Improving electron tomography of mesoporous silica structures by Ga intrusion

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Background incl. aims:
Mesoporous silica structures are widely used in the field of nanotechnology, e.g. as substrate in heterogeneous catalysis [1] and as stationary phase material in size-exclusion chromatography [2]. To understand and improve the material's properties, a precise characterization of the pore network is indispensable. Common approaches to quantitatively analyse the mesoporous space are averaging sorption/intrusion techniques [3] and three-dimensional imaging techniques such as electron tomography in high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) mode [4]. While the first mentioned techniques lack the localized spatial information, HAADF-STEM tomography resolves the mesoporous structure with a spatial resolution in the nm-range, but suffers from poor contrast between pore space and network in case of low atomic number (Z) materials, since the imaging contrast scales with $\sim Z^2$ [1]. In this study, we uniquely combine Ga intrusion of the pore space in mesoporous silica with HAADF-STEM tomography to enhance the Z-contrast between pores and silica significantly by a factor of ~9x. This enables a reliable quantitative analysis and visualizes localized information about the pore network and the process of Ga intrusion. In particular, we apply 360° HAADF-STEM tomography on pillar-shaped specimen prepared from the intruded mesoporous silica. This allows for precise 3D reconstruction of the tilt series without missing-wedge artifacts to accurately obtain important pore characteristics such as size distribution, tortuosity, and connectivity [5].

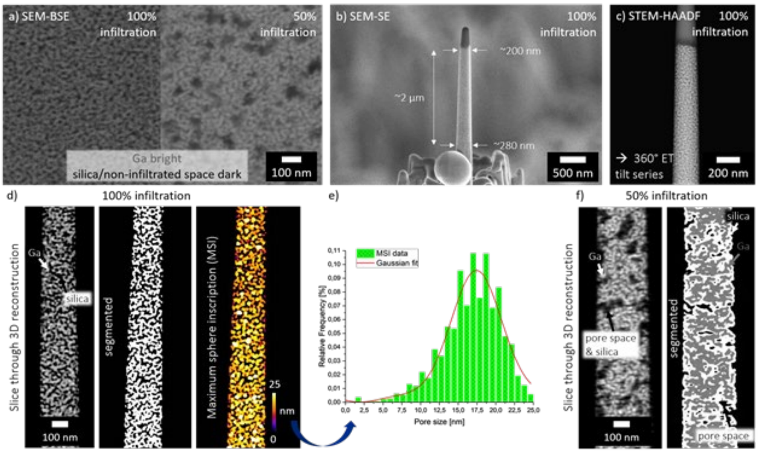
Methods:
Mesoporous silica with an average pore size of 20nm is intruded with Ga up to different filling degrees (50%, 100%) by a modified Hg intrusion porosimetry technique. From the intruded sample systems pillar-shaped specimen are prepared on a tip by scanning electron microscopy (SEM)/focused ion beam (FIB) techniques using a Helios NanoLab 660 DualBeam SEM-FIB. The samples are analysed by 360° HAADF-STEM tomography in a double Cs-corrected FEI Titan³ Themis at 300 kV.

Results:
Backscattered electron (BSE) imaging on a FIB prepared cross-section of the fully intruded silica reveals that the method of Ga intrusion leads to a homogeneous filling of the pore space in a representative volume required for STEM tomography (Figure 1a - left). The homogeneous distribution of the infiltrated Ga phase is crucial for a reliable quantitative analysis by STEM tomography. If the pressure during the intrusion process is reduced, a partial filling (50%) of the porous network can be achieved with the empty pockets being evenly distributed in the entire sample (Figure 1a - right). This finding resembles the homogenous and narrow pore size distribution of the material and hints towards smaller pore channels being present within the unfilled spaces, since the infiltration of smaller pore channels requires in general higher pressures.

From the fully- and half-intruded silica, pillar-shaped specimen can be prepared on tomography tips by common FIB lift-out technique (Figure 1b). In contrast, imaging and pillar preparation from pure silica is challenging, since the material is electron-beam sensitive and non-conductive. This leads to sample charging and causes sample drift and uneven milling during FIB preparation. Therefore, a charge neutralizer is indispensable in case of silica, which is, however, not available on any FIB instrument. Also during STEM tomography, charging effects occurring on pure silica easily cause complications resulting in bending and structure deformation, which strongly worsen the 3D reconstruction quality. Moreover, the build-up of carbon contamination during tilt series acquisition worsens the image contrast over time, due to the low atomic number difference of Si, O, empty space and C contamination in HAADF-STEM imaging mode. In contrast, specimen intruded with Ga feature a ~9x stronger contrast, so that C contamination is negligible and the pore and silica space can clearly be resolved throughout the entire tilt series (Figure 1c). As outlined, Ga intrusion of mesoporous silica features multiple advantages: (1) it improves the imaging contrast in HAADF-STEM mode, (2) increases the sample integrity, (3) mechanically stabilizes the pillar, and (4) forms a conductive pathway through the sample eliminating charging effects during preparation and STEM tomography. These benefits improve significantly the reconstruction quality of the tomographic tilt series in the fully intruded specimen (Figure 1d - left), facilitate the phase segmentation between Ga and silica (Figure 1d - middle) and enable a reliable quantitative analysis of the porosity and pore size distribution by the method of maximum sphere inscription (MSI) (Figure 1d - right, Figure 1e). For a benchmark comparison, the mesopores of the silica structures were investigated with N_2 physisorption, evaluated with the non-local density functional theory (NLDFT) method. Moreover, we investigated the 3D reconstruction of the half-intruded silica specimen (Figure 1f) to improve our knowledge regarding the Ga intrusion process and to study contrast differences of pores, Ga and silica in more detail. While the filled channels are clearly visible, the unfilled channels, which indicate bottlenecks in the pore pathways, are weakly distinguishable from the surrounding silica network (Figure 1f - left). The respective segmentation is challenging, but helps to identify bottlenecks in the pore pathways (Figure 1f - right). In sum, the findings from electron tomography can further elucidate the gallium intrusion process on the nanoscale and contribute to the development of methods for textural characterization based on liquid intrusion.

Conclusion:
This study highlights the potential of Ga intrusion for contrast enhancement of the pore space in mesoporous silica during 360° HAADF-STEM tomography to study quantitatively important pore characteristics. Vice versa, the study further helps to understand the process of Ga intrusion. The intrusion process leads to a homogeneous Ga distribution and enhances the mechanical stability of the non-conductive silica during both FIB sample preparation and acquisition of the STEM tilt series by minimizing electrical charging. The Ga intrusion process can be regarded as a potential common technique to improve electron tomography not just on mesoporous silica but also on various other porous materials.

Graphic:



Keywords:

360° ET, quantitative pore analysis

Reference:

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