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Morphological Transformations of Gold Nanorods

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Abstract – The morphology of single crystal gold nanorods has been modified through growth with either additional gold or nickel. The growth of gold nanorods can be tuned through addition of iodide ions to obtain dumbbell-like morphologies, which can be subsequently coated with silver. Transmission electron microscopy (TEM), electron diffraction techniques and scanning transmission electron microscopy coupled to X-ray energy dispersive microanalysis (STEM-XEDS) were used to characterize the shape and the crystalline structure of the initial, intermediate and final particles.

The growth of metal nanoparticles in colloidal solution has been used to obtain nanoparticles with different shapes, beyond the classical geometries predicted by Wulff construction [1]. The key issue appears to lie in the different energies between surfaces of the particles in these colloidal systems. This is why such systems can give raise to a large variety of shapes and sizes. Gold nanorods are a good example to illustrate the possibilities of tailoring nanoparticles size and shape in colloidal systems. This work illustrates the variation of shape and size from single crystal gold nanorods through overgrowth with either additional gold [2] or with other metals [3]. On the other hand it is also possible to modify the shape of gold nanorods during the synthesis step.

The overgrowth of single crystal gold nanorods usually leads to particles with a homogeneous structure, without discontinuities in the crystalline structure. Using TEM in combination with electron diffraction one can characterize the shape and the crystalline structure of the initial, intermediate and final particles. In addition, it is also possible to correlate the shape of the particles with their internal crystalline structure. In this way, we can determine the facets of the particles and to propose a growth mechanism based on surface energies. When gold nanorods are grown with nickel (Figure 1), the deposition of nickel occurs in a quasi-epitaxial mode, as demonstrated by high resolution TEM and electron diffraction. We have also been able to determine the elemental distribution, both within the core and in the shell, by using STEM-XEDS. A detailed analysis of the structure of the interface between the gold core and the nickel shell shows the presence of dislocations due to the lattice mismatch between both metals.

Another interesting example is the growth of gold nanorods in the presence of small amounts of iodide in the growth solution. The resulting nanoparticles have been found to display a dumbbell-like structure, meaning that gold salt reduction takes place preferentially at the tips (Figure 2). These particles show interesting {111} twinning planes only at the tips. Interestingly, when such gold dumbbells are coated with silver, STEM-XEDS elemental mapping confirmed epitaxial growth of silver, which however takes place preferentially at the middle, flatter part of the rods. HRTEM images demonstrate that the epitaxial growth of silver maintains the twinning planes present in the initial dumbbells.

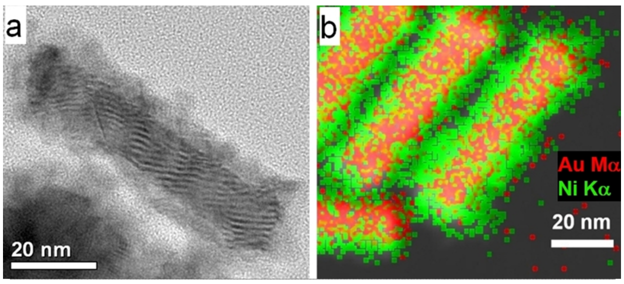

Figure 1: Nickel coated gold nanorods. **a)** Presence of Moiré fringes in Au core. **b)** STEM-XEDS elemental mapping.

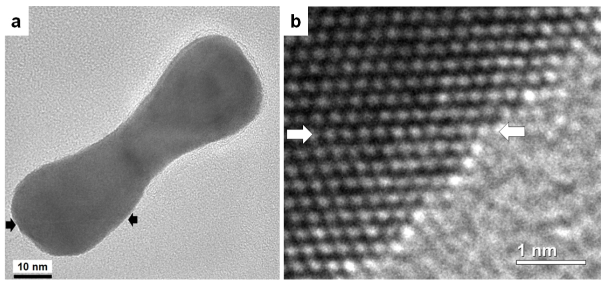

Figure 2: a) TEM image of a twinned dumbbell-like gold nanorod. **b)** HRTEM image of a twinning plane at the tip.

References

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