# A New Approach for the Au/Ag Alloy Nanoparticle Formation through the Reduction of Ag(I) to Ag(0) by Amine and Intermetallic Electron Transfer from Ag(0) to Gold(I) Complex

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A new approach for the formation of Au/Ag alloy nanoparticles is proposed; the reaction of $[Au(C_{13}H_{27}CO_2)(PPh_3)]$ and $C_{13}H_{27}CO_2Ag$ (the mole ratio 1:1) in $NEt_3$ at 80 °C for 2 h affords Au/Ag alloy nanoparticles with average diameter $3.0 \pm 0.39$ nm in large scale through the reduction of Ag(I) to Ag(0) by triethylamine and intermetallic electron transfer from Ag(0) to gold(I) complex.

Alloy nanoparticles have been attracted by distinct properties from those of monometallic nanoparticles such as electronic,[1] optical,[2–7] and catalytic[8] properties, prompting numerous preparations of multimetal nanoparticles, including core/shell bimetallic nanoparticles, partially segregated alloys, and homogeneous alloys.[1–9] In particular, preparation method of homogeneous Au/Ag alloy nanoparticles with various compositions have been studied in order to examine the relationship between the structure of nanoparticles and plasmon absorption,[4–6] because monometallic Au and Ag nanoparticles have clearly different plasmon absorption maxima in the visible region. However, Au/Ag alloy nanoparticles prepared by simultaneous reduction of both two kinds of metal ions were reported to have the average diameter from 17 to 25 nm depending on the Au/Ag composition and to show the wide particle size distribution.[6] Furthermore, the simultaneous reduction often causes the segregation of metals in a core-shell structure and the partially segregated alloy formation rather than the production of solid solutions, because the difference of reduction potentials of two metals produces the nascent core of one metal and the deposition of the other metal on the surface of core metal.[9] On the other hand, we have succeeded to control the reduction of metals by using metal complex instead of metal salts: homogeneous Au/Ag alloy nanoparticles with narrow size distribution and nearly the same average diameter (3.0–3.7 nm) for various Au/Ag compositions were quantitatively prepared by the reduction of gold(I) complex, $[Au(C_{13}H_{27}-CO_2)(PPh_3)]$,[10] in the presence of silver myristate, $C_{13}H_{27}CO_2$-Ag, in $NEt_3$ at 80 °C for 2 h. This is a new approach for the Au/Ag alloy nanoparticle formation through the reduction of Ag(I) to Ag(0) by triethylamine and intermetallic electron transfer from Ag(0) to gold(I) complex. Furthermore, this procedure can be applied to the gram-scale synthesis of alloy nanoparticles with various composition, where amine acts as reducing agent and organic ligands of the precursor metal complexes play an important role of stabilizer for the Au/Ag alloy nanoparticles to realize the nanometer size and narrow size distribution. In this paper, we describe a new synthetic approach of Au/Ag alloy nanoparticles with various Au/Ag compositions.

The preparation of representative Au/Ag alloy nanoparticles was conducted by a simple one-pot process as follows.

$[Au(C_{13}H_{27}CO_2)(PPh_3)]$ (2.06 g, 3 mmol) and $C_{13}H_{27}CO_2Ag$ (1.01 g, 3 mmol) in the mole ratio 1:1 were suspended in $NEt_3$ (17 mL, 120 mmol) and heated at 80 °C for 2 h under an $N_2$ atmosphere. The surface of precursors was turned to deep green and finally the deep green homogeneous dispersion liquid of nanoparticles was produced. The addition of methanol produced precipitates, which were collected by filtration and then washed several times with methanol. The isolated Au/Ag alloy nanoparticles (**1**) were deep green powder (0.93 g, 84% yield based on Au/Ag) which were air and moisture stable and well redispersed in toluene.

Thermogravimetry shows that the obtained nanoparticles **1**
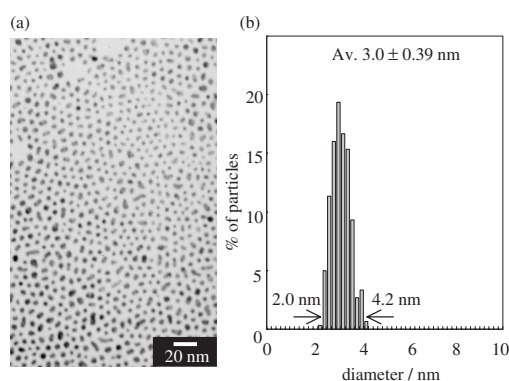


**Figure 1.** Transmission electron micrograph (TEM) image of Au/Ag alloy nanoparticles **1** with an Au:Ag ratio of 1:1 (a) and histgram of particle size distribution (b).
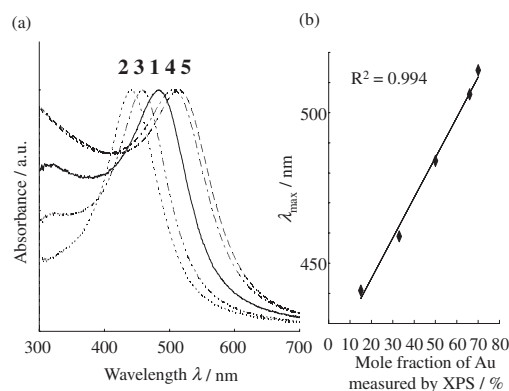


**Figure 2.** (a) UV–vis absorption spectra of Au/Ag alloy nanoparticles with various compositions, $\lambda_{max}$ 484 nm (**1**), 441 nm (**2**), 459 nm (**3**), 506 nm (**4**), 514 nm (**5**). (b) Absorption wavelength of the surface plasmon maximum plotted as a function of gold mole fraction.

**Table 1.** Properties of Au/Ag alloy nanoparticles

| Nanoparticles | (Au:Ag)[a] | Yield / % | Metal Content / %[b] | Diameter / nm[c] | $\lambda_{max}$ / nm[d] | Au:Ag Ratio of Nanoparticles[e] |
|---|---|---|---|---|---|---|
| **1** | (1:1) | 84 | 83 | $3.0 \pm 0.39$ (4.2) | 484 | 50:50 |
| **2** | (1:5) | 89 | 81 | $3.7 \pm 0.49$ (5.0) | 441 | 15:85 |
| **3** | (1:2) | 87 | 83 | $3.1 \pm 0.48$ (4.5) | 459 | 33:67 |
| **4** | (2:1) | 82 | 86 | $3.2 \pm 0.34$ (4.5) | 506 | 66:34 |
| **5** | (5:1) | 56 | 89 | $3.2 \pm 0.66$ (4.9) | 514 | 70:30 |

[a]Mole ratio of precursors. [b]TGA analysis showing total amount of metals. [c]TEM data. (XRD data.) [d]UV–vis spectral data in toluene. [e]XPS data.

contain 83% metal component and 17% organic capping ligand. GC/MS analysis clarified that the organic layers are composed of myristate and $PPh_3$ ligands and NMR estimated the ratio is approximately compatible with that of the ligands of the precursor complexes. Figure 1 shows the TEM image of nanoparticles **1** and its average particle size was $3.0 \pm 0.39$ nm with narrow size distribution. Furthermore, the distance between neighboring two nanoparticles[11] was 2.6 nm. It suggests that the myristate ligands (calcd 1.4 nm) attached on the each core are slightly spread by the coordination of $PPh_3$.

In order to confirm the composition of nanoparticles **1**, XPS and UV–vis absorption spectroscopic measurements were performed. XPS analysis shows the Au $4f_{7/2}$ (83.3 eV) and Ag $3d_{5/2}$ (367.3 eV) peaks and the estimated Au/Ag ratio is 50:50 corresponding to the mole ratio of precursor complexes (Table 1). On the other hand, UV–vis spectrum of nanoparticles **1** (Figure 2a) shows clearly only one plasmon band with maximum absorption wavelength at $\lambda_{max}$ 484 nm. If the particles were consisted of a mixture of two different monometallic particles, plasmon bands of gold and silver nanoparticles would appear at around 520 and 380 nm, respectively.[12] Thus, this result indicates the obtained Au/Ag nanoparticles are not the simple mechanical mixture of two different monometallic particles.

On the basis of these results, we have conducted to prepare Au/Ag nanoparticles with various compositions: **2** (Au:Ag = 15:85), **3** (33:67), **4** (66:34), and **5** (70:30), as shown in Table 1. The Au:Ag ratios of those nanoparticles except for **5**[13] confirmed by XPS analysis were compatible with those of the precursor complexes. The nanoparticles with various compositions show narrow size distribution and almost the same particle size in the range from 3.0 to 3.7 nm. UV–vis spectra of **2**, **3**, **4**, and **5** (Figure 2a) show the only one plasmon band at $\lambda_{max}$ 441, 459, 506, and 514 nm, respectively. It is well known that plasmon absorption maximum is drastically influenced by the difference of composition rather than by the particle size of Au/Ag alloy nanoparticles.[5] In fact, the present Au/Ag nanoparticles show a linear relationship between the mole fraction of Au estimated by XPS and UV–vis absorption peak wavelength, as shown in Figure 2b. Therefore, these results suggest that Au/Ag nanoparticles prepared in this work are the particles with homogeneous alloy structure,[5,6] but not the particles with core-shell structure nor a mixture of two different monometallic particles.

Although $C_{13}H_{27}CO_2Ag$ reacts with triethylamine at 80 °C for 2 h to afford silver nanoparticles,[11] the reaction of gold(I) complex, $[Au(C_{13}H_{27}CO_2)(PPh_3)]$, under the same condition scarcely produced gold nanoparticles. In order to confirm that the $[Au(C_{13}H_{27}CO_2)(PPh_3)]$ can be reduced in the presence of $Ag^0$, the reaction of $[Au(C_{13}H_{27}CO_2)(PPh_3)]$ with the silver nanoparticles[11] (Au:Ag ratio of 1:1) in triethylamine was carried out to afford the Au/Ag alloy nanoparticles with only one plas-

mon band at $\lambda_{max}$ 480 nm. It suggests that the $Ag^0$ can reduce Au(I) via intermetalic electron transfer and the released Ag(I) can be promptly reduced by triethylamine, because relatively faster reduction of Au(I) than that of Ag(I) may produce Au(core)/Ag(shell) nanoparticles with different plasmon absorption maximum. Furthermore, in the time-course UV–vis spectra of the reaction of $[Au(C_{13}H_{27}CO_2)(PPh_3)]$ and $C_{13}H_{27}CO_2Ag$ in triethylamine, the one plasmon absorption maximum descrived above appeared just at the initial stage of the reaction and the peak position did not change until the end of the reaction. Thus, the formation of homogeneous Au/Ag alloy core and its growth may be accomplished by simultaneous occurrence of the following reactions: the reduction of $C_{13}H_{27}CO_2Ag$ by triethylamine to produce Ag(0), the reduction of gold(I) complex by Ag(0) via intermetallic electron transfer to accompany the release of silver ion from Au/Ag alloy nuclei,[4] and the promptly reduction of the released silver ion by triethylamine.

In summary, we propose a new approach to prepare Au/Ag alloy nanoparticles with various compositions by controlling the reduction of metals using the precursor complexes. In practice, homogeneous Au/Ag alloy nanoparticles with various compositions were prepared by the reaction of $[Au(C_{13}H_{27}CO_2)(PPh_3)]$ and $C_{13}H_{27}CO_2Ag$ in $NEt_3$ at 80 °C for 2 h through the reduction of Ag(I) to Ag(0) and intermetallic electron transfer from Ag(0) to gold(I) complex. The formation of homogeneous Au/Ag alloy nanoparticles was clearly demonstrated by XPS measurements and UV–vis absorption spectroscopy.

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13　The lower amount of $C_{13}H_{27}CO_2Ag$ makes it difficult to produce the Au/Ag alloy nuclei completely, resulting the lower mole ratio of Au in the nanoparticles **5**.