may necessary when spatial resolution is dose limited.

We demonstrate the power of SCED using a solvent vapor annealed (SVA) active layer of solar cell DRCN5T:$PC_{71}BM$ (Fig. 2a-c), a highly beam sensitive nanocrystalline thin film (Fig. 2d) used as active layer in high performance organic solar cells [5]. Single diffraction patterns are shown in Fig. 1f and 1g extracted from 4D datasets with NBD and SCED setups, respectively, under identical dose budget and spatial resolution. Here we have used the following parameters for both: probe current 2 pA, dwell time 20 ms, z = 8 µm, α = 0.7 mrad, very close angular sampling size and patterns acquired using quarter area of Ceta camera at binning 2 with global rolling shutter mode. More than an order-of-magnitude improved signal intensity and high angular resolution in SCED is obvious in the extracted intensity profiles (Fig. 1h). Due to the greatly improved dose efficiency and high angular resolution, the local nanocrystalline structures, particularly location and orientation of face-on (Fig. 2f) molecular domains with their crystal b-axis aligned to viewing direction showing very small diffraction angles, is unambiguously revealed, which would not be possible with NBD (e.g., single pattern in Fig. 1f). In the map of π-stacking (edge-on) domains, the alignment of lamella to the nano-scale fiber-like structure is clearly shown (Fig. 2g). A closer analysis shows that the expected spatial resolution of SCED in the range of $\Delta R = z \cdot \alpha$ (Fig. 2d) is indeed achieved experimentally. In the present example ΔR amounts to < 10 nm, which is fully sufficient for mapping the orientation of the molecular crystals with fiber sizes in the range of 50-100 nm (short axes) and a few 100 nm (long axis).

In conclusion, SCED is capable to delivery high angular resolution diffraction patterns at extremely high dose efficiency which is suitable for the study of nanocrystalline structures of organic molecular crystals. We believe that observing growth of organic molecular crystals in situ can be possible using this method when coupling to latest generation detection technologies. More application examples will be presented in the conference.

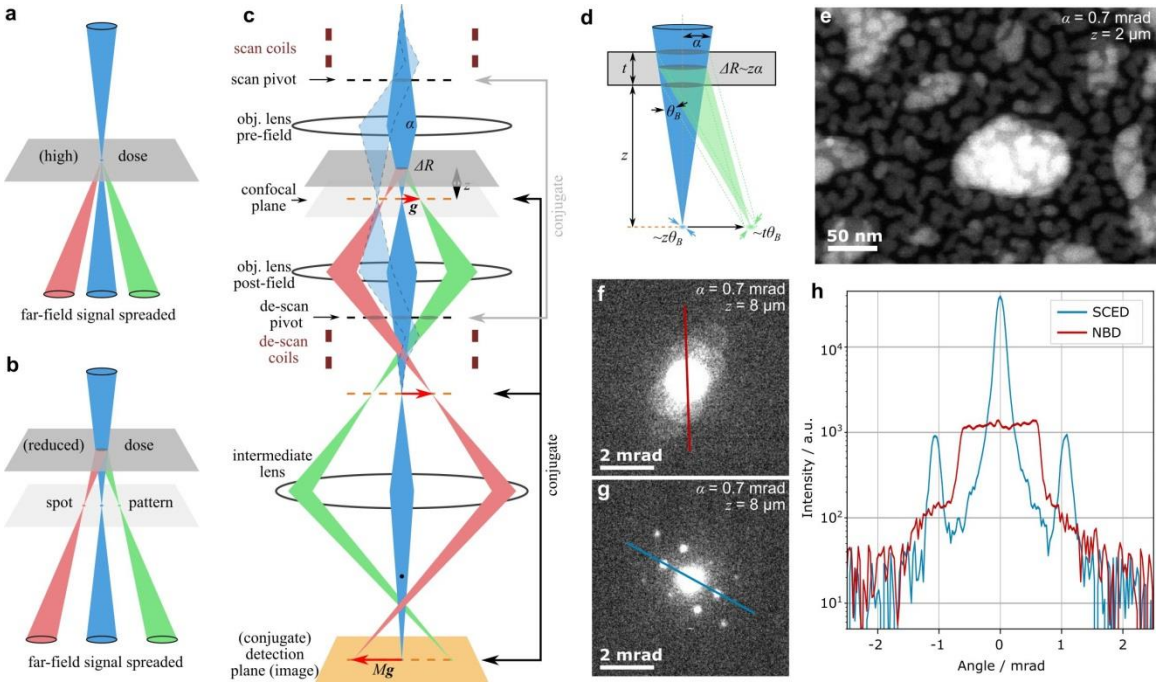

Figure 1. (a) Typical STEM setup where detector/camera is at far-field. (b) Defocusing the probe mitigate limited dose budget for radiative sensitive samples. (c) Scheme of a simplified optic path to realize scanning confocal electron diffraction. (d) A simple geometric consideration of spatial and angular resolution. With defocus far larger than sample thickness z >> t the z-dependence of the length of diffraction vector g can be

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neglected. (e) SCED ADF image of Au-Pt nano particles demonstrating resolution better than 4 nm (with α = 0.7 mrad and z = 2 µm). Single patterns extracted out of 4D datasets of similar DRCN5T domains obtained via (f) NBD and (g) SCED, respectively, with identical spatial resolution and dose budget. Order-of-magnitude improved signal and high angular resolution is obvious in the extracted intensity profiles as shown in (h).

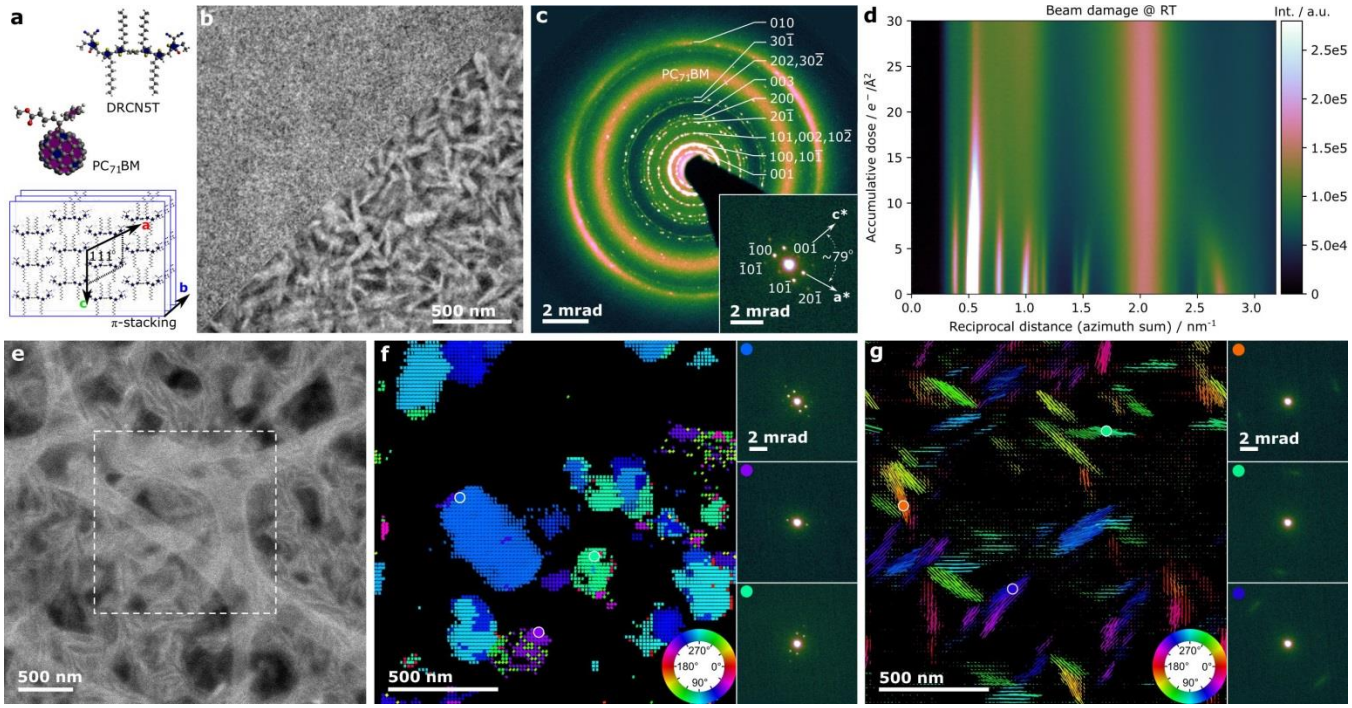

Figure 2. Highly dose-efficient mapping of the nano-crystalline domains of solvent vapor annealed (SVA) DRCN5T:PC71BM, an active layer material of high performance organic solar cell. (a) molecular and crystal structure of donner DRCN5T and acceptor PC71BM components. (b) before (left) and after (right) SVA, morphological transformation is evident by sulfur elemental maps in EFTEM, but local crystal information is not accessible. (c) (elastically filtered) selection area electron diffraction pattern from a sample region of 3.5 mm across. The inset shows a single diffraction pattern from the SCED (inset in f), indexed. (d) azimuth integrated SAED as function of the accumulative dose. (e) STEM-ADF image of area of interest. Orientation map of (f) a-axis (i.e., face-on domains) and (g) b-axis (i.e., edge-on domains) of DRCN5T crystallites, respectively. Several raw diffraction patterns as marked by the color dots are extracted and shown on the right side se insets.

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