High resolution electron tomography: from model like systems to real nanomaterials.

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Summary: Electron tomography is a powerful tool to investigate nanomaterials. However, dedicated effort is necessary to obtain atomic resolution in 3D. In addition, we should develop methodologies to investigate the 3D structure and composition of nanomaterials under realistic environmental conditions.

1. INTRODUCTION

Electron tomography has evolved into a powerful tool to investigate a broad variety of nanomaterials. Most of these results have been obtained with a resolution at the nanometer scale but different approaches have recently pushed the resolution to the atomic level. However, 3D characterisation by transmission electron microscopy (TEM) is conventionally performed in ultra-high vacuum and at room temperature! Since it is known that the morphology and consequently the activity of nanomaterials will change with temperature or pressure, one may question the relevance of such measurements at only room temperature and in ultra-high vacuum. To fully understand the connection between the 3D structure and properties under realistic conditions, innovative methodologies are required to track the fast 3D changes of nanomaterials that occur in different thermal and gaseous environments. Such experiments are very challenging and much more demanding than a simple combination of electron tomography and *in situ* TEM.

2. RESULTS

One possibility to perform electron tomography with atomic resolution is by applying reconstruction algorithms based on compressive sensing [1,2]. The methodology was applied to high angle annular dark field scanning TEM (HAADF-STEM) images acquired from defect-free Au nanorods [1]. Going further is the aim to determine the type of individual atoms in hetero-nanoparticles. Using the same approach, we were able to distinguish individual Ag from Au atoms at the interface in core-shell Au@Ag nanorods [2]. High resolution electron tomography was recently also applied to determine an unknown crystal structure. A combination of diffraction tomography and high resolution tomography in real space enabled us to investigate the distribution of Cu vacancies in $Cu_{1.5\pm x}Te$ nanocrystals. By using the outcome of these experiments as an input for first-principle calculations, the influence of these vacancies on the optical properties of the nanocrystals was determined [3].

An emerging challenge is to bring 3D characterisation of nanomaterials to the next level by tracking 3D changes of the structure and composition of nanoparticles in a realistic environment. First results will demonstrate how such experiments can help to improve the thermal stability of nanomaterials and how we can understand what happens to the 3D structure of nanoparticles while catalysis takes place. For example, to investigate the thermal stability of Au nanoparticles, a combination of a tomographic heating holder with fast tilt series acquisition has been used. We investigated the morphological evolution of a Au nanostar at 200 °C, 300 °C and 400 °C. At elevated temperatures, the sharp tips at the end of the nanobranches were observed to reshape into shorter and blunter tips.We were thereby able to quantify local volume reductions and increments [4]. To quantify nanoparticle shape dynamics in a gaseous environment in 3D, HAADF-STEM images served as an input for atom counting procedures followed by 3D relaxation of the structure. In this manner, we characterized shape changes of a Pt nanoparticle in a gaseous environment (Figure 1). The conditions have been varied from vacuum (Figure 1.a) to a 1 bar H_2 flow (Figure 1.b), followed by a 1 bar O_2 environment (Figure 1.c). To investigate the behaviour during cycling, we repeated the experiment several times using the same particle (Figure 1.d&e). We clearly observe morphology changes and we were even able to quantify the occurrence of the different surface facets [5].

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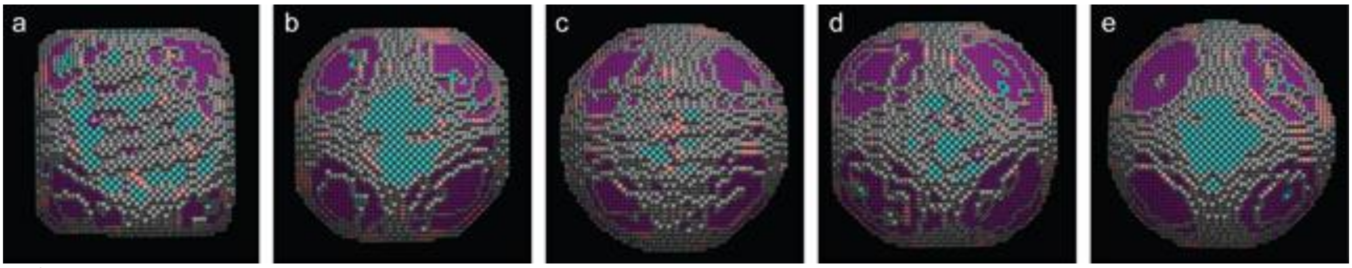

Figure 1: Figure 1: Morphology of a Pt nanoparticle in different gaseous environments. The atoms are shown using different colours, according to the type of facet: blue={100}, pink={110}, purple={111}, grey=higher index.