

# Bimetallic Nanoparticles: Kinetic Control Matters\*\*

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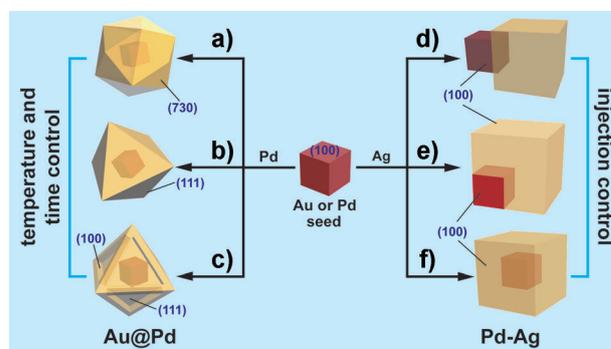
bimetallic nanoparticles · heterostructures · kinetic control · seed-mediated growth

From plasmonics to catalysis, bimetallic nanoparticles already play an important role in applications.<sup>[1]</sup> For instance, when compared to monometallic particles, bimetallic systems often exhibit greatly improved catalytic activity for many chemical reactions, even at low temperatures.<sup>[2]</sup> The observed catalytic enhancement of hybrid nanoparticles could be directly attributable to electronic coupling between the two different metals together with geometric effects caused by the different lattice constants.<sup>[3]</sup>

Bimetallic nanoparticles can be broadly classified into three types of systems. The first class is bimetallic alloys characterized by the formation of a mixture or metallic solid solution comprising two different components.<sup>[4]</sup> As a benefit of high surface energy in small-sized particles, immiscible metals at bulk state can be alloyed at the surface. The second class includes bimetallic dimers in form of supported structures with asymmetric material compositions.<sup>[5]</sup> A far more complex class of bimetallic nanoparticles concerns core-shell nanostructures. In such cases of nanostructures, the chemical reactivity and physical properties of the nanoparticles can be precisely tailored by tuning shell composition, thickness and surface structure.<sup>[6]</sup>

As more applications are envisioned, methods for preparing bimetallic nanoparticles with controlled feature size, shape, and structure are gaining significant attention. Among many synthetic methods, seed-mediated growth has been widely used to synthesize bimetallic nanoparticles.<sup>[7]</sup> When designing the synthesis, the level of the lattice mismatch between the seed and the secondary material has to be taken into consideration. If the lattice mismatch is small (< 5%), heterogeneous nucleation and growth of core-shell bimetallic nanoparticles typically occur as heterogeneous nucleation is generally more favorable than homogeneous nucleation as a result of lowered free energy barrier.<sup>[8]</sup> However, if the mismatch is considerably large (> 14%), homogeneous nucleation of the second component will compete with heterogeneous nucleation.<sup>[9]</sup> Thus, a mixture of reaction products

would be formed. On the basis of these principles, Huang and colleagues have demonstrated the synthesis of Au-Pd core-shell nanoparticles with unusual octahedral and tetrahedral morphologies using Au nanocubes as the seeds (Figure 1 a–c).<sup>[10]</sup> Notably, the symmetry of bimetallic core-shell nanoparticles can even be controlled by utilizing an eccentric polymer coating.<sup>[11]</sup>



**Figure 1.** Representative seed-mediated strategies for synthesizing bimetallic nanoparticles. a–c) Au-Pd core-shell nanoparticles with different morphologies prepared by Huang and co-workers<sup>[10]</sup> through control of reaction temperature and time. d–f) Pd-Ag bimetallic nanoparticles with tunable structures developed by Xia and co-workers<sup>[14]</sup> through control of precursor injection rate.

A formidable synthetic challenge lies in the controlled growth of a second component at selective areas of a nanoparticle seed with only one type of crystallographic facets. One innovation that is rapidly gaining momentum is associated with applying kinetic control over the reaction. For example, by controlling reduction rate of a palladium precursor, Lee et al. have shown that Pd nanocrystals can be preferentially grown at corners of a cube-shaped Pt nanoparticle rather than on its six equivalent (100) planes.<sup>[12]</sup> Another intriguing example was reported by Xia and co-workers, who utilized two different reducing reagents to control the synthesis of Pd-Au bimetallic nanocrystals using Pd nanoparticles with cubic morphology as seeds.<sup>[13]</sup> Specifically, when a strong reducing reagent (L-ascorbic acid) is used, core-shell nanostructures are formed as Au precursors tend to nucleate and grow indiscriminately on six low-index (100) planes of the Pd nanocubes. By comparison, in the presence of a weak reducing reagent (citric acid), Pd-Au dimers are synthesized as predominant products.

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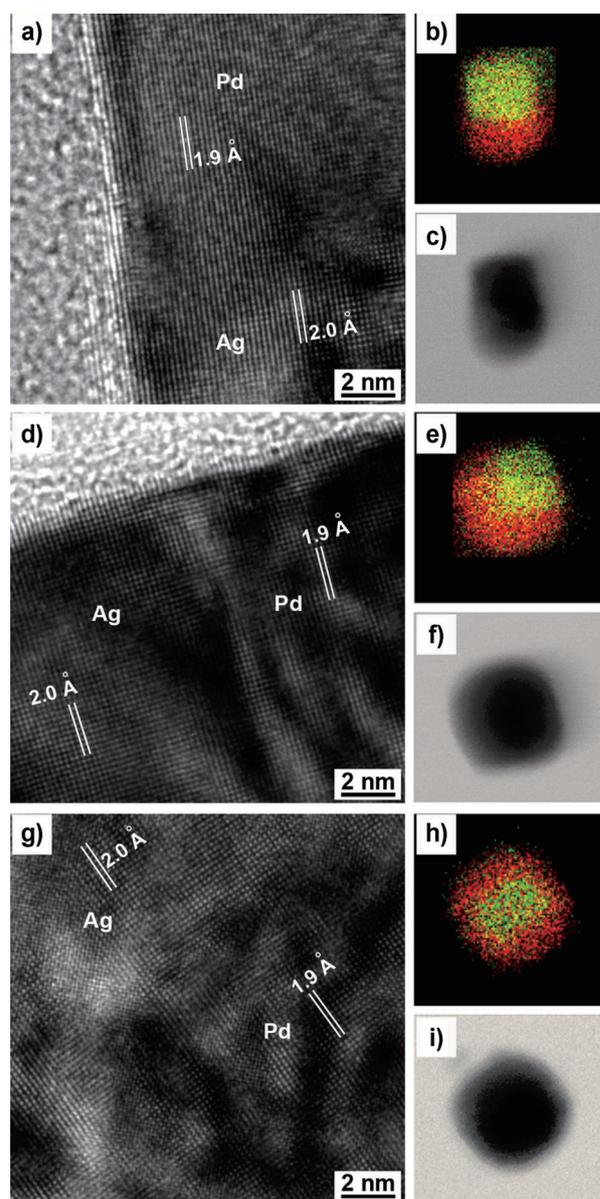
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In their recent work, Xia and his co-workers have taken one step further and reported the synthesis of bimetallic nanoparticles with remarkable control over specific surface compositions and structures.<sup>[14]</sup> They found that an alternative, through use of an appropriate syringe pump to precisely controlling the concentration of metal precursors, is even more effective than using different reducing agents. As a proof of principle, they used monodispersed Pd nanocubes about 18 nm in size as seeds. Depending on the injection rate of Ag precursor, three types of resulting nanostructures grown on the cube-shaped Pd nanoparticle seed could be readily prepared (Figure 1d–f). When injecting the Ag precursor at a slow pace, formation of Pd–Ag dimers is observed. The authors hypothesize that once Ag metal nucleates on one of six equivalent facets of Pd nanocubes, it is preferential for additional Ag to adhere and grow on that Ag seed. This proposal generally agrees with their observation of an increase in Ag particle size with extended reaction time. In contrast, when the injection rate is rapid, indiscriminate nucleation and growth of Ag on all facets of the Pd nanocube are dominated by high precursor concentration. As a result, Pd–Ag core–shell nanoparticles are obtained. Perhaps surprisingly, a rather unusual form of epitaxial growth occurs at a moderate precursor injection rate, resulting in eccentric bimetallic nanoparticles with Ag overlays covering only three adjacent facets of the Pd nanocube.

To confirm the three types of distinct structures obtained by varying precursor injection rate, the authors undertook high-resolution transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDX), and scanning transmission electron microscopy (STEM). As shown in Figure 2, the results of elemental mapping by EDX clearly reveal the exquisite control over the growth of Pd–Ag bimetallic nanoparticles using their technique. Furthermore, they measured localized surface plasmon resonance spectra of these different structures. Indeed, the data are well correlated with the prediction from theoretical calculation by the discrete dipole approximation method. However, it remains unclear whether the formation of an eccentric Pd–Ag structure is due to the kinetic-dominant reaction condition, or to the occurring of Ag atom migration, or to both. Nonetheless, the precise control of Ag atoms at a critical concentration seems to be essential. Subtle concentration changes could dramatically affect the crystal growth.

Xia and colleagues' findings clearly cannot be expected to exist in bimetallic systems with largely different lattice constants, but such discoveries of selectively depositing noble metals on one or more planes of a catalytic nanoparticle seed always represent giant steps in the rational design of bimetallic nanomaterials with unprecedented catalytic and optical properties. This is especially true for detailed investigation of the dependence of nanoparticle catalysts on their microscopic surface structure and composition, where bimetallic nanoparticles are well suited for developing simple model systems. Apart from providing insight into design of novel bimetallic systems, these findings also pose a daunting challenge. Given the notion that localized surface plasmon resonances can boost upconversion luminescence from lanthanide-doped nanocrystals,<sup>[15]</sup> will it be possible to site-



**Figure 2.** Pd–Ag bimetallic nanoparticles seen through an electron microscope. a, d, g) High-resolution TEM images of the as-synthesized nanoparticles. b, e, h) Elemental mapping of the nanoparticles by EDX. Pd green, Ag orange. c, f, i) Corresponding bright-field STEM images of the nanoparticles.<sup>[14]</sup>

specifically grow metal layers on the upconversion nanocrystals despite the constraint of large lattice mismatches? If this challenge can be met, a significant emission enhancement might be achieved to enable broader practical applications of upconversion nanomaterials.<sup>[16]</sup>

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