

Digestive ripening, nanophase segregation and superlattice formation in gold nanocrystal colloids

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Abstract

A novel digestive ripening process is shown to narrow the particle size distribution from a highly polydisperse dodecanethiol ligated gold colloid. Unlike the Ostwald ripening process, the digestion occurs through transferring materials from large particles to small particles. Temperature-induced size segregation can further select the particle sizes. By using these two methods, highly ordered superlattices using nanocrystals as building blocks can be synthesized directly from a polydisperse colloid.

Introduction

An ultimate goal of nanocrystal research is to develop the ability to manipulate the size, morphology and arrangement of these ‘superatoms’ in such a fashion that their unique optical, electrical and magnetic properties can be utilized for future device applications (Schmid, 1994). While colloid synthesis has the advantage of making bulk quantities of nanomaterials in a manner much simpler and of a smaller size than lithographic techniques, the problem of narrowing the particle size distribution has long plagued colloid scientists (Matijevic, 1996). The significance of obtaining a monodisperse colloid is that it will allow us to correlate the physical properties of the entire colloid directly to the physical properties of each single size particle. It is also one of the key requirements in forming superlattice structures using nanocrystals as building blocks, which have been extensively studied recently (Whetten et al., 1996; Murray et al., 1995; Collier et al., 1998; Weller, 1996; Motte et al., 1997; Andres et al., 1996; Wang et al., 1998; Lin et al., 1999a; Fendler, 1996). Furthermore, monodisperse colloids also provide ideal

systems to study colloidal phase transitions without being affected by the complexity of particle size distribution (Arora & Rajagopalan, 1997).

Uniform micron size particles have been prepared by LaMer et al. half a century ago using a ‘growth by diffusion method’ (Sinclair & LaMer, 1949; Johnson & LaMer, 1947), the preparation of single size nanocrystal colloids, however, are much more difficult due to their fast growth rate and their inherent stability. The success only occurred within the last several years (Murray et al., 1993; Schaaff et al., 1998; Whetten et al., Peng et al., 1998). There are generally two approaches to obtain nanocrystal colloids with uniform size distribution. The first approach is the size selective precipitation method, which is a separation technique relying on the size dependent solubility of nanocrystals in a solvent mixture. Several groups have successfully used this technique to separate different size particles from a polydisperse hydrosol (Frens, 1972) and organic phase colloids (Murray et al., 1993; Schaaf et al., 1998). The second method is a result of continuing efforts following the original idea of LaMer et al. (Sinclair & LaMer, 1949; Johnson & LaMer 1947) and Sugimoto,

(Sugimoto, 1987), in which a uniform particle size is obtained by a fast nucleation occurring at the early stage of the reaction followed by a diffusion-controlled growth process that is carefully monitored during the rest of the synthesis (Peng et al. 1998).

In our previous work, we have shown that 3D nanocrystals superlattices (NCSs) can be synthesized directly from a polydisperse colloid by modifying the surface of the colloidal particles with specific ligands and nucleating the colloid at the phase boundary (Lin et al., 1999a;b). In this paper, we further studied this process and demonstrate that formation of gold NCSs occurs through a novel digestive ripening process and a temperature dependent size segregation process. The digestive ripening process can narrow the size distribution of a polydisperse colloid significantly. Unlike the well known Ostwald ripening in which large particles grow at the expense of small particles, this process narrows the distribution by sharing the material among different sizes of particles until a thermodynamically stable size is reached in the colloid. A temperature induced size segregation can further select the specific particle sizes. By controlling the segregation process carefully, we can spontaneously form 3D superlattice structures directly in the colloid.

Experimentation and results

Particle synthesis and digestive ripening

The gold colloid was prepared at room temperature using a didodecyldimethylammonium bromide (DDAB)/water/toluene inverse micelle system. Through controlling the amount of surfactant, water, the rate of reaction and the reaction temperature, inverse micelle synthesis usually produces nanoparticles with a fairly narrow size distribution, with the average particle size depending somewhat on the size of the micelles. (Pileni, 1993; Wilcoxon, 1992). Different from our previous experiments (Lin et al., 1999a;b) we purposely used a much smaller amount of DDAB surfactant to create a polydisperse colloid. A typical synthesis is as follows. DDAB was purchased from Fluka and used as received. Sodium borohydride, dodecanethiol and gold chloride (99.99%) were obtained from Aldrich and used as received. Deionized distilled water was obtained from a Barnstead nanopure system. Toluene was purchased from Fisher and further purified by distillation with sodium and

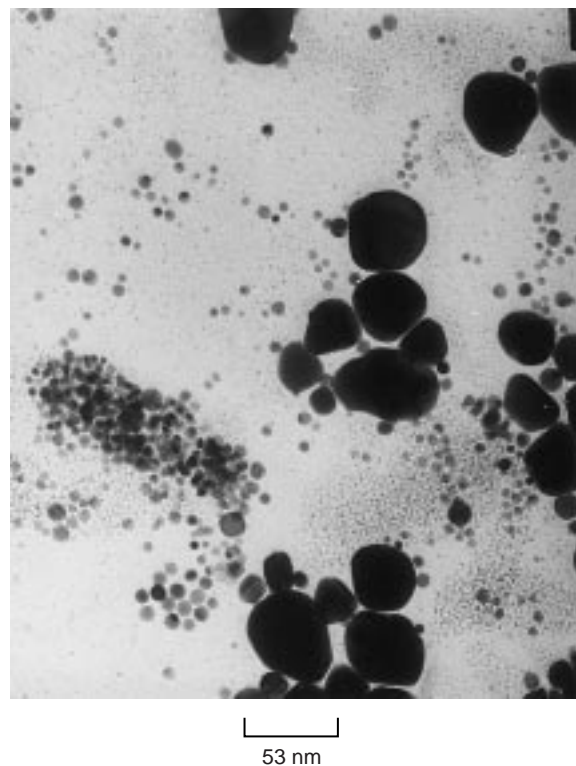


Figure 1. TEM images of the as prepared gold colloid using DDAB/water/toluene inverse micelle technique ([water]:[DDAB] ratio is 4 : 1)

potassium metal. Toluene and distilled water were first degassed by bubbling with dry argon gas for 2 h, and 156 mg of DDAB was dissolved in 15 mL toluene to form a 0.025 M micelle solution. Then, 51 mg gold chloride was dissolved in the micelle solution by sonication for 15 min, and a clear reddish brown colored solution was obtained. To this solution 54 μL of 9.4 M NaBH_4 aqueous solution was added dropwise to the reaction flask while stirring the solution at room temperature. The color of the solution turned dark red after about 20 s. The mixture was stirred for another 15 min to ensure complete reaction.

Figure 1 shows the transmission electron microscopy (TEM) image of the as prepared sample. The as prepared gold particles have a wide size distribution, from tiny particles as small as 1 nm to very large particles with the size of 80 nm. The large size distribution was apparently caused by the inhomogeneous growth of the nanoparticles due to the low DDAB concentration.

We then transferred 2.5 mL of the as prepared colloid to a separate 30 mL vial to which 0.2 mL of dodecanethiol was added. After stirring for 1 min, the color of the colloid turned from dark red to slightly purple. Dodecanethiol has a strong affinity to the gold surface (Dubois & Nuzzo, 1992) which results in a change of the interaction strength between the particles. The purple color was caused by the aggregation of the gold particles (Kreibig & Genzel, 1985). 7 mL of ethanol was then added to the vial. The mixture was shaken vigorously and let stand on the benchtop undisturbed overnight. The clear top solution, which contained reaction side products, DDAB surfactant and extra dodecanethiol ligand, was decanted. The bottom precipitates were dried under vacuum. The dried precipitates were redissolved into 2.5 mL toluene and an extra of 0.2 mL of dodecanethiol was added to the vial. The vial was then placed on a preheated hot plate and heated under reflux. The color of the colloid changed back to red within a minute during the refluxing which indicated a nonaggregated state of the particles in the colloid.

One drop of the colloid after refluxing was diluted in boiling toluene (110°C) and deposited on a carbon coated grid which was placed directly above the hot plate. The particle size and distribution after reflux digestion for 3 h are shown in Figure 2 (300 particles were measured for each histogram). It is clear that ligand modification and reflux digestion caused a dramatic improvement of particle size distribution. The average particle size was 6.2 nm, with a much narrower size distribution ($\sigma = 0.3$ nm) (Figure 2(b)). The same size particles existed throughout the entire grid. TEM analysis also showed that most of the size change happened within the first 10 min of digestion. A longer time digestion only improve the size distribution slightly.

Effect of experimental conditions

Unlike Ostwald ripening, where small particles dissolve preferentially in favor of larger particles (Tadros, 1987), the digestive ripening occurs through a process in which large particles break apart and small particles increase in size until a stable and uniform size is reached for the entire colloid. This process must be directly related to the modification of the particle surface by the ligand because similar reflux digestion was performed on the as prepared sample without adding any ligand and the size distribution changed only slightly.

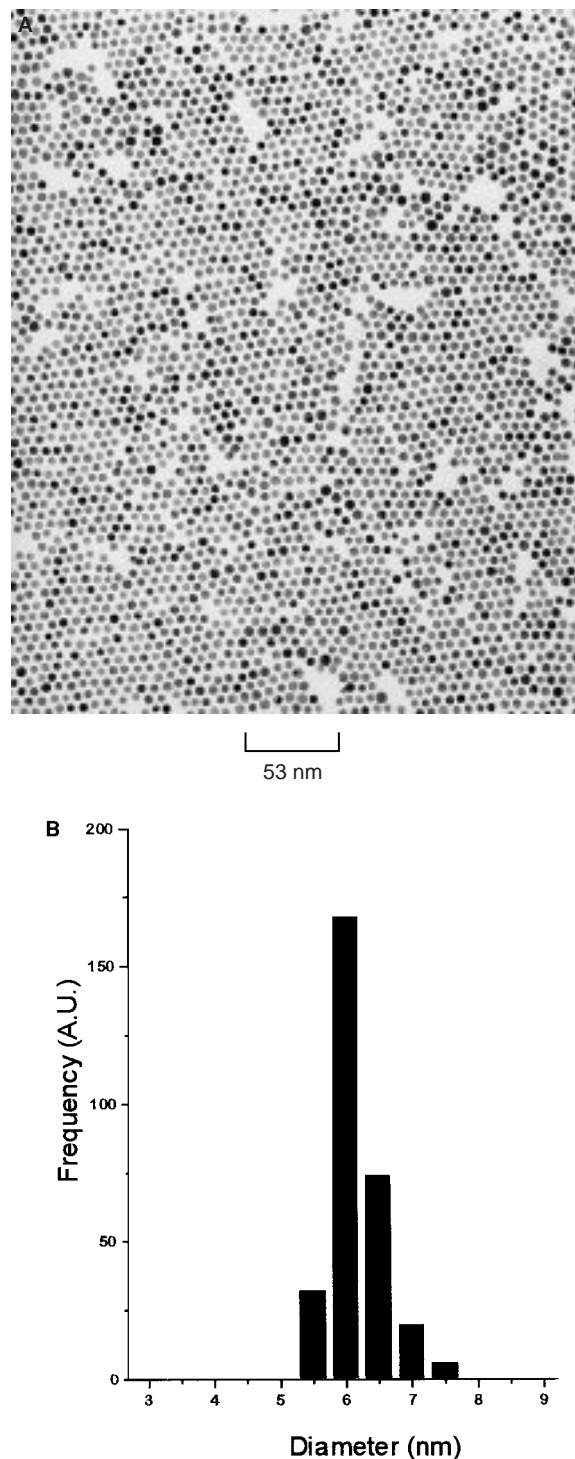


Figure 2. TEM image (a) and size histogram (b) of the dodecanethiol ligated gold colloid after three hours digestive ripening with [thiol] : [gold] ratio greater than 30.

The particle size (6.2 nm) after digestion seem to be a thermodynamically stable size for this specific system. This idea was further confirmed by performing the particle synthesis at a higher temperature (80°C) and trapping the particles by the same amount of dodecanethiol at the early stage of the borohydride reduction process. In this case we obtained a brownish colloid containing particles with majority size of 1–2 nm and a few of 4–5 nm. After cleaning the sample with ethanol precipitation followed by digestion with the same amount of dodecanethiol, we obtained the same 6.2 nm particle size with high monodispersity.

The amount of dodecanethiol also affected the final size of the system. From both experimental and theoretical calculation of the self assembly of a dodecanethiol monolayer on a (111) gold surface, we know that each thiol molecule occupies a surface area of 21.4 \AA^2 (Sellers et al., 1993). Using this value, the amount of thiol needed for a monolayer coverage of gold nanocrystals can be estimated. For 2.5 mL gold colloid containing the same concentration of 6.2 nm nanocrystals in our system, this value is about 0.5 μL . Our experiments, however, show that the amount of thiol needed to obtain 6.2 nm nanocrystals is far beyond this value. If 2 μL dodecanethiol was added to 2.5 mL colloid, a much larger particle size was observed after 3 h of digestion (Figure 3(a)), with average size of 8.7 nm and standard deviation of $\sigma = 1.5 \text{ nm}$. It is also noticed that significant amount of 6.2 nm particles also exist in the size distribution. Therefore a large amount of extra dodecanethiol molecule is needed for this complete digestion to occur.

The amount of water existent in the reaction precursor also influenced the final particle size after digestion. We increased the amount of water in the DDAB/water/toluene system by five times. Similar to Figure 1, the as prepared sample is also very polydisperse. Figure 4(a) shows the TEM image of this sample after 3 h digestion. Different from Figure 2(a), a significant amount of very smaller particles with diameter 3–4 nm appear. One possible explanation is the increased water concentration allows more nucleation sites in the system. By sharing materials between these nucleation sites, the overall particle size after digestion decreases. Long time digestion (up to 12 h), however, did not seem to further narrow the particle size distribution. Exactly how water affect the thermodynamically stable size needs to be further investigated.

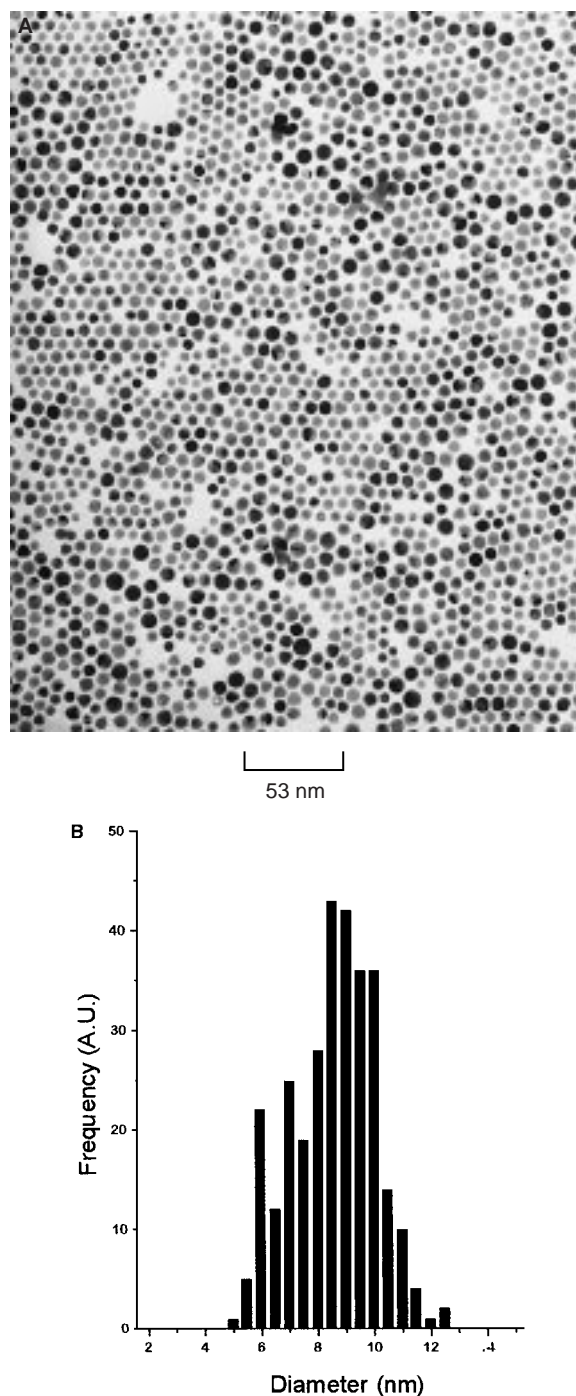


Figure 3. Effect of the amount of dodecanethiol ligands on the digestion. TEM image (a) and size histogram (b) of the dodecanethiol ligated gold colloid after 3 h digestive ripening with [thiol]: [gold] ratio equals to 0.3.

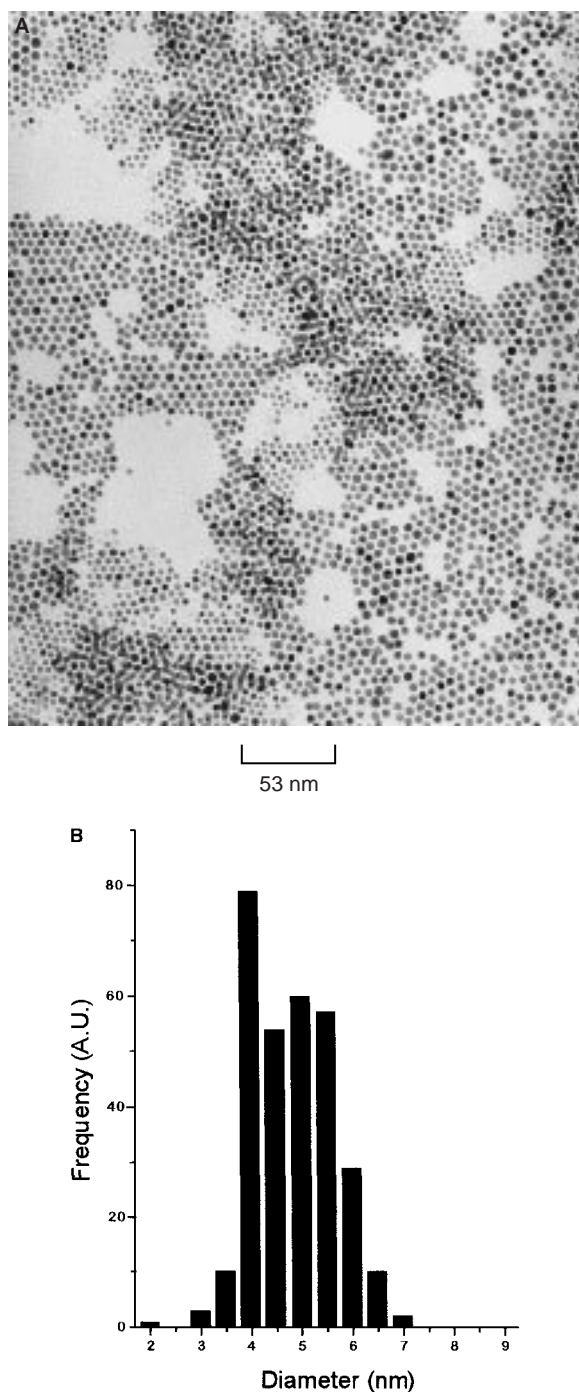


Figure 4. Effect of water on the final size of digestion. TEM image (a) and size histograms (b) of the dodecanethiol ligated gold colloid after 3 h of digestive ripening for a sample prepared with [water] : [DDAB] ratio of 20 : 1, [thiol] : [gold] ratio greater than 30.

Temperature-induced size segregation and superlattice formation

Although the size distribution of the gold nanocrystals is narrowed significantly after digestion, they are still not single sized. We found that upon lowering the colloid temperature from 110°C to room temperature, a size segregation occurs. This is especially true for the samples which were digested for a short amount of time. Figure 5 shows a TEM image of a sample which was digested for 10 min, and was diluted using room temperature toluene and was deposited onto a grid under ambient condition. Dark areas in the image correspond to the aggregation caused by some slightly larger particles. The monolayer region contains very monodisperse smaller particles. The size ratio between the smaller particle in the monolayer and the large particles in the aggregates are roughly 0.85. This result seems to be different from the previously reported work (Kiel et al., 1998), in which C₁₀thiol coated bimodal gold particles with size ratio 0.87 form random alloys

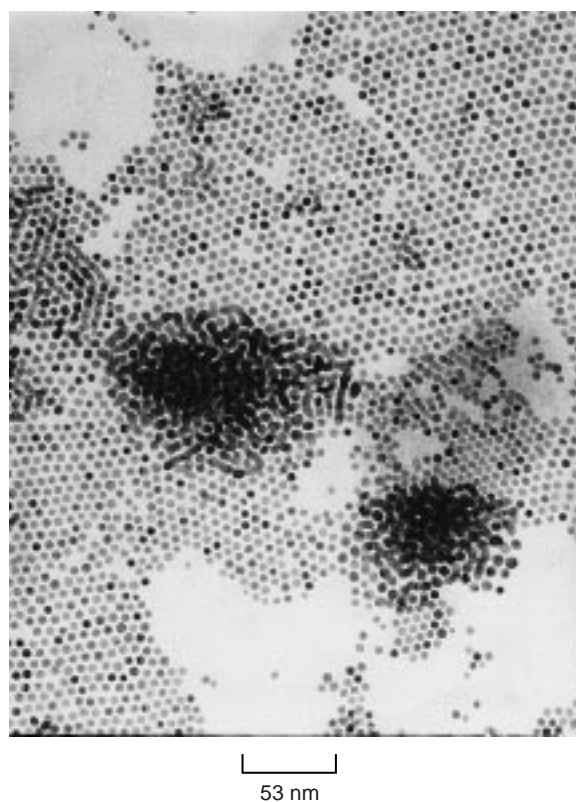


Figure 5. Segregation of different size nanocrystals on a TEM grid due to the decrease of colloid temperature.

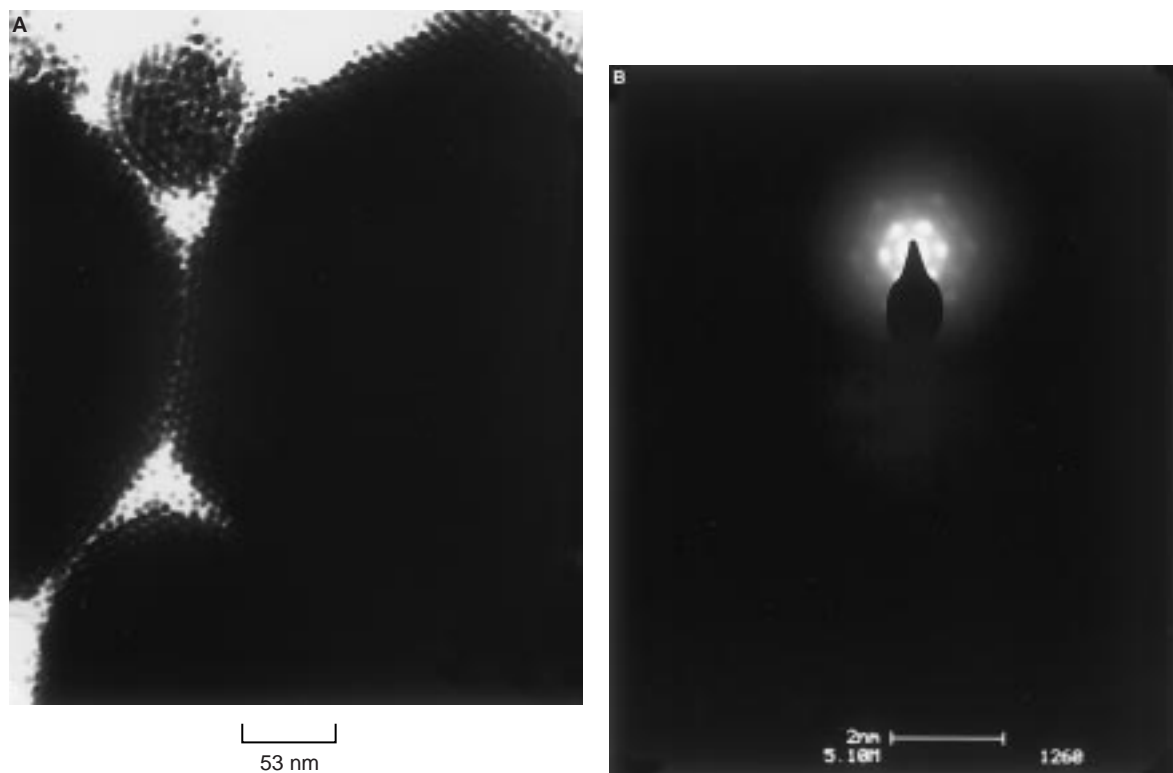


Figure 6. (a) TEM image of 3D nanocrystal superlattices formed directly in the colloid. (b) Small angle electron diffraction pattern of the nanocrystal superlattices.

at room temperature. In our case, random alloy structures only form at high temperatures ($\sim 100^\circ\text{C}$), and at room temperature, different size particles phase separated into different domains. This indicates, unlike the previous system, the interaction between nanocrystals can not be modeled by a simple hard sphere repulsion. Numerical simulation performed by Ohara et al. has also demonstrated that long range attraction between dodecanethiol ligated gold nanocrystals can cause size segregation (Ohara et al., 1995).

The size segregation phenomena also caused a problem for analyzing particle size distribution using TEM, since most of the TEM analyses are done in a local area. In our work, this was overcome by diluting the digested colloid in boiling toluene and depositing onto a grid that is placed close to the hot plate. This allows the solvent to evaporate very quickly and nanocrystals to deposit on the carbon film before they have a chance to segregate. On the bright side, temperature induced size segregation eases the strict requirement of single size particles in order to obtain 2D and 3D superlattice structures. By maintaining the colloid temperatures around the

phase separation temperature (Lin et al., 1999a), size segregation can selectively pick out large size particles from the size distribution and allows them to organize into 3D superlattices. These superlattices are formed directly in the colloid and eventually precipitate to the bottom of the vial. Figure 6(a) shows a TEM image of such 3D supercrystals with clear facets. The picture was slightly underexposed because of the thermal instability of the superlattice under the electron beam. However, the lattice fringes at the edge of the crystals are clearly visible. The small angle electron diffraction (SAED) pattern in Figure 6(b) shows the supercrystals have a fcc structure. The distance between neighboring particle surfaces is smaller than 0.5 nm, much smaller than the length of dodecanethiol carbon chain (Motte et al., 1995), which is 1.77 nm. Bundling of the passivating molecules in the supercrystals might be a reason why the interparticle distance is shorter (Luedtke & Landman, 1996).

After phase segregation, the top layer of the gold colloid is left with a very narrow distribution particles (average size 5.5 nm, with standard deviation of

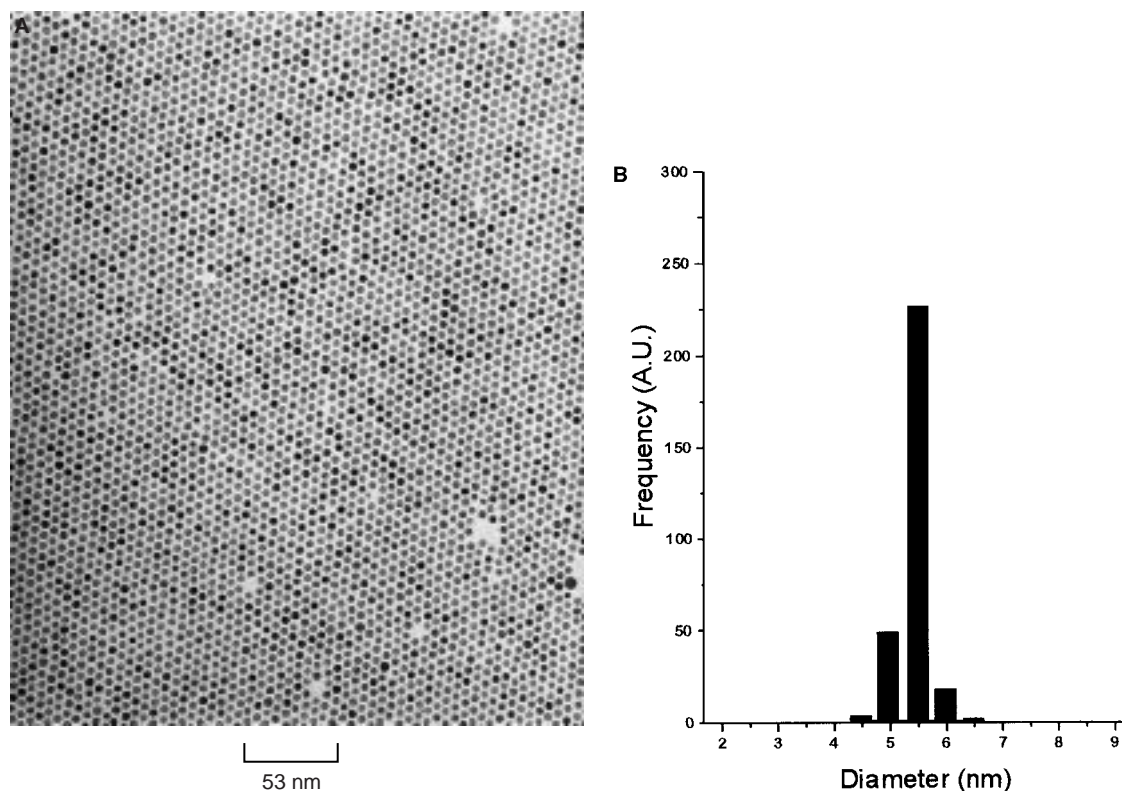


Figure 7. (a) Two dimensional superlattice structures formed by nanocrystals in the top layer of the colloid after size segregation. (b) Size histogram of nanocrystals in the two dimensional superlattices.

0.2 nm). These particles can under the right condition form hexagonal two dimensional superlattices on a flat substrate, as shown in Figure 7. Different from the three dimensional case, the distance between neighboring particle surfaces was about 1.7 nm in the 2D superlattices. This value is similar to a previous published result (Korgel & Fitzmaurice, 1998) and almost equal to the length of a carbon chain in the dodecanethiol ligand. Therefore, the carbon chains of the ligand molecules from neighboring particles may interdigitate to their full length.

Conclusion

In summary, we have demonstrated a simple and straightforward approach to obtain narrow size distribution gold nanoparticles from a very polydisperse colloid by ligating the nanoparticles with dodecanethiol followed by a digestive ripening process. Temperature induced size segregation can be used to further select the desired particle size. These two processes play an important role in 3D superlattice

formation directly in the colloid. By combining these two, one can generate well ordered structures from an initially very polydisperse system. At this time, we do not know the exact mechanism for this digestive ripening process, but we think it is largely due to the unique interaction between the gold surface and dodecanethiol ligand. Whether the same procedure can be generalized to other systems need to be further investigated.

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References

- Andres R.P., T.P. Bein, M. Dorogi, S. Feng, J.I. Henderson, C.P. Kubiak, W. Mahoney, R.G. Osifchin & R. Reifengerger, 1996. Self-assembly of a two-dimensional superlattice of molecularly linked metal cluster. *Science* 273, 1690.
- Arora A.K. & R. Rajagopalan, 1997. Applications of colloids in studies of phase transitions and patterning of surfaces. *Cur. Opi. Colloid Interface Sci.* 2, 391.
- Collier C.P., T. Vossmeier & J.R. Heath, 1998. Nanocrystal superlattices. *Annu. Rev. Phys. Chem.* 49, 371.
- Dubois L.H. & R.G. Nuzzo, 1992. Synthesis, structure, and properties of model organic surfaces. *Annu. Rev. Phys. Chem.* 43, 437.
- Fendler J.H., 1996. Nanoparticles at air/water interfaces. *Cur. Opi. Colloid Interface Sci.* 1, 202.
- Frens G., 1972. Particle size and sol stability in metal colloids. *Kolloid-Z. u. Z. Polymere* 250, 736.
- Johnson I. & V.K. LaMer, 1947. The determination of the particle size of monodispersed systems by the scattering of light. *J. Am. Chem. Soc.* 69, 1184.
- Kiely C.J., J. Fink, M. Brust, D. Bethell & D.J. Schiffrin, 1998. Spontaneous ordering of bimodal ensembles of nanoscopic gold clusters. *Nature* 396, 444.
- Korgel B.A. & D. Fitzmaurice, 1998. Condensation of ordered nanocrystal thin films. *Phys. Rev. Lett.* 80, 3531–3534.
- Kreibig U. & L. Genzel, 1985. Optical absorption of small metallic particles. *Surface Sci.* 156, 678–700.
- Lin X.M., C.M. Sorensen & K.J. Klabunde, 1999a. Ligand-induced gold nanocrystal superlattice formation in colloidal solution. *Chem. Mater.* 11, 198.
- Lin X.M., G.M. Wang, C.M. Sorensen & K.J. Klabunde, 1999b. Formation and dissolution of gold nanocrystal superlattices in a colloidal solution. *J. Phys. Chem. B* 103, 5488.
- Luedtke W.D. & U. Landman, 1996. Structure, dynamics, and thermodynamics of passivated gold nanocrystallites and their assemblies. *J. Phys. Chem.* 100, 13323.
- Matijevic E., 1976. Monodispersed colloids: art and science. *Langmuir*, 61, 24.
- Motte L., F. Billoudet & M.P. Pileni, 1995. Self-assembled monolayer of nanosized particles differing by their sizes. *J. Phys. Chem. Soc.*, 99, 16425–16429.
- Motte L., F. Billoudet, E. Lacaze, J. Douin & M.P. Pileni, 1997. Self-organization into 2D and 3D superlattices of nanosized particles differing by their size. *J. Phys. Chem.* 101, 138.
- Murray C.B., D.J. Norris & M.G. Bawendi, 1993. Synthesis and characterization of nearly monodisperse CdE (E = S, Se, Te) semiconductor nanocrystallites. *J. Am. Chem. Soc.* 115, 8706–8715.
- Murray C.B., C.R. Kagan & M.G. Bawendi, 1995. Self-organization of CdSe nanocrystallites into three-dimensional quantum dot superlattices. *Science* 270, 1335–1338.
- Ohara P.C., D.V. Leff, J.R. Heath & G.M. Gelbart, 1995. Crystallization of opals from polydisperse nanoparticles. *Phys. Rev. Lett.* 75, 3466.
- Peng X., J. Wickham & A.P. Alivisatos, 1998. Kinetics of II-VI and III-V colloidal semiconductor nanocrystal growth: 'focusing' of size distribution. *J. Am. Chem. Soc.*, 120, 5343.
- Pileni M.P., 1993. Reverse micelles as microreactors. *J. Phys. Chem.* 97, 6961–6973.
- Schaaff T.G., G. Knight, M.N. Shafigullin, R.F. Bor & R.L. Whetten, 1998. Isolation and selected properties of 10.4 kDa gold: glutathione cluster compound. *J. Phys. Chem.* 102, 10643–10646.
- Schmid G. (ed.) 1994. *Clusters and Colloids*. VCH, Weinheim.
- Sellers H., A. Ulman, Y. Schnidman & J.E. Eilers, 1993. Structure and binding of alkanethiolates on gold and silver surfaces: implications for self-assembled monolayers. *J. Am. Chem. Soc.* 115, 9389 and references within.
- Sinclair D. & V.K. LaMer, 1949. Light scattering as a measure of particle size in aerosols. *Chem. Revs.* 44, 245.
- Sugimoto T., 1987. Preparation of monodispersed colloidal particles. *Adv. Colloid Interface Sci.* 28, 65.
- Tadros T.F. (ed.) 1987. *Solid/Liquid Dispersions*. Academic Press, London.
- Wang Z.L., S.A. Harfenist, I. Vezmar, R.L. Whetten, J. Bentley, N.D. Evans & K.B. Alexander, 1998. Superlattices of self-assembled tetrahedral Ag nanocrystals. *Adv. Mater.* 10, 808–812.
- Weller H., 1996. Self-organized superlattices of nanoparticles. *Angew. Chem. Int. Ed. Engl.* 35, 1079–1081.
- Whetten R.L., J.T. Khoury, M.M. Alvarez, S. Murthy, I. Vezmar, Z.L. Wang, P.W. Stephens, C.L. Cleveland, W.D. Luedtke & U. Landman, 1996. Nanocrystal gold molecules. *Adv. Mater.* 8, 428–433.
- Wilcoxon J.P., 1992. Method for the preparation of metal colloids in inverse micelles and product preferred by the method. U.S. Patent No. 5,147,841, DOE control No. S70621.