New Type of Monodispersed Gold Nanoparticles Capped by Myristate and PPh_3 Ligands Prepared by Controlled Thermolysis of $[Au(C_{13}H_{27}COO)(PPh_3)]$

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Controlled thermolysis of gold(I) complex, $[Au(C_{13}H_{27}COO)(PPh_3)]$, at 180 °C for 5 h under an N_2 atmosphere affords the new type of monodispersed spherical gold nanoparticles capped by myristate and a small amount of PPh_3 ligands (average diameter 23 ± 1.5 nm), in spite of no use of solvent, reducing agent and stabilizer.

Much attention has been paid to the preparation and structure determination of transition metal nanoparticles, because of their widespread use in technological applications.[1] In general, the chemical reduction of metal salts and organometallic complexes[2] by the use of reducing agent is carried out to prepare gold nanoparticles. In some cases, a large amount of solvent and stabilizers such as surfactants,[3] polymers[4] and ligands[5] are used to prevent agglomeration of particles and control the particle size. For instance, Brust et al. reported a two-phase reduction of $AuCl_4^-$ by $NaBH_4$ in the presence of dodecanethiol as stabilizer to prepare gold nanoparticles.[6] On the other hand, O'Brien et al. recently reported an one-phase preparation of gold nanoparticles by the reduction of $AuCl_4^-$ by $NaBH_4$ in the mixture of tri-*n*-octylphosphine oxide and octadecylamine which act as both solvent and stabilizer, but this procedure also needs reducing agent.[7]

Recently, we have shown that thermolysis of gold(I) thiolate complex, $[C_{14}H_{29}N(CH_3)_3][Au(SC_{12}H_{25})_2]$, produced gold nanoparticles (average diameter 26 nm) passivated by alkyl groups deriving from the counter cation of the precursor complex.[8] However, the size distribution of the particles was relatively broad, ranging from 5 to 50 nm. In order to prepare the new type of monodispersed gold nanoparticles by thermolysis procedure, it may be important how to design the most suitable precursor gold complexes which decompose at low temperature and supply the organic protecting groups to prevent the agglomeration and afford the ligand stabilized nanoparticles. On the basis of this idea, we have prepared gold(I) complex, $[Au(C_{13}H_{27}COO)(PPh_3)]$, as the precursor and conducted its controlled thermolysis with no use of solvent, reducing agent and stabilizer. As a result, we have succeeded to obtain the new type of monodispersed gold nanoparticles capped by myristate and a small amount of PPh_3 ligands. The thermolysis process of gold(I) complex was also investigated in detail to reveal the role of ligands.

Thermolysis of gold(I) complex, $[Au(C_{13}H_{27}COO)(PPh_3)]$ (**1**), prepared by the transmetalation of $[AuCl(PPh_3)]$ with $C_{13}H_{27}COOAg$,[9] was conducted by the heating of the powder of complex **1** with no use of solvent under an N_2 atmosphere.[10] The complex **1** completely melted to afford the precursor liquid and then the liquid gradually decomposed at 180 °C for 5 h. The reactant changed to deep purple coloured oil, and finally afforded a mixture of gold nanoparticles and organic liquid. The gold nanoparticles were isolated as powder which were redispersed in acetone. The colloidal solution did not show any signs of aggregation over a period of two weeks.[11]

Figure 1 shows the transmission electron microscopy (TEM) image and the size distribution histgram of gold nanoparticles. The sample of TEM was obtained by placing a drop of the acetone solution of nanoparticles onto a carbon film supported on a copper mesh grid. The particles are spherical in shape and have narrow size distribution ranging from 18 to 27 nm, and almost all particles are the same particle size with a mean diameter of 23 ± 1.5 nm. The powder X-ray diffraction pattern is shown in Figure 2a. The broad peaks at $2\theta = 38.1$, 44.1, 64.4, 77.9 indicate 111, 200, 220 and 311 planes of fcc

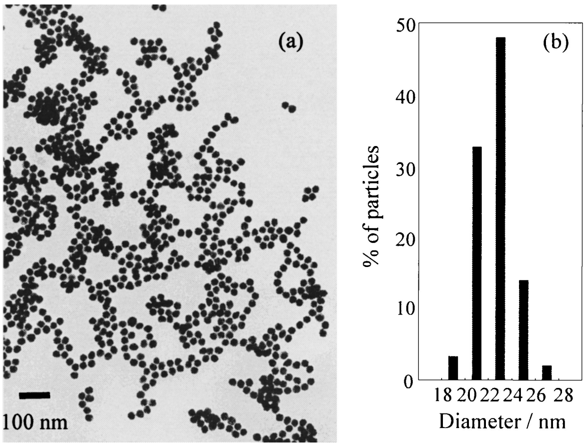

Figure 1. (a) TEM photograph of gold nanoparticles. (b) Histogram for the nanoparticle size, obtained from TEM.

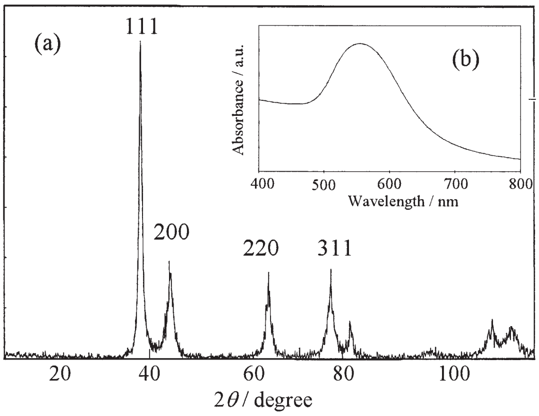

Figure 2. (a) XRD pattern and (b) UV-vis spectrum in acetone of gold nanoparticles prepared by thermolysis (180 °C, 5 h).

gold. The average particle size of the metal nuclei (17 nm) was calculated from the half-width of the intense 111 reflection by the use of Scherrer equation. The X-ray photoelectron spectrum (XPS) showed the Au $4f_{7/2}$ band (83.5 eV) instead of Au $4f_{7/2}$ band (85.4 eV) in the precursor Au(I) complex **1**. It means that the core gold in the nanoparticles must be present as Au^0 state.[12] The UV-vis spectrum of gold nanoparticles in acetone (Figure 2b) displays the surface plasmon resonance at 554 nm, the wavelength of which showed red shift compared to that of previously reported gold nanoparticles passivated by alkyl groups in spite of the same particle size and solvent.[8] The difference of the organic moieties attached on the gold surface (vide infra) may contribute to this red shift.[1] Furthermore, TG/DTA analysis of gold nanoparticles indicates the nanoparticles contain 88% gold, suggesting the presence of organic moiety around the core gold. Thus, IR, XPS, ^1H NMR and GC/MS were carried out to confirm the organic moiety. The $\nu_{C=O}$ band (1733 cm^{-1}) of myristate ligand was detected by IR and XPS of the gold nanoparticles also afforded the O 1s band (532.1 eV). The ^1H NMR spectrum of gold nanoparticles displayed resonances associated with methyl group at δ 0.83-0.88 and methylene groups at δ 1.21-1.26. In addition, the signals assigned to PPh_3 were observed at δ 7.4-7.7. With respect to PPh_3, XPS also afforded the P 2p peak (132.1 eV) compatible with that of precursor complex (132.1 eV) rather than that of free PPh_3 (130.9 eV). Furthermore, GC/MS analysis of gaseous components evolved by the decomposition of gold nanoparticles at 180 °C for 30 min showed two peaks at m/z 228 and 262 identified as $C_{13}H_{27}COOH$ and PPh_3, respectively, and estimated that the ratio of $C_{13}H_{27}COOH$ to PPh_3 was about 80:1. Therefore, these results prove that myristate and a small amount of PPh_3 ligands are coordinated to the surface of core gold.

The thermolysis process of the precursor gold(I) complex **1** producing gold nanoparticles with myristate and PPh_3 ligands was examined in detail. After thermolysis of **1**, a mixture of gold nanoparticles and organic liquid was obtained. On the basis of IR ($\nu_{C=O}$, 1716 cm^{-1}; $\nu_{O\text{-}H}$, 3419 cm^{-1}) of the organic liquid, it was confirmed that the organic liquid contained myristic acid. Furthermore, the ^{31}P-NMR spectrum of the organic liquid showed a single signal at δ 42.0, which was corresponding with that of bis(triphenylphosphine)gold(I) complex, $[Au(PPh_3)_2]^+$,[13,14] rather than that of precursor complex (δ 29.6). It is well known that $[Au(RCOO)(PPh_3)]$ is easily converted into the thermally stable bis(phosphine)gold(I) complex $[Au(PPh_3)_2][RCOO]$ in the presence of PPh_3.[13] These results suggest that thermolysis of **1** causes elimination of myristate ligand to reduce gold(I) to metallic gold(0), accompanying the protection of gold nanoparticles by myristate ligand. At the same time, the eliminated PPh_3 reacted with precursor complex **1** to produce $[Au(PPh_3)_2][C_{13}H_{27}COO]$ which was not decomposed under this reaction condition. On the other hand, when the thermolysis was carried out under the atmospheric condition, the yield of nanoparticles became quantitative which suggests PPh_3 was trapped as $O{=}PPh_3$ not to produce bis(phosphine)gold(I) complex. But the particles size became larger (70-180 nm) and its shape was not spherical. These results mean that both myristate and PPh_3 ligands directly coordinated to the gold center in the precursor complex act as useful stabilizers; the former stabilizes the gold nanoparticles and the latter stabilizes gold(0) intermediate to prevent rapid agglutination. Thus, monodispersed spherical gold nanoparticles capped by myristate and a small amount of PPh_3 ligands are formed by controlled thermolysis.

The particle size can be controlled by reaction time and temperature. The aggregation of gold nuclei was promoted by longer reaction time and higher temperature.[8] For example, thermolysis of the complex **1** at 180 °C afforded the gold nanoparticles with the average diameter 12 nm for 1 h, 19 nm for 4 h and 28 nm for 10 h. In addition, the average diameter became 42 nm under the condition at 200 °C for 5 h.

In conclusion, the new type of monodispersed gold nanoparticles bearing a surface coating of myristate and a small amount of PPh_3 ligands have been prepared by the controlled thermolysis of $[Au(C_{13}H_{27}COO)(PPh_3)]$. Further investigations on the thermolysis of organometallic precursors for the synthesis of nanoparticles and bimetallic Au/M nanoparticles are now in progress by our hands.

References and Notes

1 L. N. Lewis, *Chem. Rev.*, **93**, 2693 (1993); J. S. Bradley, in "Clusters and Colloids: From Theory to Applications," ed. by G. Schmid, VCH, Weinheim (1994), Chap. 6, pp 523-536; "Nanoparticles and Nanostructured Films: Preparation, Characterization and Applications," ed. by J. H. Fendler, Wiley-VCH, Weinheim (1998).

2 J. S. Bradley, in "Clusters and Colloids: From Theory to Applications," ed. by G. Schmid, VCH, Weinheim (1994), Chap. 6, pp 469-490.

3 Y. Nakao and K. Kaeriyama, *J. Colloid Interface Sci.*, **110**, 82 (1986); K. Torigoe and K. Esumi, *Langmuir*, **8**, 59 (1992); H. Bönnemann, W. Brijoux, R. Brinkmann, E. Dinjus, T. Jouben, and B. Korall, *Angew. Chem., Int. Ed. Engl.*, **30**, 1312 (1991).

4 H. Hirai, Y. Nakao, and N. Toshima, *Chem. Lett.*, **1976**, 905; M.-O. Delcourt, N. Keghouche, and J. Belloni, *Nouv. J. Chim.*, **7**, 131 (1983); C. H. Walker, J. V. St. John, and P. W-Neilson, *J. Am. Chem. Soc.*, **123**, 3846 (2001).

5 G. Schmid and A. Lehnert, *Angew. Chem., Int. Ed. Engl.*, **28**, 780 (1989); C. Larpent and H. Patin, *J. Mol. Catal.*, **44**, 191 (1988).

6 M. Brust, M. Walker, D. Bethell, D. J. Schiffrin, and R. Whyman, *J. Chem. Soc., Chem. Commun.*, **1994**, 801.

7 M. Green and P. O'Brien, *J. Chem. Soc., Chem. Commun.*, **2000**, 183.

8 M. Nakamoto, M. Yamamoto, and M. Fukusumi, *J. Chem. Soc., Chem. Commun.*, **2002**, 1622.

9 K. Abe, T. Hanada, Y. Yoshida, N. Tanigaki, H. Takiguchi, H. Nagasawa, M. Nakamoto, T. Yamaguchi, and K. Yase, *Thin Solid Films*, **327**, 524 (1998).

10 Typical synthesis of nanoparticles was conducted as follows. $[Au(C_{13}H_{27}COO)(PPh_3)]$ (687 mg, 1 mmol) was placed in the bottom of a two necked flask under an N_2 atmosphere, and then heated up to 80 °C to cause complete melting. Further heating up slowly to 180 °C and holding at that temperature for 5 h made the precursor complex gradually decompose to give a deep violet solution. After cooling to room temperature, the brown precipitate was separated by addition of methanol. The precipitate was washed with methanol for 2 times. The crude product was dispersed in acetone by irradiation of ultrasonic wave and again precipitated with methanol. The product was isolated as a brown solid by removing supernatant liquid or as golden leaves by slowly evaporation from acetone solution and then dried *in vacuo* (98 mg, 50% yield based on Au; Au content, 88%).

11 The plasmon absorption at 554 nm and its intensity showed no change for two weeks.

12 D. I. Nichols and A. S. Charleston, *J. Chem. Soc. A*, **1969**, 2581.

13 M. N. I. Khan, J. P. Fackler, S. P. Chum, and A. Paquet, *J. Polym. Sci., Part A: Polym. Chem.*, **31**, 2353 (1993); J. P. Fackler, Jr., W. E. van Zyl, and B. A. Prihoda, in "Gold, Progress in Chemistry, Biochemistry and Technology," ed. by H. Schmidbaur, Wiley, Chichester (1999), Chap. 20, pp 795-839; J. P. Fackler, Jr., M. N. I. Khan, C. King, R. J. Staples, and R. E. P. Winpenny, *Organometallics*, **10**, 2178 (1991).

14 M. Bardaji, P. Uznanski, C. Amiens, B. Chaudret, and A. Laguna, *J. Chem. Soc., Chem. Commun.*, **2002**, 598; J. M. Forward, Z. Assefa, R. J. Staples, and J. P. Fackler, *Inorg. Chem.*, **35**, 16 (1996).