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Synthesis and size regulation of gold nanoparticles by controlled thermolysis of ammonium gold(I) thiolate in the absence or presence of amines

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Dedicated to Professor Hubert Schmidbaur.

Abstract

Controlled thermolysis of gold(I) complex with no use of solvent was investigated as a novel synthetic method of gold nanoparticles. A series of precursors, ammonium gold(I) thiolate $[RN(CH_3)_3][Au(SC_{12}H_{25})_2]$ ($R = C_8H_{17}$, $C_{12}H_{25}$, and $C_{14}H_{29}$) and $[(C_{18}H_{37})_2N(CH_3)_2][Au(SC_{12}H_{25})_2]$, have been prepared and the thermolysis of those precursors was conducted at 180 °C for 5 h under an N_2 atmosphere, providing spherical gold nanoparticles stabilized by alkyl groups derived from the precursor, gold(I) complex. In spite of thermolysis process, the average diameter of gold nanoparticles deriving from $[C_{12}H_{25}N(CH_3)_3][Au(SC_{12}H_{25})_2]$ was 22 nm, but the size distribution ranges from 11 to 76 nm. For the purpose of the size regulation of the gold nanoparticles, equimolar primary, secondary, or tertiary alkylamines are added as stabilizer and mild reductant to the controlled thermolysis of gold(I) complex at lower temperature of 165 °C for 5 h. The gold nanoparticles obtained by the controlled thermolysis in the presence of stearylamine are well regulated and almost monodispersed nanoparticles with average diameter of 7.5 nm. Such size regulation resulted from the inhibition of the growth of gold nuclei by transforming reaction from ammonium and thiolate moieties to neutral tertiary amine, thiol and sulfide, which function as stabilizer for gold nanoparticles.

Keywords: Nanoparticles; Gold complexes; Controlled thermolysis; Size regulation; Reductive elimination

1. Introduction

Gold is the highly functional metal applied to a lot of purpose [1]. Especially in the colloid chemistry, gold is known as one of the unique metal to form stable nanoparticles. The preparation and properties of narrowly distributed metal nanoparticles have been intensively studied because of anticipation in various applications of the electronic, magnetic, catalytic and thermal properties which bring new perspective in science and technology [2–12]. The gold nanoparticles have high stability to corrosion and low annealing temperature due to the high surface energy of nanoparticles. Focusing on this point, the gold nanoparticles are especially closed up as the thermal forming electronic conductor for fine pitch electronic circuits [1]. Since Brust et al. reported the two-phase reduction of $AuCl_4^-$ by $NaBH_4$ to afford monodispersed gold nanoparticles stabilized by alkanethiolate ligands [13], plenty of preparative investigations on gold nanoparticles [14,15] and its surface modification [16] have appeared, because of their potential applications in microelectronics [17]. However, those preparative methods generally involve the reduction of $AuCl_4^-$ by reducing agent, e.g., $NaBH_4$, in the presence of suitable organic stabilizers such as alkanethiols [13–

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15], phosphines [17], quaternary ammonium salts [18], surfactants [19], or polymers [20]. On the other hand, O'Brien et al. recently reported the preparation of organically capped gold nanoparticles at 190 °C, where tri-*n*-octylphosphine oxide and/or *n*-octadecylamine are used both as a reaction medium and as a stabilizing ligand [21], but this procedure also needs $NaBH_4$ as reducing agent.

Our novel preparative method for gold nanoparticles without strong reductant such as $NaBH_4$ combines the reductive elimination of thiolate ligands with simultaneous attachment of an organic moiety on the growing nuclei. Ammonium gold(I) thiolates were useful for our preparative method. We now report the thermolysis of alkylammonium gold(I) thiolates, $[RN(CH_3)_3][Au(SC_{12}H_{25})_2]$ (**C8Au**: $R = C_8H_{17}$, **C12Au**: $R = C_{12}H_{25}$, **C14Au**: $R = C_{14}H_{29}$) and $[(C_{18}H_{37})_2N(CH_3)_2][Au(SC_{12}H_{25})_2]$ (**(C18)₂Au**), under an N_2 atmosphere, where the powder of gold(I) complexes completely melts to afford the precursor liquid and then the liquid gradually decomposes. Although there is no use of reducing agent or solvent, a reduction is thermochemically induced to afford novel gold nanoparticles stabilized by alkyl groups rather than by alkanethiolate ligand. The size of gold nanoparticles prepared via the controlled thermolysis of the gold(I) complexes is larger than that of gold nanoparticles prepared by the two-phase synthesis reported by Brust et al. It may be that the stabilizing effect of the alkyl group was not enough for inhibition of the gold core growth. In order to regulate the particle size, the controlled thermolysis of gold(I) complex was carried out in the presence of amines known as mild reductant, ligand for metal ions, stabilizer for metal nanoparticles, and solvent. In this paper, we report the novel synthetic method of gold nanoparticles by controlled thermolysis of ammonium gold(I) thiolates in the absence or presence of amines, and the size regulation of gold nanoparticles. The reaction mechanism of the thermolysis is also revealed from the detailed study on identification of organic stabilizer.

2. Experimental

2.1. Chemicals

All solvents and chemicals were of reagent grade quality, obtained commercially and used without further purification. *n*-Octyltrimethylammonium bromide, distearyldimethylammonium chloride, *n*-octylamine (**C8NH₂**), and di-*n*-octylamine (**(C8)₂NH**) were obtained from Tokyo Kasei Organic Chemicals. $KAuCl_4 \cdot 2H_2O$ were purchased from Mitsuwa Chemicals Co., Ltd. Dodecanethiol, lauryltrimethylammonium chloride, myristyltrimethylammonium bromide, sodium methylate (28% in MeOH), laurylamine (**C12NH₂**), stearylamine (**C18NH₂**), tri-*n*-octylamine (**(C8)₃N**), MeOH, acetone and toluene were obtained from Nakarai Tesque, Inc.

2.2. Measurements

Melting points (mp) were recorded on a Yanaco micro-melting point apparatus. Elemental analysis was performed on a Carlo Erba Instruments EA 1110 CHNS-O analyzer. ^1H NMR spectra were recorded on a JEOL JNM-AL300 instrument at 300 MHz. Transmission electron microscopic images were obtained on a JEOL JEM-1200EX transmissions electron microscope (TEM) operation at 100 keV. Samples for TEM were dispersed in toluene by sonication and deposited on amorphous carbon film-coated copper grid. UV–visible absorption spectra were recorded on a Shimadzu UV-3150C spectrophotometer. Powder X-ray diffractions were recorded on a Rigaku RINT 2500 diffractometer (Cu Kα radiation) equipped with a monochromator. The GC-MS spectra were taken using a pyrolizer PY-2020D for thermal extraction at 200 °C for 10 min and Hewlett-Packard 6890 GC system equipped with an HP 5973 mass selective detector. X-ray photoelectron spectroscopy was measured on a Physical Electronics (PHI) model 5700 ESCA spectrometer with an Al monochromatic source (Al Kα energy of 1486.6 eV). Thermal gravimetric analysis was carried out on a Seiko Instruments SSC/5200 thermal analyzer. Fast atom bombardment (FAB) mass spectra were obtained on a JEOL JMS-AX505HA.

2.3. Preparation of gold(I) thiolate complexes

A series of gold(I) complexes, $[RN(CH_3)_3][Au(SC_{12}H_{25})_2]$ (**C8Au**: $R = C_8H_{17}$, **C12Au**: $R = C_{12}H_{25}$, **C14Au**: $R = C_{14}H_{29}$) and $[(C_{18}H_{37})_2N(CH_3)_2][Au(SC_{12}H_{25})_2]$ (**(C18)₂Au**), were prepared as follows: a MeOH (30 ml) solution of corresponding alkyltrimethylammonium halide (10 mmol) was added to a MeOH solution (30 ml) of $KAuCl_4 \cdot 2\,H_2O$ (4.14 g, 10 mmol). Yellow suspension of ammonium chloroaurate was obtained immediately. A MeOH solution (20 ml) of dodecanethiol (8.08 g, 40 mmol) and MeONa (28% in MeOH, 7.72 g, 40 mmol) was added to the suspension of ammonium chloroaurate. The color of suspension turned to pale yellow. The obtained pale yellow powder was filtered, washed with MeOH and water, and dried under vacuum to give **C8Au** (90%), **C12Au** (91%), **C14Au** (88%) and **(C18)₂Au** (74%) as microcrystals.

C8Au: mp 85.9–87.3 °C. *Anal.* Calc.: C, 54.45; H, 9.92; N, 1.81. Found: C, 54.10; H, 9.87; N, 1.49%. ^1H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, 9 H), 1.18–1.42 (m, 52H), 1.67 (p, 4H), 1.79 (br p, 2H), 2.68 (t, 4H), 3.39 (s, 9H), 3.44–3.57 (m, 2H).

C12Au: mp 96.4–98.2 °C. *Anal.* Calc.: C, 56.56; H, 10.22; N, 1.69. Found: C, 56.56; H, 10.19; N, 1.52%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, 9H), 1.24–1.27(m, 48H), 1.32–1.39 (m, 6H), 1.67 (p, 4H), 1.79 (p, 2H), 2.76 (t, 4H), 3.41 (s, 9H), 3.53–3.60 (m, 2H).

C14Au: mp 97.5–99.5 °C. *Anal.* Calc.: C, 57.51; H, 10.36; N, 1.64. Found: C, 57.49; H, 10.32; N, 1.91%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, 9 H), 1.24–1.26 (m, 52H), 1.39–1.32 (m, 6H), 1.66 (p, 4H), 1.78 (p, 2H), 2.76 (t, 4H), 3.40 (s, 9H), 3.54–3.62 (m, 2H).

$(C18)_2Au$: mp 86.0–91.0 °C. *Anal.* Calc.: C, 64.71; H, 11.39; N, 1.22. Found: C, 64.78; H, 11.23; N, 1.53%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (t, 12H), 1.24–1.35 (m, 88H), 1.35–1.38 (m, 8H), 1.64–1.75 (m, 8H), 2.76 (t, 4H), 3.32 (s, 6H), 3.45–3.52 (m, 4H).

2.4. Controlled thermolysis of gold(I) complexes

The powder of gold(I) complex (1.0 mmol) was placed in the bottom of three necked flask under an N_2 atmosphere, then heated up to 180 °C to cause complete melting and maintained the temperature for 5 h. The liquid gradually decomposed to afford a mixture of brown precipitates and liquid, and precipitates were collected by filtration, washed with MeOH (30 ml × 2), and dried under vacuum (quantitative yield based on Au).

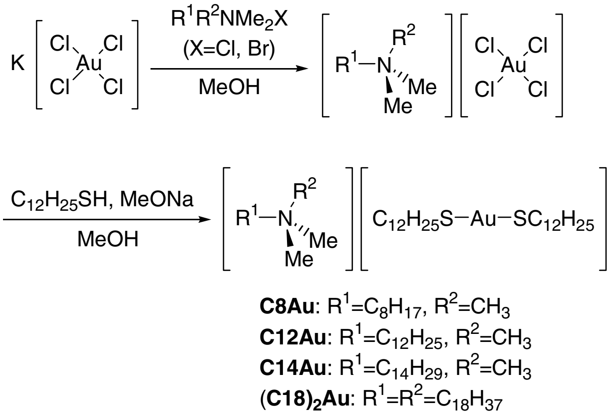
2.5. Controlled thermolysis of gold(I) complexes in the presence of amines

The powder of gold(I) complex (1.0 mmol) and amines (1.0 mmol) was placed in the bottom of three necked flask under an N_2 atmosphere, then heated up to 165 °C to afford a liquid of gold(I) complex. Heating a liquid at that temperature for 5 h caused gradual decomposition to produce a mixture of brown precipitates and liquid, and precipitates were collected by filtration, washed with MeOH (30 ml × 2), and dried under vacuum (quantitative yield based on Au).

3. Results and discussion

3.1. Synthesis and controlled thermolysis of gold(I) complexes

The synthetic route to gold(I) thiolate complexes, $[RN(CH_3)_3][Au(SC_{12}H_{25})_2]$ (**C8Au**: R = C_8H_{17}, **C12Au**: R = $C_{12}H_{25}$, **C14Au**: R = $C_{14}H_{29}$) and $[(C_{18}H_{37})_2N(CH_3)_2][Au(SC_{12}H_{25})_2]$ (**$(C18)_2Au$**) is shown in Scheme 1 [22]. In order to reduce the gold(I) to metallic gold(0) easily, the gold(I) complex was selected for precursor. For the cation exchange of $KAuCl_4$, we used the corresponding *n*-alkyltrimethylammonium halide in MeOH, respectively. The obtained ammonium chloroaurate was precipitated as yellow solid in MeOH. The freshly prepared $C_{12}H_{25}SNa$ in MeOH was added to the resulting suspension, immediately the color of suspension was turned to pale yellow. Ammonium gold(I) thiolates are isolated as pale yellow solid, characterized by ^{1}H NMR and elemental analysis.



Scheme 1.

In order to prepare gold nanoparticles, thermolysis of gold(I) complexes was carried out by a simple one-pot process. The powder of gold(I) complexes was heated up to 180 °C and maintained for 5 h under an N_2 atmosphere. In the case of the thermolysis of **C12Au**, **C14Au**, and **$(C18)_2Au$**, the melted gold(I) complex turned to brown dispersion after heating at 180 °C for 5 h. Addition of MeOH to the resulted brown dispersion afforded the black precipitate, which was centrifuged and collected, dried under vacuum. The gold nanoparticles, **C12AuNP**, **C14AuNP**, and **$(C18)_2AuNP$**, synthesized from **C12Au**, **C14Au**, and **$(C18)_2Au$**, respectively, were isolated as black powder in quantitative yield. The particles are well redispersed in nonpolar solvents such as toluene and benzene.

3.2. Physical properties of gold nanoparticles prepared by the controlled thermolysis of gold(I) complexes

Fig. 1 shows typical transmission electron microscopy (TEM) images of gold nanoparticles **C12AuNP** prepared by the controlled thermolysis of **C12Au** at 180 °C for 5 h. The TEM images indicate a controlled growth of spherical gold nanoparticles. As shown in Fig. 2, these spherical gold nanoparticles display a size distribution ranging from 11 to 76 nm. Although the particle size is larger than that of alkanethiol-stabilized gold nanoparticles (less than 5 nm) prepared by $NaBH_4$ reduction [13,14], the aggregation of gold nuclei is smoothly regulated and the growth of core gold is limited to an average diameter of 22 nm in spite of the thermal procedure. The particle size and distribution of **C14AuNP** determined by the TEM images were similar

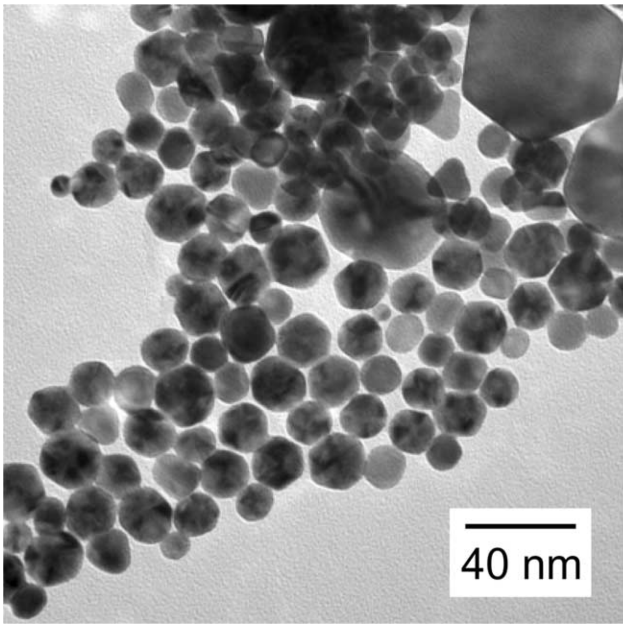


Fig. 1. TEM image of **C12AuNP**.

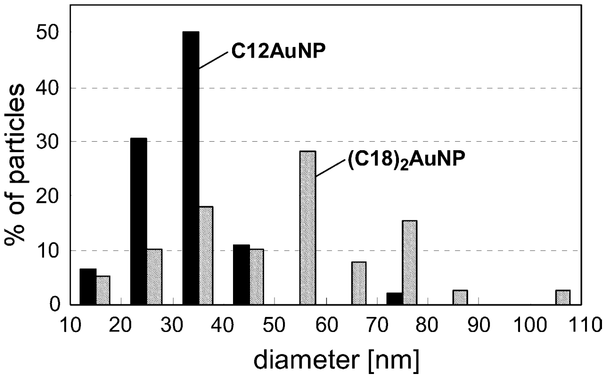


Fig. 2. Histogram for the size distribution of **C12AuNP** and **(C18)$_2$AuNP**.

to those of gold nanoparticles **C12AuNP** as shown in Table 1.

The oxidation state of gold in the nanoparticle **C14AuNP** was confirmed by X-ray photoelectron spectroscopy (XPS). Both the binding energies of Au $4f_{7/2}$ (83.4 eV) and Au $4f_{5/2}$ (87.0 eV) are characteristic of gold(0). Gold(I) peaks were not observed in the region of gold(I) complexes [23,24]. Fig. 3 shows the X-ray

Table 1
Properties of gold nanopaticles

Nanoparticles	Yield (%)	Metal content (%)	Averaged diameter (nm)	Range of diameter (nm)
C12AuNP	99	99	22	11–76
C14AuNP	93	93	26	5.0–50
(C18)$_2$AuNP	79	98	46	13–107

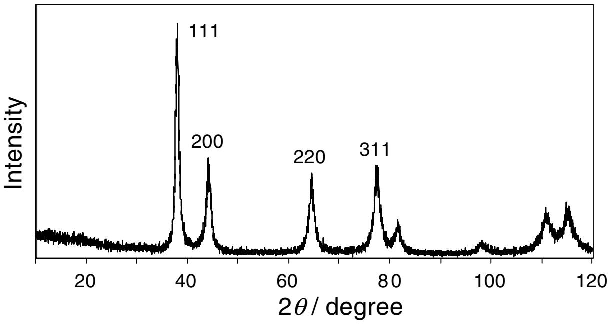


Fig. 3. XRPD pattern of **C12AuNP**.

powder diffraction (XRPD) pattern of **C12AuNP**. The XRPD pattern of **C14AuNP** was also similar. The formation of metallic gold(0) particles was confirmed by XRPD pattern, which showed slightly broad reflections for the (1 1 1), (2 0 0), (2 2 0), and (3 1 1) planes of metallic gold(0) in a face-centered cubic lattice. The average diameter of particles (19 nm) calculated by the Scherrer equation, using the half width of the intense (1 1 1) reflection, was compatible with the value obtained from TEM images.

It is well known that gold nanoparticles show the characteristic plasmon absorptions at 520–540 nm in the UV–visible absorption spectra [25]. The gold nanoparticles, **C14AuNP**, redissolved in acetone showed the absorption centered at 538 nm. The wavelength of this absorption maximum slightly shifts toward longer wavelength compared with those of the previous reported alkanethiol-stabilized gold nanoparticles with smaller particle size (520 nm). As mentioned in the literature [26], plasmon absorptions of nanoparticles tend to shift toward longer wavelengths with increasing particle size. Thus, the absorption band at 538 nm of the present gold nanoparticles is assigned to the plasmon absorption band and its peak maximum is compatible with the average particle size determined by TEM image.

Thermogravimetry shows that the obtained **C12AuNP** contain 99% metal component and 1% organic capping ligand. The metal contents of other gold nanoparticles are also measured and summarized in Table 1.

3.3. Mechanism of controlled thermolysis of gold(I) complexes

There are two possibilities for the origin of the organic components of gold nanoparticles: one is the quaternary ammonium part and the other is the dodecanethiolate ligand. In order to examine the organic moiety of the present gold nanoparticles, the ^{1}H NMR spectrum of the **C14AuNP** was measured, which showed CH_3– and –CH_2– signals of long alkyl groups, but no signal of NCH_3- and NCH_2-groups. Examination of nitrogen was also conducted by elemental analysis, but nitrogen was not left in the particles. Furthermore, XPS was examined to confirm the existence of sulfur, but no evidence for the sulfur atom was found. Thus, these results exclude the alkylamine-capped and thiol-derivatized nanoparticles, and suggest that the present gold nanoparticles are a new class of gold nanoparticles surrounded by alkyl groups (vide infra).

Thermolysis of gold(I) thiolate complexes finally afforded a mixture of gold nanoparticles and organic liquid. FAB mass spectroscopy of this organic liquid revealed the almost single substance of disulfide, $C_{12}H_{25}SSC_{12}H_{25}$, with *m*/*z* 402. The elemental analysis was also compatible with the theoretical value of $C_{12}H_{25}SSC_{12}H_{25}$. Furthermore, trimethylamine was detected in the gaseous phase by GC-MS analysis after thermolysis at 180 °C for 3 h. These results support that thermolysis of gold(I) thiolate complexes causes reductive elimination of the thiolate ligand to reduce gold(I) to metallic gold(0) and to afford disulfide, accompanying the protection of gold nanoparticles by alkyl groups derived from the quaternary ammonium cation as shown in the following equation:

$$[\mathrm{RN(CH_3)_3}][\mathrm{Au(SC_{12}H_{25})_2}] \rightarrow \mathrm{Au\ nanoparticles} + \mathrm{(CH_3)_3N} + \mathrm{C_{12}H_{25}SSC_{12}H_{25}} \quad (1)$$

On the other hand, the ammonium cations with almost the same chain lengths, $[RN(CH_3)_3]^+$ ($R = C_{12}H_{25}$, $C_{14}H_{29}$), do not show a pronounced effect on the tuning of the particle size. However, the ammonium cations containing only one longer alkyl group effectively afford gold nanoparticles compared with the ammonium cation containing two longer alkyl groups, $[(C_{18}H_{37})_2N(CH_3)_2]^+$, as shown in Fig. 2. Because the former can easily eliminate gaseous trimethylamine and supply long alkyl groups as protecting groups surrounding core gold.

3.4. Controlled thermolysis of gold(I) complexes in the presence of amines

It is well known that alkylamines function as stabilizer of nanoparticles and mild reductant. We have previously shown that trialkylamines act as effective reductant for controlled thermolysis of silver(I) myristate to produce silver nanoparticles [27]. In addition, the controlled thermolysis in the presence of amine could be carried out at lower temperature, and the particle size and its distribution of the obtained silver nanoparticles were highly regulated. In this point of view, the controlled thermolysis of the **C12Au** in the presence of amines was carried out. Various amines, such as *n*-octylamine (**C8NH$_2$**), di-*n*-octylamine (**(C8)$_2$NH**), tri-*n*-octylamine (**(C8)$_3$N**), laurylamine (**C12NH$_2$**), and stearylamine (**C18NH$_2$**), were used for investigation of particle size regulation by alkyl chain lengths and numbers.

Controlled thermolysis of **C12Au** in the presence of amines was conducted by the same manner of thermolysis in the absence of amines. The reaction was a simple one-pot process. The powder of gold(I) complexes and amines was heated at 165 °C for 5 h under an N_2 atmosphere. The thermolysis of **C12Au** with **C18NH$_2$** yielded gold nanoparticle **C12AuNP/C18NH$_2$** as a black powder. **C12AuNP/C12NH$_2$**, **C12AuNP/C8NH$_2$**, **C12AuNP/(C8)$_2$NH**, and **C12AuNP/(C8)$_3$N** were synthesized by the same procedure for **C12AuNP/C18NH$_2$**, respectively. The synthetic yields and metal contents determined by the thermal analysis are listed in Table 2.

It is noteworthy that the controlled thermolysis of **C8Au** in the absence of **C12NH$_2$** did not yield **C8AuNP** at 180 °C, but **C8AuNP/C12NH$_2$** was produced in the presence of **C12NH$_2$** at 165 °C. The gold(I) complex **C8Au** has an almost same melting point to other gold complexes, but the decomposition point is over 180 °C. In the presence of amine, the **C12NH$_2$** plays an important role in the thermolysis both as stabilizer and solvent and as reductant for lowering decomposition point. Thus, **C8AuNP/C12NH$_2$** was obtained by the controlled thermolysis in the presence of **C12NH$_2$**.

*3.5. Particle size regulation of gold nanoparticles by the controlled thermolysis of **C12Au** in the presence of amines*

Fig. 4 shows typical TEM images of spherical gold nanoparticles **C12AuNP/C18NH$_2$**, **C12AuNP/C12NH$_2$**, and **C12AuNP/C8NH$_2$**. The determined average diameters and metal contents of gold nanoparticles are listed in Table 2. On the other hand, the obtained TEM image of **C12AuNP/C8NH$_2$** shows the large aggregate of metallic gold (Fig. 4(c)). The aggregation may be caused by the instability of the gold nanoparticles with **C8NH$_2$** capping ligand at the heating temperature of 165 °C. As shown in Fig. 4(a), this spherical gold nanoparticle displays a monodispersibility. The growth of core gold is effectively limited to an average diameter of 7.5 nm by the well stabilization of **C18NH$_2$**. Furthermore, the comparison of **C12AuNP/C18NH$_2$** and **C12AuNP/C12NH$_2$** (Fig. 4(b)) apparently indicates the effect of alkyl chain length of monoalkylamines on the size regulation of gold

Table 2
Properties of **C12AuNP**/amines

Nanoparticles	Yield (%)	Metal content (%)	Averaged diameter (nm)	Range of diameter (nm)
C12AuNP/C18NH$_2$	67	95	7.5	4.0–11
C12AuNP/C12NH$_2$	99	99	23	16–91
C12AuNP/C8NH$_2$	97	98	Cannot	Cannot
C12AuNP/(C8)$_2$NH	99	98	12	5.9–17
C12AuNP/(C8)$_3$N	75	97	15	6.9–30

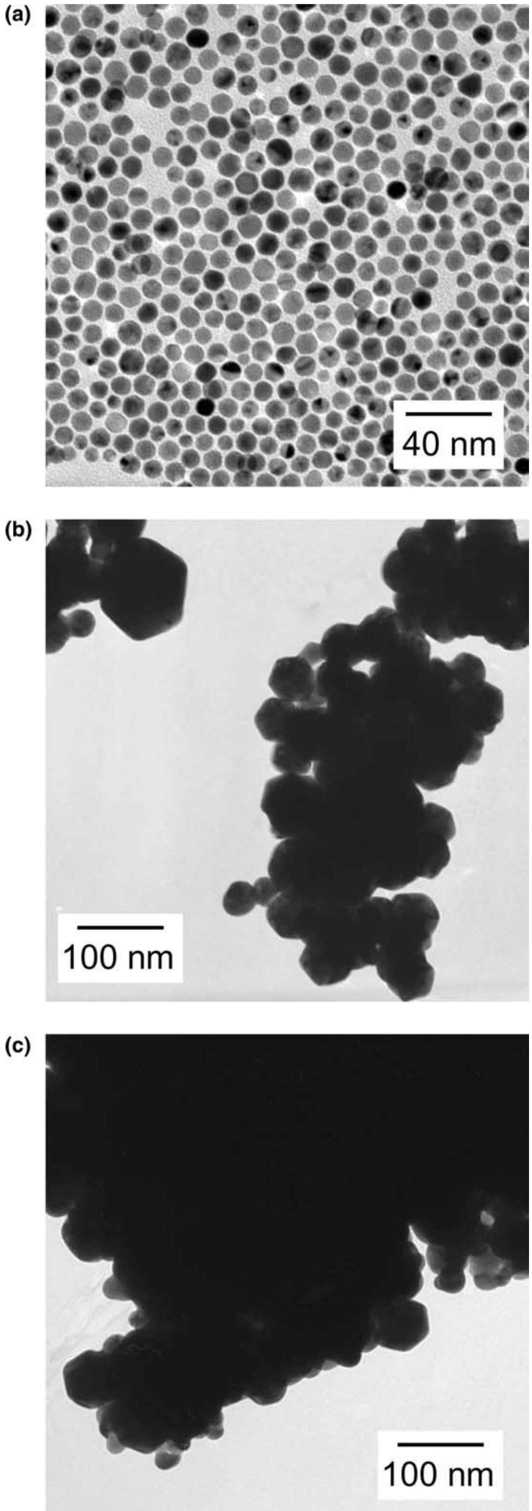


Fig. 4. TEM photographs of (a) **C12AuNP/C18NH$_2$**, (b) **C12AuNP/C12NH$_2$**, and (c) **C12AuNP/C8NH$_2$**.

nanoparticles. The average diameter of **C12AuNP/C12NH$_2$** (23 nm) are similar to that of **C12AuNP** (22 nm), but the diameter of **C12AuNP/C18NH$_2$** (7.5 nm) is obviously smaller than **C12AuNP**. These results accord with the thermostability and size regulation of alkanethiol-derivatized gold nanoparticles, where the alkyl chain length of alkanethiol strongly affected the properties of gold nanoparticles through the alkane–alkane interaction [28].

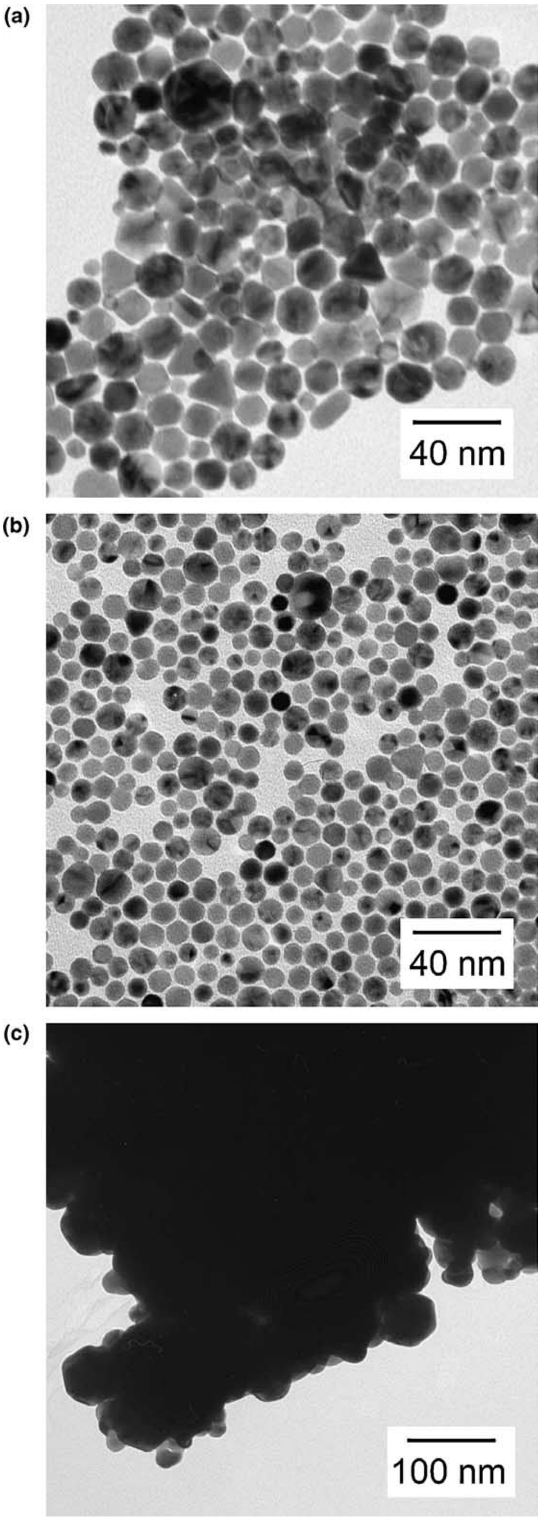
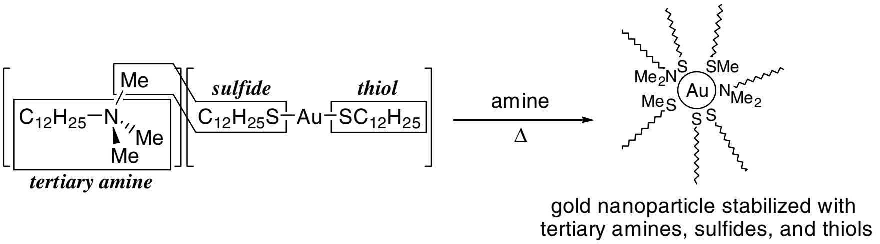


Fig. 5. TEM photographs of (a) **C12AuNP/(C8)$_3$N**, (b) **C12AuNP/(C8)$_2$NH**, and (c) **C12AuNP/C8NH$_2$**.



Scheme 2.

The number of alkyl chains of amines also affected the particle size and distribution. Fig. 5 shows the TEM images of the gold nanoparticle prepared by the controlled thermolysis of **C12Au** in the presence of di-*n*-octylamine, **(C8)$_2$NH**, or tri-*n*-octylamine, **(C8)$_3$N**. In these cases, the spherical gold nanoparticles were derived. It should be noted here that the corresponding controlled thermolysis of **C12Au** with **C8NH$_2$** did not produce the gold nanoparticles **C12AuNP/C8NH$_2$** (Fig. 5(c), vide supra). The average diameters of the gold nanoparticles were 15 nm for **C12AuNP/(C8)$_3$N** (Fig. 5(a)) and 12 nm for **C12AuNP/(C8)$_2$NH** (Fig. 5(b)). The average diameters of **C12AuNP/(C8)$_3$N** is similar to **C12AuNP/(C8)$_2$NH**, but the size distribution was broader than **C12AuNP/(C8)$_2$NH**. Such broadened size distribution of **C12AuNP/(C8)$_3$N** may be caused by the disfavorable packing of stabilizer, tri-*n*-octylamine, with steric bulkiness on the surface of gold nanoparticles. Thus, particle size and distribution of gold nanoparticles prepared by this work was strongly controlled by the alkyl chain length and number of amines.

3.6. Proposal mechanism of controlled thermolysis of gold(I) complexes in the presence of amines

The mechanism of the controlled thermolysis in the presence of amines is suggested by the analyses of the resulting liquid byproduct of the controlled thermolysis and the stabilizing organic component of gold nanoparticles. The GC-MS analysis of the organic liquid obtained as the byproduct of gold nanoparticles by the controlled thermolysis of **C12Au** with **C18NH$_2$** revealed the three organic constituents, **C18NH$_2$**, $C_{12}H_{25}SCH_3$, and $C_{12}H_{25}N(CH_3)_2$. Furthermore, the GC-MS analysis of the extracted organic components of corresponding nanoparticle **C12AuNP/C18NH$_2$** at 200 °C heating for 10 minutes revealed $C_{12}H_{25}SH$, $C_{12}H_{25}SCH_3$, and $C_{12}H_{25}N(CH_3)_2$, respectively, but not **C18NH$_2$**. These organic components, $C_{12}H_{25}SH$, $C_{12}H_{25}SCH_3$, and $C_{12}H_{25}N(CH_3)_2$, are obviously derived from **C12Au**. These results suggest that thermolysis of **C12Au** was initiated by the electronic reduction of gold(I) to metallic gold(0) by **C18NH$_2$**. Thus, with respect to the decomposition pathways, reductive elimination of disulfide was inhibited and the transforming reaction from ammonium and thiolate moieties to neutral tertiary amine, thiol, and sulfide occurred as shown in Scheme 2. The size regulation of gold nanoparticles was achieved by the existence of organic constituents, $C_{12}H_{25}SH$, $C_{12}H_{25}SCH_3$, and $C_{12}H_{25}N(CH_3)_2$, that suppress the growth of gold nuclei efficiently.

4. Conclusions

In conclusion, thermolysis of gold(I) thiolate complexes, **C12Au**, **C14Au**, and **(C18)$_2$Au**, can regulate the growth of gold nuclei and afford novel gold nanoparticles stabilized by alkyl groups. The alkyl chain length on ammonium cation of gold(I) complex strongly affects synthesizability of gold nanoparticles by thermolysis. The controlled thermolysis in the presence of amines achieved to produce narrow size dispersed small gold nanoparticles under milder condition. The synthesized gold nanoparticles in the presence of amines were stabilized by the tertiary amines, thiols, and sulfides derived from gold(I) complex, thus the reaction pathway of thermolysis is different from that in the absence of amines. Gold nanoparticle prepared in this study contains a high metal content, up to 99%. The synthetic method in this study may be highly promising as a facile new route to prepare gold nanoparticles.

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