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The Impact of Automated Electron Diffraction Tomography (ADT) in Nano Science

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With the intense use of nano particles nowadays the need for structural characterization of these particles increases. Crystal structures of µm-size particles are mainly solved by X-ray powder diffraction. With decreasing particle size this method is hampered by peak broadening especially for large crystal lattice cells. Furthermore, nano materials are often either of low crystallinity or contain a mixture of phases. Here, transmission electron microscopy (TEM) providing structural information with atomic resolution from nano volumes in both imaging and diffraction mode is an optimal tool. However, high resolution TEM images at atomic resolution demand a high electron dose that causes beam damage in organic as well as in inorganic materials, ranging from structural changes to complete amorphization. In contrast, electron diffraction that requires substantially lower electron dose provides structural data with even higher resolution. For a complete structure solution, delivering atomic positions in sub-Angstrom accuracy, three-dimensional experimental data are necessary. The electron diffraction data collected traditionally at crystallographic zones, cover only a limited amount of reflections and deliver mostly heavy atom positions but hardly lighter atoms. The dynamical scattering effects, which are strongly enhanced in oriented zones, can be reduced by electron beam precession technique [1].

In order to improve data quantity and quality, being the key to a successful "*ab-initio*" structure solution Automated electron Diffraction Tomography (ADT) was developed [2, 3]. The core idea, of the method, is to collect not-oriented diffraction patterns in a tilt sequence around an arbitrary axis with fixed tilt steps. In such a way the totality of the accessible reciprocal space can be scanned inside the tilt range of the microscope goniometer.

Data acquisition: ADT data sets have been collected with a FISCHIONE tomography holder and a cooled GATAN single-tilt holder on a Tecnai F30 S-TWIN transmission electron microscope equipped with a field emission gun working at 300 kV. STEM images, for crystal tracking, were collected by a FISCHIONE high angular annular dark field detector (HAADF). Nano electron diffraction patterns were acquired with a CCD camera (14-bit GATAN 794MSC). A mild illumination setting resulting in an electron dose rate of 10 - 15 $e/Å^2s$ was used. Nano electron diffraction was performed employing a 10 µm C2 condenser aperture with a 100-50 nm beam on the sample. The above described equipment is not mandatory for ADT data collection. It has been shown that most standard TEMs are capable to be set up for this technique [4]. A further improvement in reflection intensity collection by integration was achieved by coupling ADT with precession electron diffraction (DigiStar unit, NanoMEGAS). The precession angle was kept at 1.2° which is significantly lower than angles used for the measurement of precessed in-zone diffraction patterns [5].

Data analysis: The resulting diffraction patterns cannot be analyzed manually any more, therefore, dedicated software (ADT3D) was developed to reconstruct the three-dimensional reciprocal space after some geometrical corrections. Based on this method, the crystal cell parameters can be determined using clustering-routines [6], the diffraction spots can be indexed and intensities integrated. In addition, the three-dimensional reciprocal space reconstruction allows for a visual detection of crystallographic specialties such as disorder, twinning or other individuals.

Structure solution: Data sets collected by ADT proved to be of higher quality as compared to ones collected by conventional electron diffraction based on zone-oriented electron diffraction patterns. Because dynamical effects are reduced, a standard kinematic approach (intensities proportional to F_{hkl}^2) delivers *ab-initio* the complete structural model (direct methods or simulated annealing as implemented in SIR2008, included in the package Il Milione [7]).

Based on ADT and ADT/PED data it was possible to solve a wide range of crystal structures from nano particles down to 30 nm [8]. Remarkably, large cell porous minerals [9], zeolites (doped and calcinated) [10] beam-sensitive metal-organic frameworks [11], organic-inorganic hybrids [12] and small organic molecules [13] have been solved in the last years.

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