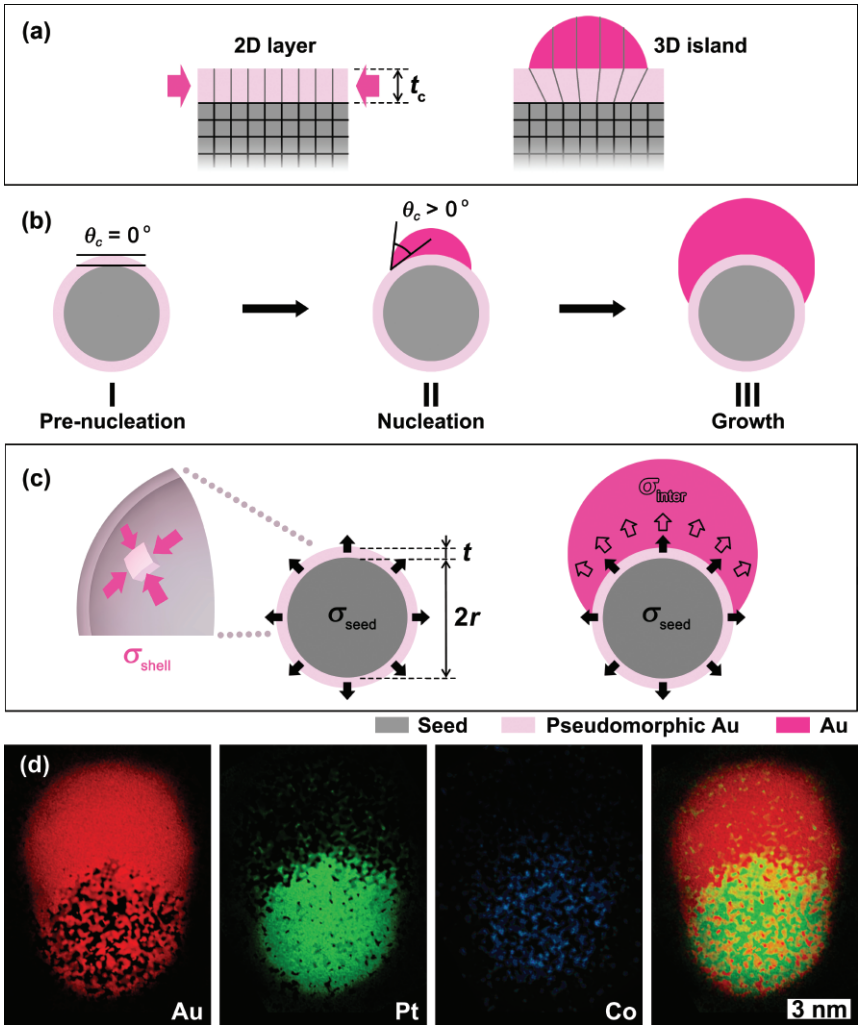
Lattice Strain and Strain Relaxation Produce Nano "Dumbbells"

Nanoparticles come in many different shapes and sizes, and their geometry is often as influential as their chemical makeup in determining behavior, from catalytic or energy storage properties to potential as a semiconductor component. The physical and chemical properties at the nanoscale can be varied by combining different materials to form heterostructured nanoparticles that can be synthesized in many different shapes, such as core/shell combination, nano-dumbbells, nano-rods, and terapods. The growing importance of heterostructured nanoparticles in various applications demands a much better understanding of how the structure appears and evolves during synthesis, an understanding that cannot be gained by studies of static structures alone, but require the kinds of real-time studies made possible by the state-of-the-art x-ray analysis facilities available at the APS. Utilizing the APS, a team of researchers followed the nucleation and growth kinetics of a gold (Au) overlayer on platinum (Pt) and Pt-alloy seeds and found that the lattice strain and subsequent strain relaxation of the seed and overlayer control the dumbbell shape of the resulting material. These nano-dumbbells could have a broad range of applications as catalysts.



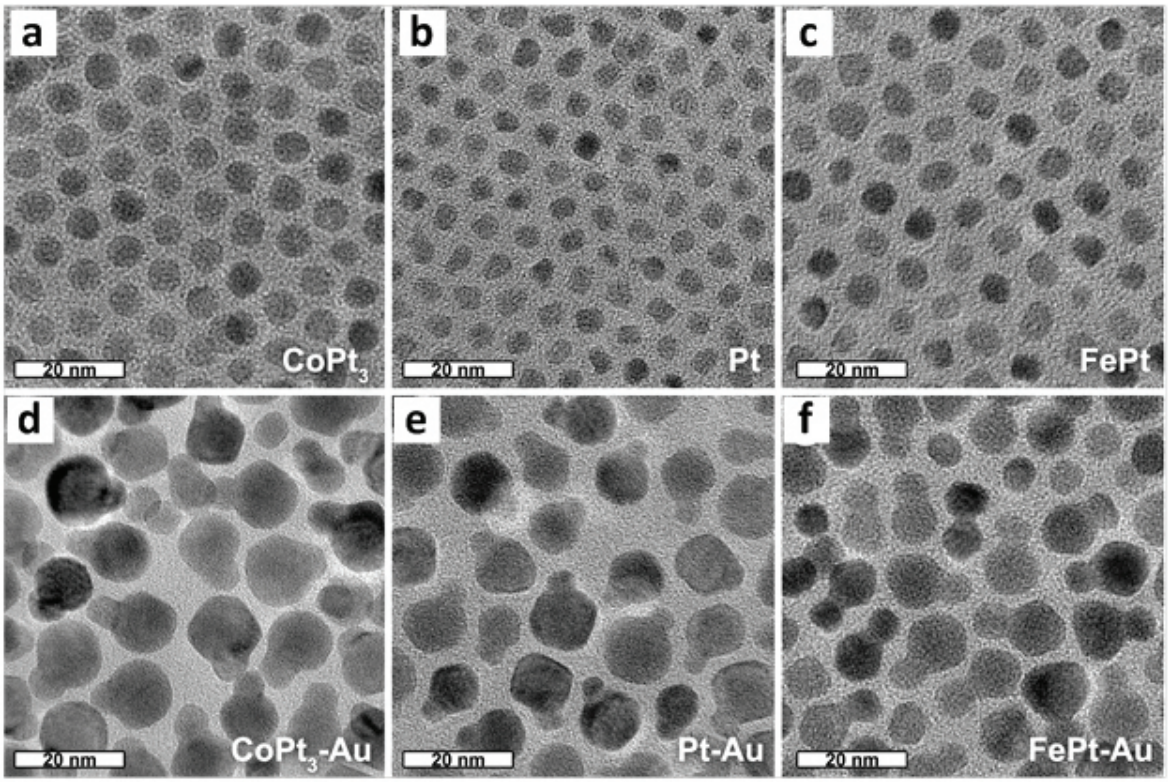


Fig. 2. TEM images of the seeds and nanodumbbells. (a)-(c): Seed NPs with the mean size of 6.2 nm ($CoPt_3$), 4.8 nm (Pt), and 6.2 nm (FePt). (d)-(f): Nanodumbbells synthesized by using the seeds shown in panels (a)-(c).

The synthetic reaction that occurs during the formation of an overgrowth layer on a seed of a different material is much more complicated than that of a single-component nanoparticle. Because the seed and overgrowth have different crystal structures, the heterogeneous nanoparticles can have a lattice mismatch (where the spacing between atoms in the two materials do not align) and consequent strain.

< Fig. 1. Core/shell to dumbbell transition of the seed/Au NP during synthesis. (a) Lattice structure of the overgrowth phase in the two-dimensional and three-dimensional mode of the Stranski–Krastanov model. (b) Morphological evolution of the seed/Au heterostructure during the pre-nucleation, nucleation and growth periods. (c) Schematic illustration of the stresses within core/shell and dumbbell NPs. (d) STEM-energy-dispersive x-ray spectroscopy mapping of a $CoPt_3$/Au dumbbell. Elemental mapping was performed by acquiring EDX spectrum images including the AuM series (red), PtM series (green) and Co L series (blue) x-rays. The right-most one is the layered image of those mappings. The electron probe size is approximately 100 pm, and the acquisition time was 287 sec. Figures from S.G. Kwon et al., Nat Mater. **14,** 215 (February 2015).

While the team of researchers from Argonne, the University of Illinois at Chicago, the Illinois Institute of Technology, and The University of Chicago studied the reaction process that occurs during synthesis of heterostructured nanocomposites, they simultaneously performed small- and wide-angle x-ray scattering measurements in real time at XSD beamline 12-ID-B of the APS under "realistic" conditions. They used the same reaction volume and stirring and heating procedures as those typically used to synthesize nanoparticles. This allowed them to track the evolution of the size and crystal structure of the nanoparticles over time at sub-Å resolution. For nanoparticle characterization, the team performed x-ray diffraction measurements at the GSECARS 13-ID-C,D beamline at the APS, and extended x-ray fine structure measurements at the MR-CAT 10-ID-B beamline, also at the APS. Separately performed at the Argonne Center for Nanoscale Materials and the University of Illinois at Chicago were transmission electron microscopy (TEM, Fig. 2) and scanning transmission electron microscopy (STEM) of the nanoparticles.

The analytical results indicated three stages in the formation of a dumbbell structure: pre-nucleation, nucleation, and growth (Fig. 1). In the pre-nucleation period (0-20 min.) the Au covers the Pt or Pt-alloy seed's surface uniformly and forms a core/shell structure. During nucleation (20 min-140 min), the huge stress created by the growth of the Au shell deforms the crystal lattice of the core/shell. The strain energy resulting from this deformation substantially increases the free energy of the core/shell and, thus, its chemical potential. Transition from core/shell to dumbbell structures results from the subsequent strain relaxation of the shell. During the growth period (140 min-240 min), no further nucleation of dumbbells occurs, and the dumbbells already nucleated grow from 97 Å up to 120 Å. The STEM analysis revealed that the relief of the lattice strain in the shell takes place through the slip of Au atomic layers at the core/shell interface.

This study represents the first observation of the kinetics of this heterogeneous nucleation process in real time under realistic conditions. The know-

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ledge gained will advance the engineering of multicomponent nanostructures and, in particular, will allow the development of a time-resolved synthesis mechanism that can be used to control the structure-property functions in these nanostructures. *— Joseph E. Harmon*

See: Soon Gu Kwon[1], Galyna Krylova[1‡], Patrick J. Phillips[2], Robert F. Klie[2], Soma Chattopadhyay[3], Tomohiro Shibata[3], Emilio E. Bunel[1], Yuzi Liu[1], Vitali B. Prakapenka[4], Byeongdu Lee[1*], and Elena V. Shevchenko[1**], "Heterogeneous nucleation and shape transformation of multicomponent metallic nanostructures," Nat. Mater. **14**, 215 (February 2015).
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10-ID-B • MR-CAT • Materials science, environmental science, chemistry • X-ray absorption fine structure, time-resolved x-ray absorption fine structure, micro x-ray absorption fine structure, microfluorescence (hard x-ray) • 4.3-27 keV, 4.3-32 keV, 15-90 keV • On-site • Accepting general users •

12-ID-B • XSD • Chemistry, materials science, life sciences, polymer science, physics • Small-angle x-ray scattering, grazing incidence small-angle scattering, wide-angle x-ray scattering, grazing incidence diffraction • 7.9-14 keV • On-site • Accepting general users •

13-ID-C,D • GSECARS • Geoscience, environmental science • Microdiffraction, x-ray absorption fine structure, microfluorescence (hard x-ray), high-pressure diamond anvil cell, high-pressure multi-anvil press • 4-45 keV • On-site • Accepting general users •