Low-Temperature Metallic Alloying of Copper and Silver Nanoparticles with Gold Nanoparticles through Digestive Ripening

Alexander B. Smetana, Kenneth J. Klabunde,* Christopher M. Sorensen, Audaldo A. Ponce, and Benny Mwale

Departments of Chemistry and Physics, Kansas State University, 111 Willard Hall, Manhattan, Kansas 66506

Received: July 19, 2005; In Final Form: December 1, 2005

We describe a remarkable and simple alloying procedure in which noble metal intermetallic nanoparticles are produced in gram quantities via digestive ripening. This process involves mixing of separately prepared colloids of pure Au and pure Ag or Cu particles and then heating in the presence of an alkanethiol under reflux. The result after 1 h is alloy nanoparticles. Particles synthesized according to this procedure were characterized by UV−vis spectroscopy, EDX analysis, and high-resolution electron microscopy, the results of which confirm the formation of alloy particles. The particles of 5.6 ± 0.5 nm diameter for Au/Ag and 4.8 ± 1.0 nm diameter for Cu/Au undergo facile self-assembly to form 3-D superlattice ordering. It appears that during this digestive ripening process, the organic ligands display an extraordinary chemistry in which atom transfer between atomically pure copper, silver, and gold metal nanoparticles yields monodisperse alloy nanoparticles.

Introduction

Since the early 1990s investigations of metal nanoparticles have become a paradigm for the burgeoning discipline of nanotechnology. Synthetic control over size, shape, and composition of the particles has led to many interesting investigations into their physical properties.[1] The synthesis of these materials has been approached from numerous angles ranging from innovative laser,[2] microwave,[3] and sonochemical techniques,[4] to elegant purely chemical synthetic routes.[5] The extraordinary properties and widespread applications of these new materials are being investigated thoroughly by many scientists across numerous disciplines. Such particles are now being employed in various technologies including improved catalysts, interfaces for SERS technology, and components in optical and electronic devices.[6] Most recently, modified synthetic techniques have allowed for the formation of alloys and heterogeneous metal particles with sizes, shapes, and compositions similar to their single-elemental counterparts, yet with new and interesting chemical and physical properties.[7−9] Here we report a remarkable low-temperature chemical process that converts a mixture of separate noble metal nanoparticles into monodisperse alloy particles of either silver or copper with gold.

Previously in our laboratories we developed the Solvated Metal Atom Dispersion (SMAD) process, capable of producing monodisperse metal nanoparticles of gold, silver, and copper in gram quantities.[10−11] This synthesis involved a coevaporation of bulk metal and a stabilizing solvent. Their vapors are frozen into a solvent depositing on the sides of a reactor wall cooled with liquid nitrogen. When the liquid nitrogen is removed, a slurry forms and the metal atoms begin to interact, form particles, and grow. An organic ligand, typically dodecane thiol, is added to this mixture to halt the growth process. This method produces a very polydisperse colloid of metal nanoparticles on the gram scale.

In a process we have termed *digestive ripening*[12] the polydisperse product colloid is subsequently heated at or near the solvent boiling point during which time the particles evolve through some, as yet not understood, dynamic process between the metal particles and their ligand environment to attain an equilibrium size. In this digestive ripening stage smaller particles experience growth, yet larger particles, some up to 50 nm in size, are eroded until the mixture becomes very homogeneous in size. This technique is very much different from the well-known Ostwald ripening, in which particles only experience growth at the expense of sacrificial, higher energy smaller particles. Our digestive ripening process allows us to refine particles' size, leading to a narrow size distribution, thereby cutting down on loss of material from size selection procedures.[13]

Since the digestive ripening process involves atomic or cluster metal transfer from one particle to another until a dynamic equilibrium is achieved, and since the process is applicable to numerous metals including Au, Ag, and Cu, it is clear that relatively low-temperature alloying might be achieved by this process. Also, alloy nanoparticle formation may yield some valuable clues about how digestive ripening occurs.

Experimental Section

Starting Materials. The reagent colloids used were prepared by a metal vapor−solvent co-condensation method (SMAD), which is mentioned above, but described in detail elsewhere.[10,11] These colloids are composed of polydisperse metal nanoparticles with a surfactant (dodecane thiol) to metal ratio of 20:1, with 4-*tert*-butyltoluene as the solvent. In a typical experiment, 0.2 g of metal is suspended in 60 mL of 4-*tert*-butyltoluene. Digestive ripening of the above colloid is conducted by refluxing under argon for 3 h. During this time the colloid matures and becomes transparent (indicating loss of large particles and aggregates). After digestive ripening, a monodisperse product of single elemental nanoparticles is achieved. The yield of monodisperse particles from this reaction is essentially 100%.

* Address correspondence to this author. Phone: 785-532-6849. Fax: 785-532-6666. E-mail: kenjk@ksu.edu.
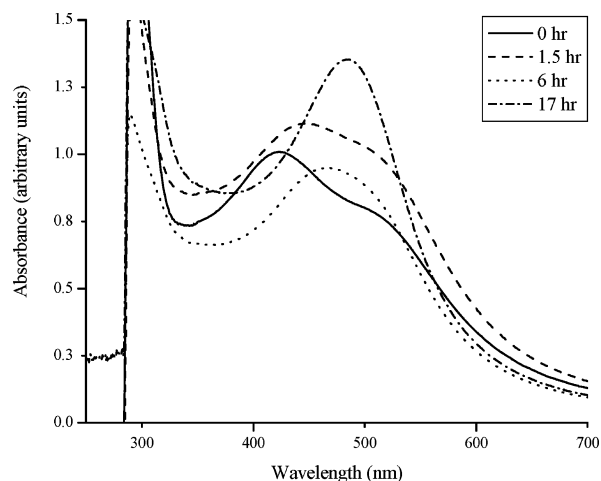
Figure 1. UV−vis spectrum displaying the progress of a digestive ripening alloying of gold and silver nanoparticles. Initially the peaks for silver (420 nm) and gold (520 nm) are quite distinct, but as the reaction proceeds the presence of elementally pure particles rapidly decreases as intermetallic species are formed. Note: Concentrations of aliquots are similar, but not exact.
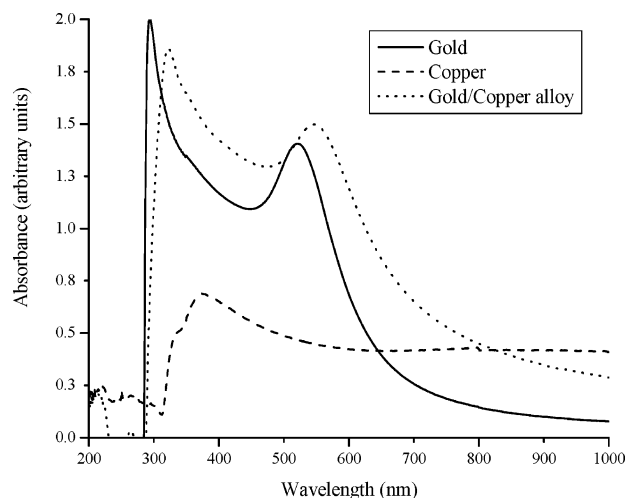

Figure 2. UV−vis spectrum showing the shape and position of the surface plasmon resonance of the reactants: gold (dashed line), copper (dotted line), and product of the Cu/Au (solid line) alloy reaction. The red shift of the Au peak at 520 nm to the Cu/Au peak at 546 nm is indicative of the alloying process.

Alloy Reaction. In an alloy experiment, separate colloids of pure metals are mixed in approximately molar ratios with an excess of 20:1 dodecane thiol to metal. This mixture is subsequently heated to the boiling point of the solvent 4-*tert*-butyltoluene at 198 °C. The reaction time is dependent on the colloid concentration, but most experiments were conducted with 0.002 g of metal/mL of solvent with a reaction time of 17 h.

Instrumentation. UV−Vis spectra were recorded on a Cary 500 UV−Vis−NIR spectrometer at 2% dilution of the initial colloid concentration against a background of 4-*tert*-butyltoluene in a separate cell. Low-magnification TEM photographs and electron diffraction measurements were taken on a FEI CM100 transmission electron microscope. The samples were prepared by depositing 3 μL of nanoparticle solution on a carbon coated copper grid. HRTEM (high-resolution transmission electron microscopy) pictures and energy-dispersive X-ray (EDX) analysis were performed on a Joel JEM-2010 F TEM/SEM microscope. The HRTEM samples were precipitated with ethanol from the 4-*tert*-butyltoluene solution and excess dodecane thiol, centrifuged, and washed twice more with ethanol before re-dispersion in hexanes and deposition on a holey carbon nickel grid.

UV−Vis Spectra. The absorption features of noble metal nanoparticles are characteristic of the size, shape, and composition of the particles in solution. This phenomenon is commonly referred to as a surface plasmon resonance (SPR) and has been studied extensively in recent years.[14,15] The position of the absorption maximum (λ_{max}) allows us to monitor the progress of the alloying reaction with a quick and simple analysis of aliquots taken periodically as the reaction proceeds. From a sample of mixed gold and silver colloids analyzed before the alloying reaction, there are clearly two superimposed peaks arising from discrete gold absorption (520 nm) and silver absorption (420 nm) as shown in Figure 1. During digestive ripening the individual plasmon absorption peaks progressively meld into a single symmetric peak at 470 nm after reflux, as seen in Figure 1. The reaction is deemed complete when the width of the absorption peak no longer narrows with time.

Core−shell heterogeneous particles have been synthesized by other groups and are known to display complex absorption peaks in the optical region.[16] The absorption features of this type of particle can be predicted theoretically, and are readily distinguishable from an alloy particle according to Mulvaney.[17] Only a solitary peak is observed in our product as demonstrated in the UV−vis spectra taken after the reaction is complete in Figure 1.

Our data suggest the formation of alloy particles, as the surface plasmon resonance appears at a wavelength intermediate between gold and silver colloids. This is indicative of the particles changing in elemental composition from pure gold or silver nanoparticles into alloy particles composed of both metals. Experiments with Ag and Au particles show that when the molar ratio of the metal precursors is altered to favor one metal over the other, the λ_{max} is shifted toward the peak of the more concentrated metal in proportion to the amount of excess metal. Similar results regarding the peak position for Ag/Au alloys have been observed by other groups.[3]

The individual spectra for the identical reaction between copper and gold particles are shown in Figure 2. The spectrum of copper particles has no distinct features, but displays a broad extinction throughout the visible spectrum. This is in agreement with theoretical calculations done by Pileni.[18] Upon digestive ripening in the presence of copper, however, the well-defined gold plasmon peak is substantially red shifted by 26 nm. This again indicates that the atomic composition of the individual particles has been altered.

TEM. The alloy particles display a very narrow size distribution. This is accentuated by the self-assembly of the particles into 2-D and extensive 3-D superlattices seen in Figure 3. The spontaneous ordering of these superlattices is a note-worthy property of the product colloid, as the formation of nanoparticle superlattices is an important precursor to the application of nanoparticles as novel optical and electrical materials.[19] The average size of the silver/gold intermetallic particles is 5.6 ± 0.5 nm, derived from a population of 200 particles. This is not very different from the particle size of the initial colloids: Au 6.7 nm, Ag 6.6 nm. While some minor size change can be expected during digestive ripening, the alloy particle size should not change much since the elements are very similar, and the capping ligand is the same as the parent particles, which is observed. It should be noted that the particle size of the alloy is smaller than that of the initial colloids. Then by conservation of mass, a greater number of particles must be
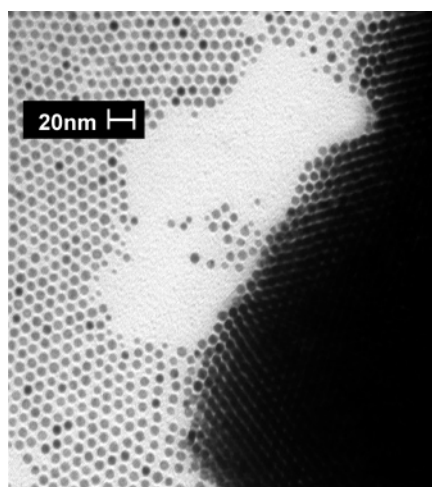
Metallic Alloying of Cu and Ag Nanoparticles

J. Phys. Chem. B, Vol. 110, No. 5, 2006 **2157**

Figure 3. Low-magnification TEM image of Ag/Au intermetallic particles. The particles have a very narrow size distribution of 5.6 ± 0.5 nm and display the ability to self-assemble into 2- and 3-dimensionally ordered superlattices.
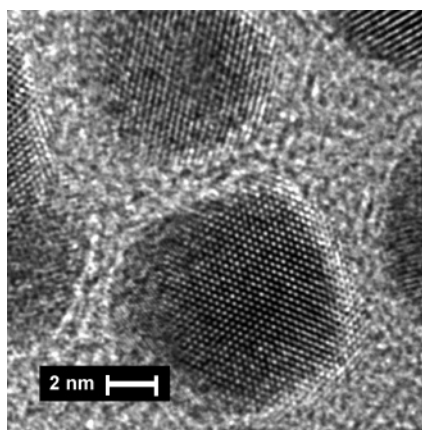

Figure 4. HRTEM image of two individual Cu/Au alloy nanoparticles displaying the homogeneity of the atoms in the particles (lack of core−shell structure).

in the product. This suggests that new particles have been nucleated in this environment.

A high-resolution image of Cu/Au nanoparticles is shown in Figure 4. The image depicts excellent atomic ordering within the individual particles. The particles also show no evidence of a core/shell structure that would appear as areas of contrasting density. The homogeneity of the particles implies atomic level mixing has occurred uniformly throughout the particle. The average particle size for Au/Cu alloys is 4.8 ± 1.0 nm.

Electron Diffraction. Electron diffractograms which were obtained for both alloys and their monometallic precursors proved to be of little help in establishing the alloy nature of the particles. All particles displayed a distinct ring pattern demonstrating crystallinity, with the exception of the copper particles which were amorphous. The diffraction patterns for gold and silver agreed with standard *d* spacing values. Unfortunately, the values for silver, gold, and their alloy are within 1% of each other due to their similar atomic radii and chemical nature, and hence were indistinguishable. Similarly, the major peaks of our Au/Cu alloy were found to be within instrumental error of the *d* spacings for bulk gold.[20] The literature values for a Au_3Cu alloy correspond to this, which is the most likely composition of the particles, since the UV−vis spectrum indicates that gold particles are no longer in solution.[20] The minor peaks for the Au/Cu alloy were too weak to distinguish in the diffractogram.

TABLE 1: List of *d* Spacings for Pertinent Metals

Au	1.23	1.40	2.01	2.38
Au/Cu alloy	1.25	1.44	2.05	2.41
Au_3Cu^a		1.45	2.05	2.36
Cu^a	1.28	1.81	2.08	

[a] Literature values for copper metal and Au_3Cu taken from the Powder Diffraction File Alphabetical Indexes for Inorganic Phases.[20]
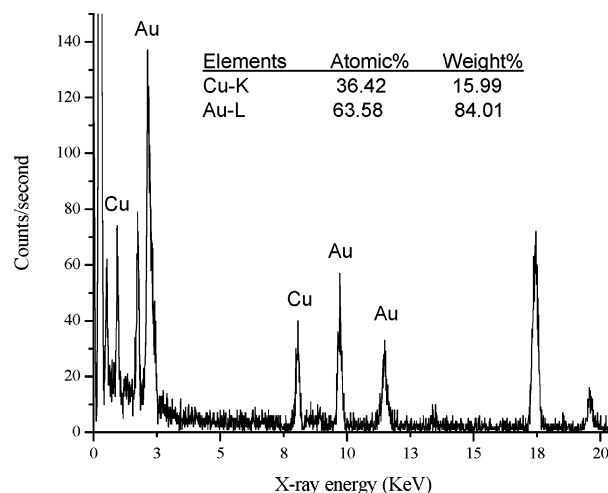

Figure 5. EDX spectrum of a solitary Au/Cu particle showing the presence of both elements in a single intermetallic particle. The unlabeled peaks arise from organic remnants on the particles and the sample grid.

A powder XRD spectra was taken of the sample after precipitation with ethanol from solution; however, due to the small size of the particles, only the major peaks can be made out from the spectrum and cannot distinctly classify the crystal composition.

A list is of *d* spacings is given in Table 1 for pertinent metals.

EDX. Energy-dispersive X-ray spectral analysis (EDX) was conducted on the intermetallic colloids to probe for the presence of both metals within a single particle. To obtain a suitable spectrum, excess surfactant molecules needed to be removed from the sample to prevent masking of the particles in the electron microscope. This was accomplished by precipitating the colloids with ethanol, centrifuging, and washing the solid twice with ethanol before being re-dispersed in hexanes. Unfortunately the particles were not completely stable in this environment and over a long period of time, and significant sintering of the particles occurred. The Cu/Au colloid remained the most stable and individual particles were still amenable to analysis. A representative EDX spectrum of Au/Cu particles is provided in Figure 5. The atomic percentages reflect an average value of two spectra. These data confirm the presence of Cu and Au in each single particle.

Discussion

The UV−vis spectra and EDX analysis demonstrate that alloyed, intermetallic particles can be created by digestive ripening of a mixture of separately prepared colloids. Moreover, the merging of both the separate silver and gold plasmon peaks into a single intermediate peak in the UV−vis spectrum and the HRTEM photographs show that the final colloid is composed of alloy particles and not core−shell heterogeneous particles. This result is somewhat curious in that if atoms of one particle are merely being transferred to the surface of a particle with different elemental composition, a core−shell structure or heterogeneous particle would be a much more reasonable product than an intimately mixed alloy. Work from Schaak and

co-workers[21] has demonstrated atomic diffusion of gold and copper in nanoparticles by solid-state annealing at 240 °C. Similarly Hodak et al.[16] showed that the irradiation of core−shell Ag/Au particles with laser light transforms them into alloys. This result was interpreted as being interparticle diffusion of the atoms. Our digestive ripening procedure is typically conducted at temperatures near 200 °C, which is comparable to the conditions above, but in a solution environment. It is a reasonable conclusion that interparticle diffusion occurs as a pathway for atoms from the surface to travel to the center of the nanoparticles. The alloying reaction has been attempted at temperatures as low as 100 °C in our laboratory. While the plasmon peaks shift toward each other under these conditions, the decreased temperature considerably lengthens the reaction time. This is probably due in large part to a much slower rate of atomic diffusion within the particles at this temperature.

In similar experimental conditions Schaff and Whetten[22] proposed that long-chain thiols can act as both a stabilizing agent and an etchant of a gold colloid, removing atoms from the surface of the particle helping to favor certain particle's sizes in solution. Similarly Liz-Marzán[23] commented on a solution phase equilibrium between particles and atoms/ions during synthesis, which facilitated lattice rearrangement between silver and gold particles to form alloys. Our data support this view and demonstrate that at higher temperatures this process is accelerated up to the point where elementally unique particles can completely interchange atoms and form a new colloid of homogeneous intermetallic particles. This process of refinement where ligands act as labile metal atom carriers by removing and transplanting atoms from one particle to another explains what we term digestive ripening.[12] We have also found that increasing the concentration of particles in solution by 300% can decrease the alloy reaction time to 60 min, a factor of 17 times faster. This evidence suggests that collisions between particles in solution may encourage the removal of atoms from the surface of particles. A reaction was also conducted in which the excess ligands were removed from the colloids before digestive ripening. The reactant colloids were precipitated with ethanol, decanted, and then redissolved in 4-*tert*-butyltoluene. The outcome of this experiment was extensive, irreversible, aggregation of the particles, proving that excess ligand in solution is *essential* for atomic transfer between nanoparticles.

The fact that thiol capped metal nanoparticles can be atomically mixed by reflux in an organic solvent is a remarkable discovery. It shows that (1) nanoparticles are quite chemically labile and are size equilibrated by the excess thiol ligands that are transferring metal atoms between particles, (2) the digestive ripening process must take place by atom or cluster transfer, as implied by the work of Lin[24] and Scherer,[25] but the exact mechanism and understanding of the process is still lacking, and (3) bulk samples of gold do not undergo digestive ripening and particle size reduction. Thus, as stated above, nanoparticles are particularly reactive and susceptible to this ligand manipulation while normal bulk gold is not. Clearly, it would be valuable to learn why nanoparticles are so active. We speculated earlier that this is because of high energy nanocrystal interfaces and increased strain energy nonexistent in bulk materials.[26]

Conclusion

We have demonstrated chemistry that involves interparticle atomic transfer of gold, silver, and copper metals to form alloys well below their melting points in a liquid solvent medium. This phenomenon is an exceptional route for the synthesis of large quantities of monodisperse alloy nanoparticles at low temperatures. It is evident that a much deeper understanding of digestive ripening, a "nanomachining" type process, would be valuable, and may point toward more environmentally benign gold mining procedures, as well as controlled metal alloying under mild conditions.

References and Notes

(1) Klabunde, K. J. *Nanoscale Materials in Chemistry*; John Wiley & Sons: New York, 2001.

(2) Mizukoshi, Y.; Okitsu, K.; Maeda, Y.; Yamamoto, T. A.; Oshima, R.; Nagata, Y. *J. Phys. Chem. B* **1997**, *101*, 7033−7036.

(3) Lee, I.; Han, S. W.; Kim, K. *Chem. Commun.* **2001**, 1782−1783.

(4) Gao, F.; Lu, Q.; Komarneni, S. *Chem. Mater.* **2005**, *17*, 856−860.

(5) Sarathy, K. V.; Raina, G.; Yadav, R. T.; Kulkarni, G. U.; Rao, C. N. R. *J. Phys. Chem. B* **1997**, *101*, 9876−9880.

(6) Daniel, M.; Astruc, D. *Chem. Rev.* **2004**, *104*, 293−346.

(7) Métraux, G.; Cao, Y. C.; Jin, R.; Mirkin, C. *Nano Lett.* **2003**, *3*, 519−522.

(8) Tsai, S.; Liu, Y.; Wu, P.; Yeh, C. *J. Mater. Chem.* **2003**, *13*, 978−980.

(9) Park, J.; Kim, M. G.; Jun, Y.; Lee, J. S.; Lee, W.; Cheon, J. *J. Am. Chem. Soc.* **2004**, *126*, 9072−9078.

(10) Stoeva, S. I.; Klabunde, K. J.; Sorensen, C. M.; Dragieva, I. *J. Am. Chem. Soc.* **2002**, *124*, 2305.

(11) Smetana, A. B.; Klabunde, K. J.; Sorensen, C. M. *J. Colloid Interface Sci.* **2005**, *284*, 521−526.

(12) Lin, X. M.; Sorensen, C. M.; Klabunde, K. J. *J. Nanopart. Res.* **2000**, *2*, 157−164.

(13) Emory, S. R.; Nie, S. *J. Phys. Chem. B* **1998**, *102*, 493−497.

(14) Link, S.; Wang, Z. L.; El-Sayed, M. A. *J. Phys. Chem. B* **1999**, *103*, 3529−3533.

(15) Kelly, L. K.; Coronado, E.; Zhao, L. L.; Schatz, G. C. *J. Phys. Chem. B* **2003**, *107* (3), 668−677.

(16) Hodak, J.; Henglein, A.; Giersig, M.; Hartland, G. *J. Phys. Chem. B* **2000**, *104*, 11708−11718.

(17) Mulvaney, P. *Langmuir* **1996**, *12*, 788−800.

(18) Pileni, M. P. *New J. Chem.* **1998**, 693−702.

(19) Taleb, A.; Petit, C.; Pileni, M. P. *Chem. Mater.* **1997**, *9*, 950−959.

(20) McClune, W. *Powder Diffraction File Alphabetical Indexes Inorganic Phases*; International center for diffraction data: Newton Square, PA, 1998.

(21) Amandeep, K. S.; Schaak, R. E. *J. Am. Chem. Soc.* **2004**, *126*, 6667−6672.

(22) Schaff, G. T.; Whetten, R. L. *J. Phys. Chem. B* **1999**, *103*, 9394−9396.

(23) Rodríguez-González, B.; Sánchez-Iglesias, A.; Giersig, M.; Liz-Marzán, L. M. *Faraday Discuss.* **2004**, *125*, 133−144.

(24) Samia, A. C. S.; Hyzer, K.; Schlueter, J.; Jiang, J. S.; Bader, S. D.; Lin, X.-M. *J. Am. Chem. Soc.* **2005**, *127*, 4126−4127.

(25) Jin, R.; Egusa, S.; Scherer, N. F. *J. Am. Chem. Soc.* **2004**, *126*, 9900−9901.

(26) Stoeva, S.; Prasad, B. L. V.; Uma, S.; Stoimenov, P. K.; Zaikovski, V.; Sorensen, C.; Klabunde, K. *J. Phys. Chem. B* **2003**, *107*, 7441−7448.