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One-Step One-Phase Synthesis of Monodisperse Noble-Metallic Nanoparticles and Their Colloidal Crystals

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Noble-metallic nanoparticles have attracted increasing research attention during the past decades due to their interesting size-dependent optical, electronic, and catalytic properties.[1,2] Nanoparticles with a narrow size distribution can further function as building blocks for the construction of higher-ordered superlattices that exhibit collective properties of individual nanoparticles.[3−8] Although several synthetic routes of noble-metallic nanoparticles have been developed, the challenge remains of obtaining monodisperse nanoparticles with size <10 nm on a large scale. Since the first report in 1994, the syntheses of metallic nanoparticles with size less than 10 nm have been dominated by the Brust method, a two-phase protocol that can be easily scaled up to gram scale. However, the nanoparticles prepared by the Brust method and its variations typically have a continuous and broad size distribution in the range of 1−4 nm.[9,10] Similarly, the method based on the solvated metal atom dispersion technique is suitable for preparation of metal nanoparticles on the gram scale,[6,11] but post-heat treatment is generally required for good size dispersivity.

Recently, efforts have been made to develop one-phase syntheses in which the reduction of metal takes place homogeneously in a selected organic solvent rather than at the two-phase interface as in the Brust method.[12−15] Even though these one-phase syntheses have been shown to significantly narrow the particle size distribution, to our best knowledge, monodisperse metallic particles with size dispersivity <5% have not yet been reported by using any one-phase synthesis without a subsequent size-selection process.

We report here a facile one-step one-phase synthetic route to achieve a variety of metallic nanoparticles by using amine−borane complexes as reducing agents. With the use of different metal sources, both mono- and alloyed metallic nanoparticles with a narrow size distribution can be obtained in a single step on a gram scale. The synthesized nanoparticles are ready to function as building blocks for the formation of large colloidal crystals (Figure 1) directly from the reaction mixtures.

All syntheses were carried out in air by mixing metal source(s) and capping ligand (e.g., thiols) in an organic solvent, such as benzene, toluene, or chloroform. An amine−borane complex was then added to the mixture and stirred until the reduction was complete. As an example, dodecanethiol-capped gold nanoparticles were prepared as follows: 0.25 mmol $AuPPh_3Cl$ was mixed with 0.125 mL of dodecanethiol in 20 mL of benzene to form a clear solution to which 2.5 mmol of *tert*-butylamine−borane complex was then added. The color of the mixture darkened gradually and became purple−red after stirring at 55 °C for 5 min. TEM samples were prepared by dipping carbon-coated Cu TEM grids directly into the solution and drying in air for at least 2 h. As shown in Figure 1A, long-range close-packed superlattices of 6.2 nm gold nanoparticles (Figure 1A) can be obtained even without control over the evaporation rate.

To prepare colloidal crystals, the mixture was sealed and cooled naturally in air upon the completion of reaction. After 2 days, tens-

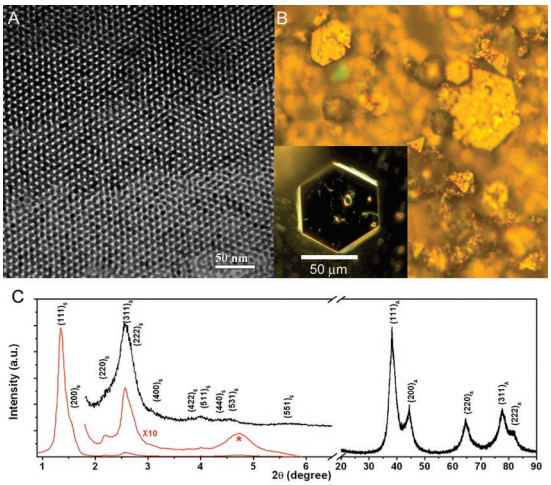

Figure 1. (A) TEM image of close-packed superlattice of 6.2 nm gold nanoparticles. (B) Optical micrograph of colloidal crystals formed directly from the reaction mixture. The inset is the dark-field micrograph. (C) Small-angle X-ray scattering (red traces) and diffraction patterns (black traces) of the colloidal crystals. The subscript "S" and "A" designate the Miller indices from the superlattice and atomic lattice of Au nanoparticles, respectively. The peak marked with an asterisk is from the window material of the scattering instrument.

of-micrometer-sized colloidal crystals (Figure 1B) were obtained. Small-angle X-ray scattering and diffraction patterns of the colloidal crystals shown in Figure 1C indicate their 3D face-centered cubic structure with $a = 11.3$ nm. Prior to this work, the formation of large metallic colloidal crystals required careful control over growth conditions even after a size-selection process.[3−8] In this work, we have found that the crystallization of as-made nanoparticles is readily induced by cooling the mixture or diffusing a polar solvent (e.g., ethanol) into the mixture.

The use of amine−borane complexes is essential for the syntheses of monodisperse metallic nanoparticles reported here. Compared to commonly used reducing agents (e.g., $NaBH_4$, $LiBH_4$), amine−borane complexes have a weaker reducing ability, which can slow the reducing rate of gold cations and allow control over the growth of nanoparticles. Upon the addition of strong reductants, such as $NaBH_4$, gold cations are reduced rapidly, resulting in an immediate color change of the reaction mixture from colorless or yellow to dark red. With the use of weaker reductants applied in our syntheses, a much slower but continuous color change from colorless to yellow, pink, brown, and finally to purple−red is observed, which indicates a relatively slow reducing rate of Au(I). In addition to *tert*-butylamine−borane, other amine (i.e., triethylamine, morpholine, and ammonia)−borane complexes were examined. While the triethylamine complex is a reducing agent comparable to the *tert*-butylamine complex, the morpholine complex exhibits much weaker reducing ability and requires longer reaction time to complete the reaction. In comparison, the reducing ability of ammonia−borane

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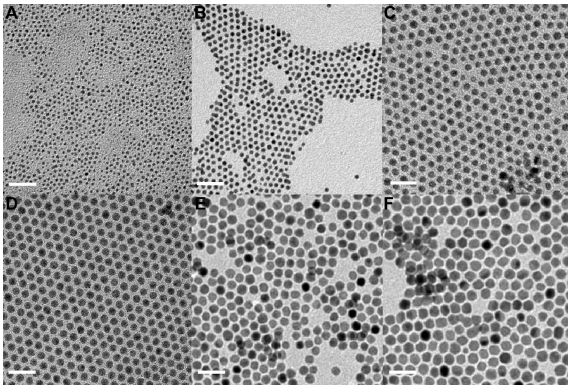

Figure 2. TEM images of as-made different-sized gold nanoparticles produced by varying reaction solvent (A−B) and temperature (C−F): (A) 2.1 ± 0.3 nm; (B) 3.5 ± 0.3 nm; (C) 5.3 ± 0.4 nm; (D) 6.2 ± 0.3 nm; (E) 7.1 ± 0.5 nm; (F) 8.3 ± 0.5 nm. All scale bars are 20 nm.

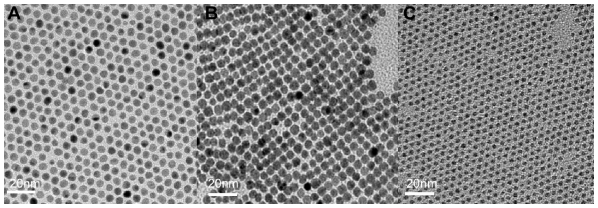

Figure 3. TEM images of different metallic nanoparticles: (A) 5.5 ± 0.3 nm Ag; (B) 6.3 ± 0.4 nm Pd; (C) 3.8 nm ± 0.2 1:1 Au/Ag alloy. All scale bars are 20 nm.

is much stronger, so that it is difficult to obtain nanoparticles with a narrow size distribution.

We found that the reducing rate of metal cations by certain amine−borane complexes is dependent on the reaction temperature and concentration of reactants. The higher the temperature or the concentration of reactants, the faster the reducing reaction. The reaction at lower temperature for a short period typically leads to a relatively broad size distribution due to the existence of small nanoparticles. When the reaction time is long enough or the reaction temperature is increased, these small nanoparticles can grow to reach the size of larger particles. For example, monodisperse gold nanoparticles can be prepared within 5 min at 55 °C but require more than 1 h at room temperature.

Some representative results obtained by varying reaction conditions are illustrated in Figure 2. While the reaction temperature is an important factor to control the reducing rate of metal cations, we also found that higher temperature gives larger average particle size. As shown in Figure 2C−F, the reduction of $AuPPh_3Cl$ in benzene gave 5.3 nm particles at room temperature, 6.2 nm at 55 °C, 7.1 nm at 85 °C, and 8.3 nm at 100 °C. Reaction solvents can also have a significant effect on determining the average size of nanoparticles. Stable smaller gold nanoparticles can be synthesized by using a polar solvent. The 2.1 nm nanoparticles were produced at room temperature when 3:1 (by volume) chloroform/ethanol was applied as solvent; the reaction in chloroform gave uniform 3.5 nm gold nanoparticles (Figure 2A,B).

It has been well demonstrated that the average size and size dispersivity of nanoparticles are mainly controlled by the balance of nucleation and growth rates.[2] Therefore, it was suggested that strong ligands, such as thiols, should be avoided in order to get monodisperse gold nanoparticles because they limit the activity of metal precursors.[13] In our syntheses, however, it was found that strong thiol ligands facilitate the formation of monodisperse nanoparticles better than weak ligands (e.g., phosphines, amines), which motivated us to study the formation mechanism of nanoparticles. Fortunately, by using low concentration and low temperatures (i.e., room temperature), the reaction rate can be significantly reduced, which allows us to monitor the formation of nanoparticles during the course of reaction. It was found that large nanoparticles formed at the very beginning of the reaction and neither grew nor aggregated with the reaction time. These large-sized nanoparticles can be considered as a thermodynamic metastable state that can be better stabilized by long-chain alkanethiols.

The synthetic route described here requires that the metal precursors be soluble in organic solvent(s). In the case of gold, $AuPPh_3Cl$ was selected because it can be synthesized easily in the form of a white powder by reacting $HAuCl_4 \cdot nH_2O$ with PPh_3 in ethanol.[16] In addition to gold nanoparticles, other noble-metallic nanoparticles with a narrow size distribution can be synthesized by substituting $AuPPh_3Cl$ with other metal precursors (e.g., $AgCF_3COO$, Pd(II) acetylacetone). As shown in Figure 3, both mono- and alloyed metallic nanoparticles can be synthesized. Furthermore, grams of monodisperse nanoparticles can be easily obtained by scaling up the reactant quantities.

In summary, a facile one-phase method has been developed for the synthesis of different metallic nanoparticles with a narrow size distribution. They can be synthesized even in the form of large colloidal crystals. The use of amine−borane complexes as reducing agents and thiols as capping ligands is essential to the synthetic route reported.

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Supporting Information Available: Detailed synthetic procedures and characterizations of nanocrystals and colloidal crystals, comparison studies on the effect of different capping agents and reducing agents, color change, and time-domain TEM images during the formation of gold nanoparticles. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Daniel, M. C.; Astruc, D. *Chem. Rev.* **2004**, *104*, 293−346 and references therein. (b) Astruc, D.; Lu, F.; Aranzaes, J. R. *Angew. Chem., Int. Ed.* **2005**, *44*, 7852−7872 and references therein.
(2) Schmid, G. *Nanoparticles: From Theory to Application*; Wiley-VCH: Weinheim, Germany, 2004 and references therein.
(3) (a) Shevchenko, E. V.; Talapin, D. V.; Kotov, N. A.; O'Brien, S.; Murray, C. B. *Nature* **2006**, *439*, 55−59. (b) Murray, C. B.; Kagan, C. R.; Bawendi, M. G. *Annu. Rev. Mater. Sci.* **2000**, *30*, 545−610.
(4) Collier, C. P.; Vossmeyer, T.; Heath, J. R. *Annu. Rev. Phys. Chem.* **1998**, *49*, 371−404.
(5) Andres, R. P.; Bielefeld, J. D.; Henderson, J. I.; Janes, D. B.; Kolagunta, V. R.; Kubiak, C. P.; Mahoney, W. J.; Osifchin, R. G. *Science* **1996**, *273*, 1690−1693.
(6) Stoeva, S. I.; Prasad, B. L. V.; Uma, S.; Stoimenov, P. K.; Zaikovski, V.; Sorensen, C. M.; Klabunde, K. J. *J. Phys. Chem. B* **2003**, *107*, 7441−7448.
(7) Wang, S. H.; Sato, S.; Kimura, K. *Chem. Mater.* **2003**, *15*, 2445−2448.
(8) Brown, L. O.; Hutchison, J. E. T. *J. Phys. Chem B* **2001**, *105*, 8911−8916.
(9) Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R. *J. Chem. Soc., Chem. Commun.* **1994**, 801−802.
(10) (a) Wuelfing, W. P.; Gross, S. M.; Miles, D. T.; Murray, R. W. *J. Am. Chem. Soc.* **1998**, *120*, 12696−12697. (b) Templeton, A. C.; Wuelfing, M. P.; Murray, R. W. *Acc. Chem. Res.* **2000**, *33*, 27−36.
(11) Stoeva, S.; Klabunde, K. J.; Sorensen, C. M.; Dragieva, I. *J. Am. Chem. Soc.* **2002**, *124*, 2305−2311.
(12) Yee, C. K.; Jordan, R.; Ulman, A.; White, H.; King, A.; Rafailovich, M.; Sokolov, J. *Langmuir* **1999**, *15*, 3486−3491.
(13) Jana, N. R.; Peng, X. G. *J. Am. Chem. Soc.* **2003**, *125*, 14280−14281.
(14) Rowe, M. P.; Plass, K. E.; Kim, K.; Kurdak, C.; Zellers, E. T.; Matzger, A. J. *Chem. Mater.* **2004**, *16*, 3513−3517.
(15) Schulz-Dobrick, M.; Sarathy, K. V.; Jansen, M. *J. Am. Chem. Soc.* **2005**, *127*, 1281.
(16) Braunstein, P.; Lehner, H.; Matt, D. *Inorg. Synth.* **1990**, *27*, 218−221.

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