Nanoparticles

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Mixing an Aqueous Suspension of Pd or Au Nanocrystals with a Less Polar Solvent Can Cause Changes to Size, Morphology, or Both**

*Byungkwon Lim, Taekyung Yu, Jinho Park, Yiqun Zheng, and Younan Xia**

Controlling the size and morphology of nanocrystals has attracted much attention in recent years because of their direct correlations with electronic and optical properties.[1] Understanding the mechanistic details involved in both nucleation and growth is a prerequisite for the synthesis of nanocrystals with desired sizes and morphologies, and thus properties. Metal nanocrystals are typically synthesized in an aqueous solution or an organic solvent. A common practice for collecting the product is to precipitate the nanocrystals with the addition of a different solvent such as acetone or hexane. It is generally assumed that the nanocrystals should retain their size and morphology during this solvent-assisted precipitation process. To our knowledge, however, this bold assumption has never been validated to any extent through careful examinations. In fact, when nanocrystals are exposed to different solvents, there might be a change to colloidal stability and such a change can lead to unexpected variations in terms of both size and morphology.

Here we demonstrate, for the first time, that nanocrystals of noble metals (at least for Pd and Au) can change size and morphology in response to variation in the solvent medium. Notably, at room temperature, Pd and Au nanocrystals with a nearly spherical profile and sizes less than 5 nm exhibited a drastic change in size and/or morphology when their as-prepared aqueous suspensions were mixed with a different solvent such as acetone or tetrahydrofuran (THF). Unlike an aging process,[2] the transformation observed in this study occurred within a relatively short period of time, typically less than 30 min. Our results not only unveil the sensitivity of nanocrystals toward the surrounding environment, but also provide an alternative, post-synthesis route to control the size and morphology of metal nanocrystals.

In a typical experiment, aliquots of a suspension of nanocrystals were dropped directly onto carbon-coated copper grids, dried at room temperature, and then analyzed using transmission electron microscopy (TEM). The Pd nanocrystals were prepared in an aqueous solution by reducing Na_2PdCl_4 with poly(vinyl pyrrolidone) (PVP) in the presence of bromide ions.[3] The color of the reaction solution containing PVP and bromide ions immediately turned into brown upon the addition of an aqueous Na_2PdCl_4 solution due to the formation of $PdBr_4^{2-}$ species. The reaction solution was then heated at 80 °C in air under magnetic stirring for 3 h, and finally cooled down to room temperature. The brown color (Figure 1 a) associated with the as-prepared, aqueous suspension of Pd nanocrystals can be attributed to the remaining $PdBr_4^{2-}$ species. Figure 2 a shows typical TEM and high-resolution TEM (HRTEM) images of the as-synthesized Pd nanocrystals, demonstrating the formation of Pd nanocrystals with relatively small sizes and a

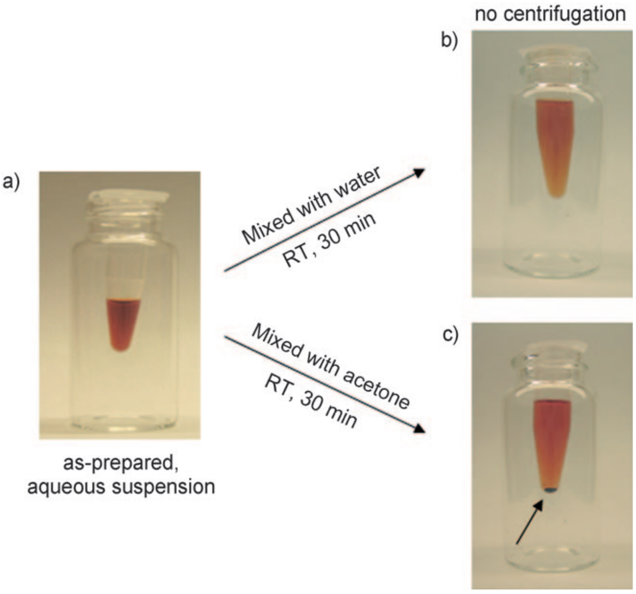

Figure 1. a) Photograph of the as-prepared aqueous suspension of Pd nanocrystals. b,c) Photograph showing samples obtained by mixing the as-prepared suspension of Pd nanocrystals with deionized water (b) and acetone (c) at room temperature. The volume ratio of the as-prepared suspension of Pd nanocrystal to the added solvent was 1:3, and the photograph was taken after mixing for 30 min.

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[*] Dr. B. Lim,[++] [+] Dr. T. Yu,[+] Prof. Y. Xia
Department of Biomedical Engineering, Washington University
Saint Louis, MO 63130 (USA)
E-mail: xia@biomed.wustl.edu
J. Park
Department of Energy, Environmental and Chemical Engineering
Washington University, Saint Louis, MO 63130 (USA)
Y. Zheng
Department of Chemistry, Washington University
Saint Louis, MO 63130 (USA)
[++] Current address: School of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon 440-746 (Korea)

[+] These authors contributed equally to this work.

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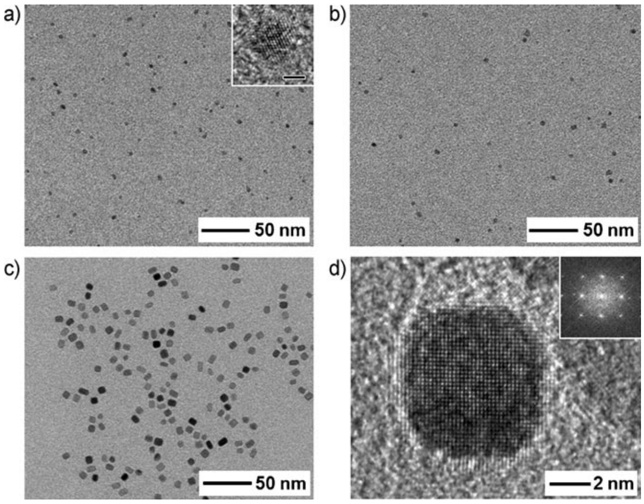

Figure 2. a) TEM image of the as-prepared Pd nanocrystals. The inset shows an HRTEM image of a Pd nanocrystal (scale bar of inset is 2 nm). b) TEM image of Pd nanocrystals obtained by mixing the as-prepared aqueous suspension of Pd nanocrystals with deionized water (volume ratio 1:3) at room temperature after 30 min. c) TEM and d) HRTEM images of Pd nanocrystals obtained by mixing the as-prepared aqueous suspension of Pd nanocrystals with acetone (volume ratio 1:3) at room temperature for 30 min. In (d), the inset shows the corresponding FT pattern.

nearly spherical shape (also see Figure S1 in the Supporting Information for nanocrystals sampled from different portions of the suspension). The Pd nanocrystals were well dispersed on the TEM grid, without forming aggregates. Dynamic light scattering (DLS) analysis indicated that the as-prepared Pd nanocrystals had an average diameter of (3.8 ± 1.1) nm (Figure S2), in agreement with the TEM results.

We did not observe any change to the Pd nanocrystals when the as-prepared aqueous suspension was mixed with deionized water and stored in a centrifuge tube at room temperature for 30 min (Figures 1b and 2b). In contrast, we observed spontaneous precipitation in the sample when the as-prepared aqueous suspension was mixed with acetone (Figure 1c). The precipitates could be re-dispersed by vortexing. An aliquot of the sample was then transferred onto a TEM grid, dried at room temperature, and then analyzed by TEM. Surprisingly, the sample mainly contained Pd nanocrystals with a cubic shape, albeit with some truncations at corners (Figure 2c). These cubic nanocrystals were 5–10 nm in edge length, and some of them had aspect ratios slightly larger than one and thus appeared like short bars. The HRTEM image and corresponding Fourier-transform (FT) pattern (Figure 2d) of a single Pd nanocube revealed that it was a piece of single crystal with its main faces being enclosed by {100} facets. Both the TEM and HRTEM results confirmed that the initial sub-5 nm Pd nanocrystals with a spherical shape had essentially disappeared from the sample. It is worth pointing out that this drastic change in size and morphology for Pd nanocrystals was consistent throughout all of the repeated (> 10 times) experiments.

We then monitored the changes in size and morphology by analyzing the samples obtained by mixing the as-prepared suspension of Pd nanocrystals with acetone for different periods of time. At $t = 30$ s, the Pd nanocrystals still maintained their spherical shape and individuality, as shown in Figure 3a. At $t = 2$ min (Figure 3b), however, we observed a large number of peanut-shaped or elongated nanocrystals. The HRTEM image taken from a peanut-shaped nanocrystal clearly shows the presence of a neck between adjacent particles (Figure 4a), indicating that this nanocrystal was most likely formed through particle coalescence (or attachment) rather than atomic addition. In the HRTEM image, the coherence of lattice planes across the attachment interface is a manifestation of oriented attachment,[4] albeit we also found examples of random aggregates (Figure 4b). For the sample taken at $t = 3$ min, the Pd nanocrystals started to take a cubic

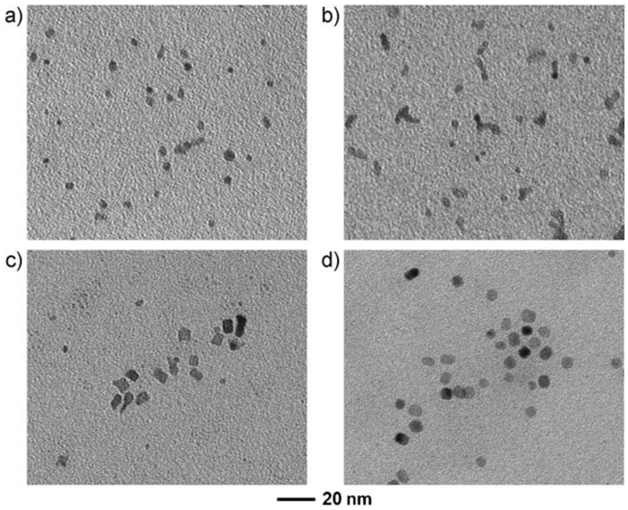

Figure 3. TEM images of Pd samples obtained after the as-prepared aqueous suspension of Pd nanocrystals had been mixed with acetone (volume ratio 1:3) at room temperature for: a) 30 s, b) 2 min, c) 3 min, and d) 5 min.

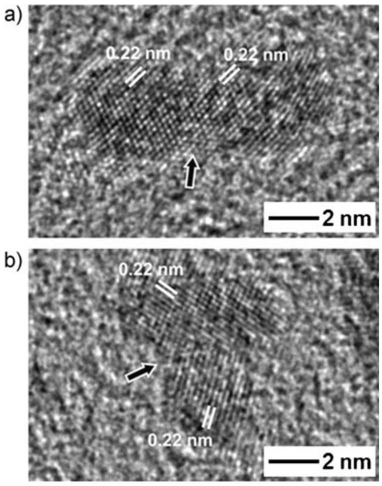

Figure 4. HRTEM images of two typical types of nanocrystals contained in the sample shown in Figure 3b. The arrows indicate the interfaces for attachment.

shape and most of them had single or multiple bump(s) on the surface (Figure 3c). In the next 2 min, the surface of the Pd nanocrystals was smoothened (Figure 3d). These observations suggest that the morphological transformation occurred through particle coalescence, followed by a reshaping process involving migration of surface atoms.

We suggest that the particle coalescence observed in this study was largely caused by the abrupt reduction in colloidal stability for the small Pd nanocrystals upon the addition of acetone. According to the Derjaguin, Landau, Verwey, and Overbeek (DLVO) theory, the stability of a colloidal system is determined by the sum of attractive and repulsive forces between the particles. The repulsive forces can arise from electrostatic charges and/or adsorbed polymers on the surfaces of particles, as well as solvation due to the surrounding solvent molecules. The result is an energy barrier to prevent the particles from approaching one another close enough to adhere and fuse together. We could exclude the role of partial removal of PVP and/or bromide ions from the surface of Pd nanocrystals due to dilution because no change in size or morphology was observed when the as-prepared aqueous suspension was diluted with water. As a polar protic solvent, water solvates negatively charged particles strongly by hydrogen bonding, whereas acetone is an aprotic solvent and has a much lower polarity than water (the dielectric constants of water and acetone are 80.1 and 21.4 at 20 °C, respectively).[5] Upon the addition of acetone, water molecules in the solvation shell will be partially replaced by acetone molecules because of the miscibility of these two solvents. Since the Pd nanocrystals had a negatively charged surface due to adsorption of bromide ions (the zeta potential value of the as-synthesized Pd nanocrystals was −14.5 mV), they were poorly solvated by acetone molecules due to their low polarility, leading to a reduction in solvation strength. The resultant reduction in repulsive forces between particles makes them more prone to aggregation as a result of particle collisions driven by Brownian motion. We have also performed similar experiments with the as-prepared aqueous suspension of Pd nanocrystals by replacing acetone with THF or dimethyl sulfoxide (DMSO). These two solvents have dielectric constants of 7.5 and 46.7 at 20 °C, respectively. In these two cases, similar changes in size and morphology were observed for the Pd nanocrystals upon mixing with THF, but not with DMSO (Figure S3). These observations support our argument that the low polarity of a solvent added to an aqueous suspension of Pd nanocrystals plays a pivotal role in reducing the colloidal stability and thus triggering particle coalescence.

The coalesced particles can rapidly change their shape by migration of surface atoms in an effort to minimize the total surface free energy, as has been demonstrated in the coalescence of Pt nanocrystals.[6] In general, the atoms on the convex region of a surface have higher chemical potentials than those on the concave region. As such, there is migration of atoms from bumps to the neck region, resulting in surface smoothening and morphological evolution.[6,7] For randomly oriented aggregates, reshaping may occur along with recrystallization. The relaxation of the stress caused by misorientation or twinning at the attachment interface provides a driving force for recrystallization.[8] During the reshaping process, evolution of Pd nanocrystals into a cubic morphology rather than a truncated octahedron with a lower surface-to-volume ratio suggests that the bromide ions play an important role in promoting the formation of {100} facets through chemisorprtion,[3] thus lowering their total surface energy. Throughout the shape transformation process, UV/Vis spectroscopy measurements showed no detectable change in the concentration of the remaining $PdBr_4^{2-}$ species (Figure S4), indicating the absence of further reduction of the remaining $PdBr_4^{2-}$ species by either PVP or acetone.

We also demonstrated the concept with aqueous suspension of Au nanocrystals less than 5 nm in size (Figure 5a). An increase in particle size was observed when the as-prepared, aqueous suspension was mixed with acetone and stored in a centrifuge tube at room temperature for 30 min (Figure 5b). The resulting Au nanocrystals exhibited both twinned and single-crystal structures (insets of Figure 5b). During this process, the characteristic absorption peak of Au nanocrystals was red-shifted, reflecting a dependence of the localized surface plasmon resonance peak (LSPR) of Au nanocrystals on the size (Figure 5c).[9] It is worth pointing out that some Au nanocrystals aggregated into rod-like structures, resulting in a more pronounced red-shift for the resonance peak than spherical aggregates. As shown in Figure 5d, no transformation in size or morphology was observed when the as-prepared aqueous suspension of Au nanocrystals was mixed with deionized water. These results clearly show that particle coalescence was only triggered when there was a partial exchange between water and a less polar solvent.

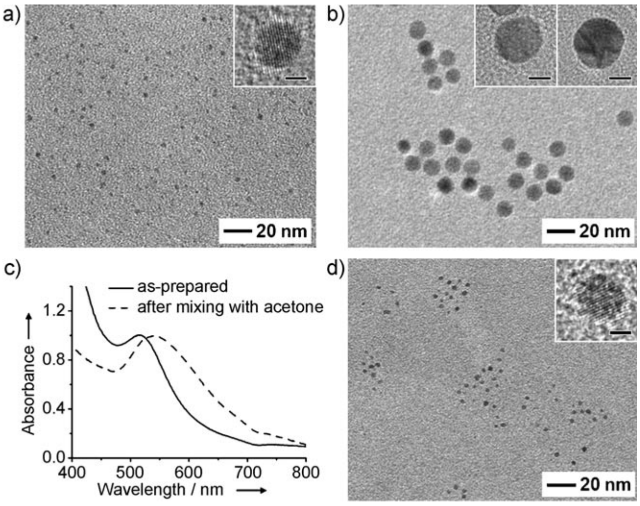

Figure 5. a) TEM image of the as-prepared Au nanocrystals. The inset shows an HRTEM image of a single Au nanocrystal (scale bar is 2 nm). b) TEM image of Au nanocrystals obtained by mixing the as-prepared, aqueous suspension of Au nanocrystals and acetone (volume ratio 3:1) at room temperature for 30 min. The insets show HRTEM images of Au nanocrystals (scale bars are 5 nm). c) Absorbance spectra recorded from the samples (aqueous suspensions) shown in (a) and (b). d) TEM image of Au nanocrystals obtained by mixing the as-prepared aqueous suspension of Au nanocrystals with deionized water (volume ratio 3:1) at room temperature for 30 min. The inset shows an HRTEM image of a Au nanocrystal (scale bar is 2 nm).

In summary, we have demonstrated that small Pd and Au nanocrystals could be triggered to coalesce at room temperature when their aqueous suspensions were mixed with a solvent much lower polar than water. The phenomenon observed in this study not only demonstrates the ability for nanocrystals to change their size and morphology in response to variations in the surrounding environment, but also offers a simple and potentially useful method for controlling the size or morphology of metal nanocrystals.

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