

Synthesis of Silver Nanocrystallites by a New Thermal Decomposition Method and Their Characterization

Don Keun Lee and Young Soo Kang

We formed silver nanocrystallites by the thermal decomposition of a Ag^+ -oleate complex, which was prepared by a reaction with AgNO_3 and sodium oleate in a water solution. The resulting monodispersed silver nanocrystallites were produced by controlling the temperature (290 °C). Transmission electron microscopic (TEM) images of the particles showed a 2-dimensional assembly of the particles with a diameter of 9.5 ± 0.7 nm, demonstrating the uniformity of these nanocrystallites. An energy-dispersive X-ray (EDX) spectrum and X-ray diffraction (XRD) peaks of the nanocrystallites showed the highly crystalline nature of the silver structure. We analyzed the decomposition of the Ag^+ -oleate complex using a Thermo Gravimetric Analyzer (TGA) and observed the crystallization process using XRD.

Keywords: Silver nanoparticle, thermal decomposition, silver-oleate complex.

I. Introduction

The area of nanotechnology is witnessing an increase in research activity due to its immense potential in various industrial applications such as optoelectronic devices [1], nonlinear optics [2], light-emitting diodes [3], and quantum dot lasers [4]. One of the goals in nanotechnology is the organization of nanocrystallites in crystalline arrays, with the ability to tailor the size and separation of the nanocrystallites and thereby the optical and electronic properties of the assembly [5]. However, the synthesis of colloidal inorganic nanocrystals, particularly with respect to the control of their shape, remains underdeveloped and complicated. A new direction for synthetic methods and an understanding of the mechanisms by which the size and shape of the nanocrystals can be easily varied are key issues in nanochemistry. For the past few years, various methods have been developed for the synthesis of 1-dimensional nanomaterials including pulsed sonoelectrochemical [6], photochemical [7], colloidal micellar [8], capping [9], and thermal dynamic processes [10]. Here we report on a very easy, economical, and nontoxic thermal decomposition method for fabricating highly crystalline silver nanocrystallites. Our silver nanoparticles have a crystal structure due to a high decomposition temperature of 290 °C under a low pressure of 0.3 Torr and a very narrow size distribution of 9.5 ± 0.7 nm.

II. Experimental Section

We obtained AgNO_3 (99+%) and sodium oleate (98%) from

Manuscript received May 14, 2003; revised Jan. 20, 2004.

This work was supported by the Brain Busan 21 project in 2004.

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Aldrich Chemical Co. and used them without further purification. To prepare a Ag^+ -oleate complex, we dissolved 1.7 g of AgNO_3 (10 mmol) in deoxygenated water (300 mL, 18 M Ω , nitrogen gas bubbling for 30 minutes), and added the resulting solution into 3.05 g of sodium oleate (10 mmol) under vigorous stirring for two hours. We separated the precipitate by filtration and washed it with doubly deionized water to free it of sodium and nitrate ions. After drying, the Ag^+ -oleate complex was transferred into a pyrex tube. The complex was then flushed with nitrogen, and the tube sealed at 0.3 Torr. We slowly heated the sample from room temperature to 290 °C at 2 °C/min and annealed it at 290 °C for 1 hr before cooling it to room temperature again. The complex color changed to black, indicating the formation of silver nanocrystallites, which can be easily redispersed in octane or toluene. Transmission electron microscopy (TEM) examinations of the samples were carried out on the HITACHI H-7500 (low-resolution) and JEOL JEM2010 (high-resolution). We prepared the TEM samples on a 400 mesh copper grid coated with carbon and measured the size distributions of the particles using enlarged photographs of the TEM images. The nanocrystallite structure was analyzed by X-ray diffraction (XRD) using a Philips X'Pert-MPD System with a $\text{Cu K}\alpha$ radiation source ($\lambda = 0.154056$ nm). We conducted our elemental analysis of the nanocrystallites using the Energy-dispersive X-ray (EDX) on the JEOL JEM2010 TEM operating under an acceleration voltage of 200 kV. The decomposition of the Ag^+ -oleate complex was analyzed by a thermo gravimetric analyzer (TGA), the Perkin Elmer model TGA-7, and the crystallization process was observed using XRD.

III. Results and Discussion

We studied the decomposition of the Ag^+ -oleate complex by TGA analysis. Figure 1 shows the weight loss for the Ag^+ -oleate complex during heat treatment under an air flow. A strong endothermic peak was observed at 287 °C. The peak indicates the evaporation of oleate molecules formed by the decomposition of the Ag^+ -oleate complex. Figure 2 illustrates the following: (a) the XRD patterns of the Ag^+ -oleate complex, (b) its aging at 300 °C, and (c) its aging at 600 °C. No crystalline signature of silver in the pristine Ag^+ -oleate complex was observed in the XRD analysis, as shown in Fig. 1(a), indicating that the complex is amorphous. However, a signature of silver was observed at 300 °C, as shown in Fig. 2(b). The broadened peaks are due to the nanocrystalline nature of silver. The sharp diffraction patterns of the XRD spectra obtained by the annealing at 600 °C, as shown in Fig. 2(c), indicate a pure crystalline silver structure, JCPDS card no. 04-0783. Figures 2(b) and 2(c) show three peaks at 2θ values of 38.2°,

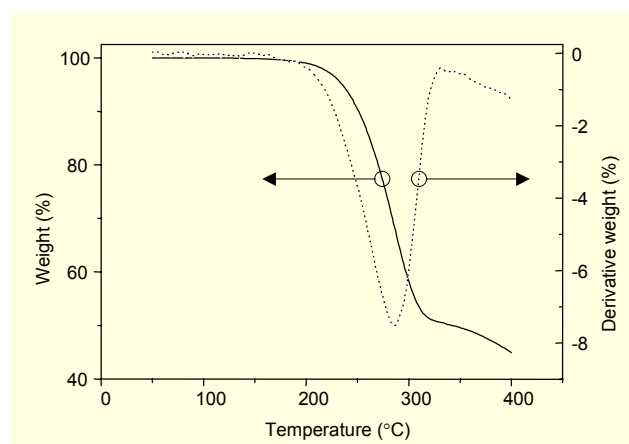


Fig. 1. Weight loss for a Ag^+ -oleate complex during heat treatment under an air flow.

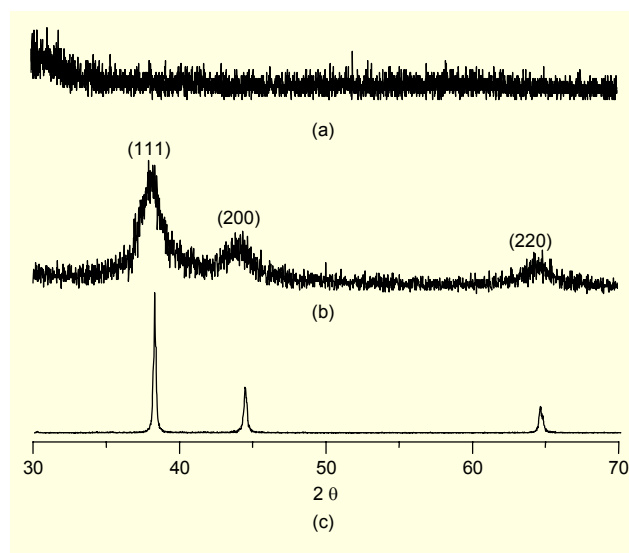


Fig. 2. (a) X-ray diffraction pattern ($\text{Cu K}\alpha$ -radiation) of the Ag^+ -oleate complex, (b) 300 °C aging of Ag^+ -oleate complex, and (c) 600 °C aging of Ag^+ -oleate complex.

44.5° and 64.5° corresponding to 111, 200, and 220 planes of silver, respectively. We observed no impurity peak in the X-ray diffraction pattern.

Thermal decomposition of the Ag^+ -oleate complex at high temperature (over 200 °C) results in a Ag atom and an oleate molecule. Crystallite growth appears consistent with “Ostwald ripening,” where the higher surface-free energy of small crystallites makes them less stable than larger crystallites with respect to dissolution in the solvent. The net result of this stability gradient within a dispersion is a slow diffusion of material from the surfaces of small particles to the surfaces of larger particles [11]. Reiss has shown how growth by this kind of transport can result in the production of colloidal dispersions from systems that may initially be polydispersed [12]. The

Ostwald ripening process accentuates any kinetic or thermodynamic “bottleneck” in the growth of the crystallites. As a bottleneck is approached (e.g., a closed structural shell), sharpening of the sample size distribution reduces the thermodynamic driving force for further growth.

Both the average size and size distribution of the crystallites in the sample are dependent on the growth temperature, consistent with surface-free energy considerations. The temperature necessary to maintain steady growth increases with the expansion of the crystallite’s size. As the size distribution sharpens, the reaction temperature must be raised to maintain steady growth. Conversely, if the size distribution begins to spread, the temperature required for slow steady growth drops. Capping groups present a significant steric barrier to the addition of material to the surface of a growing crystallite, slowing the growth kinetics. The oleate molecule coordinates the surface of silver nanocrystallites and permits slow steady growth at temperatures above 290 °C. Steady controlled growth results in nanoparticles of a consistent crystal structure.

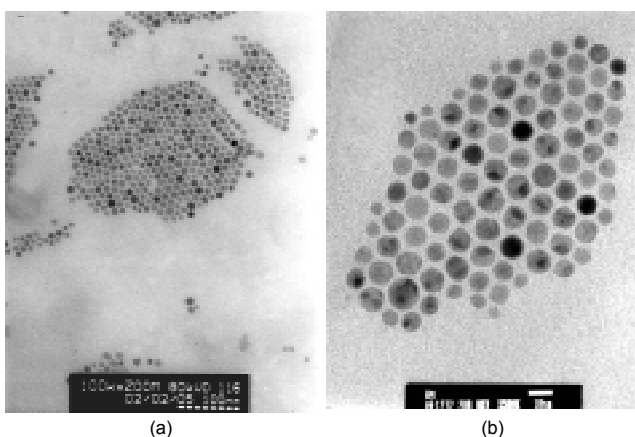


Fig. 3. Transmission electron micrographs of silver nanocrystallites synthesized at 290 °C and taken at (a) 100,000 and (b) 500,000 magnifications. The particle size shown is 9.5 ± 0.7 nm.

Figure 3(a) shows a low-resolution TEM image of silver nanocrystallites while Fig. 3(b) shows the same image in high-resolution. A silver nanocrystallite monolayer is formed by self-assembly when a drop of the nanocrystallite isooctane solution is carefully placed on the grid and air dried. Most of the silver particles are spherical. A monolayer of nanocrystallites was observed from the low-resolution image with almost no multilayer on it. Figure 3(a) shows an example of an extended area where particles are packed in a highly organized state. This figure shows that the nanocrystallites were arranged in a 2-dimensional hexagonal close-packed way, demonstrating the uniformity of the particle size. In particular, the interparticle spacing is very even. Here, as in most cases,

adjacent silver nanocrystallites were separated by a distance of approximately 2 nm and did not exhibit any diffraction contrast. This distance is considerably less than twice the expected oleate length (1.75 nm); therefore, interdigitation of the alkyl chains from the nearest-neighboring silver particles can be inferred. Figure 4 shows the histogram of the size distribution of silver nanocrystallites obtained from the TEM picture. The mean size of the silver nanocrystallites is 9.5 nm with a standard deviation of 0.7 nm. This shows that the silver nanocrystallites have a very narrow size distribution. Figure 5 shows the EDX spectra of silver nanocrystallites excited by an electron beam (200 kV). Only peaks for the elements of Ag

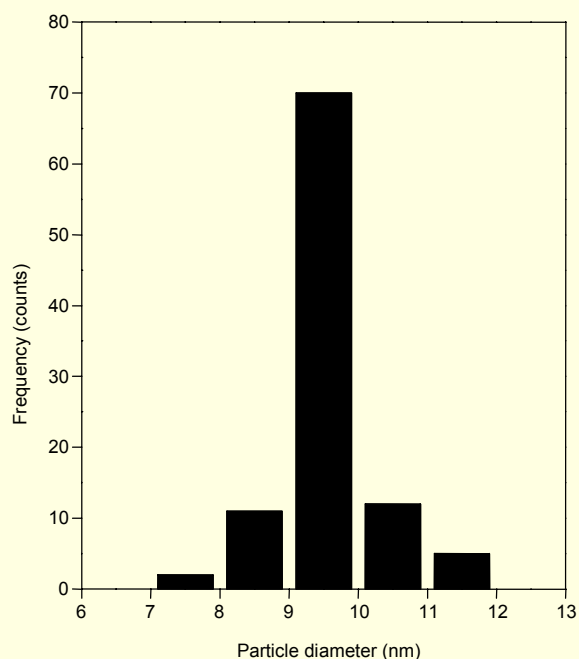


Fig. 4. Particle size statistics over 100 particles in a TEM micrograph of silver nanocrystallites synthesized at 290 °C.

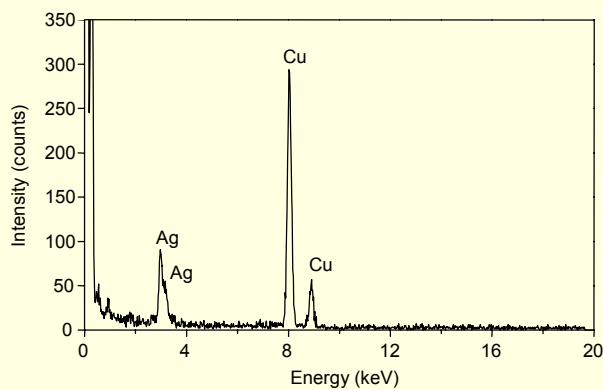


Fig. 5. An energy-dispersive X-ray spectra of silver nanocrystallites synthesized at 290 °C.

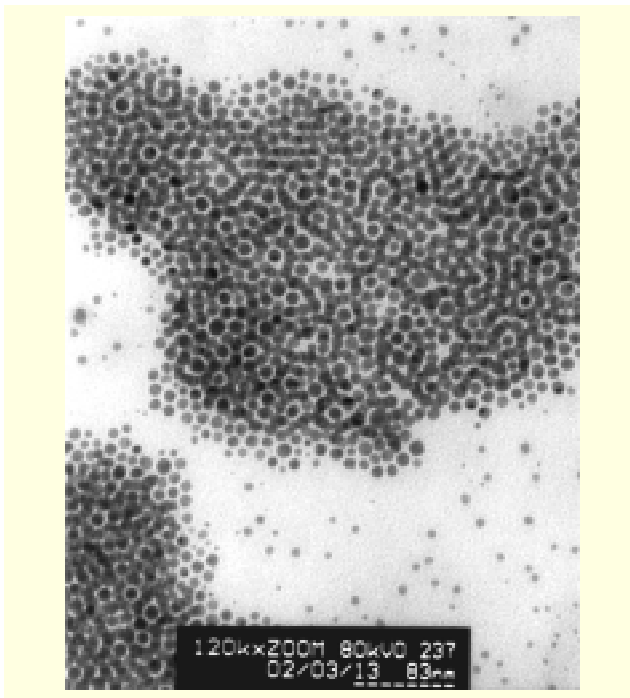


Fig. 6. Transmission electron micrographs of Ag nanocrystallites synthesized at 290 °C after storage for four weeks under ambient conditions.

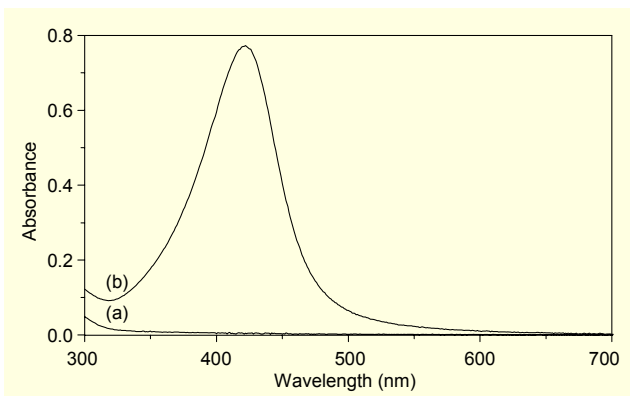


Fig. 7. A UV-Vis spectrum of (a) a Ag^{+1} -oleate complex and (b) Ag nanocrystallites synthesized at 290 °C. $\lambda_{\text{max}} = 421$ nm dispersed in an isooctane solution.

and Cu were observed. Since the Cu peaks are due to the 400 mesh copper grid, we can say that there are only silver atoms in the nanocrystallites. Accordingly, from the EDX spectra, we confirmed that the nanoparticles in the TEM images are pure silver particles. Figure 6 relates to the long-term stability of silver nanocrystallites synthesized at 290 °C. When silver atoms are allowed to crystallize at 290 °C, the protective oleate coating can be degraded slowly under ambient conditions, and it becomes energetically favorable for the Ag particles to minimize their surface energy by sintering. The silver particles have effectively connected to form a semi-continuous network

in which the regular isolated silver particle is embedded. The TEM image shows an ordered honeycomb shape. This raises the possibility that the nanocrystallite stability might be exploited for nanopatterning, such as in source and drain formation in single-electron transistor structures [13]. Figure 7 shows a UV-Vis spectrum of the Ag^{+1} -oleate complex and Ag nanocrystallites where $\lambda_{\text{max}} = 421$ nm dispersed in an isooctane solution. No absorption band in the Ag^{+1} -oleate complex has been observed. The Ag nanocrystallites display an optical absorption band peaked at 421 nm (~ 3 eV), which is typical of the absorption of metallic Ag nanocrystallites due to the surface plasmon resonance [14]. The colloidal suspensions of our silver particles were a bright yellow-greenish color due to the intense bands around the excitation of the surface plasmon resonance [15]. Although the conduction and valence bands of semiconductors are separated by a well-defined band gap, metal nanocrystallites have close-lying bands, and electrons move quite freely. The free electrons give rise to a surface plasmon absorption band in metal clusters, which depends on both the cluster size and chemical surroundings. This absorption band is a little blue-shifted compared with the plasmon absorption band of silver colloids prepared by the citrate reduction method ($\lambda_{\text{max}} = 434$ nm) [16] due to the fact that our silver nanocrystallites have a narrower size-distribution and smaller diameter than silver nanocrystallites prepared by the citrate reduction method.

IV. Conclusion

We discovered a new synthetic method to produce silver nanocrystallites using the thermal decomposition of a Ag^{+1} -oleate complex, which was prepared by the reaction of AgNO_3 and sodium oleate in a water solution. Using a TGA measurement, we observed the thermal decomposition of the Ag^{+1} -oleate complex at 287 °C. Transmission electron micrographs show that the silver nanocrystallites (9.5 ± 0.7 nm) are packed in a highly organized state. This work easily extends to other metals and to alloys made up of two or more metals.

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