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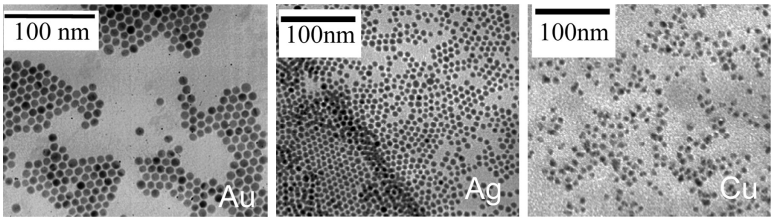


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# Single-Phase and Gram-Scale Routes toward Nearly Monodisperse Au and Other Noble Metal Nanocrystals

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Au and other noble metal nanocrystals play important roles in different branches of science,[1] such as chemical catalysis, catalysts for the growth of nanowires, nanomedicines, nanoelectronics, etc. For most of those applications, their size and size distribution control are of key importance. At present, the Brust method[2]—a two-phase and gram-scale approach—and its variations[1f,3] are the most popular synthetic schemes in the field, although some other approaches are also available.[4] However, the size range of the Brust method is limited to between about 1 and 4 nm, and size distribution is broad. Some postsynthesis treatments, such as ligand exchange[5] and thermal annealing,[6] are reported to improve the size distribution of the Au nanocrystals formed through either the Brust method or other synthetic approaches. The other drawback of the Brust method is that the resulting nanocrystals are coated with a monolayer of strong ligands, thiols, which makes it difficult to carry out the surface modification and functionalization needed for certain purposes. In comparison to Au nanocrystals, synthesis of other noble metal nanocrystals is less developed.[1f,7]

Formation of many types of nearly monodisperse semiconductor nanocrystals became routine recently because of the organometallic approach[8] and its alternative approaches.[9] The key to this success, as revealed by the mechanism studies,[8b,9b,c,10] is to maintain balanced nucleation and growth by tuning the activity of the precursors. The knowledge learned in the synthesis of semiconductor nanocrystals is unlikely to be applicable for the Brust method[2] because it is a biphasic process, for which both nucleation and growth can only occur at the interface of the two liquid phases. It was also reported that very strong ligands used for the semiconductor nanocrystals should be avoided because they typically fix the activity of the monomers at a very low level.[9b] To this standard, thiol ligands used in the Brust method may not be desirable for the formation of monodisperse noble metal nanocrystals.

The single-phase system described below is as follows (details in Supporting Information). $AuCl_3$, $Ag(CH_3COO)$, anhydrous $Cu(CH_3COO)_2$, or $PtCl_4$ was dissolved in toluene with an ammonium surfactants. Either tetrabutylammonium borohydride (TBAB) or its mixture with hydrazine in toluene was used as the reducing reagents. Fatty acids or aliphatic amines were added as ligands. The reducing reagents were always in excess to convert metal precursors completely into nanocrystal form. This made it possible to estimate the number of nuclei for a reaction after the final particle size was determined, assuming no ripening at room temperatures. The reactions were typically carried out at room temperature, although heating treatments of the products were also studied.

Figure 1 illustrates representative transmission electron microscope (TEM) images of the Au nanocrystals obtained using the single-phase approach. A plausible control over the size and size distribution of the nanocrystals is evident (Figure 1).

Several strategies are applied to achieve this level of control. The concentration and chain length of the surfactants (and/or the weak ligands) played a key role in determining the concentration

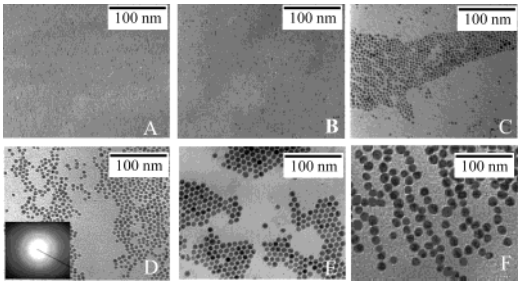


***Figure 1.*** TEM images of as-synthesized Au nanocrystals. A typical electron diffraction pattern of Au nanocrystals is shown as the inset in D.

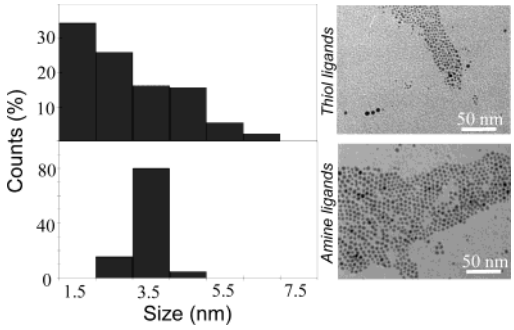


***Figure 2.*** Size distribution of Au nanocrystals formed with thiol (top) and amine (bottom) as the ligands.

of the nuclei formed in the solution, judged by the final average particle size. Similar to the synthesis of semiconductor nanocrystals in noncoordinating solvents, a high concentration of ligands or ligands with a bulky tail suppressed the activity of the monomers.[9,10] Consequently, the number of nuclei formed was low, which results in relatively large nanocrystals. This strategy yields nearly monodisperse Au nanocrystals between 1.5 and 7 nm in size (Figure 1B, C, and D).

Control experiments with thiols in place of the weak ligands (amines or fatty acids) were performed. The average nanocrystal size was limited in the range between 1 and 3 nm, which is similar to the Brust method. The size distribution of very small-sized Au nanocrystals (Figure 1A) synthesized using thiols was decent, but the samples for relatively large nanocrystals all showed a significantly broader size distribution (Figure 2). These control experiments verified the hypothesis that very strong ligands should be avoided for the synthesis of noble metal nanocrystals. When the formed nanocrystals were coated by strong ligands, the subsequent growth at room temperature was hindered, and the remaining monomers in the solution supported a continuous nucleation process, which resulted in samples being rich with very small particles (Figure 2).

The final size achievable through the first strategy was limited to roughly smaller than 7 nm. The second strategy was developed for the synthesis of large nanocrystals, 6−15 nm in size, by decreasing the reducing power of the reducing reagents. This was


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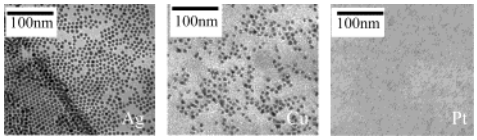


***Figure 3.*** TEM images of as-synthesized Ag, Cu, and Pt nanocrystals.

done by replacing a part of TBAB—a strong reducing reagent—with hydrazine that is relatively weak at room temperature. Presumably, TBAB was mostly used for the nucleation, and hydrazine was consumed in the growth stage. As a result, the final size of the resulting nanocrystals increased by decreasing the relative concentration of TBAB. Images E and F of Figure 1 illustrate some nanocrystals synthesized via this strategy with the thermal treatment to be discussed later.

The third strategy was the secondary injection technique used in the synthesis of semiconductor nanocrystals,[8] which is also similar to the seeding growth of noble metal nanocrystals.[4f] In this strategy, small-sized nanocrystals were formed using the first strategy. After that, more reactants—metal precursor and reducing reagents—were added into the growth solution in a dropwise fashion. The volume increase of the nanocrystals grown by this strategy roughly matched the amount of the metal precursors added in each injection, indicating an insignificant secondary nucleation. Different from the seeding growth,[4f] the entire synthesis was conducted in a one-pot fashion although multiple-pot schemes also worked. The nanocrystals obtained in this way were similar to the ones grown by the second strategy.

Finally, heating treatments of the reaction mixture without any purification were investigated for varying the size and size distribution of noble metal nanocrystals. For the single-phase approaches described here, thiol ligands were simply added into the final reaction mixture, in which the particle growth stopped at room temperature. The improvement of the size distribution was undoubtedly observed after the thermal annealing of the thiol-coated nanocrystals at ~120 °C (see Figure 1E as an example). In all our heating treatments, the average nanocrystal size increased, and a disappearance of the relatively small nanocrystals in the sample was observed when the size distribution of the nanocrystals was improved. This is similar to most observations in the literature,[5,6a,c] and different from the systems studied by Klabunde's group.[4e,6b] Klabunde's group observed that the size distribution of the Au nanocrystals was improved along with a reduction of the average particle size.

The Au atomic concentration in the approaches described above was similar to that of the Brust method, and gram-scale quantity of nearly monodisperse nanocrystals can be readily synthesized. For instance, a reaction yielding 0.5−1.0 g of nearly monodisperse Au nanocrystals was performed in ~100 mL of toluene. The preliminary results also revealed that the new approaches developed for Au nanocrystals can be readily extended to other noble metal nanocrystals, such as Ag, Cu, and Pt (Figure 3, and details in the Supporting Information).

The surface ligands of noble metal nanocrystals may need to be varied for certain purposes. For instance, biomedical applications[1d,e] require water-soluble nanocrystals. Because weak ligands were used in the current synthetic schemes, the surface modification of the Au nanocrystals was quite straightforward by reacting the as-synthesized nanocrystals with strong ligands, such as thiols. Depending on the terminal groups of the thiols used, Au nanocrystals can be made to either maintain its hydrophobic nature or become water soluble (Figure 4). To avoid significant growth of the nanocrystals during the ligand exchange process, a prompt purification of the modified nanocrystals was needed by precipitating the resulting nanocrystals from the solution containing excess thiol ligands (see Supporting Information). The characteristic peaks of the ligands in the NMR spectra (Figure 4) are broad, indicating the removal of the free ligands.

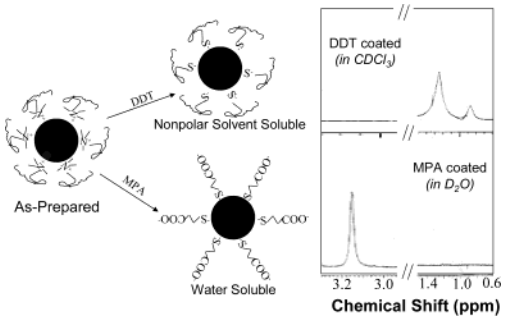


***Figure 4.*** Schemes of the surface modification of Au nanocrystals (left panel) with dodecanethiol (DTT) and mercaptopropanic acid (MPA), and the $^1$H NMR spectra of the resulting nanocrystals (right).

In summary, the size and size distribution control of Au and other noble metal nanocrystals in growth was found to be feasible by adopting single-phase and one-pot approaches using generic chemicals. The key to the success of the single-phase approaches is to maintain a tunable activity for both metal precursors and the reducing reagents. The weak ligands on the surface of the as-synthesized nanocrystals also make it possible to vary the surface function of the nanocrystals.

**Supporting Information Available:** Detailed synthetic procedures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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