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Thermal Stability of Au@Pt Nanoparticles Investigated by Electron Tomography

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Understanding the thermal stability of bimetallic nanoparticles is of vital importance to preserve their functionalities during a variety of applications. More specifically, anisotropic platinum coated gold nanorods (Au@Pt NRs) are promising candidates for photo and catalytic applications [1]. Unfortunately, NPs are often found to be extremely sensitive to thermal annealing or air exposure, altering their properties [2]. Therefore, the investigation of their thermal stability and the distribution of the chemical composition of these nanoparticles upon heating are of high interest for their practical applications since it has been shown that the shape and the surface coverage of the coating can directly affect the optical properties of the Pt coated Au nanorods [1, 3].

There are a limited number of investigations concerning the stability of Au@Pt NRs. He et al. [2] studied the stability of Au@Pt NRs by both, *ex situ* annealing at 200 °C and exposing the sample to air for long periods, followed by TEM characterization using two-dimensional (2D) HAADF-STEM images. Nevertheless, projection images are in general clearly insufficient to shed light on the complex transformations in nanostructures with three-dimensional (3D) morphological features. Therefore, since most NP properties are directly connected to their 3D structure, including composition and distribution of the elements in the core-shell structure, a 3D visualization is of great importance. Thus, electron tomography can be used as a key tool to investigate changes in the surface features and morphology of Au@Pt NRs. Furthermore, recent progress in TEM holders even allows 3D *in situ* measurements when combined with electron tomography, providing crucial information on the morphological and compositional changes in bimetallic NPs at a local scale [4].

The chemical synthesis of the sample is crucial to control the 3D structure of bimetallic NPs. Consequently, in order to study the effect of the 3D structure in the thermal stability, samples with different morphology of the Pt were prepared. Hereby, three differently synthesized Au@Pt NPs presented in this contribution differed in their Pt shells, with their own morphology and distribution of elements in the resulting core@shell nanostructures. More specifically, the samples were synthesized applying a surfactant-driven seed-mediated approach, either with or without chiral additives, and temperature reaction. By adding chiral additives, it was possible to direct the growth of regular surface Pt spikes on Au NRs [5], and by controlling the temperature different length of the Pt spikes were obtained.

To investigate the structural changes induced by the thermal instability of the three differently synthesized Au@Pt NRs we implemented 2D and 3D electron microscopy characterization techniques (HAADF-STEM, EDX-STEM). This thorough characterization at room temperature revealed the main characteristics of the different samples: a Au@Pt system with high continuity and two Au@Pt sample with a discontinuous, but regular, shell consisting in Pt spikes which differ in the length of such spikes (Figure 1).

Later, the aforementioned TEM characterization techniques were combined with *in situ* heating using a dedicated tomography holder (DENSsolutions Wildfire) to investigate the heat-induced morphological transformations on the selected samples. Upon heating at only 200 °C, temperature well below the bulk melting temperatures of the individual elemental components, the *in situ* TEM observations and tomographic reconstructions of Au@Pt NRs exhibited a low-temperature structural instability (Figure 2). Moreover, the mentioned instability was represented by voids and indentations in the Au core of the bimetallic system.

3D HAADF-STEM reconstructions and orthoslices through the volumes (Figure 2) indicated the heat-induced formation of indentations or voids in all three samples. In case of having a sample with high continuity of the Pt shell small voids appeared in a few particles. Whereas, when heating Au@Pt NPs with a discontinuous shell in form of Pt spikes have a dramatic effect leading to the extrusion of Au from the central nanorod through the free surface in all the investigated particles. However, this effect was highly dependent on the amount and coverage of Pt on the surface. The sample with shorter Pt spikes mostly showed indentations, whereas in the sample with long Pt spikes huge voids were especially noticeable. These experimental observations suggested that the percentage of the Pt coating is a major factor influencing the thermal instability and that such coating is acting as a barrier against the deformation mechanism.

Moreover, we applied MD simulations to understand the underlying deformation mechanism by using the experimentally determined three-dimensional morphology as input. According to the combination of the experimental observations and the computational simulations, we could conclude that the observed low thermal stability is strongly influenced in short-term by two main factors: the continuity of the Pt shell and the amount of Pt in the spikes on the surface of the Au NR due to a delicate balance between Au and Pt, as well as their geometric arrangement and amount around the Au surface [6].

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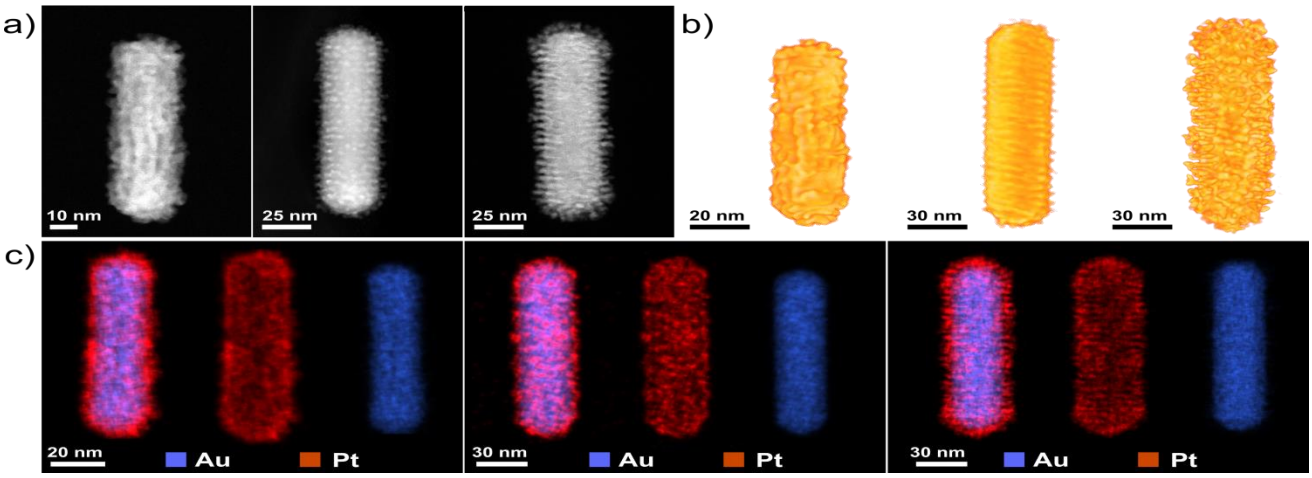

Figure 1. (a) HAADF-STEM images of different Au@Pt NRs prepared using two different surfactants and temperature. (b) 3D visualizations and orthoslices through the HAADF-STEM tomography reconstructions obtained for the different samples at room temperature. (c) EDX-STEM maps of the different Au@Pt NPs.

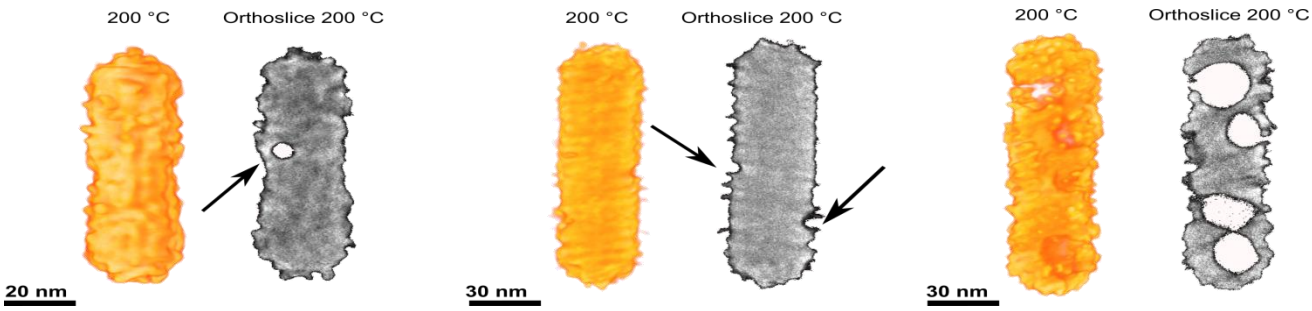

Figure 2. 3D visualizations and orthoslices through the volume of HAADF-STEM tomography reconstructions obtained under *in situ* conditions for the selected samples after heating at 200 °C. Small voids and indentations observed in the samples are marked by black arrows in the orthoslices.

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