JACS
ARTICLES

Gram-Scale Synthesis of Monodisperse Gold Colloids by the Solvated Metal Atom Dispersion Method and Digestive Ripening and Their Organization into Two- and Three-Dimensional Structures

Savka Stoeva,[†] Kenneth J. Klabunde,*[,†] Christopher M. Sorensen,[‡] and Iovka Dragieva[§]

Contribution from the Departments of Chemistry and Physics, Kansas State University, Manhattan, Kansas 66506, and the Central Laboratory for Electrochemical Power Sources, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

Received August 30, 2001

Abstract: We describe a synthetic procedure for preparation of large quantities of monodisperse thiol-stabilized gold colloids in toluene solution. The method is based on the solvated metal atom dispersion technique (SMAD), which is very suitable for preparation of large amounts of metal colloidal solutions, as well as of metal sulfide, metal oxide, and other types of dispersed compounds in different solvents. A combination of two different solvents like acetone and toluene is used for the preparation of the gold colloids. The necessity of initially carrying out the SMAD reaction in acetone comes from its high degree of solvation of gold particles. Acetone acts as a preliminary stabilizing agent. After its removal from the system, the particles are stabilized by dodecanethiol molecules, which enable their very good dispersion in toluene solution. A digestive ripening procedure is carried out with the gold−toluene colloid, and for this purpose pure toluene as solvent is necessary. This has a dramatic effect on the narrowing of particle size distribution and almost monodisperse colloids are obtained (some discussion of the probable mechanism of this remarkable digestive ripening step is given). These colloidal solutions have a great tendency to organize in two- and three-dimensional structures (nanocrystal superlattices, NCSs). We believe that this procedure provides a real opportunity to synthesize large amounts of gold nanocrystals as well as NCSs.

Introduction

Organization of nanoparticles into two- and three-dimensional structures (nanocrystalline superlatices, NCSs) leads to the formation of materials characterized by very different properties compared to those of the discrete species. The manifestation of novel and technologically attractive properties is due to the collective interactions of the particles, as well as to the finite number of atoms in each crystalline core.[1] Synthesis and characterization of such materials are interesting from both fundamental and industrial points of view. Regularly arranged nanosized particles find applications in the development of optical and electronic devices, magnetic recording media, etc.[1−4] Nanoparticles of gold and other noble metals have attracted significant attention not only because of ease of preparation but also due to their potential application in nano- and microelectronics.[5] As stated by Andres et al.,[5] a challenging point is to form a structure of a planar array of small metal islands separated by tunnel barriers for use in electronics. Gold nanoparticles are excellent candidates in this respect.

Numerous methods for synthesis of particles arranged in 2D and 3D NCSs have been reported.[6] The most common procedures include reduction of a suitable metal salt in the presence of different stabilizing agents.[7−10] In all methods, the most

---

[†] Department of Chemistry, KSU.

[‡] Department of Physics, KSU.

[§] CLEPS, Bulgarian Academy of Sciences.

(1) Andres, R. P.; Averback, R. S.; Brown, W. L.; Brus, L. E.; Goddard, W. A.; Kaldor, A.; Louie, S. G.; Moskovits, M.; Percy, P. S.; Riley, S. J.; Siegel, R. W.; Spaepan, F.; Wang, Y. *J. Mater. Res.* **1989**, *4*, 704.

(2) Schmid, G.; Chi, L. *Adv. Mater.* **1998**, *10* (7), 515−525.

(3) Schmid, G.; Baumle, M.; Geerkens, M.; Heim, I.; Osemann, C.; Sawitowski, T. *Chem. Soc. Rev.* **1999**, *28*, 179−185.

(4) Rao, C. N.; Kulkarni, G. U.; Thomas, P.; Edwards, P. *Chem. Soc. Rev.* **2000**, *29*, 27−35.

(5) Andres, R. P.; Bielefeld, J. D.; Henderson, J. I.; Janes, D. B.; Kolagunta, V. R.; Kubiak, C. P.; Mahoney, W. J.; Osifchin, R. *Science* **1996**, *273*, 1690−1693.

(6) Murray, C. B.; Kagan, C. R.; Bawendi, M. G. *Science* **1995**, *270*, 1335. (b) Weller, H. *Angew. Chem.* **1996**, *35*, 1079. (c) Yin, J. S.; Wang, Z. L. *Phys. Rev. Lett.* **1997**, *79*, 2570; *J. Phys. Chem. B* **1997**, *101*, 8979. (d) Whetten, R. L.; Khoury, J. T.; Alvarez, M. M.; Murthy, S.; Vermar, I.; Wang, Z. L.; Stephens, P. W.; Cleveland, C. L.; Luedtke, W. D.; Landman, U. *Adv. Mater.* **1996**, *8*, 428. (e) Harfenist, S. A.; Wang, Z. L.; Alvarez, M. M.; Vermar, I.; Whetten, R. L. *J. Phys. Chem.* **1996**, *100*, 13904. (f) Wang, Z. L.; Harfenist, S. A.; Vermar, I.; Whetten, R. L.; Bentley, J.; Evans, N. D.; Alexander, K. B. *Adv. Mater.* **1998**, *10*, 808. (g) Motte, L.; Billoudet, F.; Lacaze, E.; Pileni, M. P. *Adv. Mater*. **1996**, *8*, 1018. (h) Motte, L.; Billoudet, F.; Pileni, M. P. *J. Phys. Chem*. **1995**, 99, 16425. (i) Motte, L.; Billoudet, F.; Lacaze, E.; Douin, J.; Pileni, M. P. *J. Phys. Chem.* **1997**, *101*, 138. (j) Ohara, P. C.; Leff, D. V.; Heath, J. R.; Gelbart, W. M. *Phys. Rev. Lett*. **1995**, *75*, 3466. (k) Heath, J. R.; Knobler, C. M.; Leff, D. V. *J. Phys. Chem. B* **1997**, *101*, 189. (l) Markovich, G.; Collier, C. P.; Heath, J. R. *Phys. Rev. Lett*. **1998**, *80*, 3807. (m) Keely, C. J.; Fink, J.; Brust, M.; Bethell, D.; Schiffrin, D. J. *Nature* **1998**, *396*, 444. (n) Pahl, K.; Bartelt, M. C.; de la Figuera, J.; Bartelt, N. C.; Hrbek, J.; Hwang, R. Q. *Nature* **1999**, *397*, 238. (o) Collier, C. P.; Vossmeyer, T.; Heath, J. R. *Annu. Rev. Phys. Chem.* **1998**, *49*, 371. (p) Ohara, P. C.; Gelbart, W. M. *Langmuir* **1998**, *14*, 3418.

(7) Green, M.; O'Brien, P. *J. Chem. Soc., Chem. Commun.* **1999**, 2235−2241.

10.1021/ja012076g CCC: \$22.00 © 2002 American Chemical Society

important requirement is the ability to produce monodisperse particles that can order over a long range. Crystalline arrays of particles covered by organic molecules have become of great interest, especially since the improved synthesis of thiol-stabilized gold nanoparticles by Brust et al.[11] Their advantage is that they behave as simple chemical compounds in the respect that they can be dissolved, precipitated, and redispersed without change in properties,[7] much as molecular crystals can.

Here, we describe the synthesis of monodisperse thiol-protected gold nanoparticles prepared by the solvated metal atom dispersion technique (SMAD). The SMAD method involves vaporization of a metal under vacuum and co-deposition of the atoms with the vapors of a solvent on the walls of a reactor cooled to 77 K (liquid nitrogen temperature). After the warmup stage, particles are stabilized both sterically (by solvation) and electrostatically (by incorporation of negative charge).[12] This approach was first reported by Klabunde and co-workers for the preparation of nonaqueous colloidal gold solutions.[13] Since then a variety of metal colloids have been synthesized and investigated in our laboratory.[12,14] The major advantage of the SMAD technique is that no byproducts of metal salt reduction are present and pure metal colloids are formed.[12] Although most laboratories are not equipped with SMAD reactors, an important aspect of the SMAD method is the possibility for scaling up the process. Industrial applications of nanocrystalline materials require their preparation in large amounts and reproducible quality. However, the inverse micelle and reductive procedures for metal colloid preparation are usually very problematic for scale-up because of the difficulty of maintaining the exact same reaction conditions in a large volume, the large volume of solvents required, and difficult purification procedures.

In the present study, thiol-stabilized gold nanoparticles are reproducibly synthesized in gram quantities in toluene solution. A greatly modified SMAD process is used that utilizes a novel combination of solvents and thiol ligand, at controlled times and temperatures. The narrow size distribution of the particles is achieved by the remarkable procedure of “digestive ripening”.[15] This simple procedure is based on the reflux of a polydisperse nanoscale colloid for a certain amount of time, resulting in a dramatic improvement of the size distribution of the particles. Their subsequent organization in 2D and 3D superlattices is investigated by transmission electron microscopy (TEM). UV−vis studies are also presented.

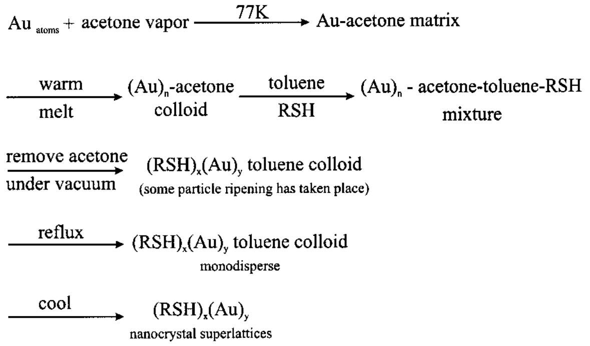

Figure 1. Flow diagram of synthetic steps for preparation of nanocrystal superlattices.

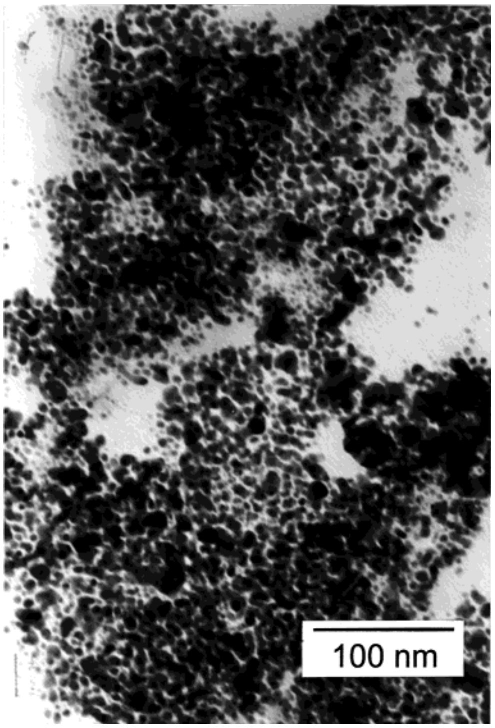

Figure 2. TEM micrograph of gold particles from Au−acetone−toluene−thiol colloid (colloid 1).

Experimental Section

(a) Preparation of Au−Acetone−Toluene−Thiol Colloid (Colloid 1). A stationary reactor described in detail in ref 16 was used for the synthesis of Au−acetone−toluene−thiol colloid. Acetone and toluene solvents were purchased from Fisher. Acetone was dried over molecular sieve. Both acetone and toluene were degassed five times by the standard freeze−thaw procedure prior to the reaction. Dodecanethiol was purchased from Aldrich and used as received. All glassware was rigorously cleaned before use.

Typically, a W−Al_2O_3 crucible was assembled in the SMAD reactor and the whole system was pumped down. This was followed by a stepwise heating of the crucible and the pressure was allowed to reach 4×10^{-3} Torr at each heating step. The crucible was heated to red in about half an hour; then the heating was decreased and the whole reactor was left under vacuum overnight while the crucible was gently heated. This process ensured no contamination of the crucible. After overnight, the reactor was filled with air and the crucible was charged with ∼0.3 g of Au metal. At the same time, 8 mL (6.8 g, 3.4×10^{-2} mol) of dodecanethiol was placed in the bottom of the reactor chamber together with a stirring bar. Degassed acetone and toluene solvents were placed in Schlenk tubes and attached to the SMAD reactor. The whole system was evacuated, with a liquid nitrogen-filled Dewar placed around the vessel. Dodecanethiol was frozen in this way in the bottom of the reactor. When the vacuum reached 4×10^{-3} Torr, 40 mL of toluene was evaporated in ∼15 min and frozen on the walls of the reactor. The liquid nitrogen Dewar was removed and toluene was allowed to

---

(8) Sarathy, K. V.; Kulkarni, G. U.; Rao, C. N. R. *J. Chem. Soc., Chem. Commun.* **1997**, 537−538.

(9) Taleb, A.; Petit, C.; Pileni, M. P. *J. Phys. Chem. B* **1998**, *102*, 2214−2220.

(10) Martin, J. E.; Wilcoxon, J. P.; Odinek, J.; Provencio, P. *J. Phys. Chem. B* **2000**, *104*, 9475−9486.

(11) Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D.; Whyman, R. *J. Chem. Soc., Chem. Commun.* **1994**, 801−802.

(12) Franklin, M.; Klabunde, K. J. *High-Energy Processes in Organometallic Chemistry*; Suslick, K. S., Ed.; ACS Symposium Series; American Chemical Society: Washington, DC, 1987; pp 246−259.

(13) Lin, S.; Franklin, M. T.; Klabunde, K. J. *Langmuir* **1986**, *2*, 259−260. (b) Klabunde, K. J. Method of Coating Substrates with Solvated Clusters of Metal Particles. U.S. Patent 4,877,647, 1989.

(14) Trivino, G.; Klabunde, K. J.; Dale, E. *Langmuir* **1987**, *3* (6), 986−992.

(15) Lin, X. M.; Wang, G. M.; Sorensen, C. M.; Klabunde, K. J. *J Phys. Chem. B* **1999**, *103*, 26, 5488−5492.

(16) Klabunde, K. J.; Timms, P. L.; Skell, P. S.; Ittel, S. *Inorg. Synth.* **1979**, *19*, 59−86; Shriver, D., Ed.

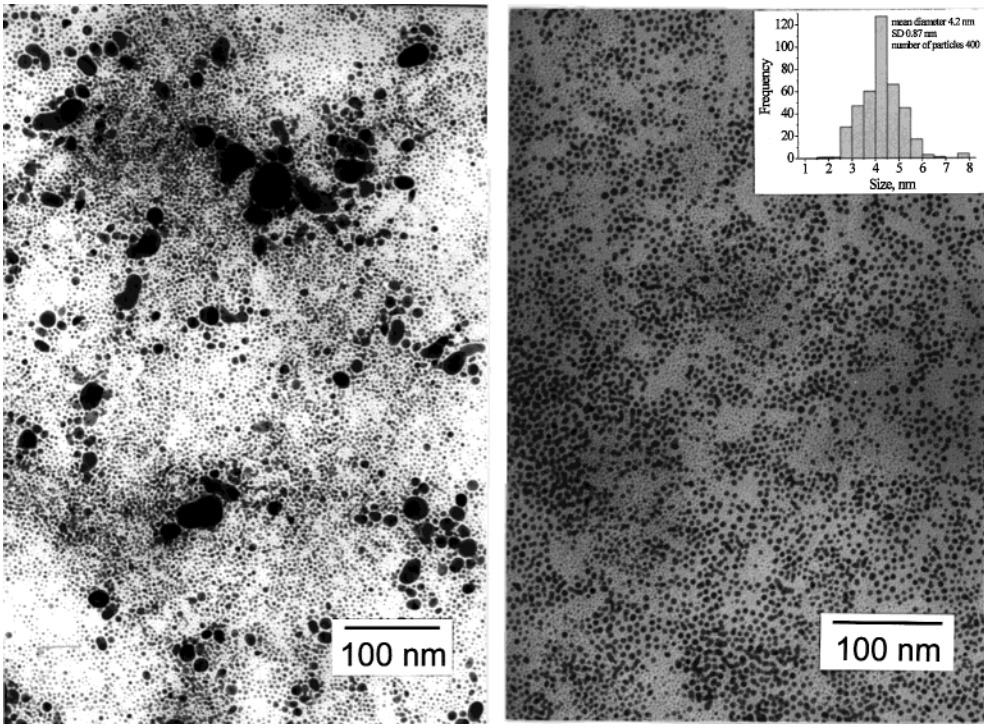

Figure 3. TEM micrographs of gold particles from Au−toluene−thiol colloid (colloid 2) from different areas of the grid.

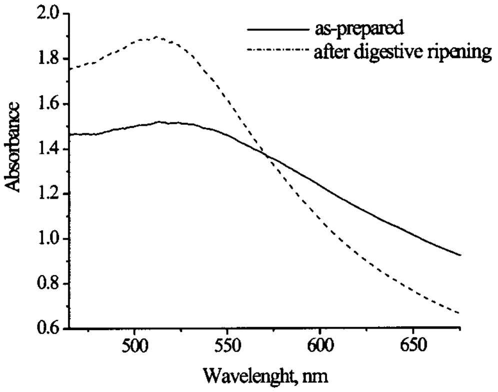

Figure 4. UV/vis absorption spectra of as-prepared colloid 2 (—) and the digestive ripened colloid (---).

melt undisturbed and fall to the bottom of the reactor. The liquid nitrogen Dewar was again put in place, and Au vapor (0.27 g, 1.4 × 10^{-3} mol) and acetone (100 mL) were co-deposited over a period of 3 h. During this time, the pressure was maintained at about 4 × 10^{-3} Torr. The frozen matrix had a deep red color at the end of the deposition. After the process was complete, the liquid nitrogen Dewar was removed and the matrix was allowed to warm slowly over a period of ∼1 h. During the warmup process, argon gas was allowed to fill the reactor system. Upon melting, the Au−acetone matrix mixed with the toluene and the color became deep brown. When the dodecanethiol started to melt, stirring was started and the whole solution was agitated for another 45 min. The as-prepared dark brown Au−acetone−toluene−thiol colloid (colloid 1) was siphoned under argon into a Schlenk tube.

(b) Preparation of Au−Toluene−Thiol Colloid (Colloid 2). The Schlenk tube containing the as-prepared Au−acetone−toluene−thiol colloid (colloid 1) was connected to a vacuum line and the acetone was evaporated until a constant 1 × 10^{-2} Torr pressure was reached (the more volatile acetone was removed along with some of the toluene). At this time, the Au−toluene−thiol colloid was diluted to 80 mL by addition of degassed toluene. Thus, the total volume of the final dark brown Au−toluene−thiol colloid was 80 mL, containing about 0.20 g of gold.

(c) Digestive Ripening. The digestive ripening process is the key step for formation of a monodisperse colloid from the polydisperse Au−toluene−thiol colloid (colloid 2). The procedure involves heating under reflux of a certain amount of Au−toluene−thiol colloid for 1.5 h. The heating temperature is the boiling point of the colloidal solution (∼120 °C). The digestive ripening was carried out under an argon atmosphere.

(d) Isolation of a Dry Product. Isolation of a dry product was done after the gold−toluene−thiol colloid (colloid 2) was subjected to digestive ripening for 1.5 h. After cooling to room temperature, 10 mL of the digested colloid (containing 0.025 g Au) was precipitated with 50 mL of absolute ethanol. After overnight, the precipitation was complete and the supernatant was carefully sucked out with a Pasteur pipet. The remaining precipitate together with a small amount of remaining toluene, thiol, and ethanol was dried under vacuum until constant pressure (5 × 10^{-3} Torr). After drying, the color of the product was brown-red and it had the appearance of a wet paste. An additional 3 mL of ethanol was added and the system was left undisturbed overnight. The supernatant was removed and the sediment again was dried under vacuum until constant pressure. After drying, the precipitate (0.0214 g) was a powder with small shiny dark crystals. It was washed again with 3 mL of ethanol and left overnight, the supernatant was removed, and the residue was dried under vacuum. After drying, the precipitate was 0.0207 g and no change of the mass was recorded after additional washing with ethanol and drying under vacuum. The yield is 84% based on gold. If the adsorbed thiol is taken into account, the yield is ∼73%.[17]

The final dry product is in the form of soft, shiny dark crystals, which are readily soluble in toluene or hexane. After addition of the solvent, the crystals immediately dissolve, giving wine-red-colored colloidal solution. However, the crystals are not soluble in ethanol or acetone.

(e) UV−Vis Spectroscopy. UV/Vis absorption spectra were obtained on a fiber optic CCD array UV−vis spectrophotometer of Spectral Instruments, Inc.

(f) Transmission Electron Microscopy. TEM is a suitable technique for investigation of size and shape changes of small particles. TEM studies were performed on a Philips CM100 operating at 100 kV. The

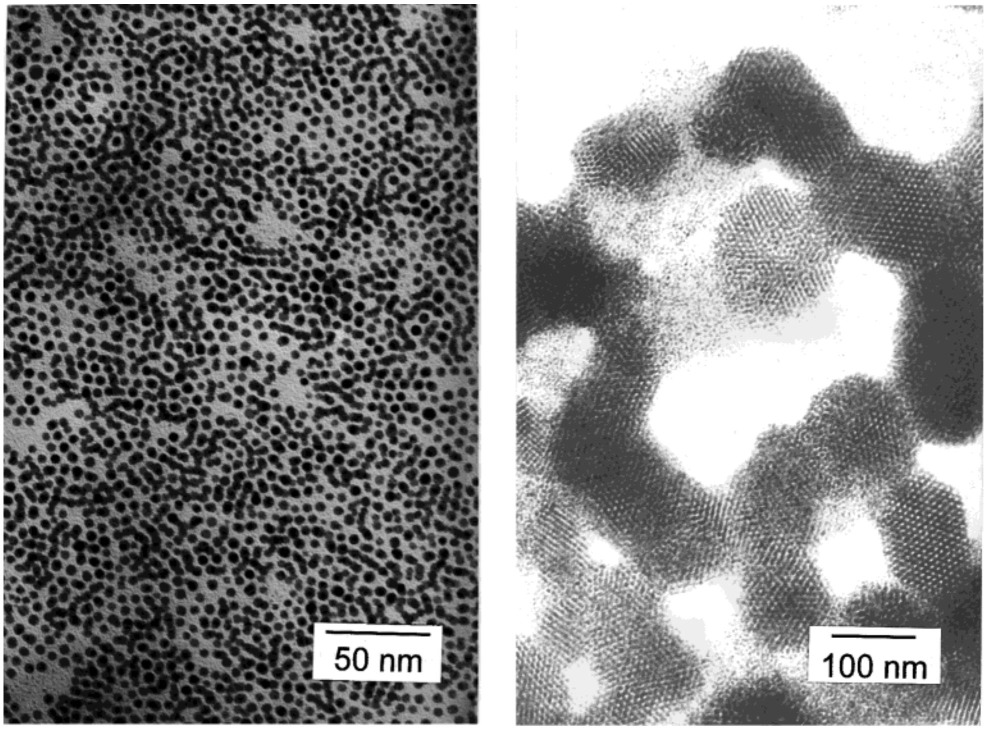

Figure 5. TEM micrographs of gold particles after digestive ripening where sampling was done from the hot colloidal solution.

TEM samples were prepared by placing a 3 μL drop from the colloidal solution onto a carbon-coated Formvar copper grid. The grids were allowed to dry in air for 1 h and left undisturbed at ambient conditions.

Results and Discussion

Since the first report in 1986[13] of the synthesis of nonaqueous colloidal gold solutions by the SMAD method, considerable work has been carried out on the preparation and characterization of several nonaqueous metal nanoscale particles.[12,14] Colloidal solutions of gold in acetone have been one of the most intensively studied and well-understood systems. Acetone, as a polar solvent, solvates the metal atoms and clusters during the warmup stage.[13] In this way steric stabilization is achieved and gold colloids are stable for months.

These earlier results have been the main motivation for choosing acetone as an initial solvent in our present work. Preliminary attempts to improve size distribution of particles from pure acetone solutions by the digestive ripening procedure turned out to be unsuccessful. An additional stabilizing agent like dodecanethiol was needed. However, when only acetone was used as the solvent, addition of dodecanethiol caused immediate precipitation of the colloid. For example, the precipitate formed after addition of dodecanethiol to Au−acetone colloids, when separated and dried under vacuum, was only partially redispersable in toluene. Digestive ripening of the partially redispersed Au colloids led to the size improvement of only those particles that were redispersed. The particles that remained in the sediment did not change their shape and size during this procedure. Obviously, a combination of acetone and toluene was needed during the SMAD reaction and subsequent cluster growth and ligation by the thiol. The role of acetone was simply to stabilize the gold nanoparticles in a preliminary way.

The size and shape changes of nanoparticles in the different samples were investigated by TEM. Representative transmission electron micrographs of the gold colloids at each step of the preparative procedure of the monodispersed colloid are displayed in the figures. A flow diagram of the major synthetic steps is given in Figure 1. The results from the separate preparative stages are discussed below.

Formation of Monodisperse Thiol-Protected Au Colloid:

(a) Au−Acetone−Toluene−Thiol Colloid (Colloid 1). The initial Au−acetone−toluene−thiol colloid has a dark brown color. TEM studies of this colloid (Figure 2) show particles ranging from 5 to 40 nm with no definite geometrical shapes. These particles are very similar to the ones obtained in pure acetone solvent.[12,13] As reported in previous results,[12,14] two types of stabilization are characteristic for these systems:

(1) steric stabilization (by solvation with the acetone molecules) and (2) electrostatic stabilization (by acquiring electrons

---

(17) Yield determination and the number of gold particles and thiol molecules are calculated as follows: yield (%) = [(experimentally measured Au mass − theoretical mass of adsorbed thiol)/(theoretically expected Au mass)] × 100. Eighty milliliters of colloid contains 0.2 g of Au metal; therefore, 10 mL of colloid contains 0.025 g of Au. The volume of 0.025 g of Au metal is 1.3×10^{-3} cm^3 = 1.3×10^{-9} m^3 [ρ(Au) = 19.28 g/cm^3]. If all gold is in the form of 2.25 nm radius particles (4.5 nm average diameter determined by TEM), then the volume of a single particle is $V = {}^4/_3\pi r^3 = {}^4/_3\pi(2.25 \times 10^{-9})^3 = 4.77 \times 10^{-26}$ m^3. For 10 mL of colloid: number of particles approximately = Au volume/Au particle volume = 1.3×10^{-9} m^3/4.77×10^{-26} m^3 = 2.73×10^{16} particles. The surface area of a single particle is $S = 4\pi r^2$, where $r = 2.25$ nm; $S = 6.36 \times 10^{-17}$ m^2. From the literature it is known that the surface area occupied by a single thiol molecule adsorbed on a gold surface is 21.4 Å = 2.14×10^{-19} m^2. The number of the thiol molecules forming a *monolayer* on the average Au particle should be $N = S_{\text{particle}}/S_{\text{thiol}} = 6.36 \times 10^{-17}/2.14 \times 10^{-19} = \sim 297-300$ thiol molecules per particle on average; in 10 mL of colloid, the total amount of the present thiol adsorbed as monolayer is $297(2.73 \times 10^{16}) = 8.1 \times 10^{18}$ molecules. This number corresponds to $8.1 \times 10^{18}/6.02 \times 10^{23} = 1.35 \times 10^{-5}$ mol (2.73×10^{-3} g, 3.23×10^{-3} cm^3). Ratio of gold/thiol in 10 mL of colloid = 0.025 g/2.73×10^{-3} g $\sim$ 10, For 10 mL of colloid: mass of adsorbed thiol is 2.73×10^{-3} g, theoretically expected Au mass is 0.025 g, and experimentally determined Au mass after ethanol washing is 0.021 g. Yield (without taking into account adsorbed thiol) = 84% or (taking into account adsorbed thiol) = 73%.

from the reaction vessel walls, electrodes, solvent medium). Another indication that the gold particles are negatively charged is the occasionally observed blinking in the electron microscope due to the interaction of the particles with the negatively charged electron beam. However, it should be pointed out that in no case was change in the shape or morphology of the particles observed under the influence of the electron beam. Both stabilization processes take place during the warmup step, which has to be carried out slowly in order to ensure good stabilization.

(b) Au−Toluene−Thiol Colloid (Colloid 2). Au−toluene−thiol colloid (colloid 2) was obtained by vacuum evaporation of all the acetone from colloid 1. TEM micrographs of two representative types of particles found in the colloid are shown in Figure 3. Drastic change of the size and shape of the particles is characteristic at this stage. Nearly spherical particles with sizes in the range of 1−6 nm are dominant.

There are also a small number of larger particles (10−40 nm) like those in the initial acetone-containing colloid.

The UV/vis absorption spectrum (Figure 4) of colloid 2 is in agreement with the sizes of the particles observed in TEM. It is characterized by a broad plasmon absorption band with no definite maximum.[15,18]

One possible explanation for the change of size and shape of the gold particles induced by the removal of acetone is the following. In colloid 1 the amount of acetone is in great excess. It strongly solvates the gold particles and the attachment of dodecanethiol molecules on the particles' surface is suppressed. Acetone, with its nonbonding electron pairs, can serve as a reasonably good ligand for gold but can only compete with RSH at high acetone concentrations. Therefore, as acetone is removed, the thiol competes better and better. This effect would be enhanced by the fact that the long-chained thiol is less soluble in acetone than in toluene.

Thus, acetone acts as a preliminary stabilizing agent, which is substituted by dodecanethiol molecules when acetone is evaporated. This ensures good dispersity of the thiol-ligated gold particles in the toluene medium. In addition, toluene is anticipated to achieve much better wetting of the thiol molecules on the gold particles' surface compared to the more polar solvent acetone. In favor of this are results obtained for the wetting of undecanethiol self-assembled monolayers on gold surface by water and hexadecane.[19] It was found that hexadecane as a nonpolar solvent wetted the thiol molecules on the gold surface much better (an advancing contact angle of ∼44°) compared to water (an advancing contact angle of ∼110°).[19] It is reasonable to expect a similar wetting trend for acetone and toluene due to their different polarities.

The fact that most of the particles in the Au colloid after evaporation of acetone have sizes in the region of 1−6 nm suggests that some ripening has already taken place, presumably due to the strong adsorption of dodecanethiol molecules on their surface. At this stage, the colloid is ready for final digestive ripening.

(c) Digestive Ripening of Colloid 2: Organization of Gold Particles. The digestive ripening process is the key step for obtaining monodisperse thiol-protected gold nanoparticles. Heating of colloid 2 under reflux results in a dramatic narrowing of the particle size distribution. TEM studies (Figure 5) of a hot colloidal solution show formation of spherically shaped particles with sizes of about 4 nm. They have a tendency to organize into 2D layers. Some of the particles from the hot colloid organize in nice 3D structures.

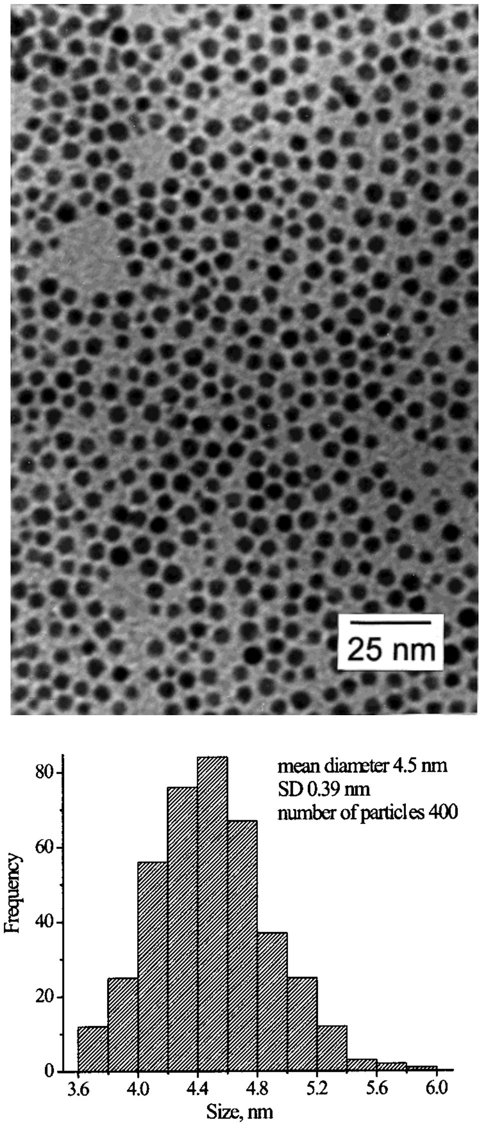

Figure 6. TEM micrograph of gold particles after digestive ripening (hot sample) and the corresponding histogram from measurement of 400 particles.

The remarkable effect of the digestive ripening procedure is the great improvement of the size distribution. A polydisperse colloid containing particles with sizes ranging from 1 to 40 nm is transformed into an almost monodisperse colloid with particle sizes of about 4−4.5 nm. A photograph taken at higher magnification (Figure 6) reveals that the shape of the particles is more polyhedral rather than spherical. The average size diameter is 4.5 nm and the size distribution is log normal, as typical for colloidal systems. The UV/vis absorption spectrum of the colloid after cooling to room temperature (Figure 4) shows an appearance of a definite plasmon absorption maximum at 513 nm, which is in agreement with the size and monodispersity of the obtained particles.

---

(18) Jirgensons, B.; Straumanis, M. E. *Colloid Chemistry*; Macmillan: New York, 1962; pp 119, 130, 258, and 306. (b) Mie, C. *Ann. Phys. (Leipzig)* **1908**, *25*, 377. (c) Ferrell, T. L.; Callcott, T. A.; Warmark, R. J. *Am. Sci.* **1985**, *73*, 344.

(19) Bain, C. D.; Evall, J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1989**, *111*, 7155−7164.

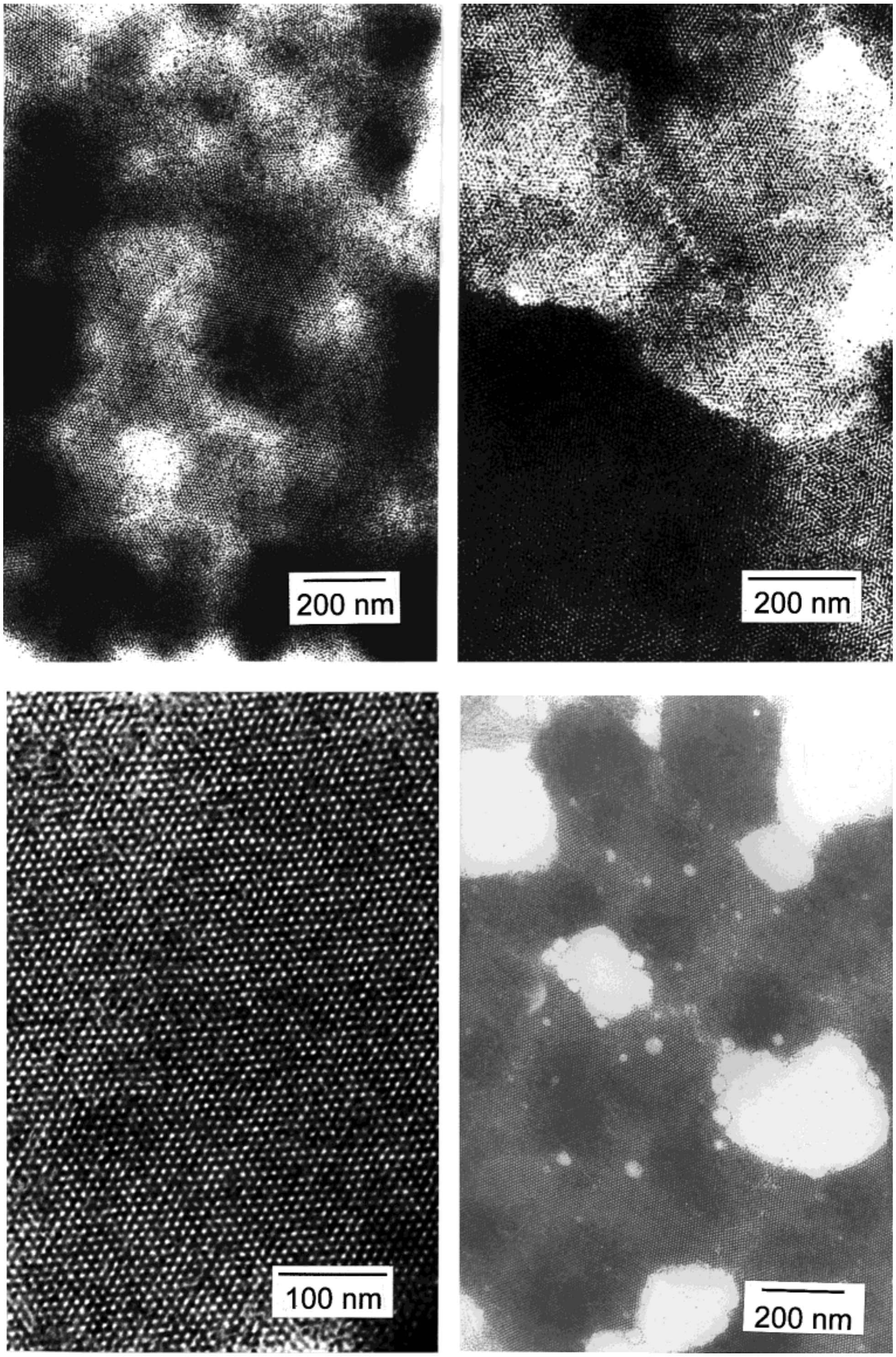

Figure 7. TEM micrographs of gold particles at different amounts of time since the digestive ripening process: (a, upper left panel) after 15 min; (b, upper right panel, and c, lower left panel) after 1 day; (d, lower right panel) after ∼2 months.

Interesting results are obtained by TEM from the digestive ripened colloids after they cool from reflux temperature. The TEM micrographs of colloids cooled for a different amount of time are shown in Figure 7. The amazing result is that the particles predominantly organize on the TEM grid in large 3D structures in only about 15 min after the digestive ripening process is finished (Figure 7, upper left panel). A small number of areas of 2D arrangement are also observed.

Even larger 3D structures ($>3\ \mu$m) are observed after 1 day (Figure 7, upper right and lower left panels) and after ∼2 months (Figure 7, lower right panel). The results suggest that the activation energy for 2D organization is lower compared to that of 3D organization.

Of course, one of the most interesting features of the synthetic sequence reported herein is the digestive ripening step, and the mechanism for this remarkable process is not entirely clear. Only a few useful facts are known. First of all, *nanoparticles* are the necessary starting material; that is, normal gold powder is not susceptible to digestive ripening, showing again that nanosized particles are intrinsically more chemically reactive than bulk samples.[20]

The ripening process probably involves the dissolution of surface atoms or clusters of atoms by the ligand molecules, which are in excess in the solution. This phenomenon is best known for gold nanoparticles,[10,15,21] but other metals can behave in a similar way with the appropriate ligands.[22] So a dissolving and reprecipitation process is likely, and reactive sites (corners, edges) would be the first atoms susceptible. The most intriguing question, though, is why all the particles become the same size, and why 4−5 nm? One possible rationale is that at 4−5 nm the thiol headgroups and the 12-membered carbon chain are close-packed in the most orderly fashion (which would be akin to formation of a crystalline surface coating) for the curvature in a 4−5 nm gold particle. Although this must be at least part of the explanation, our data with different chain lengths and different headgroups are not entirely supportive.[23] That is, even with different ligands of different chain lengths, the 4−5 nm size is still favored. Obviously, other factors must be involved as well, such as atom count, sometimes referred to as magic numbers. Further work is ongoing in an attempt to clarify the forces involved.

Acknowledgment. The support of the National Aeronautics and Space Administration (NASA) and partial support of the NSF are acknowledged with gratitude.

JA012076G

---

(20) Klabunde, K. J.; Mulukutla, R. S. *Nanoscale Materials in Chemistry*; Klabunde, K. J., Ed.; Wiley Interscience: New York, 2001; Chapt. 7, pp 223−261.

(21) Maye, M. M.; Zheng, W.; Leibowitz, F. L.; Ly, N. K.; Zhong, C. *Langmuir* **2000**, *16*, 490−497.

(22) Petrowski, J. M.; Wang, Z. L.; Grean, T. C.; El-Sayed, M. A. *J. Phys. Chem. B* **1998**, *102*, 3316−3320. (b) Murray, C. B.; Sun, S.; Gaschler, W.; Doyle, H.; Betley, T. A.; Kagan, C. R. *IBM J. Res. Dev.* **2001**, *45*, *1*, 47−56. (c) Puntes, V. F.; Krishnan, K. M.; Alivisatos, A. P. *Science* **2001**, *291*, 2115−2117.

(23) Unpublished work of B. L. V. Prasad.