Water Soluble Silver Nanoparticles Functionalized with Thiolate

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Stable carboxylate-functionalized silver nanoparticles (1.4 - 5.7 nm in diameter) which can be separated as pure water-redispersible powder are synthesized by the reduction of silver nitrate with sodium borohydride in the presence of mercapto-succinic acid (MSA) in methanol. The results show that the particle sizes can be controlled through varying the initial molar ratio of MSA to $AgNO_3$. MSA exists in the form of sodium carboxylate and adsorbs H_2O molecules on the particle surface.

Controlling function-directed nanostructure is currently a central interest throughout materials research.[1] As surface modifier materials thiolates are found very effective in stabilizing II-VI[2] and I-VII[3] semiconductor, as well as metal[4] nanoparticles. Since the successful synthesis of gold nanoparticles stabilized by long chain methyl-terminated thiolates,[4] other thiolate derivatives have been reported such as hydroxyl,[5] cyano, bromo, vinyl,[6] trimethoxysilane,[7] as well as carboxylate.[8] In contrast, for silver, despite long chain methyl-terminated thiolates,[9] direct synthetic routes have rarely been reported for the generation of thiolate stabilized silver nanoparticles. Here, we present a large-scale preparation and characterization of carboxylate-functionalized silver nano-particles which can be purified as stable pure powder like normal molecular compounds.

Basic procedure is based on a process recently developed for Au nanoparticles.[10] The silver nanoparticles with diameters ranging from 1.4 - 5.7 nm were synthesized by changing the initial molar ratio of mercaptosuccinic acid (MSA) to $AgNO_3$ (denoted as S/Ag) with a fixed concentration of $AgNO_3$. For a typical preparation of 2.2 nm particles, 0.5 mmol of $AgNO_3$ dissolved as 5% (w/v) aqueous solution and 1.0 mmol of MSA were mixed in 100 ml methanol, followed by the addition of 25 ml freshly prepared 0.2 M aqueous sodium borohydride. The color of the solution turned yellow, dark-red and finally dark-brown, with the pH changing from 1.3 to 9.5. After one hour of further stirring, the dark-brown precipitate was collected under a centrifugation force, then washed twice with 20%(v/v) water-methanol solution through ultrasonic redispersion-centrifugation process to remove the inorganic or organic impurity. This process was repeated with using 99.8% methanol to remove unbound MSA/MSA-Ag complexes. At last, the precipitate was dispersed in ethanol and dried in vacuo less than 40 °C. Yield: 86 mg (88% based on powder containing 55% of silver from elemental analysis).

Structure assignment and size estimation are conducted using X-ray diffraction (XRD). Figure 1 shows the XRD patterns of Ag samples prepared with varied S/Ag ratios. The diffraction peaks for all the samples can be indexed to that of fcc , indicating the formation of pure silver metallic particles. The average particle sizes estimated from the Scherrer's equation according to the half-width of (111) peak corrected with that of bulk Ag were given in Table 1. They increase with the decrease of S/Ag ratio.

Table 1. Analytical data from XRD, Thermogravimetry and Elemental Analysis for Particles Prepared with Different S/Ag Ratios

S/Ag	Diameter /nm [a]	Elemental analysis/% C	H	organics[c]	Thermogrametric analysis/%[d] H_2O	organics
3.0	1.4	10.75	1.49(1.68)[b]	32.9	5.6	15.2(46)[e]
2.5	1.9	10.29	0.93(1.10)	31.5	5.7	19.0(60)
2.0	2.2	10.05	0.85(1.03)	30.8	3.9	17.9(58)
1.5	3.7	9.55	0.76(0.95)	29.2	4.0	17.4(60)
1.0	4.3	8.95	0.77(1.10)	27.4	3.6	16.5(60)
0.5	5.7	8.11	0.64(0.95)	24.8	3.1	14.8(60)

[a] Calculated from Scherrer's equation from XRD data. [b] Values in parentheses represent the relative atomic ratios of hydrogen to carbon. [c] Calculated organics content based on that of carbon. [d] Obtained from the mass loss during heating. [e] Values in parentheses show the relative percentage of the decomposed organics.

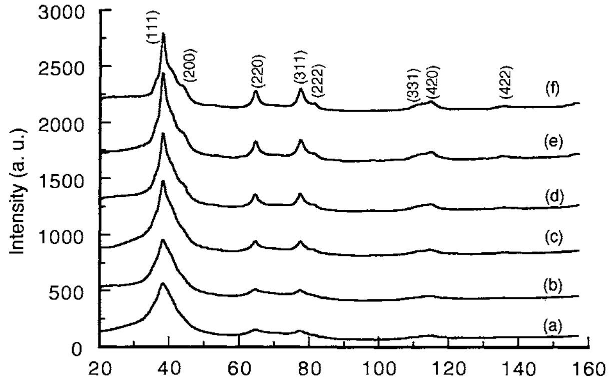

Figure 1. Wide angle XRD patterns of Ag powders prepared with S/Ag ratio of a) 3.0, b) 2.5, c) 2.0, d) 1.5, e) 1.0 and f) 0.5. The positions of lattice fringes from bulk Ag were also indicated.

Transmission electron microscopic (TEM) study reveals that the silver particles smaller than 3 nm are very unstable under electron beam irradiation of normal intensity. Care should thus be taken to use extensively dried sample (evacuated on a vacuum line <0.1 Torr for 2 days) and to keep the electron beam as weak as possible during observation. Figure 2 shows the electron micrograph of the Ag nanoparticles prepared with S/Ag = 2.0. The size distribution was studied by counting 177 particles showing a Gaußian distribution with particles ranging from 1.2 to 6.8 nm and a mean diameter of 3.3 nm. The most frequently observed particles on the monitor screen of an Image Intensifier (total magnification 2×10^7) display 5-15 (111) lattice planes of Ag, corresponding to 1.2-3.6 nm; this result is in agreement with that of XRD measurements (2.2 nm). When S/Ag = 1.0 or 0.5, particles as large as 10-15 nm were also observed. Although the average diameter of the particles was only 4-6 nm from XRD measurements, the formation of large particles can be explained as caused by the incomplete complexing of MSA with free silver ions due to the low S/Ag ratio. In fact, the starting solution of S/Ag =

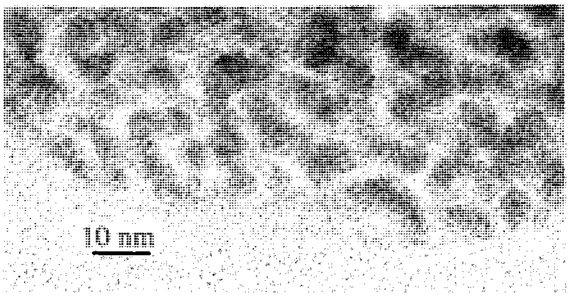

Figure 2. Electron micrograph of Ag particles prepared with initial S/Ag ratio of 2.0.

0.5 suffered from by-products such as white precipitate of AgOH which should act as a source to quickly release free Ag^+ ions enhancing the rapid particle growth on certain nuclei.

Ag particles are not dispersible in normal organic solvents, but easily in water. A strong plasmon band of silver was found at 397 nm on the UV-Vis spectrum. The solution is brownish yellow. Other sized particles show a similar spectrum, with a surface plasmon band at 397-403 nm, as well as a shoulder near 230 nm. The shape of these spectra is similar with that of dodecanethiolate stabilized silver particles in cyclohexane.[10]

The structure of organics adsorbed on Ag particle surface was found different from that of pure MSA through comparing their IR spectra (Figure 3). The existence of two strong peaks at 1570 cm^{-1} and 1404 cm^{-1} in Figure 3a, which can be attributed to the asymmetric and symmetric stretching vibration of carboxylate ions, respectively, indicated that MSA exists in the form of carboxylate anions on the particle surface. From elemental analysis, the counter ion was found Na^+. The absence of S-H vibration peak at 2548 cm^{-1} of pure MSA in the spectrum gives strong evidence that the organics combine with silver surface through sulfur in thiol group. A strong O-H band at 3410 cm^{-1} indicated the presence of adsorbed water on the particle surface.

The existence of water molecules in the Ag powder was further confirmed by thermogravimetric analysis. For a Ag sample prepared with S/Ag = 1.0, there exist at least four mass loss steps at 55, 203, 313 and 405℃. The mass loss below 100℃ was found for all Ag samples whereas this was not observed for pure MSA. This is because, dimers are formed for pure MSA through hydrogen bonding between neighbor carboxylic acid groups. However, on the particle surface, MSA exists as sodium carboxylate, making it possible for carbonyl groups to interact with water through hydrogen bonding. The mass loss (3.1-5.7%, Table 1) clearly shows that water exists in the particles. Further heating (100-499℃) resulted in the decomposition of the organics with the amount around 60% of the total organics, it is most likely that two carboxylate groups are removed from the particles (the mass percentage of two carboxylate groups in a MSA molecule is 60 %).

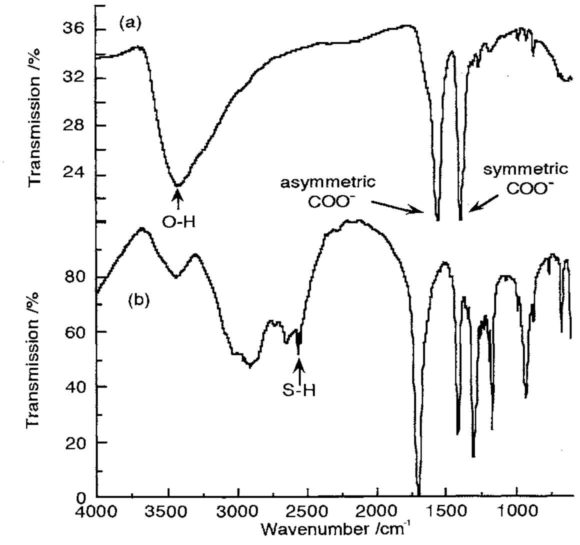

Figure 3. IR spectra of (a) Ag powder prepared with S/Ag = 3.0 and (b) pure MSA, using KBr method.

Elemental analysis of the Ag powder shows atomic ratios of hydrogen to carbon are 0.9 -1.68 (Table 1), which are higher than expected if only carboxylates exist (H/C = 3/4), supporting that water should adsorb on the particle surface. Elemental analysis of 1.4 nm particles gave (in %): C, 10.75; H, 1.49; O, 21.61; S, 6.17; Ag, 48.75; Na, 8.80. The summation of all the element amounts to 97.57%, showing that other impurity such as B or Cl is not present in a significant amount. This also confirmed that the purification steps during preparation are successful. A calculation supposing that a sodium carboxylate monolayer was formed on the silver particle surface gives a mass percentage of 53% (provided that occupation area of thiolate on silver is 15 $Å^2$ per sulfur), which is near the value obtained from elemental analysis. All these findings coincide generally with those obtained for Au nanoparticles[10] and suggest that the surface structure does not differ so much from that of Au particles.

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