Thermolysis of gold(I) thiolate complexes producing novel gold nanoparticles passivated by alkyl groups

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Thermolysis of gold(I) thiolate complex, $[C_{14}H_{29}(CH_3)_3N][Au(SC_{12}H_{25})_2]$, at 180 °C for 5 h under an N_2 atmosphere produces novel gold nanoparticles passivated by alkyl groups derived from the precursor complex, the TEM image of which shows spherical particles with average diameter 26 nm.

Since Brust *et al.* reported the two-phase reduction of $AuCl_4^-$ by $NaBH_4$ to afford mono-dispersed gold nanoparticles passivated by alkanethiolate ligands,[1] plenty of preparative investigations on gold nanoparticles[2,3] and its surface modification[3,4] have appeared, because of their potential applications in microelectronics.[5] However, those preparative methods generally involve the reduction of $AuCl_4^-$ by reducing agent $NaBH_4$ in the presence of suitable organic stabilizers such as alkanethiol,[1–4] phosphane,[5] quarternary ammonium salts,[6] surfactants[7] or polymers.[8] 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 passivating ligand,[6] but this procedure also needs $NaBH_4$ as reducing agent.

Our novel preparative method for gold nanoparticles combines the reductive elimination of thiolate ligands with simultaneous attachment of an organic moiety on the growing nuclei. Gold(I) thiolate complexes with ammonium cations were useful for our preparative method. We now report the thermolysis of gold(I) thiolate complexes, $[R(CH_3)_3N][Au(SC_{12}H_{25})_2]$ and $[R(CH_3)_3N][Au(SC_6H_4\text{-}p\text{-}R')_2]$ (R = $C_{14}H_{29}$, $C_{12}H_{25}$; R' = C_8H_{17}, CH_3),† under an N_2 atmosphere, where the powder of gold(I) thiolate complexes completely melts to afford the precursor liquid and then the liquid gradually decomposes. In spite of no use of reducing agent or solvent, a reduction reaction is thermochemically induced to afford novel gold nanoparticles passivated by alkyl groups rather than by alkanethiolate ligands.‡

Fig. 1(a) shows a typical transmission electron microscopy (TEM) image of gold nanoparticles prepared by thermolysis of $[C_{14}H_{29}(CH_3)_3N][Au(SC_{12}H_{25})_2]$ at 180 °C for 5 h, indicating a controlled growth of spherical gold nanoparticles. As shown in Fig. 1(b), these spherical gold nanoparticles display a size distribution ranging from 5 to 50 nm. Although the particle size is larger than that of thiol-derivatized gold nanoparticles (less than 5 nm) prepared by $NaBH_4$ reduction,[1–3] the aggregation of gold nuclei is smoothly regulated and the growth of core gold is limited to an average diameter of 26 nm in spite of the thermal procedure.

The oxidation state of gold in the nanoparticles 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 Au(0).[1] Au(I) peaks were not observed in the region of gold(I) complexes.[10,11] The powder X-ray diffraction pattern of the gold nanoparticles, as shown in Fig. 2, afforded slightly broad reflections for the (111), (200), (220), and (311) planes of metallic gold in a face-centred cubic lattice. The average particle size of metal nuclei (19 nm) was calculated by the Scherrer equation, using the half width of the intense (111) reflection.

It is well known that gold nanoparticles show the characteristic plasmon absorptions at 520–540 nm in the uv-visible absorption spectra.[3,12] The present gold nanoparticles redissolved in acetone showed an absorption centred at 538 nm. The wavelength of this absorption maximum slightly shifts toward longer wavelength compared with those of the previous reported thiol-derivatized gold nanoparticles with smaller particle size (520 nm).[1,2] As mentioned in the literature,[13] plasmon absorptions of nanoparticles tend to shift toward longer wavelengths with increasing particle size.[13] Thus, the absorption band at 538 nm of the present gold nanoparticles is assigned
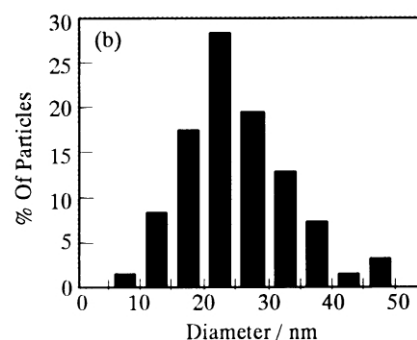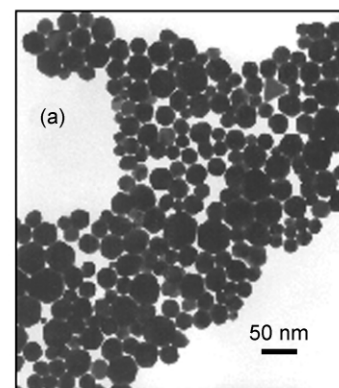

Fig. 1 (a) TEM photograph of Au nanoparticles prepared by thermolysis of $[C_{14}H_{29}(CH_3)_3N][Au(SC_{12}H_{25})_2]$ (180 °C, 5 h). (b) Histogram for the size distribution of Au nanoparticles.
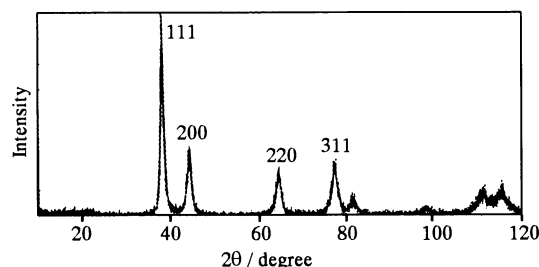

Fig. 2 XRD pattern of Au nanoparticles prepared by thermolysis of $[C_{14}H_{29}(CH_3)_3N][Au(SC_{12}H_{25})_2]$ (180 °C, 5 h).

to the plasmon absorption band and its peak maximum is compatible with the average particle size determined by TEM image.

With respect to the composition of the present gold nanoparticles, thermogravimetric analysis was conducted to indicate the gold content of 92.5% and the existence of 7.5% organic moiety. The gold content depended on the preparative conditions, but was almost regulated between 90 to 97% gold.

There are two possibilities for the origin of the organic moiety: the quaternary ammonium part or the dodecanethiolate ligand. In order to examine the organic moiety of the present gold nanoparticles, the ^{1}H-NMR spectrum of the gold nanoparticles 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 conditions such as reaction temperature and reaction time affect the particle size. Under the conditions at 160 °C for 5 h, gold nanoparticles with an average diameter of 20 nm were obtained. However, thermolysis at 180°C for 5 h promoted the growth of gold nuclei to give the product with an average diameter of 26 nm. In comparison with the reaction time at the same temperature, reactions over 7 h accelerated the aggregation of gold nuclei to afford larger average diameters.

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 $(C_{12}H_{25}S)_2$ with *m/z* 402. The elemental analysis was also compatible with the theoretical value of $(C_{12}H_{25}S)_2$. 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 quarternary ammonium cation as shown in eqn. 1.

$$[R(CH_3)_3N][Au(SC_{12}H_{25})_2] \rightarrow \text{Au nanoparticles} + (CH_3)_3N + (C_{12}H_{25}S)_2 \quad (1)$$
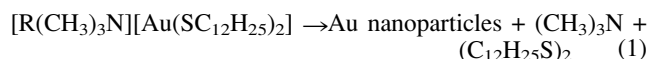
It is noteworthy that disulfide, $(C_{12}H_{25}S)_2$, plays a role of stabilizer, which was confirmed by the thermolysis of gold(I) benzenethiolate complexes, $[C_{14}H_{29}(CH_3)_3N][Au(SC_6H_4\text{-}p\text{-}R')_2]$ (R' = C_8H_{17}, CH_3). Fig. 3 shows particle size distributions of gold nanoparticles prepared by the thermolysis of those precursors at 180 °C for 8 h, respectively. The difference of the alkyl chains on the benzene rings strongly reflects the particle
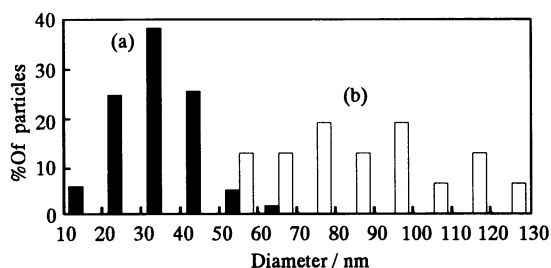
size distributions. Disulfide with longer octyl groups prevents the aggregation of gold particles and effectively regulates the growth of core nuclei compared with the methyl group. Thus, disulfide produced through thermolysis plays an important role of size control.

On the other hand, the ammonium cations with almost the same chain lengths, $[R(CH_3)_3N]^+$ (R = $C_{14}H_{29}$, $C_{12}H_{25}$), do not show a pronounced effect on the tuning of the particles size. However, the ammonium cations of $[R(CH_3)_3N]^+$ (R = $C_{14}H_{29}$, $C_{12}H_{25}$) containing only one longer alkyl group effectively afford gold nanoparticles compared with the ammonium cation containing two longer alkyl groups, $[(C_{18}H_{37})_2(CH_3)_2N]^+$. The reason may be due to the decomposition pathway as shown in eqn. 1, because the former can easily eliminate gaseous trimethylamine and supply long alkyl groups as protecting groups surrounding core gold.

In conclusion, thermolysis of gold(I) thiolate complexes, $[R(CH_3)_3N][Au(SC_{12}H_{25})_2]$ (R = $C_{14}H_{29}$, $C_{12}H_{25}$), can regulate the growth of gold nuclei and afford novel gold nanoparticles passivated by alkyl groups. Work to develop a thermolysis approach to prepare smaller size gold nanopartilces less than 5 nm and other metal nanoparticles is now in progress.

Notes and references

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Fig. 3 Ligand substituent effect on the particle size distributions for the precursors (a) $[C_{14}H_{29}(CH_3)_3N][Au(SC_6H_4\text{-}p\text{-}C_8H_{17})_2]$ and (b) $[C_{14}H_{29}(CH_3)_3N][Au(SC_6H_4\text{-}p\text{-}CH_3)_2]$.