

Digestive-Ripening Agents for Gold Nanoparticles: Alternatives to Thiols

B. L. V. Prasad,[†] Savka I. Stoeva,[†] Christopher M. Sorensen,^{*,‡} and Kenneth J. Klabunde^{*,†}

Departments of Chemistry and Physics, Kansas State University, Manhattan, Kansas 66506

Received June 6, 2002. Revised Manuscript Received September 17, 2002

Several ligands, such as alkylthiols, -amines, -silanes, -phosphines, -halides, and simple alkanes, were employed for digestive ripening, a process in which a colloidal suspension in a solvent is refluxed at the solvent boiling temperature in the presence of a surface-active ligand to convert a highly polydisperse colloid into a nearly monodisperse one. Apart from thiols, which are the only established digestive-ripening ligands, amines, silanes, and phosphines were found to be similarly efficient for this purpose. The important steps involved in the digestive ripening were identified to be (1) breaking the polydisperse colloid into smaller size particles upon addition of the ligand, (2) isolating this colloid from the reaction side products, and finally (3) heating this isolated colloid in the presence of the ligand to form a nearly monodisperse colloid. The successful ligands could be differentiated from the others based on their effectiveness to perform the different tasks in each step. Namely, they broke the bigger nanoparticles into smaller ones in the first step, formed a stable redispersible colloid in toluene after the second step, and at the end of the third step led to a nearly monodisperse colloid. The ability of the different ligands to break the bigger, prismatic as-prepared particles in the first step varied as $RSH \approx RNH_2 \approx R_3P \approx RSiH_3 > RI > ROH \approx RBr$ and simple alkanes completely failed to induce any changes in the size and shape of the as-prepared colloid. Ligands such as RI, RBr, and ROH failed in the second step, possibly because of the poor ligand–gold interaction. The ligand–gold interaction trends observed here could be rationalized semiquantitatively by invoking the hard and soft acid and base theory, which suggests that a soft acid-like gold likes to interact with softer bases such as RSH and R_3P rather than hard bases such as ROH. After the third step, the sizes of the nearly monodisperse particles depended on the ligand used for digestive ripening and correlated well with the ligand–gold interaction trends.

Introduction

The motivation for the preparation of gold nanoparticles include their potential utility in nanoelectronics, sensors, and the vast basic knowledge we can gain from these novel materials.¹ Colloids of gold nanoparticles are also one of the most stable and easiest to manipulate. However, preparing monodisperse gold particles is still not easily accomplished on a useful synthetic scale, especially if the stabilizing ligand of these particles is changed from the often used alkylthiols.

The general synthetic procedure to prepare nearly monodisperse gold colloids involves the reduction of metal salts in the presence of surfactants and then stabilizing their sizes with a capping ligand already present in the solution.² The size distribution is further

narrowed by size-selective precipitation.³ Recently, we demonstrated the advantage of a “digestive-ripening” procedure to prepare monodisperse colloids directly, avoiding the size-selective precipitation.⁴ In this procedure a polydisperse colloid is refluxed at the solvent boiling temperature in the presence of a capping ligand, resulting in the narrowing of the size distribution to a great extent. This protocol has already been established to work very well when alkanethiols are used as digestive-ripening agents.⁴ A host of alternative procedures have been reported for the synthesis of monodisperse gold and other metal nanoparticles including dissociation of metal salts with lasers, using heterogeneous seeds to prepare monodisperse particles and even utilizing biological methods to produce metal nanoparticles.⁵ Similarly, several reports have also appeared on the capping of gold nanoparticles, prepared through the standard micelle and inverse micelle techniques, with

* Corresponding authors. K. J. Klabunde: phone, 785-532-6849; fax, 785-532-6666; e-mail, kenjk@ksu.edu. C. M. Sorensen: e-mail, sor@phys.ksu.edu.

[†] Department of Chemistry.

[‡] Department of Physics.

(1) See the special Issue of *Sci. Am.* **2001**, 285.

(2) Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R. *J. Chem. Soc., Chem. Commun.* **1994**, 801. (b) Andres, R. P.; Bielfeld, J. D.; Henderson, J. I.; Janes, D. B.; Kolagunta, V. R.; Kubiak, C. P.; Mahoney, W. J.; Osifchin, R. G. *Science* **1995**, 273, 1690. (c) Spatz, J. P.; Roescher, A.; Moller, M. *Adv. Mater.* **1996**, 8, 337.

(3) Schaff, T. G.; Knight, G.; Shafiqullin, M. N.; Bor, R. F.; Whetten, R. L. *J. Phys. Chem. B* **1998**, 102, 10643.

(4) (a) Lin, X. M.; Sorensen, C. M.; Klabunde, K. J. *J. Nanopart. Res.* **2000**, 2, 154. (b) Lin, X. M.; Wang, G. M.; Sorensen, C. M.; Klabunde, K. J. *J. Phys. Chem. B* **1999**, 103, 5488. (c) Lin, X. M.; Jaeger, H. M.; Sorensen, C. M.; Klabunde, K. J. *J. Phys. Chem. B* **2001**, 105, 3353. (d) Prasad, B. L. V.; Stoeva, S. I.; Sorensen, C. M.; Klabunde, K. J. *Langmuir* **2002**, 18, 7515.

ligands other than the thiols. The list includes several modified thiols,⁶ the other chalcogenides,⁷ amines,⁸ phosphines,^{8b,9} phosphine oxides,¹⁰ carboxylates,¹¹ xanthates,¹² porphyrines,¹³ polymers,¹⁴ and dendrimers.¹⁵ However, the synthetic conditions used in these reports are quite different from each other and some even involve the usage of highly toxic chemicals, rendering the scaling up an arduous task. Since “digestive ripening” offers great promise in scaling up the synthesis¹⁶ of monodisperse nanoparticles, it would be interesting to study whether any ligands other than thiols could be used as digestive-ripening agents. Moreover, because a fundamental explanation of how digestive ripening works is lacking, more empirical data involving other ligands will be useful in finding an explanation. In this study we present our results when thiols, amines, phosphines, alcohols, halides, silanes, and simple alkanes were used as digestive-ripening ligands. Only thiols, amines, silanes, and phosphines were found to be effective digestive-ripening agents. It was also observed that the final sizes of the particles stabilized by these ligands and the ability to form superlattices varies greatly from ligand to ligand, suggesting a qualitative dependency of these functionalities on the ligand–gold interaction.

Experimental Procedure

Because detailed synthetic procedures have appeared earlier,⁴ they are not reported here. Briefly, AuCl₃ (34 mg) was dissolved in 10 mL of toluene solution of 0.02 M didodecyltrimethylammonium bromide (DDAB). The metal salt solution was then reduced under vigorous stirring by dropwise addition of 36 μ L of 9.4 M aqueous NaBH₄. The original orange-red DDAB–AuCl₃–toluene solution turned very dark bluish-red within a few minutes, indicating the formation of gold nanoparticles. The stirring was continued for 15 min to ensure the completion of reaction. All the above steps were performed in anaerobic conditions in the presence of Ar. All the solvents were degassed by bubbling with Ar gas for 4 h prior to use. All the reagents mentioned above and the ligands used in this report were procured from Aldrich and were used without any further purification. The specific ligands used were dodecanethiol (RSH), dodecylamine (RNH₂), octadecyl silane (RSiH₃), trioctyl phosphine (R₃P), dodecyl bromide (RBr), dodecyl iodide (RI), dodecanol (ROH), and decane (RH).

The “as-prepared” colloid was split into 2.5-mL portions and the ligands to be tested for digestive ripening were added to these portions by keeping the molar ratio of Au:ligand as 1:30. To this an excess amount of ethanol or acetone was added to isolate the ligand-capped gold particles from DDAB and the reaction side products by precipitation. In the cases of thiols, amines, and silanes, the colloids retained their red color and the reaction side products were removed by decanting and vacuum-drying. The precipitated colloids were then re-dispersed into 2.5 mL of toluene, mixed with another dose of the ligand (with the same molar ratio of Au:ligand = 1:30) and were allowed to reflux for about 90 min. Phosphine and other ligand-stabilized colloids resulted in the irreversible precipitation of the colloid after ethanol or acetone addition, and they could not be re-dispersed in toluene. However, we could adopt a slightly different procedure in the phosphine-stabilized colloid case and carry out digestive ripening. Here, the ligand-capped as-prepared colloids were shaken with 1 mL of water three or four times and this effectively removed all the unwanted side products into the water. To the remaining colloid a second dose of phosphine was added with the same molar ratio of 1:30 (based on the initial gold concentration in the as-prepared colloid) and was refluxed for 90 min. In all the other cases (ROH, RBr, RI, and RH) both ethanol or acetone addition caused rapid de-colorization of the red colloid and formed a greenish black precipitate that could not be re-dispersed in toluene, even at elevated temperatures. On the other hand, water addition led to the formation of emulsions, again destabilizing the colloid very rapidly.

TEM images were taken with a Phillips EM100 microscope operating at 100 kV by casting 3- μ L portions of the colloids on a carbon-coated Formvar-copper grid after vigorously shaking the sample vials. The particle size distributions were determined from a sample of a minimum of 300 particles and were determined from several samples.

Results and Discussion

We used the inverse micelle procedure to synthesize the gold colloid and we intentionally prepared a highly polydisperse colloid.¹⁷ This was done (i) to mimic the larger quantity preparations of gold nanoparticles, which generally result in a polydisperse colloid, and (ii) to validate the ligand’s capacity as a digestive-ripening agent. We consistently obtained the as-prepared colloid as prismatic-shaped particles with sizes ranging from a few nanometers to a few hundred nanometers (Figure

- (5) (a) Walker, C. H.; St. John, J. V.; Wisian-Neilson, P. *J. Am. Chem. Soc.* **2001**, *123*, 3846. (b) Esumi, K.; Hosoya, T.; Suzuku, A.; Torigoe, K. *Langmuir* **2000**, *16*, 2978. (c) Fukuoka, A.; Araki, H.; Sakamoto, Y.; Sugimoto, N.; Tsukuda, H.; Kumai, Y.; Akimoto, Y.; Ichikawa, M. *Nano Lett.* **2002**, *2*, 793. (d) Okitsu, K.; Yue, A.; Tanabe, S.; Matsumoto, H.; Yobiko, Y. *Langmuir* **2001**, *17*, 7717. (e) Mafune, F.; Kohno, J.-y.; Takeda, Y.; Kondow, T.; Sawabe, H. *J. Phys. Chem. B* **2001**, *105*, 5114. (f) Jana, N. R.; Gearher, L.; Murphy, C. J. *Langmuir* **2001**, *17*, 6782. (g) Henglien, A.; Meisel, D. *Langmuir* **1998**, *14*, 7392. (h) Ravaine, S.; Fanucci, G. E.; Seip, C. T.; Adair, J. H.; Talham, D. R. *Langmuir* **1998**, *14*, 708. (i) Yee, C. K.; Jordon, R.; Ulman, A.; White, H.; King, A.; Rafilovich, M.; Sokolov, J.; *Langmuir* **1999**, *15*, 3486. (j) Gardea-Toredey, J. L.; Parsons, J. G.; Goemz, E.; Peralta-Videa, J.; Troiam, H. E.; Santiago, P.; Yacamán, M. J. *Nano Lett.* **2002**, *2*, 397. (k) Yu, H.; Gibbons, P. C.; Kelton, K. F.; Buhro, W. E. *J. Am. Chem. Soc.* **2001**, *123*, 9198. (l) Mukherjee, P.; Ahmad, A.; Mandal, D.; Senapati, S.; Sainkar, S. R.; Khan, M. I.; Parishcha, R.; Ajaykumar, P. V.; Alam, M.; Kumar, R.; Sastry, M. *Nano Lett.* **2001**, *1*, 515. (m) Harfenist, S. A.; Wang, Z. L.; Whetten, R. L.; Vezmor, I.; Alvez, M. M. *Adv. Mater.* **1997**, *9*, 817.
- (6) (a) Kim, B.; Tripp, S. L.; Wei, A. *J. Am. Chem. Soc.* **2001**, *123*, 7955. (b) Yonezawa, T.; Onoue, S.; Kimizuka, N. *Langmuir* **2001**, *17*, 2291. (c) Shon, Y.-S.; Mazzitelli, C.; Murray, R. W. *Langmuir* **2001**, *17*, 7735. (d) Wuelfing, W. P.; Murray, R. W. *J. Phys. Chem. B* **2002**, *106*, 3139. (e) Shelly, E. J.; Ryan, D.; Johnson, S. R.; Couillard, M.; Fitzmaurice, D.; Nellist, P. D.; Chen, Y.; Palmer, R. E.; Preece, J. A. *Langmuir* **2002**, *18*, 1791.
- (7) Brust, M.; Stühr-Hansen, N.; Norgaard, K.; Christensen, J. B.; Nielsen, L. K.; Bjornholm, T. *Nano Lett.* **2001**, *1*, 189.
- (8) (a) Leff, D. V.; Brandt, L.; Heath, J. R. *Langmuir* **1996**, *12*, 4723. (b) Brown, L. O.; Hutchison, J. E. *J. Phys. Chem. B* **2001**, *105*, 8911. (c) Brown, L. O.; Hutchison, J. E. *J. Am. Chem. Soc.* **1999**, *121*, 882.
- (9) (a) Schmid, G. *Chem. Rev.* **1992**, *92*, 1709. (b) Weare, W. W.; Reed, S. M.; Warner, M. G.; Hutchison, J. E. *J. Am. Chem. Soc.* **2000**, *122*, 12890.
- (10) Green, M.; Hutchison, J. E. *Chem. Commun.* **2000**, 183.
- (11) Yao, H.; Momozawa, O.; Hamatani, T.; Kimura, K. *Chem. Mater.* **2001**, *13*, 4692.
- (12) (a) Sawant, P.; Kovalev, E.; Klug, J. T.; Efrima, S. *Langmuir* **2001**, *17*, 2913. (b) Tzhayik, O.; Sawant, P.; Efrima, S.; Kovalev, E.; Klug, J. T. *Langmuir* **2002**, *18*, 3364.
- (13) Sloufova-Srnova, I.; Vlckova, B. *Nano Lett.* **2**, 121.
- (14) (a) Corbierre, M.; Cameron, N. S.; Sutton, M.; Mochrie, S. G. J.; Lurio, L. B.; Ruhm, A.; Lennox, R. B.; *J. Am. Chem. Soc.* **2001**, *123*, 10411. (b) Youk, J. H.; Park, M.-K.; Locklin, J.; Advincula, R.; Yang, J.; Mays, J. *Langmuir* **2002**, *18*, 2455. (c) Zhou, Y.; Itoh, H.; Uemura, T.; Naka, K.; Chujo, Y. *Langmuir* **2002**, *18*, 277. (d) Pastoriza-Santos, I.; Liz-Marzan, L. M. *Langmuir* **2002**, *18*, 2888.
- (15) (a) Esumi, K.; Satoh, K.; Torigoe, K. *Langmuir* **2001**, *17*, 6860. (b) Crooks, R. M.; Zhao, M.; Sun, L.; Chechik, V.; Yeung, L. K. *Acc. Chem. Res.* **2001**, *34*, 181.
- (16) Stoeva, S. I.; Klabunde, K. J.; Sorensen, C. M.; Dragieva, I. *J. Am. Chem. Soc.* **2002**, *124*, 2305.
- (17) Borohydride reduction of AuCl₃ in a 0.35 M DDAB micelle solution leads to a fairly monodisperse colloid. See Lin, X. M.; Sorensen, C. M.; Klabunde, K. J. *Chem. Mater.* **1999**, *11*, 198. However, taking 0.02 M DDAB micelle solution makes the as-prepared gold colloid highly polydisperse.

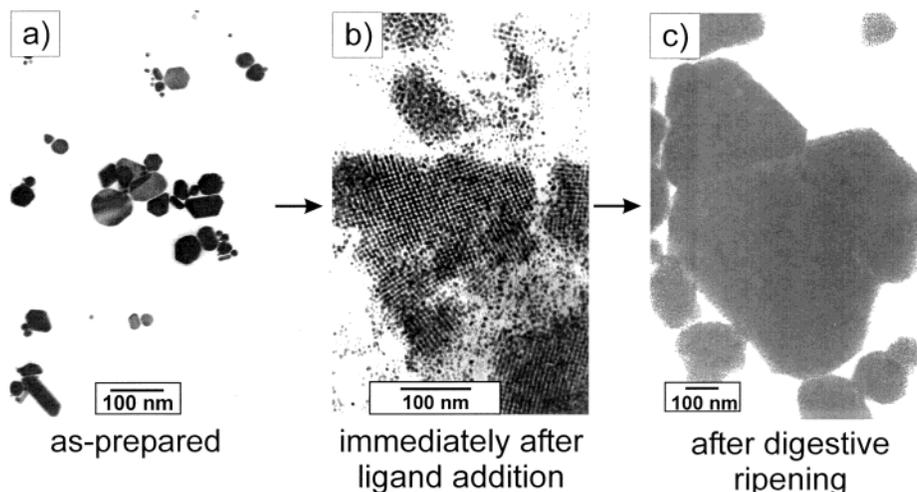


Figure 1. Pictorial demonstration of digestive ripening. The ligand used was dodecanethiol.

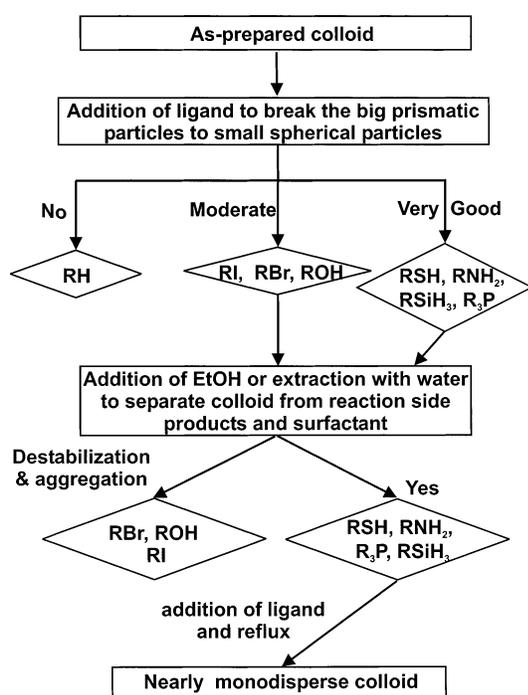


Figure 2. Flowchart of the different steps involved in the digestive-ripening procedure and the results obtained with different ligands.

1a). Figure 1 also depicts the effect of digestive ripening with dodecanethiol as the ligand and the results were similar for phosphines, amines, and silanes. As can be seen from this figure, mere addition of the ligands at room temperature induces drastic changes in the appearance and sizes of these prismatic particles, resulting in more narrowly size-distributed smaller spherical particles (Figure 1b). Refluxing these particles with additional ligand causes these particles to grow and further narrows the size distribution, and the monodisperse particles start to self-assemble into long-range lattices (Figure 1c).

The extension of the digestive-ripening process to other ligands is summarized in the flowchart in Figure 2. The entire process from an as-prepared colloid to a digestively ripened one can be categorized into three steps, namely, (1) addition of the ligand to the as-prepared colloid to break the bigger particles into

smaller ligand-capped particles, (2) isolation of the ligand-capped particles from reaction side products, and (3) refluxing the isolated colloid from step 2 with additional ligand to obtain the digestively ripened colloid. There are two important steps in the above process, which differentiate useful ligands from the rest. In the first step the ligands (except alkanes) break the big prismatic-shaped as-prepared particles into nearly spherical and relatively monodisperse colloids (Figures 3 and 4) and the ability varies as $RSH \approx RNH_2 \approx R_3P \approx RSiH_3 > RI > ROH \approx RBr$ with simple alkanes failing to make any impact. The sizes of the particles after the addition of RSH, RNH_2 , R_3P , and $RSiH_3$ and after digestive ripening are given in Table 1.

The next step involves the isolation of these ligand-stabilized small spherical particles from the reaction side products. Two slightly different protocols were employed for this. In the first one the ligand-stabilized colloids were precipitated by adding excessive amounts of ethanol or acetone. This worked well for thiol-, amine-, and silane-coated particles. In all the other cases the ligands were probably not securely attached to the particle surface, leading to the coagulation of particles when ethanol or acetone were added, and they could not be re-dispersed in toluene. Alternative methods like extracting the side products and surfactants with water were effective for only phosphine-stabilized particles. In all the other cases shaking with water formed emulsions and the colloids decomposed rapidly, making them useless for digestive ripening.

The successfully isolated colloids were either re-dispersed in toluene (thiol-, amine-, and silane-capped) or were taken as it is (phosphine); a second dose of ligand was added to them and were subjected to reflux, resulting in the formation of a nearly monodisperse gold nanoparticles in all the cases. The average size of the colloidal nanoparticles for the dodecanethiol-, trioctylphosphine-, octadecylsilane-, and dodecylamine-capped cases were 4.7, 7.2, 7.2, and 8.6 nm, respectively, after this final step (Table 1). It was also observed that whereas dodecanethiol-capped particles formed large superlattices, no such ordering was observed in the other cases. Representative figures of the resulting colloids digestively ripened with RSH, R_3P , RNH_2 , and $RSiH_3$ are all presented in Figures 5, 6, 7, and 8,

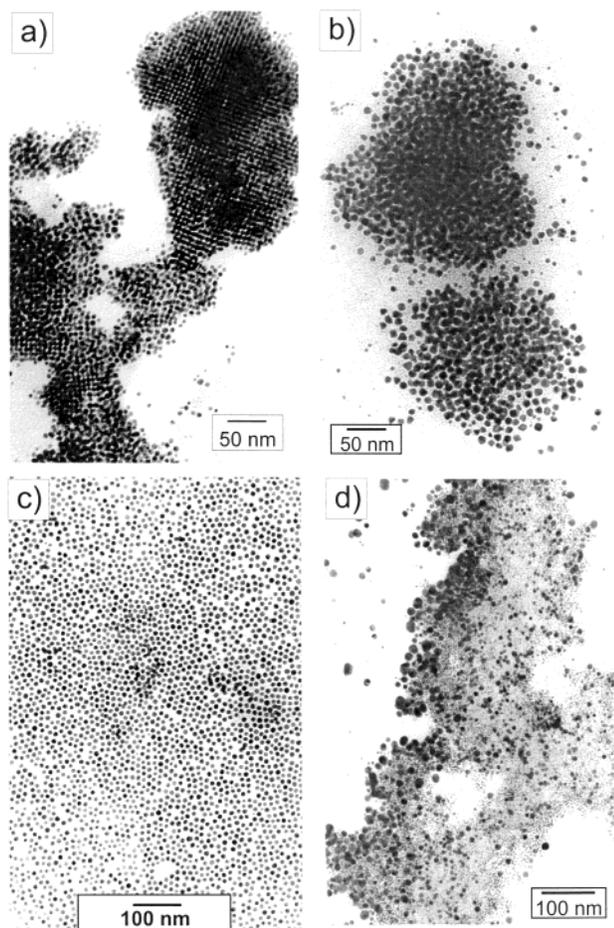


Figure 3. Effect of the addition of different ligands on the as-prepared colloid (Representative picture of as-prepared colloid is shown in Figure 1a.) (a) $C_{12}H_{25}SH$, (b) $(C_8H_{17})_3P$, (c) $C_{12}H_{25}NH_2$, and (d) $C_{18}H_{37}SiH_3$.

respectively. These figures clearly establish the efficacy of the digestive-ripening procedure as the final colloids are more monodisperse compared with the as-prepared colloid.

It is not clear presently whether our ripening procedure is completely different from Ostwald ripening or something similar is occurring in one of the steps. Heat-induced size evolution of gold nanoparticles in the presence of surface-capping ligands has been observed by other groups.¹⁸ It is argued that the capping ligand is ripped off the surface of the nanoparticle under heat treatment and small spherical particles coalesce together, leading to bigger particles. These are then restabilized by the ligand.^{18b} This mechanism is similar to Ostwald ripening where larger particles, which are favored due to their lower surface energies, grow at the expense of smaller particles. On the other hand, there is also evidence that thiol causes etching of the surface of bulk gold or gold nanoparticles upon heat treatment.¹⁹ In the case of gold nanoparticles heating with neat thiol under an inert atmosphere led to the stabilization of

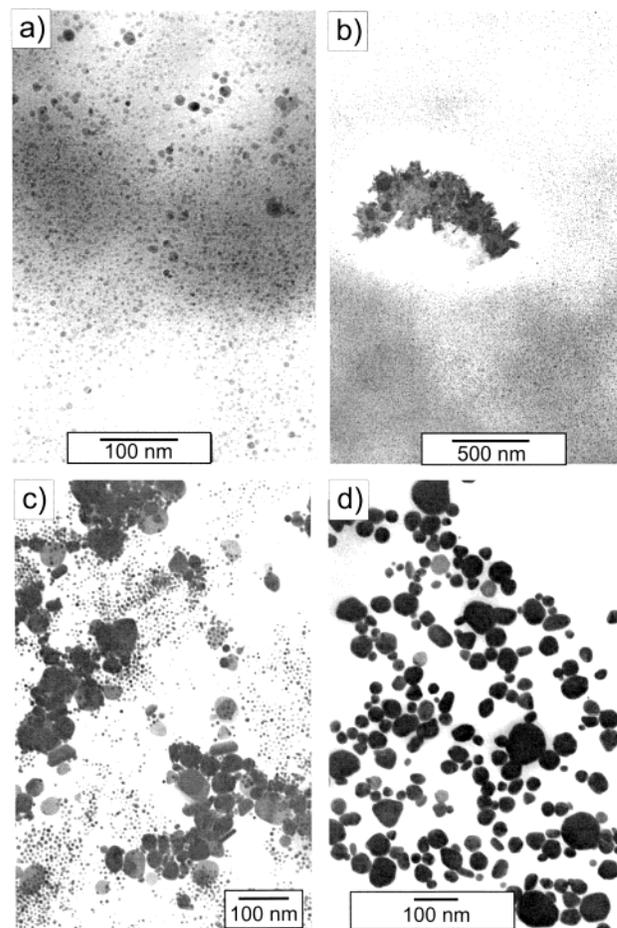


Figure 4. Effect of the addition of different ligands on the as-prepared colloid. (Representative picture of as-prepared colloid is shown in Figure 1a.) (a) $C_{12}H_{25}I$, (b) $C_{12}H_{25}Br$, (c) $C_{12}H_{25}OH$, and (d) $C_{10}H_{22}$. Although the pictures show here the regions on the grid where broken particles were only observed, there are several other places on the grid where prismatic particles were intact.

Table 1. Size Analysis of the Gold Nanoparticles after the Addition of RSH , R_3P , RNH_2 , and $RSiH_3$ and after Digestive Ripening

ligand added	size range (nm)	
	after addition of ligand	after digestive ripening
dodecanethiol	2–6	4.7 ± 0.4
trioctylphosphine	6–12	7.2 ± 1.1
dodecylamine	4–12	8.6 ± 1.3
octadecylsilane	3–20	7.2 ± 1.0

smaller sizes.^{19b} In our case both these mechanisms are possibly working side by side, influencing the size of the particles. Initial addition of ligand to as-prepared particles results in the formation of an assorted size of particles both bigger and smaller than the final size obtained after digestive ripening. Among these, the smaller particles could come together to form bigger particles as the capping agent is removed from their surfaces by heat treatment. At the same time, the surfaces of the bigger particles might be etched by the excess thiol, leading to a smaller equilibrium size. Thus, numerous factors are also possibly influencing the size of our particles apart from Ostwald ripening. A more detailed explanation on these is presented later in the text. Below, we discuss briefly the details of our digestive-ripening procedure step by step.

(18) (a) Maye, M. M.; Zhong, C.-J. *J. Mater. Chem.* **2000**, *10*, 1895. (b) Maye, M. M.; Zheng, W. X.; Leibowitz, F. L.; Ly, N. K.; Zhong, C.-J. *Langmuir* **2000**, *16*, 490. (c) Zhong, C.-J.; Zheng, W. X.; Leibowitz, F. L.; Eichelberger, H. H. *Chem. Commun.* **1999**, 1211. (d) Teranishi, T.; Hasegawa, S.; Shimizu, T.; Miyake, M. *Adv. Mater.* **2001**, *13*, 1699.

(19) (a) Edinger, K.; Golzhauser, A.; Demota, K.; Woll, C.; Grunze, M. *Langmuir* **1993**, *9*, 4. (b) Schaff, T. G.; Whetten, R. L. *J. Phys. Chem. B* **1999**, *103*, 9394.

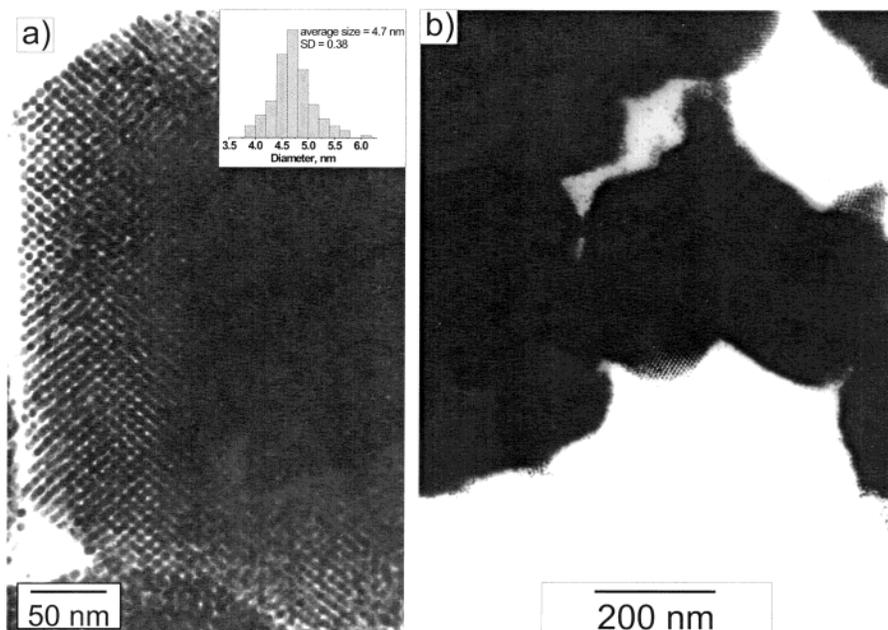


Figure 5. Au colloid digestively ripened with $C_{12}H_{25}SH$. (a) and (b) are pictures taken from different samples.

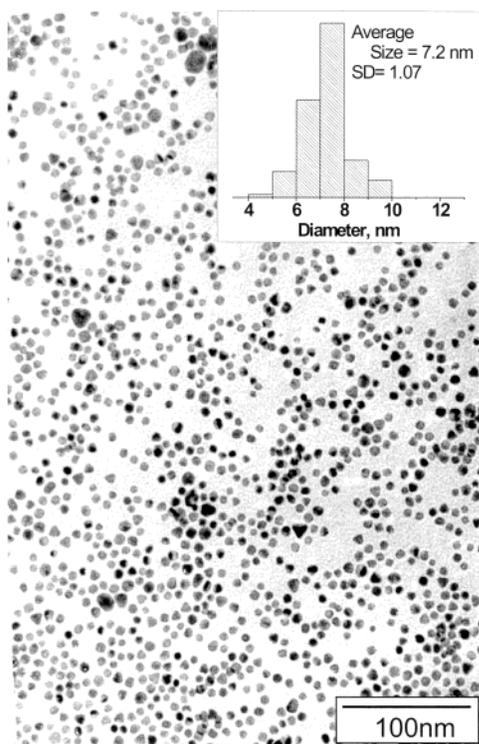


Figure 6. Au colloid digestively ripened with $(C_8H_{17})_3P$.

The first remarkable observation is the ability of the ligands to break the big as-prepared particles into smaller particles. This, in itself, is very interesting as the mere addition of a ligand is able to induce such drastic changes. In the usual synthetic conditions the nanoparticles are synthesized in the presence of a capping ligand, usually thiol.² These stabilize the nascent metal clusters to particular sizes by arresting their growth. The size of the resulting nanoparticles are usually restricted by carefully controlling the amount and nature of surfactant, water, the rate of the reaction, and the reaction temperature. In our synthetic conditions we do not have any capping ligand in the solution,

and we use a lower quantity of the surfactant, which leads to larger polydisperse nanoparticles. Defects²⁰ in these particles probably result from the rapid coalescence of smaller “as-prepared” particles in the dynamic synthetic environment as there is not enough surfactant to protect their entire surfaces. Then, the resulting bigger prismatic-shaped particles might also possess many sites, which are not protected by DDAB, making them amenable to attack by the ligands. The ligands are expected to interact with the gold surface through the lone pairs of electrons available on their headgroup. This explains the failure of simple alkanes to induce any changes in the as-prepared colloid. The addition of ligands listed in Figure 3 produce smaller, spherical-shaped particles and no prismatic particles remain in the colloid. The size distribution is already narrowed to a considerable extent in these cases and digestive ripening further improves the situation, as can be gauged by the sizes given in Table 1. Although the other three ligands employed in Figure 4 could break the big as-prepared particles to some extent, they were not as good as the set of ligands in Figure 3. In fact, no bigger prismatic particles remained when RSH , R_3P , RNH_2 , and $RSiH_3$ were added whereas the addition of RI , ROH , and RBr leaves some prismatic particles intact and the size analyses of these cases were not undertaken. These differences among the ligands could be directly related to the stronger interaction of gold with thiols, amines, phosphines, and silanes as compared with the halides and alcohols, as will be discussed in the subsequent paragraphs.

The next step of the digestive ripening involves the removal of the surfactant and the reaction side products from the ligand-capped gold nanoparticles. In some control studies we did not remove the surfactants and refluxed the colloid directly by adding the ligand to the as-prepared colloid. In such cases the resultant particles retained the prismatic shapes and even grew somewhat larger in some cases. In an independent study we

(20) Stoeva, S. I.; Zaikovski, V. Unpublished results.

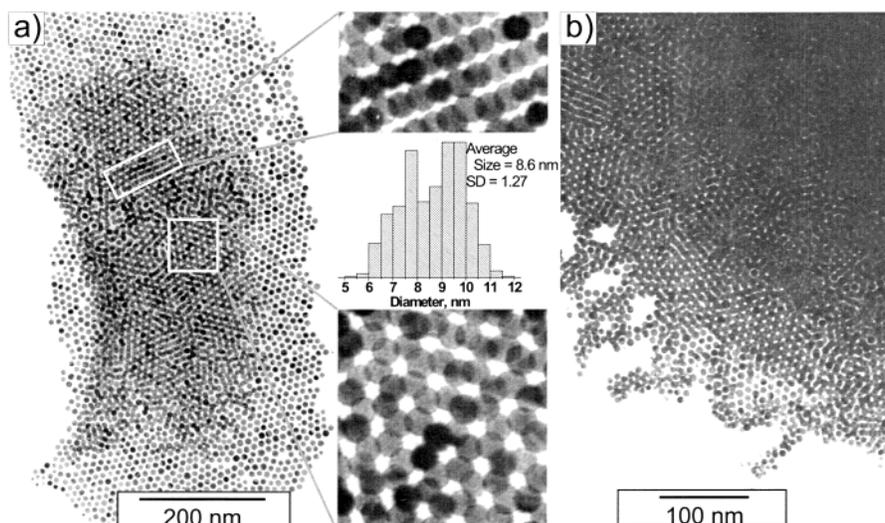


Figure 7. Au colloid digestively ripened with $C_{12}H_{25}NH_2$. (a) and (b) are pictures taken from different samples. The different types of ordering observed are highlighted.

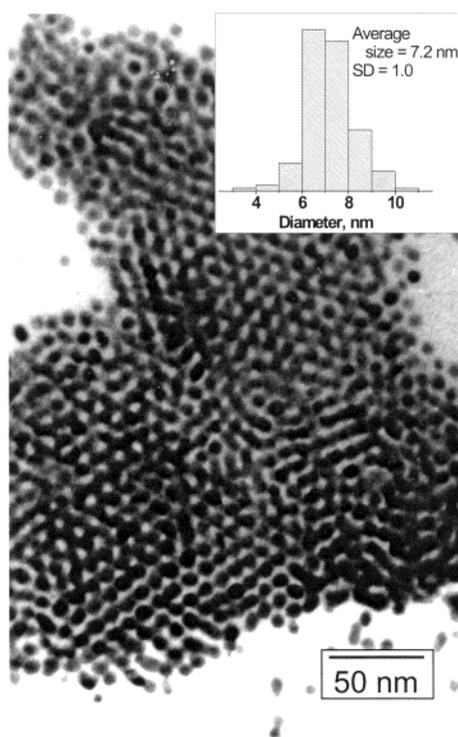


Figure 8. Au colloid digestively ripened with $C_{18}H_{37}SiH_3$.

observed that even spherical ≈ 5 -nm-size gold particles (prepared by alternative methods as described in ref 16) could be converted to prismatic-shaped particles when they were refluxed with excess cationic surfactants such as DDAB.²¹ These results indicate that when gold particles are refluxed with both the surfactant and ligand present, bigger prismatic-shaped particles are favored. In such instances, there probably is competition between the added ligand and the surfactant for the gold particle's surface. Here, the ligand is trying to make the particles smaller and the surfactant favors bigger particles, and the surfactant most likely prevails at elevated temperatures. It could also be possible that the

added ligands form some kind of adduct with the surfactants present in the solution, making it unavailable for digestive ripening. Then, at elevated temperatures, the unprotected gold nanoparticles might come into contact with each other and coalesce, resulting in the big prismatic-shaped particles. Thus, the step of isolating the pure ligand-capped gold particles free of any surfactant or reaction side products becomes crucial for the digestive ripening.

The observations in the first two steps suggest that some of the ligands used in this study are more strongly attached to the gold's surface than other ligands and that they possess a better chance of succeeding as digestive-ripening agents. It is difficult to obtain quantitative estimates on the ligand-gold binding energy because the nature of the ligand-gold bonding is still poorly understood. For example, even in the most studied thiol-Au case, there is uncertainty as to whether thiol is bound to the gold surface as a thiolate²² or it retains the hydrogen, binding just as a thiol.²³ However, the trends in some of the ligand's interaction with a gold surface are well reflected in their ability to form self-assembled monolayers on an Au(111) surface. It was reported that the potential to form self-assembled monolayers on Au(111) surfaces varies in a fashion similar to that observed here, that is, $RSH > R_3P > RNH_2$, although the exact reasons for such behaviors are not clear.²⁴

Empirical guidelines for identifying potential digestive-ripening ligands could be obtained from semiquantitative theories such as hard and soft acids and bases. Gold or any metal in the zero oxidation state is usually considered a soft acid and interacts well with soft bases.²⁵ Among the ligands we selected, RSH and R_3P are listed as soft bases and ROH and RNH_2 are hard

(21) Stoeva, S. I.; Prasad, B. L. V. Unpublished results.

(22) Biebuyck, H. A.; Bain, C. D.; Whitesides, G. M. *Langmuir* **1994**, *10*, 1825.

(23) Hasan, M.; Bethell, D.; Brust, M. *J. Am. Chem. Soc.* **2002**, *124*, 1132.

(24) (a) Bain, C. D.; Ewall, J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1989**, *111*, 7155. (b) Ulaman, A. *Chem. Rev.* **1996**, *96*, 1533. (c) Ulman, A. *An introduction to ultrathin organic films: from Langmuir-Blodgett to self-assembly*; Academic Press: New York, 1991.

(25) Huheey, J. E. In *Inorganic Chemistry: Principles of Structure and Reactivity*; Harper and Row: Cambridge, 1983; p 321.

bases. Thus, it is easy to understand the stronger affinity of RSH and R_3P toward gold as opposed to ROH. The main exception is RNH_2 . Contrary to expectations, RNH_2 was found to work very well as a digestive-ripening agent even though it is considered a hard base. This illustrates the difficulty in understanding such complex phenomenon, and it is important to remember that the terms hard and soft are only relative and there is no sharp dividing line. Several other factors might be working in tandem, and pinpointing the exact reason for the observed trends could be highly difficult.

Another ligand which acts as a good digestive-ripening agent (but offering a reasonable explanation is difficult) is $RSiH_3$. However, it is known that when silanes are attached to the gold surface, the silicon hydrogen bond becomes very weak.²⁶ In our studies when ethanol was added to the silane-capped gold particles, rapid evolution of hydrogen gas was observed. Thus, it could be possible that the silanes are attached in a more covalent fashion to the gold surface, unlike the other cases. Similar observations have been made when alkylsilanes were adsorbed on a bulk gold surface.^{26b} The easy evolution of hydrogen gas from silanes when adsorbed on gold could have important ramifications in catalysis and other areas, and we are currently undertaking more studies to understand this feature.

Among all the digestively ripened colloids, thiol-capped particles are the best in terms of monodispersity or their nature to self-assemble into superlattices (Figure 5). The nanoparticles, after digestively ripened with dodecanethiol, have an average size of 4.7 nm and form a *fcc* structure with an *ABCABC...* type ordering. Digestive ripening by amines, phosphines, and silanes generally lead to larger particles with the average size varying as $RNH_2 > R_3P \geq RSiH_3 > RSH$ as shown in Table 1. Simple reasoning like "lengthier ligands stabilize larger particles"^{4d,27} fails to explain this phenomenon because ligands with similar lengths (dodecylamine and dodecanethiol) lead to very different sizes. The rationale for this size dependency could be the strength of the ligand attachment to the gold surface with weaker ligands such as amines stabilizing larger particles. There are some reports in the literature proposing that the stabilization of a particular size of nanoparticles is controlled by thermodynamics rather than by the kinetics of nucleation and crystal growth.²⁸ They argue that the free-energy minimum resulting from a combination of a curvature-dependent surface energy and the ligand-gold binding energy leads to the particular size of nanoparticle observed. Here, the surface free energy increases with the surface curvature (smaller particle-larger curvature) and favors larger particles. The ligand-gold binding energy, on the other hand, favors larger surface area, that is, smaller particles. Therefore, these two opposing effects lead to a

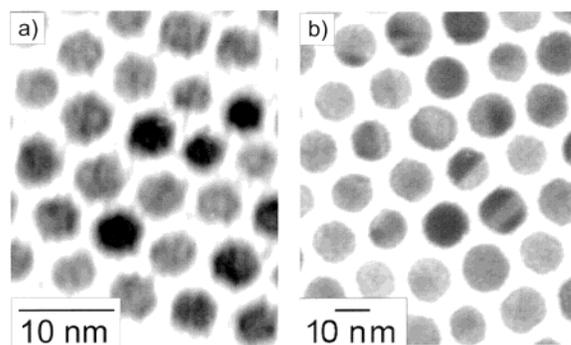


Figure 9. High-magnification TEM images of (a) $C_{12}H_{25}SH$ and (b) $C_{12}H_{25}NH_2$ digestively ripened colloids highlighting the interparticle distances.

free-energy minimum preferring a thermodynamically favored size for each of the ligands used. Among the ligands we have used, thiol is strongest and amine is the weakest attached to the gold surface. Therefore, thiol should favor the smallest particles and amines the largest, which is exactly the trend we observed.

It is also interesting to note that the coherence in the packing order as observed for the thiol-coated particles is absent for the other three cases (see the highlighted images of amine-coated particles in Figure 6 showing the coexistence of different types of ordering), although they should have more attraction between the particles²⁹ considering their larger sizes, and hence should form better superlattice structures. It is clear from the literature that the thiols are firmly attached to the gold surfaces, leading to the fixation of the alkyl chain in an *all trans* conformation.³⁰ This makes it easy for two alkanethiols on adjacent gold particles to interdigitate, paving the way to the superlattice structures observed. Amines and phosphines on the other hand may not be as firmly attached to the gold surface,²⁴ allowing more rapid exchange, and therefore less tendency to form ordered alkyl chains. This could also lead to the formation of multilayers of these ligands on a gold nanoparticle surface, with some ligands not directly attached to the particle surface. Thus, it becomes difficult for the alkyl chains on the adjacent particles to interdigitate and to form superlattices. Partial evidence for this could be found from the interparticle separation of thiol- and amine-coated particles. Dodecanethiol (alkyl chain length ~ 1.6 nm) coated gold particles are separated from each other by about 1.9 nm, suggesting a strong interdigitation of alkyl chains on adjacent particles. For dodecylamine-coated particles, which has a similar alkyl chain length, the separation is more than 3.5 nm, suggesting end-to-end separation of ligands on adjacent amine-coated particles (Figure 9).

Another point to consider is the different shapes of the particles. In all the successful cases, digestive ripening leads to spherical particles within the resolution of our TEM, except for phosphines where many triangular or polyhedral shapes are observed. The main difference between the phosphine and all the other ligands used in this study is their bulkiness. Trio-

(26) (a) Nicholson, K. T.; Zhang, K. Z.; Banaszak Holl, M. M. *J. Am. Chem. Soc.* **1999**, *121*, 3232. (b) Owens, T. M.; Nicholson, K. T.; Banaszak Holl, M. M.; Suzer, S. *J. Am. Chem. Soc.* **2002**, *124*, 6800. (c) Marchenko, A.; Katsonis, N.; Fichou, D.; Aubert, C.; Malacria, M. *J. Am. Chem. Soc.* **2002**, *124*, 9998.

(27) Whitesides, G. M.; Love, J. C. *Sci. Am.* **2001**, *285*, 39.

(28) (a) Chikan, V.; Kelley, D. F. *J. Phys. Chem. B* **2002**, *106*, 3794. (b) Sugimoto, T. *Adv. Colloid Interface Sci.* **1987**, *28*, 65. Leff, D. V.; Ohara, P. C.; Heath, J. R.; Gelbart, W. M. *J. Phys. Chem.* **1995**, *99*, 7036.

(29) (a) Hamaker, H. C. *Physica (Utrecht)* **1937**, *4*, 1058. (b) Ohara, P. C.; Leff, D. V.; Heath, J. R.; Gelbart, W. M. *Phys. Rev. Lett.* **1995**, *75*, 3466.

(30) Badia, A.; Singh, S.; Demers, L.; Cuccia, L.; Brown, G. R.; Lennox, R. B. *Chem. Eur. J.* **1996**, *2*, 359.

cylphosphine is much bulkier than the other monoalkyl ligands. Whereas all the other ligands could be assumed to have a cylindrical shape, the trioctylphosphine will definitely have a more conical shape. Thus, it will be difficult for the trioctylphosphine to have an ordered packing on the surface of the spherical particles, and therefore the driving force for the formation of spheres is diminished. It has been reported in the literature that ligands such as phosphonic acids and phosphine oxides allow the growth of specific lattice planes, leading to the formation of different shapes of nanoparticles,³¹ which is consistent with our results.

Conclusions

The effectiveness of digestive ripening with thiols, amines, silanes, and phosphines has been demonstrated. The important steps in the digestive-ripening process have been delineated. It was also shown that it is important to reflux the colloid only in the presence of the digestive-ripening agent without surfactant or other impurities. To achieve this, different protocols for separating the colloid from reaction side products were employed. Although the reasons for the success of different ligands in the digestive-ripening process could not be exactly established, this study clearly shows that these features are crucially controlled by the strength

of the Au–ligand interaction. Useful guidelines for the gold–ligand interactions could be obtained from the hard and soft acid–base theory. This is also the first study that proves the efficacy of silanes as capping ligands for gold nanoparticles. The stabilization of differently sized particles with different ligands is recognized to be thermodynamical in nature with weaker ligands stabilizing larger particles and vice versa. Overall, this study demonstrates that different ligands other than thiols can be employed to give nearly monodisperse gold nanoparticles. Efforts are currently underway to apply these results to large-scale synthesis of gold nanoparticles and also to extend this digestive-ripening procedure to other metals.

Acknowledgment. We gratefully acknowledge financial support from the National Aeronautics and Space Administration (NASA) and the National Science Foundation. We thank the Kansas State University Biology Research Microscope and Image Processing Facility, which has been supported in part by the NSF EPSCoR Program, by the NASA EPSCoR Program, by University resources, and by the Kansas Agricultural Experiment Station.

Supporting Information Available: Large area TEM images for several ligand-capped gold particles before and after digestive ripening (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

(31) Hu, J.; Li, L.-S.; Yang, W.; Manna, L.; Wang, L.-W.; Alivisatos, A. P. *Science* **2001**, *292*, 2060.

CM0206439