In situ 3D characterization of metal nanoparticles while heating

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A powerful way of studying processes at the nanoscale are in situ measurements allowing, for example, to follow heat-induced morphological transformations and compositional changes in time. However, in situ experiments conventionally only provide 2D projections of a 3D object. Therefore, they may not be sufficient to understand the complex 3D changes in anisotropic nanosystems. Ideally, in situ experiments should be performed by utilizing electron tomography to gain access to the full 3D morphology. The recent development of specialized holders such as a heating tomography holder makes it possible to follow in situ processes in 3D [1]. One obstacle, however, is the time resolution since the acquisition of a conventional tomography series takes about 30 min - 45 min. For processes that happen on the order of minutes, morphological transformations are finished before the process can be visualized in 3D. A limited number of results based on fast TEM tomography have been published, but for crystalline samples, diffraction contrast in bright field TEM violates the projection requirement for electron tomography [2,3].

Here, we will show in situ results of heating tomography experiments made possible by a new methodology to apply fast tomography in HAADF-STEM mode. Our new approach makes it possible to follow morphology transformations in real-time with a time resolution of a few minutes. As a proof of principle, Figure 1 shows preliminary results obtained by fast HAADF-STEM tomography. A Au nanodumbell was investigated by conventional electron tomography with a total acquisition time of more than 1 hour (Figure 1.a). Next, a fast tilt series was acquired by continuously tilting the same particle over ±70° (Figure 1.b). More than 700 images were acquired in less than 10 minutes. The equal quality of Figure 1.a and 1.b proves the reliability as well as the enormous potential of fast HAADF-STEM tomography. In this example, the shape of the dumbell changes to a rod like structure at 300˚C (Figure 1.c).

By adjusting the heating profile (ramping speed and temperature) to the acquisition time of 1 or several tilt series, we can capture the 3D dynamics of the nanoparticle while heating. During 3D reconstruction, we compensate for motion artefacts. A proof of concept is illustrated in Figure 2 for a Au nanostar. Given the anisotropic nature of these nanoparticles, quantitative information can not be extracted from 2D images. Fast electron tomography, based on continuous tilting, while heating enables us to characterise intermediate stages of deformation at high temperature quantitatively. It is clear that the sharp tips of the nanostar disappear first, which will have major impact on the optical and catalytic properties. For example, the sharp tips result in localised surface plasmon resonance, but reshaping of the tips will drastically reduce the local field enhancement.

Finally, we will not only follow morphological transformations, but will also focus on compositional changes of bimetallic nanoparticles induced by heating in situ by combining electron tomography and EDX mapping.

[1] www.denssolutions.com

[2] Roiban et al, Journal of Microscopy 268 (2018) p 117

[3] Migunov et al, Scientific Reports 5 (2015) p 14516

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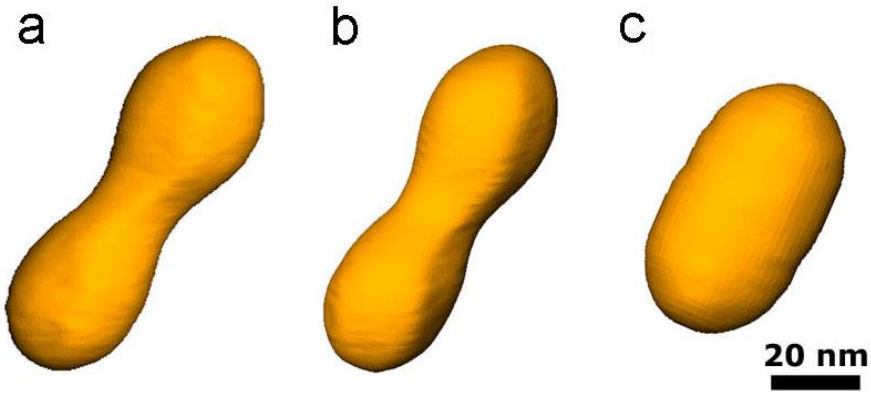

Figure 1. Fast HAADF-STEM tomography applied to Au nanodumbells a) A conventional electron tomography reconstruction of a Au nanodumbell. b) The 3D reconstruction of the same nanodumbell obtained using fast electron tomography. c) After heating the dumbells, the morphology changes to a nanorod.

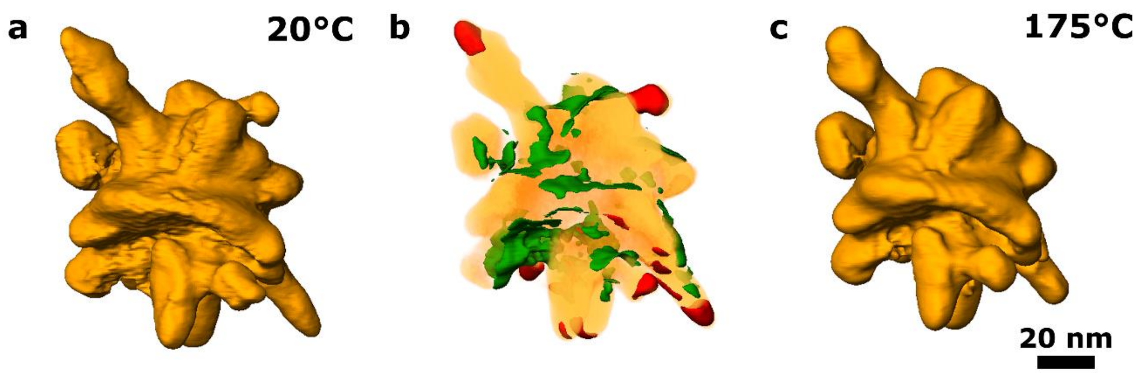

Figure 2. Fast tomography of a Au nanostar while heating a) at 20°C and c) at 175°C. b) The volume increase/decrease while heating is depicted in green/red, respectively.