Characterization of core–shell type and alloy Ag/Au bimetallic clusters by using extended X-ray absorption fine structure spectroscopy

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Abstract

Bimetallic silver and gold nanoparticles, a core–shell type structure, have been prepared by NaBH 4 reduction method. The optical absorption spectra are recorded and compared with various ratios of Ag/Au alloy nanoparticles. The absorption spectra of bimetallic nanoparticles suggested the formation of core–shell structure. On the other hand, the high resolution transmission electron microscopy image of the nanoparticles confirmed the core–shell type configuration directly. Moreover, we studied the surrounding environment of core–shell type and alloy nanoparticles around gold atoms by using extended X-ray absorption fine structure spectroscopy.

1. Introduction

The intense research in the field of nanoparticles by chemists, physicists, and materials scientists is motivated by the search for new materials in order to further miniaturize electronic devices [1–4]. Metal nanoparticles have mainly been studied because of their unique optical properties as especially nanoparticles of the noble metals such as copper, silver, and gold have a broad absorption band in the visible region of the electromagnetic spectrum [5–11]. These characteristics are attributed to the collective oscillation of the free conduction electrons induced by an interacting electromagnetic field. These resonances are also denoted as surface plasmons [12]. The size effect on the surface plasmon absorption has been of major interest [6,13]. Fabrication of bimetallic nanoparticles can be divided into two types: alloy and core–shell structured bimetallic nanoparticles. Alloy nanoparticles have been studied because of their catalytic effect and spectral properties [12,14–16]. For the core–shell structure, a second metal must be deposited on the surface of the preformed particles, and the preformed monometallic nanoparticles should be chemically surrounded by the deposited element. Layered core–shell bimetallic silver–gold colloids have been prepared by the seed-growth method and analyzed with transmission electron microscopy (TEM) images and electron diffraction pattern [17]. Additionally, bimetallic gold and silver particles, a core–shell type structure, have been prepared by a UV-photoactivation technique [18]. Tomohiro et al. [19] reported spontaneous alloying of Ag into gold at ambient temperature. They used extended X-ray absorption fine structure spectroscopy (EXAFS) to analyze the change of the Ag–Au nanoparticles. EXAFS is a powerful tool for investigation of the metal nanoparticles in colloidal dispersions and small metal particles on local structure. The measurements can give information on the environment about a particular atom in the metal clusters. Toshima and co-workers reported the coordination numbers of Au/Pd [20,21] and Pt/Pd [22] bimetallic clusters that were obtained from experimental result and structure simulation.

In this study, a Ag core-Au shell structure has been produced by NaBH 4 reduction of metal salts. We are interested in the neighboring environment about absorbing atoms between core–shell type and alloy bimetallic clusters.
Therefore, we compared the extended X-ray absorption fine structure of Au atoms between these two types of structures. By observing the EXAFS, a relationship between the composition of neighboring atoms and spectral oscillation could be obtained.

2. Experimental

2.1. Materials

Hydrogen tetrachloroaurate(III) hydrate, trisodium citrate dehydrate (99%), sodium borohydride (98%), and silver nitrate (99%) were obtained from Across Organics. The water used throughout this work was reagent-grade water produced by a Milli-Q SP ultrapure-water purification system of Nihon Millipore Ltd., Tokyo.

2.2. Preparation of the core–shell type bimetallic clusters by successive reduction

For a typical preparation, we prepared the colloidal nanoparticles by adding 0.8 mL of NaBH4 (1%) and 5 mL of citric acid (1%) to silver metal salt (AgNO3) solution. A solution of 0.4 mM Ag+ and 0.1–0.4 mM AuCl4− was prepared by dissolving the corresponding salt in water. Solutions of NaBH4 and trisodium citrate dehydrate were prepared by stirring dispersions of NaBH4 and trisodium citrate powders in water. The reaction mixture was stirred for 15 min at 100 °C, then gold metal salt solution (0.1–0.4 mM AuCl4−) was added to the solution of Ag nanoparticles. Eventually, heating was stopped and stirring continued for 10 min.

2.3. Preparation of the Au/Ag alloy clusters by simultaneous reduction

Ag–Au alloy nanoparticles were synthesized with varying initial Au/Ag molar ratios (0:1, 0.25:0.75, 0.5:0.5, 0.75:0.25, and 1:0, respectively). This synthesis was performed by reducing HAuCl4 and AgNO3 with NaBH4 in the presence of sodium citrate at room temperature. Five 125 mL flasks were cleaned with deionized water and then filled with 100 mL of deionized water and 50 μL of 0.01 M sodium citrate. Varying mole fractions of 26 mM HAuCl4 and 58 mM AgNO3 were added to each solution for a total metal salt concentration of 0.005 mM. The above method has been reported to fabricate sub 10 nm Ag–Au alloy nanoparticles [16].

2.4. Characterization of the Au/Ag bimetallic clusters

The UV/Vis spectra of the colloidal nanoparticle solutions were measured by a Hitachi U-3000 spectrophotometer with a 10 mm quartz cell. The surface morphology of the samples was examined by transmission electron microscope (TEM) with energy dispersive spectrometer (EDS) analyses (JEM-2010, 200 kV). The specimens were obtained by placing several drops of the colloidal solution onto a Formvar-covered copper grid and evaporating it in air at room temperature. Prior to specimen preparation, the colloidal solutions were sonicated for 1 min to obtain a better particle dispersion on the copper grid. For each sample, generally over 100 particles from different parts of the grid were used to estimate the mean diameter and size distribution of particles.

The samples for the EXAFS measurement were prepared by concentrating 200 mL of the previously obtained colloidal dispersions to 5–10 mL of nitrogen under reduced pressure. A series of EXAFS measurements of the synthesized samples were recorded with synchrotron radiation at room temperature. A few samples are required for this measurement. It could be emphasized that colloidal nanoparticles disperse well in solution. The measurements were performed at Au LIII edge (11918 eV) with the sample at room temperature. Due to low metals concentration in the samples, the measurements involved X-ray fluorescence detection with a thin X-ray filter to reduce scattering background [23]. The EXAFS oscillations, χ(k) (where k is the photoelectron wave number), were extracted by a standard procedure [24]. The Fourier transformed data were analyzed using the UW package [25]. The Wigglar-C beam line of the national synchrotron radiation research center (NSRRC), Taiwan, has been designed for such experiments.

3. Results and discussion

Fig. 1 shows the absorption spectra for gold, silver, and a series of gold–silver alloy nanoparticles with varying gold concentration. The absorption peaks at 520 and 410 nm belong to surface plasmon absorption of Au and Ag nanoparticles, respectively. If gold and silver ions are reduced simultaneously by sodium borohydride in the same solution, then gold–silver alloy particles are formed. The alloy formation is concluded from the fact that the optical absorption spectrum shows only one plasmon band and the wavelength at which maximum absorbance occurred

![Absorbance vs Wavelength](image-url)
in a linear fashion. The results of this study are similar to the literature results [12,16]. Calculation of the extinction spectra of Au–Ag nanoparticles, based on Mie theory, support our results that the nanoparticles are alloys rather than core–shell structures [26,27]. The divergence of absorbance between Au, Ag, and Au–Ag alloy is due to the difference of extinction coefficients at the plasmon maximum. These results have been reported in [12]. Fig. 2 shows the absorption spectra of Ag nanoparticles and Ag nanoparticles with various amounts of Au shell. In general, the core–shell type structure nanoparticles show two plamon bands in Ag–Au bimetallic system. As the metal of shell layer formed a thin uniform film (3–4 nm) on the core particles, the surface plasmon absorption band showed only one peak which resulted from the metal of shell layer [18]. By observing the color of the reaction solution, the formation process of the particles is suggested. In this study, the color of the reaction solution turned from colorless to yellow during the formation of the Ag nanoparticles. After adding the gold metal salt solution to the above product, the color of this solution changed from yellow to red instantaneously. The formation of AgcoreAushell structure nanoparticles leads to the disappearance of the surface plasmon peak of Ag. For Ag:Au = 0.4:0.1 sample, the plasmon absorption band of silver slightly showed red-shift while the plasmon peak of silver still existed. These results indicated that the shift of peak depends on the ratio of the metal salts. For this reason, we suggest that Au and Ag formed alloy on the surface. This brings about the shift of surface plasmon band. Additionally, spontaneous alloying of Au–Ag nanoparticles has been reported [19]. The nanoparticle alloying can, in principle, result from an increase in the diffusion coefficient of the metals, because the melting point lowers as their size decreases [28]. There is one other thing that is important for this contention. Atomic size of Ag is similar to that of Au, so that interdiffusion between Au atoms and Ag atoms is easy. Judging from the above, it would be possible to argue that Au and Ag formed alloy.

Fig. 3 shows the TEM and HRTEM image of AgcoreAu shell nanoparticles (Ag:Au = 0.4:0.2). The inset shows the electron diffraction pattern of this sample. The gold deposited on the surface and formed an uniform shell. This was consistent with the absorption spectrum observed. The elemental ratio of Au/Pt bimetallic particles was measured by HRTEM with EDS. The size of electron beam is 1.5 nm, thus the composition of different parts of nanoparticles can be examined independently. The composition was Ag (87%) and Au (13%) in the core part of core–shell nanoparticle. This confirmed that the main composition of core part was silver. A certain quantity of silver resulted from the shell layer. In addition to this, the composition was Ag (37%) and Au (63%) in the shell layer of
this nanoparticle, the main composition being gold. The reason for the appearance of Ag in shell layer is due to the diffusion of incident electron. The incident electron diffused into the core part of the particle and excited the characteristic X-ray, the detector would receive the signal of silver. The deviation could be due to the low number of particles chosen for detection and analysis errors. In summary, the EDS analysis confirms directly the formation of Ag_{core}, Au_{shell} bimetallic nanoparticles.

Fig. 4a shows the Au L III edge EXAFS spectra ($\chi(k)$) of the Ag–Au alloy. Note the change of the oscillation above approximately $k = 2$ Å$^{-1}$. This results from the increase of the neighboring Ag atoms, because Au and Ag have quite different backscattering phase shifts. This large difference facilitates the coordination analysis of the Au–Ag system. Au–Ag in the first shell that appears as a doublet in the amplitude from Fourier transform of $\chi(k)$ (Fig. 4b), where $k = 3–10$ Å$^{-1}$ is transformed. The peak intensity at a larger distance increases relative to that at smaller distance with increasing Ag amount due to changes in interference between Au and Ag oscillation. It is worth pointing out that both peaks come from the first neighbor (with a single distance), and they appear at a shorter distance from the actual bond lengths. This arises from the backscattering phase shift. It can be best summarized in the following sentences: both EXAFS oscillation of $\chi(k)$ and Fourier transform of $\chi(k)$ for this series of samples show a continuous change with increasing of Ag amount. Fig. 5a shows the Au L III edge EXAFS spectra ($\chi(k)$) of the Ag–Au core–shell structure. Similarly, it is easy to observe the difference of oscillation at $k = 2$ Å$^{-1}$. However, the result in Fig. 5a differs from the result in Fig. 4a. The oscillation of Ag:Au = 0.4:0.1 sample differs from the others. At the same time, the oscillation of Ag:Au = 0.4:0.1 sample (core–shell structure) are similar to the oscillation of Ag:Au = 3:1 sample (alloy). Moreover, the other core–shell structure samples show similar oscillation. The most likely explanation is that the surroundings of Au atoms at Ag:Au = 0.4:0.1 sample (core–shell structure) is similar to the surroundings of Au atoms at Ag:Au = 1:1 sample (alloy). We may now conclude that Ag and Au atoms formed alloy on the surface in Ag:Au = 0.4:0.1 sample. Moreover, the Au and Ag atoms shows continuous change with various Ag amounts. Table 2 shows coordination numbers and interatomic distances around Au atoms of core–shell structure. The results of interatomic distance at Ag:Au = 0.4:0.1 sample are different from the other samples, and the value is similar to that of Ag:Au = 1:1 sample (alloy). Fig. 5b shows the amplitude of the Fourier transform of $\chi(k)$ for the Ag_{core}, Au_{shell} samples. It is important to note that the peak comes from the first neighbor. The peak does not separate into two parts except for the Ag:Au = 0.4:0.1 sample. From the result already stated, we suggest that the structure is still faced-center cubic, in spite of the formation nanoparticle of Ag and Au atoms. The interatomic distance around
Ag atoms interdiffused randomly and formed Au–Ag alloy. For Ag: Au = 0.4:0.2, 0.4:0.3, and 0.4:0.4 samples, there are no remarkable differences in Fourier transform of $\chi(k)$ and interatomic distance around Au atoms. This result reveals that the surrounding sites around Au atoms are Au atoms and shows that the Au atoms formed a uniform layer. In summary, Ag and Au atoms formed Ag$_{\text{core}}$Au$_{\text{shell}}$ structure nanoparticles.

### 4. Conclusions

The Ag–Au alloy and Ag$_{\text{core}}$Au$_{\text{shell}}$ nanoparticles can be successively prepared by simultaneous reduction of the corresponding ion. UV/Vis absorption spectra of Au–Ag alloy show continuous shift with varying gold mole fraction. The optical absorption spectra reveal that the nanoparticles have been prepared for alloy structure nanoparticles. For Ag: Au = 0.4:0.1 sample (core–shell), spontaneous alloying was observed. The EXAFS spectra oscillation of Ag: Au = 0.4:0.1 sample (core–shell) above approximately $k = 2 \text{Å}^{-1}$ is similar to that of the alloy samples. This result is due to the existence of the neighboring Ag atoms. This result is consistent with the investigation of EXAFS results. Studies in Ag–Au alloy with EXAFS measurements reveal that the peak intensity at larger distance increases relative to that of the peak at smaller distance with increasing Ag amount. From the EXAFS analysis as well as HRTEM observation, the Ag core structure, in which the Au atoms are on the surface of the nanoparticles, is presented.

### Acknowledgement

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### References


### Table 1

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<th>Ag/Au</th>
<th>Coordination number, $N$</th>
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<td>2.86 ± 0.03</td>
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### Table 2

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<td>2.86 ± 0.08</td>
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<td>2.83 ± 0.15</td>
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<tr>
<td>1/1(Au = 50%)</td>
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<tr>
<td>3/1(Au = 25%)</td>
<td>11.9 ± 1.2</td>
<td>2.77 ± 0.06</td>
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**Fig. 5.** (a) Au L$_{III}$ edge oscillations, $\chi(k)$, for Ag$_{\text{core}}$Au$_{\text{shell}}$ nanoparticles with varying gold mole fraction. (b) Fourier-transformed EXAFS spectrum at Au L$_{III}$ edge of Ag$_{\text{core}}$Au$_{\text{shell}}$ nanoparticles with varying gold amount.
[25] Data were fit by FEFFIT using the theoretical paths produced by FEFF702.