

# Synthesis of Size-Controlled and Shaped Copper Nanoparticles

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*Received December 4, 2006. In Final Form: February 21, 2007*

The synthesis of stable, monodisperse, shaped copper nanoparticles has been difficult, partially because of copper's propensity for oxidation. This article reports the findings of an investigation of a synthetic route for the synthesis of size-controllable and potentially shape-controllable molecularly capped copper nanoparticles. The approach involved the manipulation of reaction temperature for the synthesis of copper nanoparticles in organic solvents in the presence of amine and acid capping agents. By manipulating the reaction temperature, this route has been demonstrated for the production of copper nanoparticles ranging from 5 to 25 nm. The size dependence of the melting temperature of copper nanoparticles, especially for surface melting, is believed to play an important role in interparticle coalescence, leading to size growth as the reaction temperature is increased. Control of the reaction temperature and capping molecules has also been demonstrated to produce copper nanoparticles with different shapes such as rods and cubes. The previously proposed combination of the selective formation of a seed precursor and a selective growth direction due to the preferential adsorption of capping agents on certain nanocrystal facets is believed to be responsible for shape formation by kinetically controlling the growth rates of crystal facets. The nanoparticles are characterized using TEM, XRD, and UV

Alfa Aesar. 1,2-Hexadecanediol (90%), octyl ether (99%), oleyl amine (70%), hexane, and other common solvents used were obtained from Aldrich.

**Synthesis.** The synthesis of copper nanoparticles in organic solution was achieved through the modification of a previous method that was reported for the synthesis of FePt nanoparticles<sup>8a</sup> and PtVFe nanoparticles.<sup>11</sup> In the modified synthesis, copper(II) acetylacetonate was added to octyl ether to create a 20 mM solution of copper(II). Then 1,2-hexadecanediol (a reducing agent)<sup>8b</sup> was added to the solution (60 mM). The solution was heated under argon gas to a temperature of 105 °C with stirring. The solution was held at 105 °C for 10 min, and then both oleic acid and oleyl amine capping agents were added to the solution to create 20 mM solutions of each. The solution was heated to higher temperatures, which was varied from 150 to 210 °C. Once at high temperature, the solution was left to react for 30 min. The solution was then cooled to room temperature. Finally, the reacted solution was mixed with ethanol, and the particles were allowed to precipitate overnight. The supernatant was removed, and the nanoparticle sediment was washed and dried using a stream of nitrogen gas. We note that we have not yet determined the synthetic yields, but a complete determination of the yields at different reaction temperatures is part of our ongoing work, which will be reported in the near future. The nanoparticles were suspended in hexane and were ready for analysis.

**Instrumentation and Measurements.** The nanoparticles were characterized using thermogravimetric analysis (TGA), UV–vis spectroscopy, transmission electron microscopy (TEM), and X-ray powder diffraction (XRD).

TGA analysis was performed on a Perkin-Elmer Pyris 1-TGA to determine the weight of the organic shell. Typical samples weighed ~4 mg and were heated in a platinum pan. Samples were heated in 20% O<sub>2</sub> at a rate of 10 °C/min.

UV–vis spectra were acquired with an HP 8453 spectrophotometer. A quartz cell with a path length of 1 cm was used, and spectra were collected over the range of 200–1100 nm.

TEM was performed on a Hitachi H-7000 electron microscope (100 kV). Copper nanoparticle samples were suspended in hexane solution and were drop cast onto a carbon-coated copper grid, followed by solvent evaporation in air at room temperature.

XRD data was collected on a Philips X'Pert diffractometer using Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The measurements were made in reflection geometry, and the  $2\theta$  diffraction (Bragg) angles were scanned at a step of 0.025°. Each data point was measured for at least 20 s, and several scans were taken of the sample.

## Results and Discussion

The reaction for the synthesis of copper nanoparticles of different sizes, as shown in Scheme 1, was accomplished by

varying the reaction temperature in the range of 150–190 °C. As the temperature of the reaction was raised, solutions with the resulting nanoparticles were found to become darker in color. The size evolution and shape formation, which are highly dependent on the reaction temperature, will be detailed in the next two subsections. As a general observation, the color evolution of the reaction solution under different temperatures was found to

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above 190 °C, the nanoparticles showed increased standard deviations (e.g.,  $24.0 \pm 6.5$  nm (190 °C)).

Figure 4 shows a plot of the average particle size versus the reaction temperature. The average size of the nanoparticles was found to increase approximately linearly with temperature. The linear regression of the data yields 0.46 nm/°C. This finding is significant, demonstrating the important role of reaction temperature in the control of particle size.

A close examination of some of the large particles seems to reveal subtle cluster features. This observation may hint at the possibility of coalescence of smaller particles, which provides some implications to the understanding of the mechanistic origin of the size dependence on temperature. It is known that the growth of nanoparticles is influenced by the strength of adsorption of the encapsulating ligands and the competition between the interparticle aggregation for the growth of particles and the molecular encapsulation for the stabilization of nanoparticles. For growth to occur, desorption of an encapsulating ligand on the particle must occur, allowing a metal atom or neighboring particle to gain access to the particle surface.<sup>13</sup> The adsorption of capping molecules on the copper nanoparticles is favored at lower temperatures, thus limiting the particle growth rate. However, as the temperature is increased, desorption of the capping ligand from the nanoparticle surface is favored, increasing the opportunities for interparticle coalescence. On the basis of the TGA data, desorption of the capping molecules from the nanoparticle surface likely occurs at  $\sim 150$  °C. Below  $\sim 150$  °C, there were no nanoparticles detected. Therefore, the nanoparticles synthesized at 150 °C acted as seed particles for the growth of larger particles at elevated reaction temperature. In addition to the theoretical basis for the decreased melting point of nanoscale copper particles, there are experimental studies indicating that nanoscale copper materials exhibit depressed melting points. For example, copper nanorods have recently been shown to exhibit a range of melting temperature as low as 350–550 °C.<sup>17</sup> A DSC

began to form at temperatures above 190 °C. Figure 6 shows a representative TEM image of the as-synthesized particles derived from the reaction temperature of 210 °C and careful control of the initial heating rate in the presence of the capping agents. Copper nanoparticles shaped as cubes, rods, and tetrahedrons are evident, in addition to a certain percentage of spherically shaped particles. Shape formation began at 190 °C but was not prominent until 200 °C, for which shapes such as rods and cubes became common among the particles. In all of the samples that formed shapes, rods were the most common shape, demonstrating that the formation of copper nanoparticles at high temperature favors the formation of rods. As indicated by the enlarged views, the cubes, rods, and tetrahedrons have well-defined shapes. The cube-shaped particles are 200 nm in size. The rod-shaped particles are around 700 nm in length and about 100 nm in width, with an aspect ratio as high as  $\sim 7$ . It is important to note that these shaped particles do not show any hint of the possibility of coalescence of smaller particles as observed for the spherical particles described earlier, thus ruling out the simple coalescence mechanism for shape formation. The observation of these shapes is remarkable considering the relatively small change in the synthetic temperature that was required to initiate their formation.

There is a remarkable resemblance between the shapes of the nanoparticles synthesized using our method and those reported by Pileni and co-workers.<sup>9</sup>

A key question is what synthesis parameters are necessary to achieve precise control of the formation of the precursor seed particles and the relative adsorption of the two capping agents on the nanocrystal surfaces. Preliminary experiments have indicated that the manipulation of the reaction temperature and the relative ratio of the two capping agents could lead to variations