

Tuning the Gold Nanorods Morphology

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The synthesis of metal nanoparticles with precise morphology (shape and size) control is a key stage in realizing the fabrication of functional materials at the nanoscale. This is due to the strong correlation between the morphology and the chemical, physical, optical, electronic and catalytic properties of the nanoparticles. In particular, gold and silver are widely studied metals due to potential multiple applications arising from their unique optical properties, in fields such as surface-enhanced Raman scattering (SERS), plasmonics and biosensing. The important role of shape and size on the properties of metal nanoparticles makes it indispensable to understand the processes and mechanisms involved in their growth so as to design synthetic strategies that allow shape tuning. Many of proposed methods are based on the growth of preformed seeds to avoid uncontrolled nucleation and thereby direct particle growth, the seeds often also acting as catalysis to favour reduction of the metal salt on their surface. Therefore, understanding the growth mechanism over a particular type of seed and subsequent shape-guiding process is crucial to fabricate particles with a specific shape and crystalline structure. Anisotropic particle growth is directly related to the differences in growth rate of different crystallographic facets while in general, metals tend to grow into thermodynamically stable particles.

An interesting route toward the production of metal nanoparticles with tailored morphology is the use of preformed gold nanocrystals as templates, on which other metals could be grown. Herein, we describe three different growth processes where gold nanorods, single crystal and pentatwinned, act as seeds. Thus, single crystal Au nanorods were grown with Au and Ag and the pentatwinned ones with Au. The overgrowth of gold nanorods, single crystal and pentatwinned, with gold, is carried out in organic media (N,N-dimethylformamide, DMF) and in the presence of poly(vinylpyrrolidone), PVP. Nevertheless the core-shell Au@Ag nanoparticles are obtained through the use of hydroquinone as reducing agent in aqueous medium.

While the overgrowth of the single crystal gold nanorods, independently of the metal, leads to particles with octahedral geometry, the pentatwinned gold nanorods give rise to particles with quasi-decahedral geometry. Furthermore, particles with intermediate shapes between the original Au nanorods and the final octahedral or quasi-decahedral particles can be obtained by simply tuning the [metal salt] to [seeds] ratio. As a result of the particle growth and concomitant decreased anisotropy, a progressive blue-shift of the surface plasmon resonance bands of the nanoparticles which allows a remarkable control over the optical response spanning the whole visible range and into the near IR. In all the cases, the growth mechanism was elucidated through a combination of different techniques, including transmission and scanning electron microscopy, high resolution TEM and selected area electron diffraction. Thus, from the thorough structural analysis of all the intermediate morphologies obtained, it can be concluded that gradual morphology changes are related, as previously commented, with the preferential growth of higher energy crystallographic facets.

References

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Figures

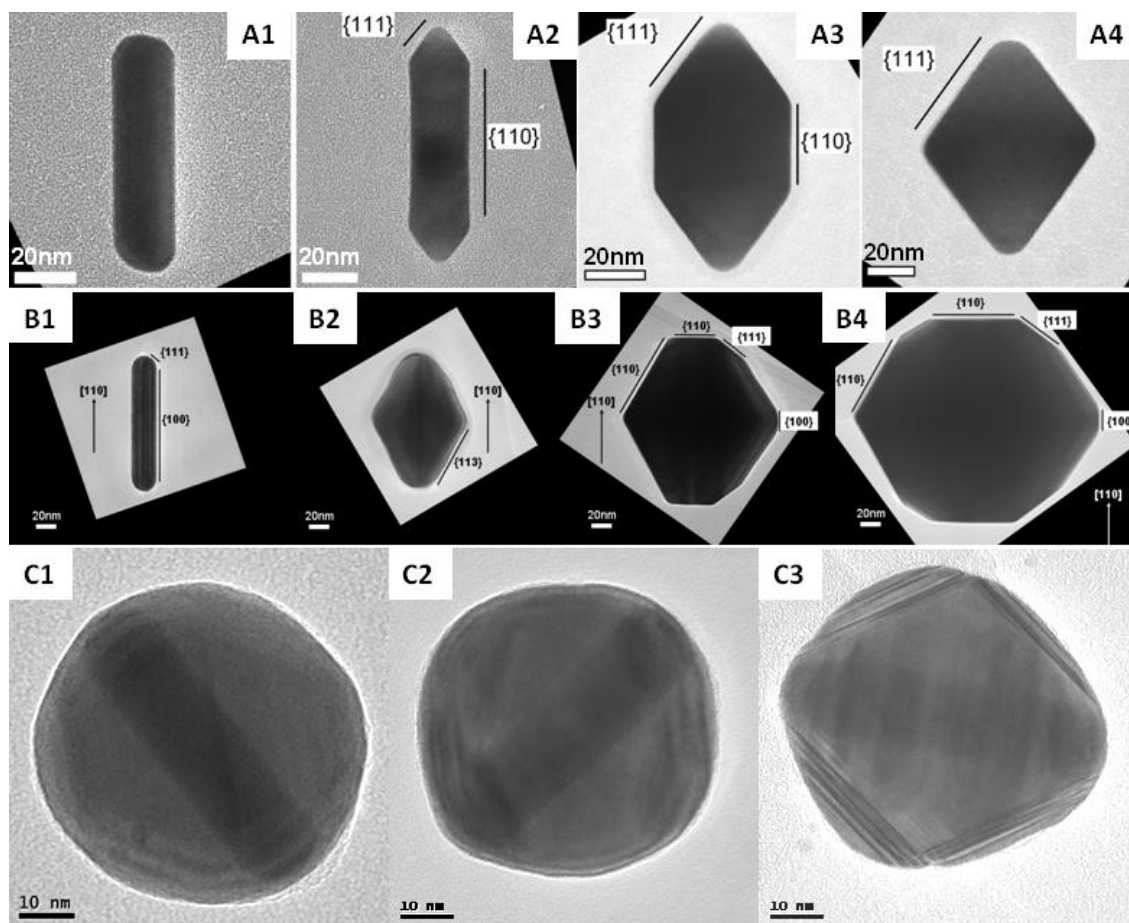


Figure 1. A and B) Representative TEM images of the overgrowth of single crystal (A1-A4) or pentatwinned (B1-B4) gold nanorods with Au through the reduction of gold salt with DMF in the presence of PVP. In these sequences of images the evolution from cylindrical shape (A1 and B1) to octahedral shape (A4) or quasi-decahedral shape (B4) can be observed. C) TEM images (C1-C3) of the very same Au nanorod@Ag rounded octahedron oriented in different zone axes. The particles were produced through the reduction of a silver salt with hydroquinone on the single crystal Au nanorods surface.