Shape-controlled synthesis of plasmonic nanorattles via galvanic replacement-seeded growth method.

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Control over the morphology of metal nanoparticles (NPs) in combination with mechanic understanding is a crucial step for the development of modern nanoscience and nanotechnology. Nanoscale galvanic replacement reaction has been widely used as a convenient approach for the transformation of solid NPs into corresponding porous/hollow NPs, in which pore size and chemical composition controls their optical and catalytic properties. Galvanic replacement reaction on Au@Ag core-shell NPs lead to the formation of nanorattles with complex chemical composition, while preserve the morphology of sacrificial template. The internal electromagnetic hot spots of plasmonic nanorattles make them ideal for plasmon-enhanced applications. However, the three-dimensional (3D) morphological and chemical architectural transformations associated with the formation process of nanorattles have not been well understood by means of conventional electron microscopy.

Here we demonstrate an unconventional shape transformation of Au@Ag core-shell nanorods (NRs) and nanocubes (NCs) into octahedral nanorattles comprised of Au NRs and Au nano-octahedra as cores respectively via galvanic replacement reaction at room temperature. [1] We used state-of-the-art quantitative EDX tomography technique for simultaneous elucidation of 3D morphological and chemical architectural transformations involved during the transformation. The presence of reducing agent lead to such unconventional mechanistic path, in which galvanic replacement dominates in the initial stages of the reaction, while overgrowth suppress the dealloying process in the later stages of the reaction.

This work will help to understand the processes involved in galvanic replacement combined with co-reduction. In principle, the analytical approach we presented here can be applied to a wide range of complex hetero nanostructures for clear understanding of unknown nanoscale growth process as well as their precise chemical compositions, which will help to further advance the field of shape-controlled synthesis.

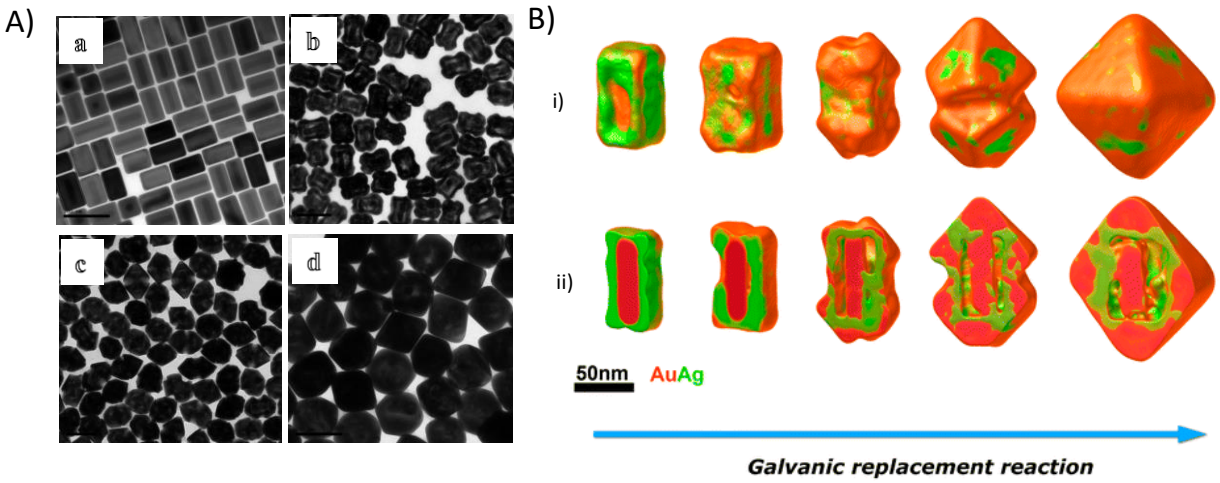

Fig. 1 A) TEM images of Au@Ag core-shell NRs before (a) and after (b–d) galvanic replacement with increasing amounts of 0.5 mM $HAuCl_4$. B) Quantitative XEDS tomography imaging. Transformation of Au@Ag NRs into octahedral nanorattles with addition of increasing amounts of $HAuCl_4$ in consecutive reactions (stages i-v). (i) 3D reconstructions showing Au (orange) and Ag (green) at each transformation. (ii) Inner view of the 3D reconstructions

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