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Signal Enhancement of Low-Dose Cryogenic 4D-STEM Data for Mapping of Beam Sensitive Materials

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Recent advances in cryogenic scanning nanobeam electron diffraction (cryo-NBED) methods have allowed extraction of the crystalline-domain morphology in organic materials such as polymer thin films and organic semiconductors [1]. Nonetheless, mapping such morphology in beam sensitive systems with suppressed crystallinity such as semicrystalline copolymer membranes used for fuel cell applications presents a new challenge [2].

NBED of radiation sensitive materials with suppressed crystallinity requires careful consideration of the experimental setup in order to optimize the signal-to-noise ratio (SNR) while minimizing dose. Here, we demonstrate SNR optimization in low-dose, cryogenic 4D-STEM mapping of phosphonium-functionalized norbornene (5:1 hPN-co-iPrMe) copolymer membranes [3] with ~2nm resolution. In systems such as this one where the domain size (down to ~5nm) is a fraction of the sample thickness (~70 nm), a higher electron dose will be required to achieve a detectable signal as scattering from the amorphous regions above and below the crystalline domain has to be taken into account. Low-dose cryo-NBED was performed on a TFS Titan Themis at 300 kV with a ~0.5 mrad convergence angle and a step size of 2-6 nm.

Figure 1 demonstrates the use of both reciprocal and real-space information encoded in cryo-NBED data to enhance the SNR for extremely low-dose mapping of crystalline domains. First, 2-fold symmetry is imposed on each diffraction pattern in order to yield a dataset that leverages the scattering intensity in both conjugate Bragg disks. Next, a gaussian kernel is applied such that the signal in each diffraction pattern from a given scan position is summed with additional signal from its adjacent scan pixels. This results in an increased signal when neighboring scan pixels exhibit reflections in the same location, thus making use of the real-space information in the data. Crystalline domain maps of the original, 2-fold symmetry imposed, and gaussian filtered data are shown in Figs. 1A,D,G and were obtained by assigning the angular orientation value of the brightest detected Bragg disk in each diffraction pattern to its corresponding real-space pixel. The real-space crystalline-domain maps as well as individual diffraction patterns (Fig. 1C,F,I) illustrate the increase in SNR of the data following this process.

In order to work near the detection limit for identifying crystalline regions, a dose assessment is used to quantify the critical dose of the material of interest. The second-generation electron pixel array detector (EMPAD-G2) was used in this work and allowed for low-dose NBED with 10 kHz framerates and negligible dead time [4]. Figure 2 shows the results of a dose series acquired over a ~750 nm field of view of a similar copolymer membrane with slightly larger crystalline domains on the order of 10-100 nm in size. The data were recorded with an acquisition time of 0.5 ms per scan pixel and a ~6 nm step size. No noticeable drift is

observed (Fig. 2A-B) despite the use of a cryogenic side-entry TEM holder which exhibits reduced stability compared to room temperature holders [5]. The benefit of the signal enhancement procedure described above is demonstrated in Fig. 2B where the reduced noise level in the crystallinity maps gives a clear real-space visualization of the destruction of the crystalline domains with increasing dose. Integration over the crystalline reflection in the radial profiles of the summed diffraction patterns for each dataset in the series (Fig. 2C) results in an expected exponential decay, yielding a critical dose, D^* of 10 $e^-/Å^2$ [6]. Working near the critical dose at cryogenic temperatures using a highly sensitive detector and making use of both real and reciprocal-space information in the 4D dataset allows robust crystalline-domain mapping of highly beam sensitive materials with crystallites merely a few nanometers in size.

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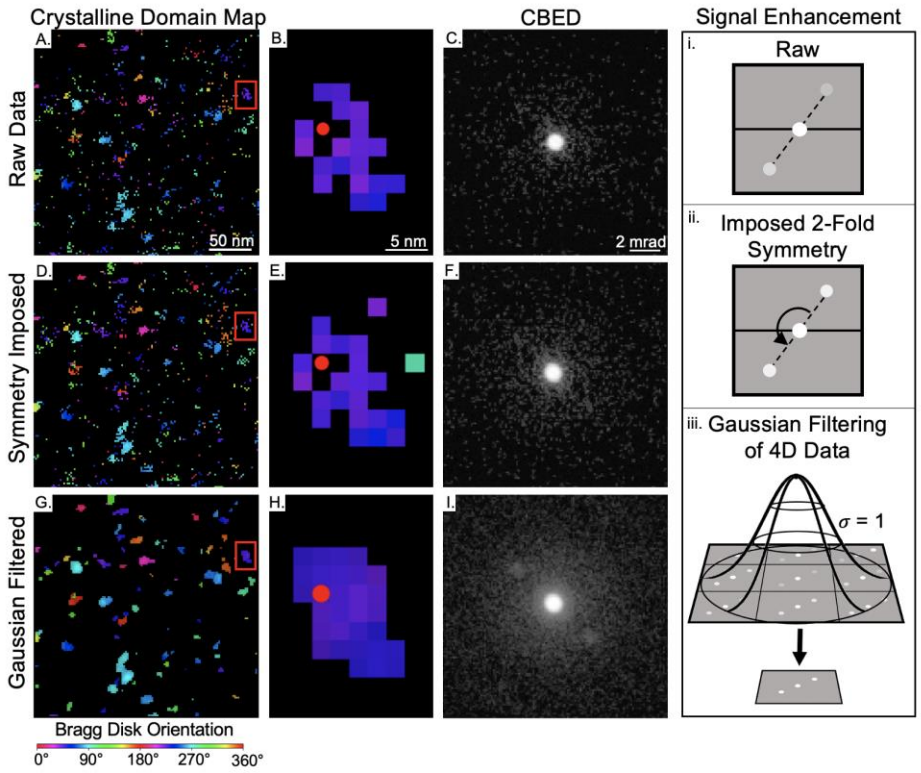

Figure 1. Signal enhancement process for low-dose cryo-4D-STEM data taken from a ~70 nm thick cross section of a cation-functionalized norbornene copolymer at ~9.5 $e^-/Å^2$ and ~2 nm step size. (A) The

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crystalline-domain map of the copolymer with (B) an inset of one crystalline domain and (C) one convergent beam electron diffraction (CBED) pattern corresponding to the pixel indicated by the red dot in (B) and illustrated in (i). (D-F) and (G-I) show the same map and diffraction pattern as (A-C) after imposing 2-fold symmetry as illustrated in (ii) and then gaussian filtering with $\sigma = 1$ as in (iii).

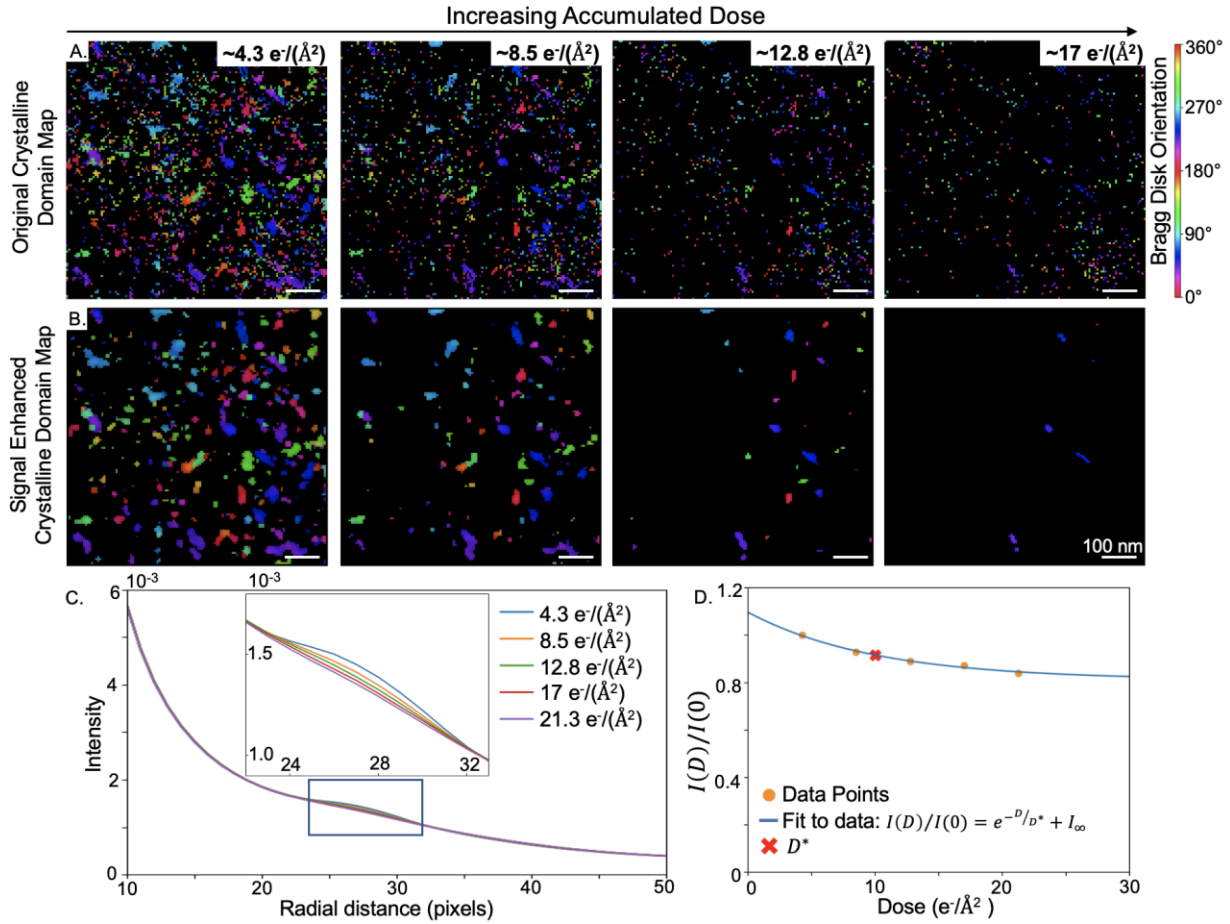

Figure 2. Dose series and critical dose assessment in a similar copolymer membrane to that mapped in Fig.1. (A) Crystalline-domain maps of the copolymer exposed multiple times to ~4.3 $e^-/Å^2$. (B) The same dose series, with crystalline-domain detection after signal enhancement. (C) Radial profiles of the summed diffraction patterns from five datasets with increasing total accumulated dose. (D) Critical-dose analysis of the crystalline domains based on the radial profiles in (C), yielding a critical dose, D* of ~10 $e^-/Å^2$.

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