Oral presentation

3D Electron Diffraction for accurate structure analysis of nanoparticles

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So-called 3D electron diffraction (3D ED) approaches [1] have become an alternative for overcoming the size limitations of single-crystal X-ray diffraction. Nevertheless, the literature remains poor on the limits of 3D ED and what can be expected for the analysis of very small crystals. To address this point, we report here our results on the accurate structure analysis of individual nanoparticles (NP).

The model materials used in this methodological study were nanoparticles of TiO_2 (brookite), $In_{2-x}Sn_xO_3$ (ITO), and $MgTi_2O_5$. To assess the capability to localize light elements, lithium was incorporated into the brookite TiO_2 structure, resulting in the compound Li_xTiO_2. The feasibility and efficiency of various data acquisition protocols are first established for different particle sizes using a JEOL F200 electron microscope equipped with an ASI Cheetah M3 hybrid pixel detector as our main experimental setup. Beam precession motion, when applied, was achieved using a Nanomegas DigiStar unit. We also found advantages in employing a Gatan Elsa cryogenic and tomographic holder. For larger NPs, around 100 nm in size, rapid automated data acquisition is possible for different beam sizes. However, for NPs around 10 nm in size, only precession-assisted 3D ED with a small parallel beam has proven effective for subsequent accurate structure refinement (see Figure 1.1). In this case, it becomes possible to achieve atomic position precision on the order of 0.01 Å or 0.03 Å depending on whether we consider dynamical effects in refinement [2] or not. Another approach, related to serial ED, was also successfully tested in cases where the NPs are subjected to uncontrolled movement induced by an external stimulus. NPs were set in motion by beam energy that modifies the amorphous support (see Figure 1.1), the induced rotation of NPs can be used advantageously to collect hundreds of diffraction patterns from different NPs. In the final part of this contribution, we successfully applied the established 3D ED data acquisition protocol and analysis (i.e. precession-assisted 3D ED and 'dynamical refinement') to two case studies. Firstly, we explored the feasibility of localizing lithium atoms in Li_xTiO_2 (x=0.4) brookite nanorods, which have a maximum width of approximately 100 nm (see Figure 1.2). Second, we addressed the challenge of determining the ratio of magnesium to titanium atoms sharing the same atomic positions within a $MgTi_2O_5$ NP of about 30 nm in size (see Figure 1.3).

Our research highlights the ability of 3D ED to perform accurate structural analysis of NPs as small as 10 nm. As examples, we demonstrate the localization of light elements, such as lithium, and the determination of element ratios in atomic positions with a mixed occupancy (in this case Mg/Ti). We are confident that these findings will capture the interest of the community and enhance the understanding of crystallographic structures of new nanoparticles, which are vital for applications in energy materials and catalysis.

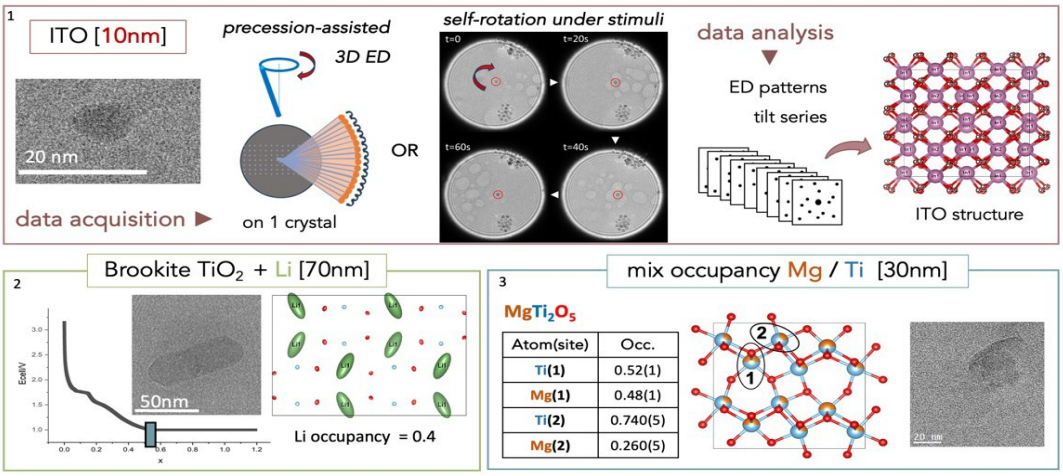

Figure 1. 1) Accurate structure solution for 10nm NP using precession-assisted 3D ED and an alternative approach, related to Serial ED, based on NPs induced self-motion. 2) Lithium detection on 70nm NPs. Green ellipsoids represent atomic displacement parameters. 3) Element ratios for atomic positions with mix occupancy.

[1] Gemmi, M. et al. 3D electron diffraction: the nanocrystallography revolution. ACS Central Science 5 (2019) 1315-1329.

[2] Palatinus, L. et al., Structure refinement using precession electron diffraction tomography and dynamical diffraction: theory and implementation. Acta Crystallogr. A 71 (2015) 235-244.

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