A Simple and Effective Chemical Route for the Preparation of Uniform Nonaqueous Gold Colloids

M. Y. Han,*,† C. H. Quek,† W. Huang,‡ C. H. Chew,† and L. M. Gan‡

Department of Chemistry and Institute of Materials Research & Engineering, National University of Singapore, Singapore 119260

Received December 1, 1998. Revised Manuscript Received February 15, 1999

In this paper, we report a simple and clean method of producing uniform nonaqueous gold colloids by the chemical reduction of chloroauric acid ($HAuCl_4$) using the oxygen-free organic supporting medium formamide itself as reducing agent in the presence of the stabilizer poly(vinylpyrrolidone) (PVP). The reduction of $HAuCl_4$ can take place easily at room temperature in the new reducing system without introducing foreign reducing agents. A two-step reaction process to gold particles was suggested from the kinetics analysis for the formation of gold colloids in formamide systems. The difference in the production of gold particles in formamide solution from the established route in aqueous solution was also depicted. This new and effective chemical route also provides an alternative method to produce other uniform transition-metal particles in nonaqueous solvents.

Introduction

Although the production of gold colloids has been known since M. Faraday's time, there is a considerable renaissance to be observed during the past decade due to the potential applications in a new generation of optical and electronic devices.[1−4] The preparation of gold particles in aqueous systems has been extensively studied. Many synthetic schemes for the production of gold particles in organic media have also emerged recently, such as solvent extraction/reduction techniques, gas evaporation techniques, chemical reduction, and phase transfer methods, etc.[5−9] Although the most successful synthetic procedures for the production of uniform gold particles so far use aqueous systems,[5−9] starting with the pioneering and representative work of M. Brust,[10] a useful chemical route to uniform gold colloidal particles in nonaqueous systems is now also widely used. However, the latter involves a complicated two-phase reduction via reducing agent, and the gold colloids bear a surface coating of thiol. Here we present a new and simple chemical route of producing uniform gold colloids in a nonaqueous reducing system in which the oxygen-free organic solvent formamide itself serves as a reducing agent in the presence of a stabilizing polymer. Unlike conventional chemical routes, the simple method can be performed at room temperature without introducing a foreign reducing agent. The production of colloidal gold particles in the organic solution is quite different from that in aqueous solution, caused by the difference in redox equilibria and kinetics, polarity, and viscosity. The nonaqueous reducing environment permits reduction at more moderate conditions and results in higher colloid uniformity than in an aqueous system, associated with the higher viscosity of the new reducing system. The simple, clean, and effective chemical route can also be used to prepare other uniform transition-metal particles in organic media. For example, the preparation of uniform silver nanoparticles in formamide will be reported elsewhere.

Experimental Section

Chloroauric acid ($HAuCl_4$) of high purity was supplied by Sigma, poly(vinylpyrrolidone) (PVP, M_w 40 000) was obtained from Fluka, and analytical grade formamide from Merck was used as received. All glassware used in all preparations was scrupulously cleaned with chromic acid solution and rinsed in turn with deionized water from a Millipore system and formamide. Gold particles were prepared from the chemical reduction of $HAuCl_4$ in the oxygen-free formamide solutions containing 3.0×10^{-4} or 6.0×10^{-4} M $HAuCl_4$ at a PVP/$HAuCl_4$ molar ratio of 1/5 or 3/5, respectively. The oxygen-free formamide was produced first in a 250-mL round-bottom flask by purging with purified argon at 60 °C for 2 h. The vacuum-degassed $HAuCl_4$ and PVP were then added into the flask with 100 mL of the freshly prepared solutions at room temperature. After being mixed thoroughly, the resulting colorless solution was stirred continuously at room temperature (30 °C) until no further changes in the color of the solutions were observed. To characterize the formation kinetics of the gold particle, aliquots (2 mL) of the resulting colloid were

---

* To whom correspondence should be addressed at the Department of Chemistry, Indiana University, Bloomington, IN 47405. E-mail: mihan@indiana.edu.

† Department of Chemistry.

‡ Institute of Materials Research & Engineering.

(1) Lewis, L. N. *Chem. Rev.* **1993**, *93*, 2693.

(2) Andres, R. P.; Bein, T.; Dorogi, M.; Feng, S.; Henderson, J. I.; Kubiak, C. P.; Mahoney, W.; Osifchin, R. G.; Reifenberger R. *Science* **1996**, *272*, 1323.

(3) Freeman, R. G.; Grabar, K. C.; Allison, K. J.; Bright, R. M.; Davis, J. A.; Guthrie, A. P.; Hommer, M. B.; Jackson, M. A.; Smith, P. C.; Walter, D. G.; Natan, M. J. *Science* **1995**, *267*, 1629.

(4) Shi, J.; Gider, S.; Babcock, K.; Awschalom, D. D. *Science* **1996**, *271*, 937.

(5) Turkevich, J.; Stevenson, P. C.; Hillier, J. *Discuss. Faraday Soc.* **1951**, *11*, 55.

(6) Frens, G. *Nature, Phys. Sci.* **1973**, *241*, 20.

(7) Ahmadi, T. S.; Wang, Z. L.; Green, T. C.; Henglein, A.; El-Sayed, M. A. *Science* **1996**, *272*, 1924.

(8) Siiman, O.; Hsu, W. P. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 851.

(9) Quinn, M.; Mills, G. *J. Phys. Chem.* **1994**, *98*, 9840.

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

10.1021/cm9810943 CCC: $18.00

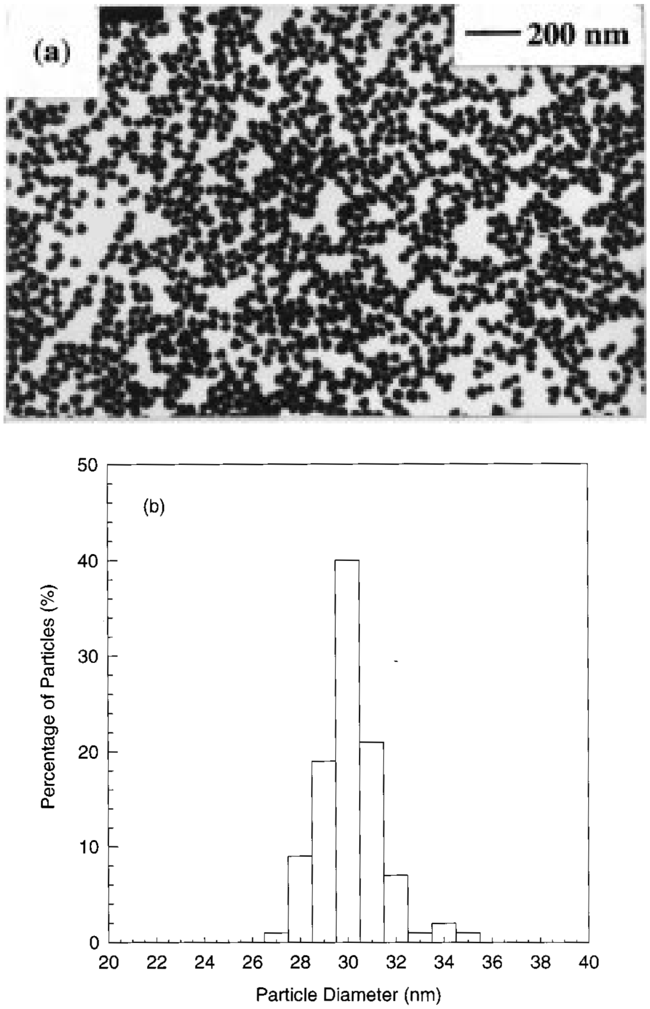

Figure 1. (a) Transmission electron micrograph and (b) particle size distribution of gold particles prepared from 3.0×10^{-4} M $HAuCl_4$ at a $PVP/HAuCl_4$ molar ratio of 1/5.

removed from the reaction solution to a quartz cell at fixed times. The reduction reaction in the removed colloid was quenched immediately by exposing the colloid to oxygen to avoid further reaction.

The samples for transmission electron microscopy (TEM) were prepared by putting one drop of the gold colloid on a Formvar-coated copper grid followed by drying in a desiccator. Electron micrographs were taken with a JEOL JEM-100CXII electron microscope operated at 100 kV. Absorption spectra were recorded using a HP 8452A diode array spectrophotometer at 1 cm path length.

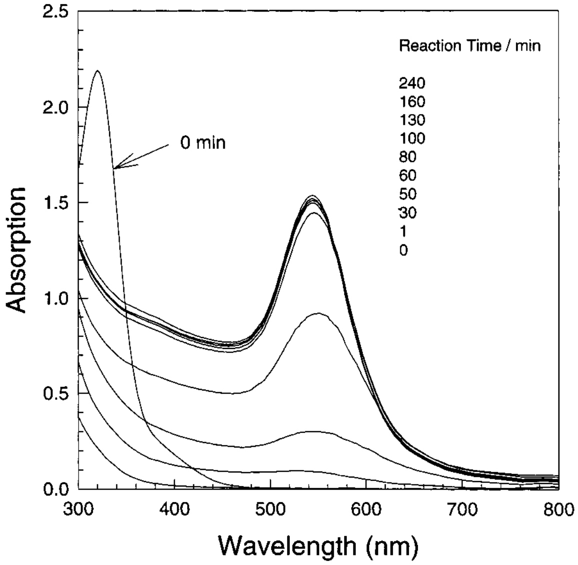

Figure 2. Evolution of absorption spectra with reaction time for the formamide solution containing 3.0×10^{-4} M $HAuCl_4$ at a $PVP/HAuCl_4$ molar ratio of 1/5.

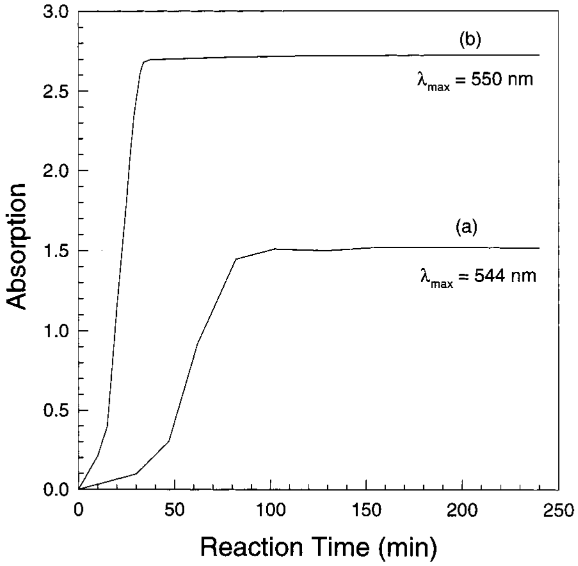

Figure 3. Evolution of the absorption at the λ_{max} in the formamide solution of (a) 3.0×10^{-4} M $HAuCl_4$ at a molar ratio of 1/5 and (b) 6.0×10^{-4} M $HAuCl_4$ at a $PVP/HAuCl_4$ molar ratio of 3/5.

Results and Discussion

Unlike conventional chemical routes, the reduction reaction described here can be performed at room temperature, and introduction of an additional reducing agent into the reaction system is not required. The uniform nonaqueous gold colloids can form quickly in the oxygen-free formamide solutions of $HAuCl_4$ at suitable molar ratios of $PVP/HAuCl_4$. The nearly monodisperse gold particles of ~30 nm diameter shown in Figure 1 were prepared in such a reducing system containing 3.0×10^{-4} M $HAuCl_4$ at a $PVP/HAuCl_4$ molar ratio of 1/5. Figure 2 shows the evolution of absorption spectra with increasing reaction time for this formamide solution. The formation kinetics of gold particles shown in Figure 3 a were also followed by measuring changes in the absorption of the resulting gold particles at the maximum absorption wavelength (λ_{max}). The ligand-to-metal charge transfer (LMCT) band of the $AuCl_4^-$ at ~322 nm decayed fast and disappeared within 1 min. The reduction reaction of $HAuCl_4$ then took place at a low initial formation rate of gold particles. The formation of gold particles was first evident after 30 min, indicated by a broad absorption band at ~550 nm. The intensity of this band increased fast with increasing reaction time from 30 to 80 min and reached its maximum at 100 min. A blue shift of the λ_{max} of gold particles from 550 to 544 nm was observed in the final stage of the reduction reaction. The red shift of the absorption band of gold particles of ~30 nm in formamide, as compared to the gold particles of similar size in aqueous solution, is believed to arise from the larger refractive index of formamide instead of smaller particle sizes.[11]

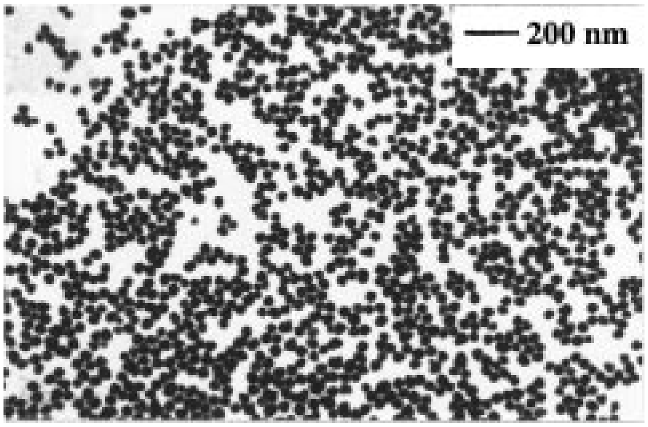

Figure 4. Transmission electron micrograph of gold particles prepared from 6.0×10^{-4} M $HAuCl_4$ at a PVP/$HAuCl_4$ molar ratio of 3/5.

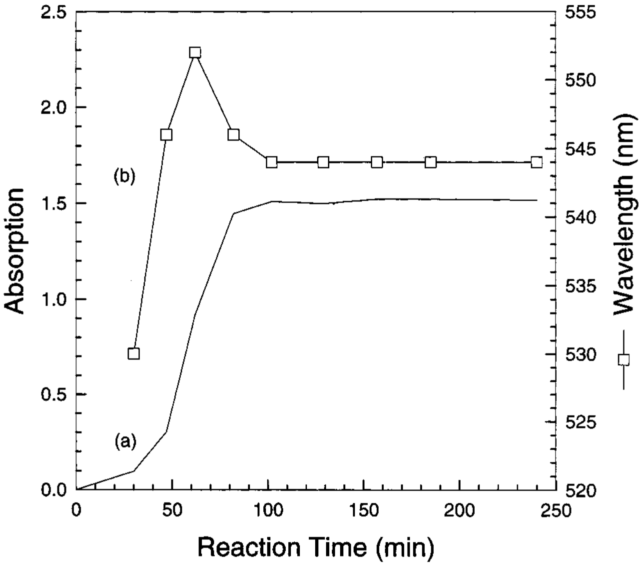

Figure 5. (a) Evolution of the absorption of the λ_{max} and (b) the λ_{max} as function of reaction time in the formamide solution containing 3.0×10^{-4} M $HAuCl_4$ at a PVP/$HAuCl_4$ molar ratio of 1/5.

The stable and nearly monodisperse gold colloid shown in Figure 4 was also successfully prepared in a formamide solution containing 6.0×10^{-4} M $HAuCl_4$ at a PVP/$HAuCl_4$ molar ratio of 3/5. Although a higher concentration of $HAuCl_4$ was used, uniform gold particles of ~32 nm, almost the same size as the above, were still produced by changing the molar ratio of PVP/$HAuCl_4$. The formation of gold particles was evident within 10 min. It was completed just after 35 min, whereas the 3.0×10^{-4} M $HAuCl_4$ system took as long as about 100 min, and the maximum absorption intensity of the colloid nearly doubled as the $HAuCl_4$ concentration was doubled as shown in Figure 3b. These results show that the formation rate of gold particles is strongly dependent on the concentration of $HAuCl_4$.

Under typical reaction conditions for producing gold particles in aqueous solutions, i.e., when boiling chloroauric acid and citrate solutions were mixed, there was an almost instantaneous appearance of deep red color, indicating the formation of gold particles of 15−25 nm diameter.[12] The reacting solution progressively went from clear and colorless at the time of mixing through black, purple, blue, and then red. The relative big particles can produce first, and then fall apart later as the reaction proceeds, resulting in the uniform sols.[12] For the preparation of gold particles in the currently used formamide system, the reaction solution changes from faint pink through blue to magenta at room temperature, as shown in Figure 5 , as the reduction reaction proceeds. A blue shift of the absorption band of the gold particles appeared at the final stage of the reduction. Relatively large and irregular gold particles from the nearly completed reaction were also observed by TEM as compared to the particles from the completed reduction reaction. These results indicate that small gold particles can form at the initial stage of the reduction reaction, grow as the reaction proceeds, and shrink at the final stage of chemical reduction, resulting in the uniform gold particles.[12] Only a small variation of the absorption band of gold particles from 530 to 550 nm shown in Figure 5 was observed in the formamide reducing system with 3×10^{-4} M $HAuCl_4$, which exhibits a small change in the particle size during the particle formation process. However, a wide variation in the range from 520 to 600 nm was observed in the typical aqueous system.[12] Our results show that the reactivity of $HAuCl_4$ is much higher in the new reducing system and that the room-temperature chemical reduction of $HAuCl_4$ can be carried out more completely than in water.[12]

The formation mechanism of gold colloids in the oxygen-free formamide is discussed in the following. As the dielectric constant of formamide is higher than that of water or alcohol, the salt of chloroauric acid dissolved in it can exhibit a much higher degree of dissociation,[13] and the LMCT band of the $AuCl_4^-$ thus decays much faster by displacing Cl^- from $AuCl_4^-$ as compared to the alcohol or aqueous solutions.[9,14] A similar ligand-substitution reaction can also occur in alkylamine solution.[15] However, the LMCT band remains unchanged in dimethylformamide having no primary amino group but an aldehyde group as in formamide. It is thus assumed that the amino group instead of the aldehyde group in formamide participates in the ligand-substitution reactions as hydroxyl groups do in the aqueous or alcohol solutions. Although ligand-substitution reactions can also proceed in polar media such as water, alcohol, or alkylamine, the chemical reduction of $HAuCl_4$ to gold particles can occur only in oxygen-free formamide solutions. The reduction reaction can be quenched easily by exposing it to oxygen, and it cannot be initiated in an oxygen-containing formamide solution. This indicates that only the ligand-substitution reaction is not sufficient for the formation of gold particles, and that the aldehyde group with the reducing ability in formamide is required to participate in the reduction reaction in the oxygen-free formamide solution. It is known that the aldehyde group can reduce gold com-

---

(11) Underwood, S.; Mulvaney, P. *Langmuir* **1994**, *10*, 3427.

(12) Chow, M. K.; Zukoski, C. F. *J. Colloid Interface Sci.* **1994**, *165*, 97.

(13) Zamudio, W.; Garcia, A. M.; Baraona, R. *Transition Met. Chem.* **1995**, *20*, 518.

(14) Belevantsev, V. I.; Kolonin, G. R.; Ryakhovskaya, S. K. *Russ. J. Inorg. Chem.* **1972**, *17*, 1303.

(15) Nagel, Y.; Beck, W. *Z. Anorg. Allg. Chem.* **1985**, *529*, 57.

plexes in basic aqueous solution.[5,8] The chemical reduction of chloroauric acid to gold particles in the new reducing system therefore involves two-step reaction processes, which are ligand substitution and chemical reduction.

Since electrostatic stabilization is generally not effective in the relatively low polarity of typical organic media, and the medium viscosity is often lower than that of water, there are more frequent encounters between the colloidal particles in such organic phases, leading to a more rapid aggregation than in water. The production of colloidal gold particles in typical organic media is thus quite different from that in aqueous solution. In our experiment formamide was chosen as the organic supporting medium because of its higher polarity, dielectric constant, and viscosity. For the preparation of well-dispersed colloidal gold particles, it is helpful to use solvents with a larger dielectric constant.[16] Due to the high solvating ability of the organic medium formamide, all gold complexes are dissociated completely, and the resulting intermediates are thus surrounded closely by formamide molecules. The direct reduction of $HAuCl_4$ by the surrounding formamide molecules enhances the nucleation rate of gold particles and reduces their growth rate. The stabilizer polymer can absorb to the gold nuclei, reducing their growth and preventing the flocculation of the organosols by steric stabilization. During the formation process of gold particles, the competition between particle growth and nucleation is also partially controlled by diffusion. For low-viscosity reducing solutions, the rate of diffusion is fast and the reduced gold atoms can migrate to the surface of nuclei before they form a new nucleus. The time of nucleation and length of the growth period of different nuclei are not the same, giving particles with different sizes at the end of the growth process. However, in the highly viscous formamide solution the rate of diffusion is slow, resulting from the high viscosity of formamide and the addition of stabilizer. In summary, we believe that the successful formation of nearly monodisperse colloidal gold particles arises from the sufficiently high nucleation rate but the low growth rate of particles.[17]

Conclusions

We present the synthesis of uniform nonaqueous gold particles in formamide, acting as a reducing agent, in the presence of the stabilizing polymer PVP. The chloroauric acid in the oxygen-free formamide solutions can be reduced to gold particles quickly at room temperature. Unlike conventional chemical routes, the efficient formation of uniform gold particles does not require the introduction of additional reducing agent because the organic solvent can serve as reducing agent as well as supporting medium. This new chemical route is also very promising for the production of other uniform transition-metal particles such as copper and silver.

CM9810943

---

(16) Satoh, N.; Hasegawa, H.; Tsujii, K. *J. Phys. Chem.* **1994**, *98*, 2143.

(17) Kreibig, U.; Vollmer, M. *Optical Properties of Metal Clusters*; Springer: Berlin, 1995.