Controlled Synthesis and Characterization of Bimetallic Nanocrystals

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Bimetallic nanocrystals synthesized by heterogeneous seeded growth have the advantage of coupling the optical or catalytic properties of one metal with those of another metal and form multifunctional nanocrystals. Recently, we have studied various bimetallic nanostructures consisting of noble metals such as Au, Rh, Pd, and Pt by this approach, including polyhedral nanocrystals with core-shell structures of Pd-Au, nanodendrites of Pd-Rh consisting of branched arms made of one metal supported on a core of another metal, and Pd-Pt bimetallic nanocrystals with a Concave Structure. High resolution transmission electron microscopy (HRTEM), High angle angular dark field (HAADF) - scanning transmission electron microscopy (STEM) with electron energy loss spectroscopy (EELS) or energy dispersive x-ray spectroscopy (EDS) have been proven to be an unique and effective site-specific analysis tool at atomic and nano scale to study the crystal structure and chemistry of nanocrystals. We report here the structure and chemistry of bimetallic nanocrystals synthesized by controlled heterogeneous seeded growth and characterized by HRTEM, HAADF-STEM/EELS-EDS techniques.

Figure 1 demonstrates two different types of bimetallic nanostructures, namely, core-shell nanocrystals and dimers, can be selectively produced via controlled overgrowth of Au on the well-defined surface of the cubic Pd seeds by selection of the reducing agent for the synthesis. Using this approach, we were able to not only control the morphology of the Pd-Au bimetallic nanostructures but also tune their localized surface plasmon resonance (LSPR) peaks in the visible region.

Figure 2 shows Pd–Rh bimetallic nanodendrites consisting of Rh branches anchored to a Pd nanocrystal core. Palladium nanocrystals with various shapes, including truncated octahedron, cube, octahedron, and thin plate, have all been successfully employed as seeds to grow Rh branches. The degree of Rh branching could be controlled by varying the concentration of Na₃RhCl₆ involved in a synthesis. Electron microscopy analysis revealed that growth of Rh branches proceeded via attachment of small Rh particles that had been formed via homogeneous nucleation in solution.

Figure 3 shows Pd-Pt nanocrystals with a concave structure on the surface. Nanocrystals with a concave structure have physical/chemical properties different from those enclosed by a flat or convex surface; which have many potential applications in catalysis, optical sensing, and localized surface plasmon resonance (LSPR).

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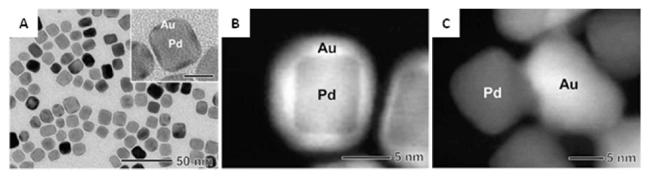


Figure 1. (A) TEM images of Pd-Au core-shell nanocrystals at initial stage. (B) HAADF-STEM image of a Pd-Au core-shell nanocrystal. (C) HAADF-STEM image of a Pd-Au dimer consisting of a Pd nanocube and a Au nanoparticle.

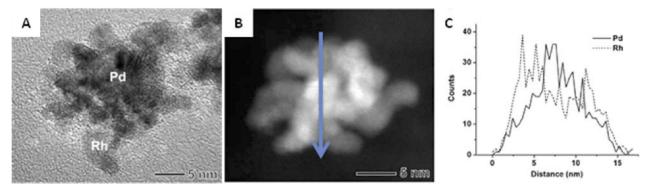


Fig. 2. (A) HRTEM and (B) HAADF-STEM image of a single Pd–Rh nanodendrite, (C) Chemical line profiles of Pd and Ph on the Pd–Rh nanodendrite recorded along the line shown in the HAADF-STEM image.

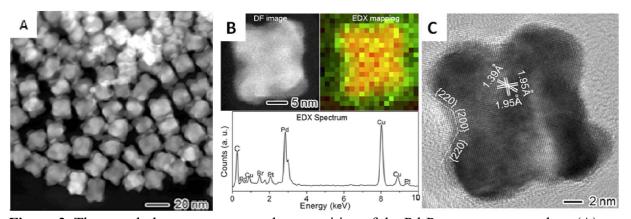


Figure 3. The morphology, structure, and composition of the Pd-Pt concave nanocubes. (A) HADDF-STEM image, (B) HADDF-STEM of one nanocrystal and EDX mapping/analysis (yellow and green represent Pd and Pt, respectively), and (C) HRTEM image of one concave nanocrystal viewing alone [001] orientation.