In the framework of the development of nano-sized materials with new optical properties induced by the size effect or by a specific morphology, the study of noble metal nanoparticles takes nowadays a prominent position, due in particular to their plasmonic properties. Attention has been paid to the quest for a synthesis method able to provide Au nanostructures with precise shape and crystallographic orientation. Thus, it was demonstrated that by using a seed mediated technique [1] and tuning the Au seeds concentration that play the role of nucleation centers, one can synthesize Au bipyramids (BPs) with various aspect ratios inducing various symmetries in the basal plane. From a fundamental point of view, it is expected that changing the morphology of these NPs may induce modifications of their optical properties. To synthesize Au BPs with controlled aspect ratios a good understanding of the nucleation and growth mechanisms is needed. The goal of this work is to perform a comprehensive analysis based on an approach combining modern TEM techniques: conventional TEM imaging mode, HR imaging using both TEM and STEM HAADF modes [2] and STEM-HAADF electron tomography. This type of analysis provides reliable information regarding the morphology and the crystallographic structure of both Au seeds and Au BP and thus allows elaborating reliable hypothesis on the nucleation and growth processes of these anisotropic NPs. We present here a detailed study performed on Au NPs presenting aspect ratios of 2, 3, and 5. An icosahedral (penta-twinned decahedron) shape of Au seeds NPs presenting a 4 nm size was firstly evidenced (Fig. 1). In a second step, a detailed HRTEM analysis on Au BP allowed us to directly observe the highly stepped nature of the BP surface constituted by \{151\} lateral facets (Fig. 2). Finally, the analysis of the reconstructed volumes obtained by electron tomography showed that the bipyramidal morphology is preserve for all the studied nanoparticles (Fig. 3a). However, some differences between them can be observed regarding the shape of their tips, the symmetry of the equatorial plane and the characteristics of the steps present on the surface (Fig. 3b). Particularly, the larger the BP is, the sharper the tips and higher the surface steps are. In addition, the analysis of the transversal sections for each volume showed that the symmetry of the equatorial plane changes from a hexagonal one for high aspect ratios to a pentagonal one for low ratios.

References:

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Fig. 1: (a) HR-STEM HAADF image of a 4 nm Au seed NP; (b) Projection at 0° extracted from the tilt series used to reconstruct the volume of an area containing several Au seeds NP; (c) XY slice through the reconstructed sub-volume of an individual Au seed NP evidencing its icosahedral morphology.

Fig. 2: (a), (b) High Resolution TEM micrographs of an Au bipyramid showing the crystallographic nature of the stepped lateral facets; (c) Schematic representation illustrating the oriented assembling of Au seeds icosahedrons.

Fig. 3: (a) 3D Models of Au bipyramids with three various aspect ratios obtained by electron tomography; (b) Illustration of the presence of steps on the external surface of the BP.