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4D-STEM of Beam-Sensitive Materials

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4D-STEM (four-dimensional scanning transmission electron microscopy) [1] is able to extract quantitative structural information from electron beam-sensitive materials that can be challenging to image in the TEM [2]. A converged electron beam is stepped across the sample, and a pixelated camera records a diffraction pattern at each scan position. The four dimensions refer to the two dimensions in the scanned real-space image and the two dimensions in the reciprocal-space diffraction pattern. From the four-dimensional data set one can reconstruct maps of local crystal orientation, structural distortions, crystallinity, or different structural classes. As an exploratory characterization technique 4D-STEM can be used to probe structure over length scales from microns to nanometers, and one can optimize the acquisition parameters in an empirical manner to produce the highest signal to noise for a given material.

4D-STEM can be applied to both organic and inorganic materials; they can be highly crystalline, semicrystalline, mixed phase, or amorphous. Examples of several classes of materials that are 'beam-sensitive' [3] include organic polymers and molecular solids, framework materials such as chalcogenide frameworks or metal-organic frameworks, silicate and carbonate compounds such as those found in clays or in mollusk shells, halide perovskite materials, and battery materials. Figures 1 a-f provide examples of individual diffraction patterns taken from 4D-STEM scans from some of these materials. In addition to being beam-sensitive, many of these materials are also weakly scattering due to their low atomic number and/or low crystallinity making the diffracted signal weak and often noise-limited.

For samples that are easily damaged by the electron beam, irradiating the sample to find the right location, to carefully focus, and to acquire spectroscopic data as a function of position is sometimes not possible. While it is not easy in practice to keep track of the area exposed in parallel beam TEM, it is easy to control both the electron dose and the area scanned using STEM (Figure 1 g-i). Often times one is simply trying to acquire a weak diffracted signal, and so using a small convergence angle probe to make the diffracted signal sharp in reciprocal space is advantageous. These more 'parallel' convergent beams (0.1 to 0.5 mrad) are made possible by a combination of small probe-forming apertures and 3-condenser illumination; their probe size in real space is diffraction-limited and is inversely proportional to the aperture diameter, sometimes called the numerical aperture (Figure 1 j-l). Consequently, the probe full-width at half-maximum (FWHM) can be 1 to 20 nm. The probe size and scanning step size can then be judiciously chosen to optimize signal-to-noise ratio (SNR) and spatial resolution. Multiple data sets can be acquired with different parameters to then empirically determine the optimal parameters for a given material, which are not possible to practically predict. We will discuss over- and under-sampling of the scan positions and how to optimize these parameters to conduct the most successful experiments (Figure 1 m). Ultimately, the goal is to optimize SNR in the raw data and enable dose control, both of which can be achieved using 4D-STEM.

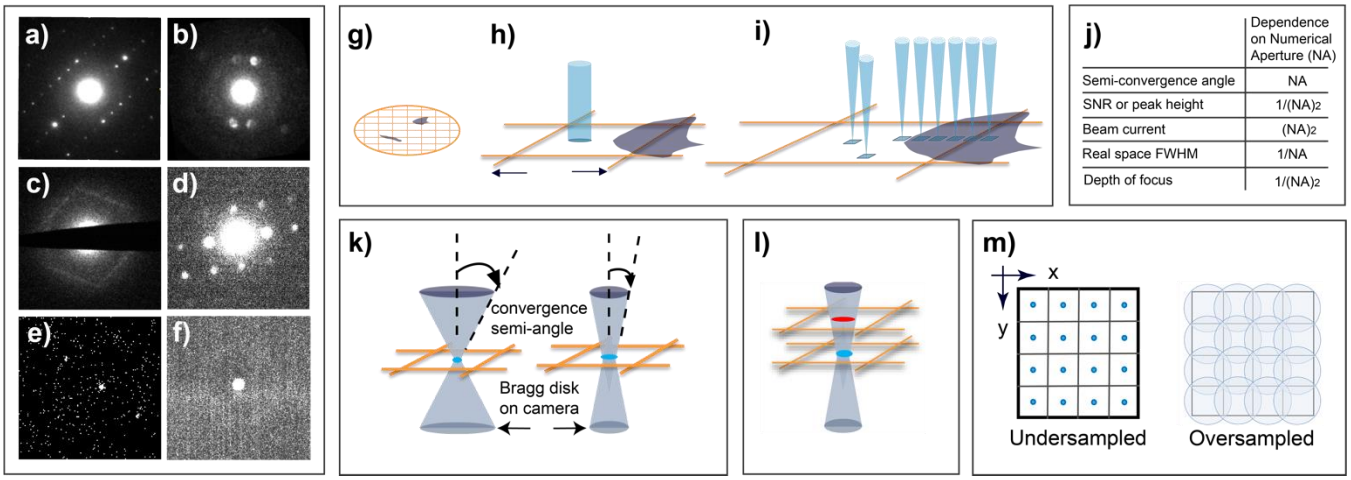

Figure 1. Example diffraction patterns and experimental parameters. a) Protein crystallite [4]; b) Organic polymer [5]; c) Peptoid nanosheet [6]; d) ZIF-8 metal-organic framework nanoparticle; e) Polypropylene on detector in counting mode [7]; f) Polyethylene, amorphous halo used for radial distribution function phase map [7]; g) Schematic of microtome slices on a copper TEM grid; h) Parallel TEM; i) STEM allowing to keep track of areas exposed; j) Dependence on probe-forming aperture; k) Relationship between convergence angle and size of reflections on camera; l) An in-focus probe intersects the sample at the blue disk; an under-focused probe intersects at the red disk; m) Step sizes much larger than probe size are often necessary to avoid sample damage from the previous scan position.

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