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Synthesis of spherical silver nanoparticles by digestive ripening, stabilization with various agents, and their 3-D and 2-D superlattice formation

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Abstract

Capped nanoparticles of silver were synthesized via the solvated metal atom dispersion (SMAD) technique followed by a digestive ripening procedure producing gram quantities of monodisperse spherical nanoparticles. This shows for the first time that a digestive ripening protocol is possible for an element other than gold. The particle size and optical spectra were found to be dependent on the capping agent used. Particles capped with dodecane thiol had a mean diameter of 6.6 ± 1 nm, while trioctyl phosphine capped particles were 6.0 ± 2 nm determined via TEM microscopy. These particles were found to organize into two- and three-dimensional superlattices with a well defined geometry through self-assembly in a liquid solution, that was dictated by the ligand used resulting in a triangular or circular lattice.

Keywords: Digestive ripening; Self-assembly; 3-D superlattice; Gram scale

1. Introduction

The synthesis of metal nanoparticles has been the focus of numerous research groups worldwide in the past few years [1–10]. Some very successful techniques have been developed for producing gold, silver, and to a lesser extent other materials as nanoparticles. In the most successful of these techniques control of parameters by subtle changes in the experimental procedure is possible [1,2]. Some of these methods are the use of phase transfer agents [3], inverse micelle solutions [4], and laser induced evaporation techniques [5]. Their fundamental limitation lies in the small quantities produced, and their resistance to scaling up. If this niche of materials science is going to thrive it will need a way to provide enough material to perform adequate experimentation, and eventually, to distribute to needful applications. The solvated metal atom dispersion (SMAD) technique in conjunction with digestive ripening, previously developed in our laboratories, has been proven to produce gold colloids of similar or better quality than other methods, and on the gram scale [11]. This method is related to CVD and laser lithography in that bulk metal is heated under vacuum to liberate atoms and/or small clusters of the metal in question, then attempting to control the aggregation of these clusters to prevent them from reverting to the bulk state. The SMAD technique lends itself to scale up readily by at least 5000-fold compared to inverse micelle techniques. The colloids are then further refined by heating them in inert atmosphere in the presence of selected ligands that encourage the particles to reach a narrow size range. Our laboratory has done extensive studies on gold colloids produced in this manner and we have now adapted this method to synthesize silver nanoparticles [12–16]. This was done in the hope of taking advantage of the biocidal and optical properties of silver, and attempting to extend this synthetic method to other materials [17–26].

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2. Materials and methods

Silver shot 99.9999% was purchased from Strem Chemicals. Tungsten crucibles were purchased from R.D. Matthis and Co. and coated with an aluminum oxide cement from Zircar. Dodecane thiol 98+%, 4-*tert*-butyl toluene 95%, and trioctyl phosphine 90% were purchased from Aldrich, dried overnight over molecular sieves and bubbled with argon for a minimum of one hour before use. Methyl ethyl ketone was bought from Fisher, dried with CaO, fractionally distilled, and degassed via the freeze–thaw method with a minimum of 5 cycles.

2.1. Solvated metal atom dispersion method

The initial metal nanoparticles were synthesized in a manner similar to that recorded previously [11]. An aluminum oxide coated tungsten crucible was degassed by placing it into a reaction vessel (Fig. 1) and heating to ~1400 °C in vacuum. 0.3 g (1 eq.) silver shot was placed into the crucible while the capping agent (20 eq.) and 60 ml of 4-*tert*-butyl toluene were added to the bottom of the reactor flask with a stir bar. This system was sealed to vacuum and the liquids in the reactor were degassed. The reactor was surrounded by liquid nitrogen and evacuated for 3 h typically reaching pressures of 1×10^{-3} Torr. Then 40 ml of 2-butanone was slowly (roughly 1 h) deposited on the walls of the reactor flask forming a layer of frozen solvent. Simultaneously the crucible was slowly heated to the evaporation temperature of Ag (~1200 °C at reaction conditions). The flow of 2-butanone was slightly increased and the crucible temperature was maintained throughout the reaction. Once the silver begins to evaporate a yellow color appears in the frozen matrix which slowly turns to brown as the concentration of the metal increases in the solvent bed. Once evaporation has ceased, an additional 40 ml of 2-butanone was evaporated on top of the metal–solvent matrix. The liquid nitrogen was removed at this stage and the vessel was allowed to warm under a static vacuum. Stirring of the product was begun as soon as the stir bar was free of the frozen mixture on the bottom of the flask. At this point the product became a black solution that picked up a brown color as it warmed to room temperature. Argon was introduced into the vessel and the mixture was siphoned out into a schlenk flask for storage. Under argon, methyl ethyl ketone (a total of ~120 ml) was evaporated under vacuum from the prepared product mixture, leaving the dispersion containing only *t*-butyl toluene, silver, and capping agent.

2.2. Digestive ripening procedure

The product from the SMAD preparation was heated in the original schlenk flask under a flow of argon to reflux at 190 °C. The dispersion was refluxed from 90 min to 2 days in inert atmosphere. The resulting colloid was a dark solution of a vibrant yellow color when diluted. The entire synthetic process is illustrated in Fig. 1.

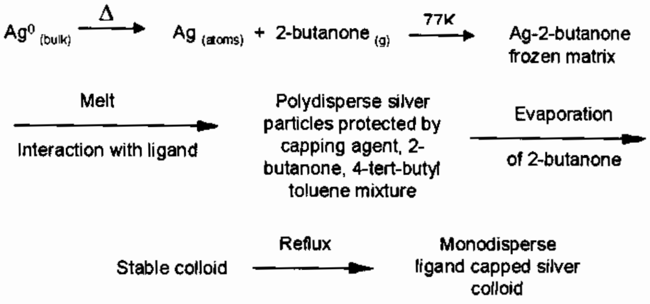


Fig. 1. Reaction sequence during SMAD synthesis and digestive ripening of particles.

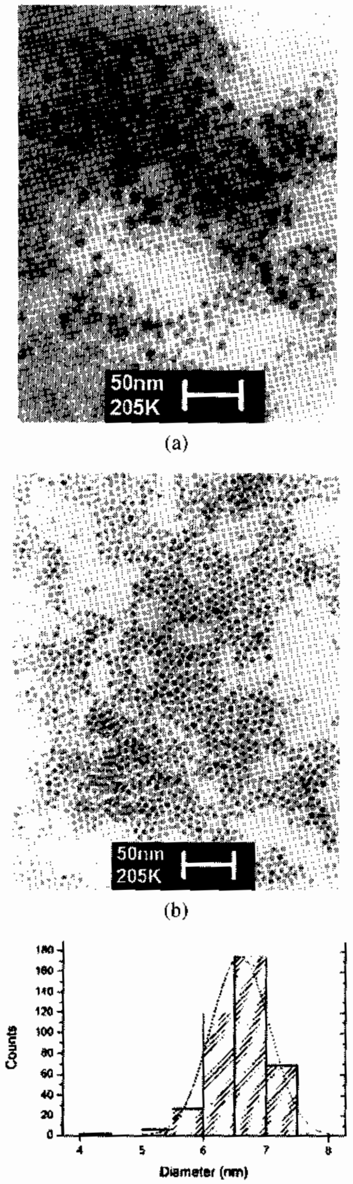
2.3. Instrumentation

The absorption spectra were obtained using a Cary 500 Scan UV–vis–NIR spectrophotometer. The size and morphology of particles were determined by TEM on a Phillips EM 201 microscope operating at 100 kV. Samples were prepared on formvar coated copper grids from Electron Microscopy Sciences by placing 2 μl of the Ag colloid on the grid and allowing it to dry in an inert atmosphere overnight on anticapillary tweezers. Preparing grids on the benchtop results in poor quality grids thought to be caused by oxidation of the product.

3. Results and discussion

3.1. Synthesis

The 2-butanone in the synthesis was used as an initial stabilizing agent to trap the initial clusters of Ag atoms and to prevent extensive aggregation of the Ag nanoparticles before they can come into contact with the capping agent. The *t*-butyl toluene has a two-fold purpose: providing a medium for the capping agent and the nanoparticles to interact in, and as a high boiling point solvent for the digestive ripening stage. After 90 min the majority of the colloid was broken down into small monodisperse particles; further refluxing serves to narrow the size distribution of the particles. Experiments were conducted in toluene akin to the earlier Au nanoparticle studies, however, the resulting colloid was of poorer quality with a large amount of small background particles (less than 2 nm in diameter), and of poorer distribution. This was attributed to the lower temperature of digestion. The choice of methyl ethyl ketone as the initial stabilizing solvent was dictated by previous experiments conducted independently of a stabilizing organic ligand, which included several polar and apolar solvents. The selection of capping agent, and molar ratio of capping agent to metal were all identical to previous synthetic procedures obtained from studies on Au and were confirmed to be acceptable for reactions with Ag [12,14].



(a)

(b)

(c)

Fig. 2. (a) Dodecane thiol stabilized silver nanoparticles prepared by SMAD method. (b) Same colloid after digestive ripening. (c) Histogram depicting the size distribution of the particles in (b).

As can be seen from the TEM pictures in Fig. 2a, the SMAD process produces polydisperse nanoparticles with spherical and some nonspherical shapes. This step is necessary, however, to produce large amounts of metal nanoparticles reactive enough to partake in the digestive ripening step. Then merely refluxing the mixture causes the size distribution of the particles to narrow drastically. It should be noted that bulk silver is inert to digestive ripening when placed in a similar chemical and physical environment. This is another example of the greatly increased reactivity of nanomaterials with respect to their macroscopic counterparts.

Long chain thiols have commonly been the choice for stabilizing Ag and Au nanoparticles in colloidal solution. The polar sulfur head group ligates to the metal surface while the alkane chain creates a boundary that insulates the reactive metal particles from each other, preventing aggregation. Trioctyl phosphine acts similarly in our study. However, the identity of the ligating head group and number of alkyl chains show considerable differences in behavior and properties of the product colloid.

Among the main advantages of this synthetic procedure is the lack of purification needed of the product. There are no reducing agents, or counterions that need to be removed from solution. Also, the yield is extremely high for there is no need for a size selective precipitation, or filtration procedures to isolate monodisperse particles as in other methods [8]. This method also allows for a high degree of tuneability, as the metal and capping agent can be interchanged allowing for a series of products ranging from metals to semiconductors, all with unique and adjustable properties.

3.2. *UV–vis absorption spectrum*

The visible absorption spectra for metal nanoparticles in the vicinity of group 11 are dominated by a surface plasmon resonance (SPR) peak, which is characteristic of the particle and its surrounding environment. This SPR phenomenon has been extensively studied in other papers, and can be predicted using the Mie theory [27–30]. It has been found that as particle size decreases this peak is blue-shifted, with respect to identical larger particles. Also, as the size distribution of the particles narrows it is reasonable to assume that this absorption peak will narrow with it. So as the range of particles in solution decreases the absorption will be focused at a more specific location. As can be seen from the spectra of the trioctyl phosphine capped particles (Fig. 3), the absorption peak from the SMAD prepared silver dispersion becomes considerably sharper and symmetric upon digestively ripening the sample. It should be noted that the spectra in Fig. 3 are from samples that have approximately the same concentration of silver atoms, yet the density of particles has undoubtedly increased as the larger particles have all been broken down to 6 nm causing an increase in the absorption spectra. While aggregates are known to cause a red shift in the absorption spectra [14] it is believed that the broadness of the peak in the SMAD prepared sample is due to the presence of the numerous particles of different size still solvated in the 4-*tert*-butyl toluene that are evident in the TEM pictures. The absorption peak is also observed to be blue-shifted by 15 nm. This alludes to the formation of a tighter size distribution of smaller particles. This trend is observed for both the trioctyl phosphine and dodecane thiol capped particles, and supports the TEM pictures. Although the sizes of the particles protected by the separate capping agents are nearly identical, a shift in the peak maximum can be seen for the two species (Fig. 4). This is likely due to slightly different electronic environments of the particles caused by the difference of the interaction of the sulfur vs the phosphorous ligating functionality in contact with silver nanoparticle. Their difference in electronegativity alone

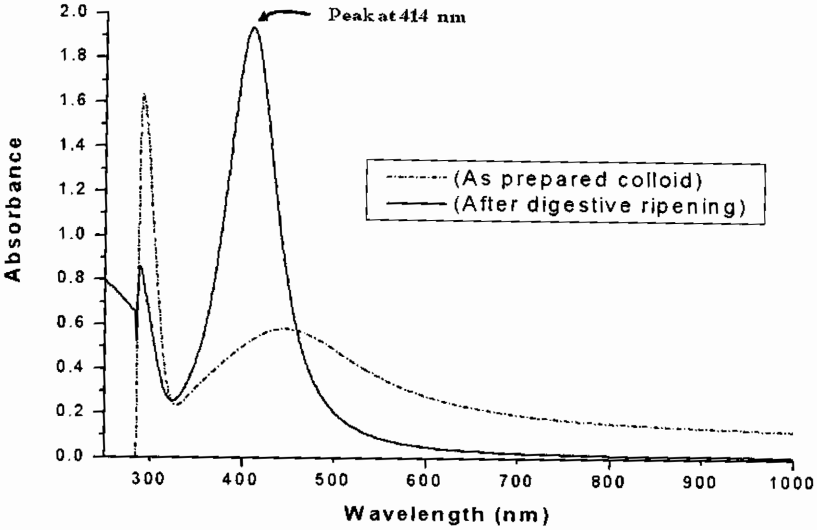


Fig. 3. Comparison of the surface plasmon resonance of a trioctyl phosphine protected silver colloid before and after narrowing the size distribution by digestive ripening.

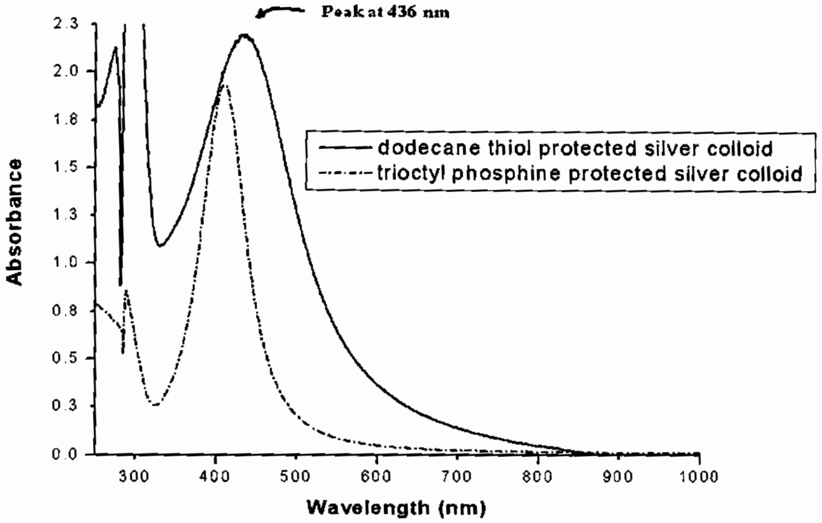
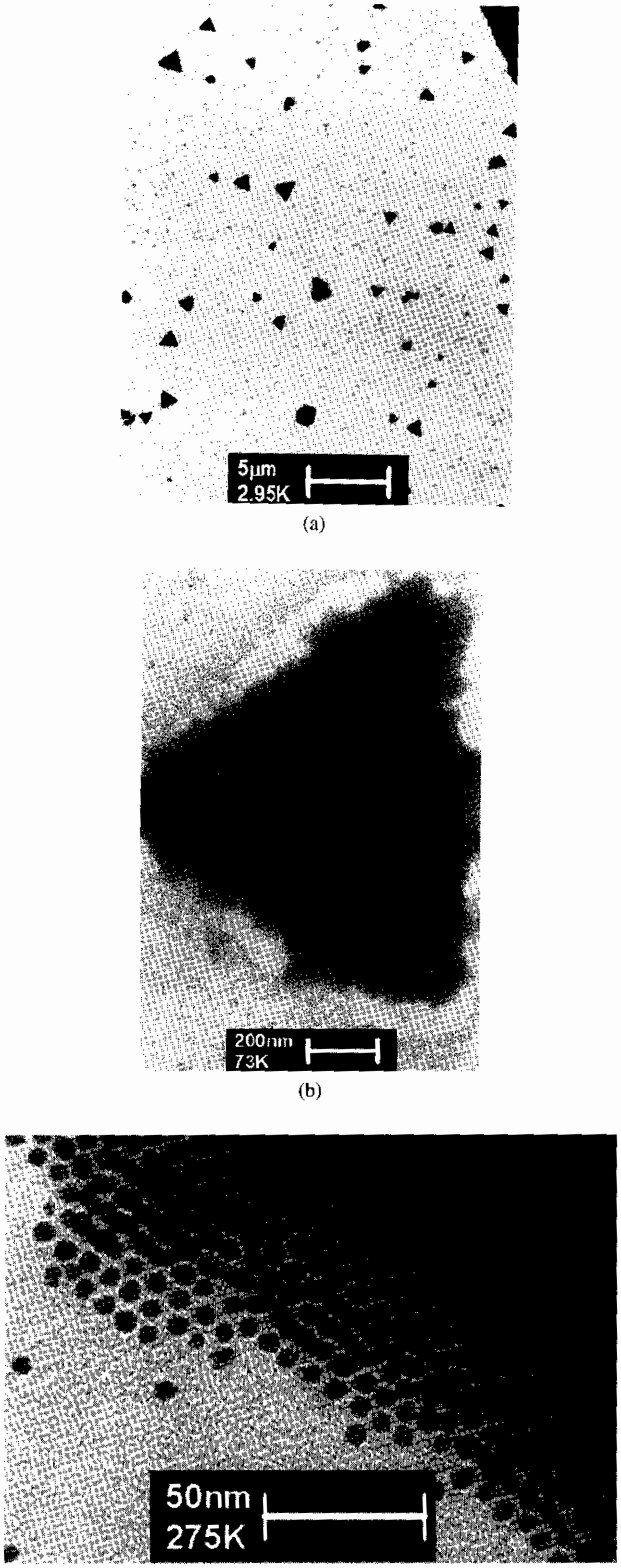


Fig. 4. Comparison of absorbance spectra for dodecane thiol capped silver nanoparticles and trioctyl phosphine capped silver particles.

should affect the amount of displacement of the electron gas associated with the particle.

3.3. Nanocrystal superlattice formation

One of the many remarkable properties of spherical metal nanoparticles that are very close in size is their ability to form ordered crystals, as atoms will, only on a dimension an order of magnitude larger. Often it has been reported that thiol passivated silver and gold nanoparticles have formed two-dimensional ordered arrays aided in some cases by the use of various substrates [15,31,32]. However, reports of 3-D arrays are rarer and their structures have been reported as completely amorphous. Three-dimensional superlattices are so difficult to construct that even with the use of thiol passivated self-assembled monolayers, as templates in the laboratories of Brust and Rao, defects commonly exist in even small areas [34,35]. In the present work, while both the dodecane thiol and trioctyl phosphine samples were able to produce 2-D arrays on TEM grids, there was almost exclusive formation of triangular 3-D crystals by the dodecane thiol sample (Fig. 5). A similar phenomenon was seen for the formation of circular superlattices for the trioctyl phosphine ligated particles (Fig. 6). The stark difference in geometry of these superlattices cannot be attributed to the difference in particle size. The phenomenon for forming triangular superlattices for dodecane thiol capped particles is akin to the results from reports by Wang, yet the particle sizes differ by almost 2 nm in diameter due to differences in synthetic preparations [33]. What must be weighed more heavily are the surface characteristics of the particles. Dodecane thiol protected particles are known to interdigitate very well with each other, and can arrange themselves on a surface in a close orderly fashion. There are three alkyl chains for each trioctyl phosphine ligand opposed to the single chain in do-

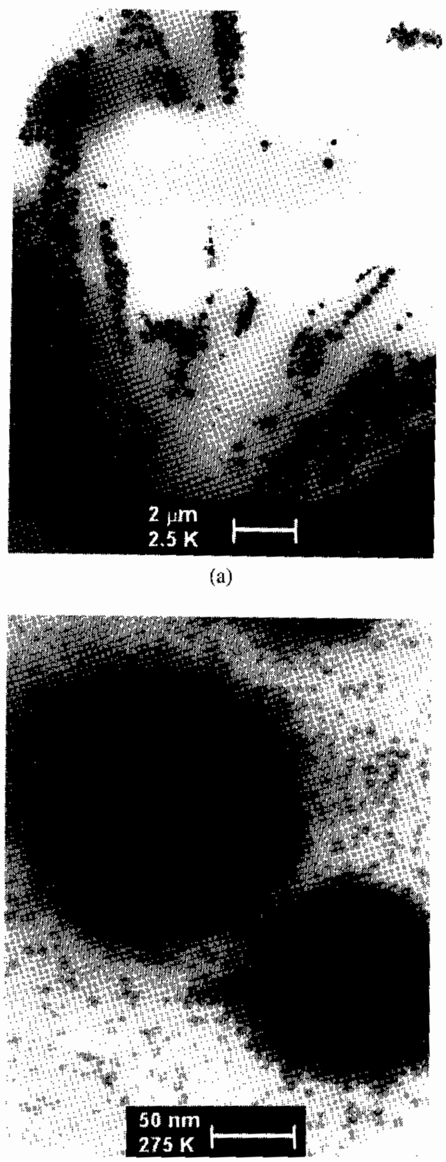


(a)

(b)

(c)

Fig. 5. (a) Low magnification image of triangular superlattices formed from dodecane thiol capped silver nanoparticles. (b) Medium magnification of a superlattice. (c) Magnified image of a triangular superlattice displaying the methodical ordering of the individual particles of the superlattice.



(a)

(b)

Fig. 6. (a) Low magnification picture of circular superlattices formed by trioctyl phosphine capped silver nanoparticles. (b) Magnified image of the superlattices.

decane thiol. This most likely causes a unique packing on the surface of the particles and probably gives rise to a different mode of interdigitation, and this gives rise to superlattices with a new structure, observed by the spherical crystals formed on precipitation.

4. Summary

We have successfully prepared monodisperse ligand protected silver colloids in gram quantities. This synthesis has added depth to the solvated metal atom dispersion method for preparation of nanoparticles and has confirmed the refining ability of ligands when heated in solution with metal nanoparticles in the digestive ripening stage. These SMAD prepared and digestively ripened particles are noted especially for their extensively ordered 3-D superlattice formation in geometrical shapes dependent upon the capping agent used. While the synthetic procedure is similar to that for gold nanoparticles, some alterations in the experiment were needed to safeguard against the greater ease of oxidation of the silver particles. Also a solvent system more suited to this metal had to be found to properly stabilize the initial particles and allow for complete digestion. Our goal is to be able to extend this synthetic procedure to many metal elements as well as to other areas of the periodic table by tailoring the synthesis to the chemical properties of the element involved. This will allow us to produce gram-scale quantities of a myriad of new monodisperse nanomaterials and their superlattices.

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