Multi-scale electron tomography in liquid state and its application to the study of beam-sensitive nanomaterials

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Background incl. aims

Electron tomography is a technique that allows 3D data analysis at the nanometer scale. In its early days, it was performed in high vacuum and only beam-resistant samples were analyzed due to its time-consuming nature. In the last decade, tremendous technical developments have been made to make tilt series acquisition faster and faster, and to make fast electron tomography compatible with environmental electron microscopy. [1,2] Environmental electron tomography in gas, and even more so in liquid state, is very sensitive to the electron beam, so acquiring fast tilt series in STEM mode with a very low electron dose received by the sample is a real challenge even for the most experienced users. In this presentation the application of the M-SIS software, developed in our group, in the analysis of aluminum hydrogel suspended in liquid will be shown.

Methods

$Al(OH)_3$ is an extremely beam sensitive sample, so care must be taken to avoid beam damage, especially when the sample is in a liquid state. An aqueous suspension of aluminum hydrogel was inserted into the ESEM in the liquid state, then dried and rehydrated in situ. At each hydrated state, a fast tilt series in STEM mode from -70° to +70° was recorded on the region of interest at low electron dose in order to preserve the sample. In addition, ETEM experiments were carried out without encapsulating the sample. A careful control of the sample temperature and the water vapor pressure enabled the 3D study of the hydrated material at nanometer scale and the pore size distribution was measured. The tilt series were recorded using the custom code M-SIS build in Python that is an automatic tool for electron tomography and can be installed on an ESEM and on an ETEM.[1-3]

Results

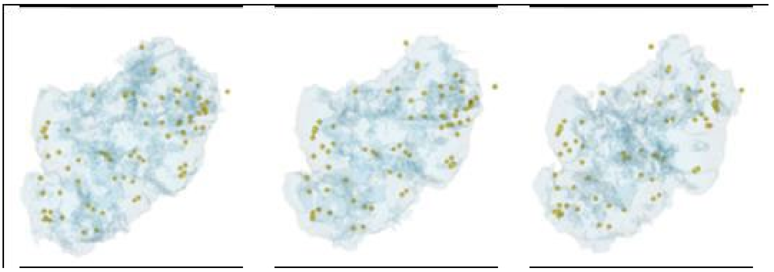
Three hydration states of $Al(OH)_3$ were investigated in 3D by ESEM. It was found that the global volume of the sample does not change its structure during the dehydration-rehydration cycle. Its change in volume was measured to be about - 3.4 ± 1.3% during dehydration, followed by a + 1.2 ± 1.0% expansion during rehydration. The spatial resolution of the tomograms was

about 10 nm and the total electron dose of each tomogram was between 1050 and 1250 e-nm-1.
In ETEM, tilt series could be acquired with 260 frames in 12 min, with a pixel size of 0.6 nm and a total electron dose of 16,000 e-nm-1. No significant change of the sample structure could be detected during acquisition. The pore size distribution in the hydrated state was found to vary from 5 to 30 nm (Figure 1).

Conclusion
Thanks to the development of the M-SIS software, we are now able to study beam-sensitive materials in liquid in 3D. Al(OH)3, an extremely beam-sensitive material, was analyzed in ESEM in 3D in different hydration states. The morphological changes were quantified with a spatial resolution of 10 nm. The pore size distribution in the hydrated sample was quantified with higher resolution in liquid using electron tomography in ETEM.

Figure 1: 3D model of Al(HO)3 in the initial state in liquid, then after dehydration and finally after rehydration. The yellow particles are Au particles used as fiducial model.

Graphic:



Keywords:

In-situ, liquide, beam sensitive, tomography

Reference:

[1] S. Koneti et al, Fast electron tomography: Applications to beam sensitive samples and in situ TEM or operando environmental TEM studies. Materials Characterization 151, 2019.
[2] X. Jiao et al, Electron tomography on latex particles suspended in water using environmental scanning electron microscopy, Micron, 2019, 117.
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