

Local Structure of Ag/Au Core/shell Nano-Particles Studied by XAFS*

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We have measured Ag K - and Au L_{III} -edge EXAFS (extended x-ray absorption fine structure) for Ag/Au core/shell particles. The structural parameters were obtained from EXAFS curve-fitting analyses and were discussed in comparison to the structure estimated from TEM (transmission electron microscope) analyses. The thickness of the shell and diameter of the core can be evaluated from EXAFS that are fairly consistent with the results estimated from TEM. From EXAFS two-shell model analyses the Ag-Ag distance decreases and Au-Au distance increases in the thinner shell. This result suggests that the electrons transfer from Ag atom to Au atom at the interface between core and shell atom. [DOI: 10.1380/ejsnt.2006.138]

Keywords: XAFS; Core/shell particle; Ag/Au

I. INTRODUCTION

It is well established that small particles in the nanometer size exhibit physical and chemical properties, which are different from those of bulk materials. The nano-scaled fine particles are also interested in presenting new optical properties [1, 2] because of their mesoscopic characters. The enormous surface area-to-mass ratio of the nano-particles leads to excess the surface free energy that is comparable to the lattice energy. Ag fine particles are typical examples to be studied by EXAFS (extended x-ray fine structure) [2] and optical properties [1]. Recently the core-shell type particles are expected to be a hybrid system and have a different lattice parameter from original bulk or particle structure affected by lattice mismatch or electron transfer between core and shell atoms. The Ag/Au core/shell nano-particles are quite interesting systems structurally and optically because of their stabilities of the materials. Shibata *et al.* [3] studied the size dependence of the alloying of Au/Ag core/shell nano-particles by EXAFS and MD (molecular dynamics). They showed an interesting result that there is clear Au-Ag first nearest neighbor contribution in Au L_{III} -edge EXAFS for thin Au-shell particle. However, they discussed only the coordination number but the interatomic distance was not appeared and the inverse system of Ag-shell particle has not been presented. In this paper we study the local structures of Ag/Au and Au/Ag core/shell particle by Ag K - and Au L_{III} -EXAFS. It should be noted that the local structure of Ag or Au thinner shell particles is different from the more thick shell or bulk materials.

II. EXPERIMENTAL

All sample particles were synthesized by chemical reduction and dispersed in the comb-type copolymer consisted of an acrylate and styrene maleic acid at Nippon Paint LTD [4].

In this paper we present the results for 6 samples of Ag/Au core/shell particles as listed in Table I.

Figure 1 shows the TEM (transmission electron microscope) photograph for sample (a) 001a, (b) 002a and (c) 003a (Ag-shell and Au-core).

We extract one of the particles in each photograph as an example and show them in Table II. TEM photograph shows a quite clear Au-core and Ag-shell structure. We present the schematic model for the core/shell particles calculated from the average size and the volume ratio [5] in Table I. Figure 2 shows the TEM photograph for sample (a) 001b, (b) 002b and (c) 003b (Au-shell and Ag-core). The scale bars in the photograph are 20 nm for (a), (b) and 50 nm for (c). We also show more detailed photograph for the core/shell particle in Table III. This Table presents the same as Table II but the core and shell structure is less clear than that in Table II because the shell material Au is heavier atom than core element Ag so the electron beam cannot penetrate through Au shell.

Ag K - (25.5 keV) and Au L_{III} -edge (11.9 keV) x-ray absorption spectra were obtained at BL-10B (Si(311) monochrometer) and 9A (Si(111) monochrometer) at Photon Factory (KEK), respectively, in transmission mode with the detector of the ionization chamber. The XAFS analyses were performed by XANADU code [6]. In order to obtain the structural parameters, non-linear least-square-fitting was applied to the experimental data as described as

$$\xi(k) = \sum_j \frac{S_0^2 N_j}{k r_j^2} f_j(k, r_j) \exp(-2\sigma^2 k^2) \exp(-2r_j/\lambda(k)) \times \sin \left[2kr_j + \varphi_j(k) - \frac{4}{3} C_3 k^3 \right], \quad (1)$$

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TABLE I: List of the sample Ag/Au core/shell particles. Volume ratio is determined at the sample preparation. Average sizes are estimated from TEM photograph [5]. Core diameter and shell thickness is calculated from the volume ratio and the average size.

Samples	core/shell	volume ratio	average size (nm)	core diameter (nm)	shell thickness (nm)
001a	Au / Ag	1/2	20	6.9	3.1
002a	Au / Ag	1/8	30	7.2	7.8
003a	Au / Ag	8/1	15	7.2	0.30
001b	Ag/ Au	1/2	13	4.5	2.0
002b	Ag / Au	1/8	27	6.5	7.0
003b	Ag / Au	8/1	9	4.3	0.19

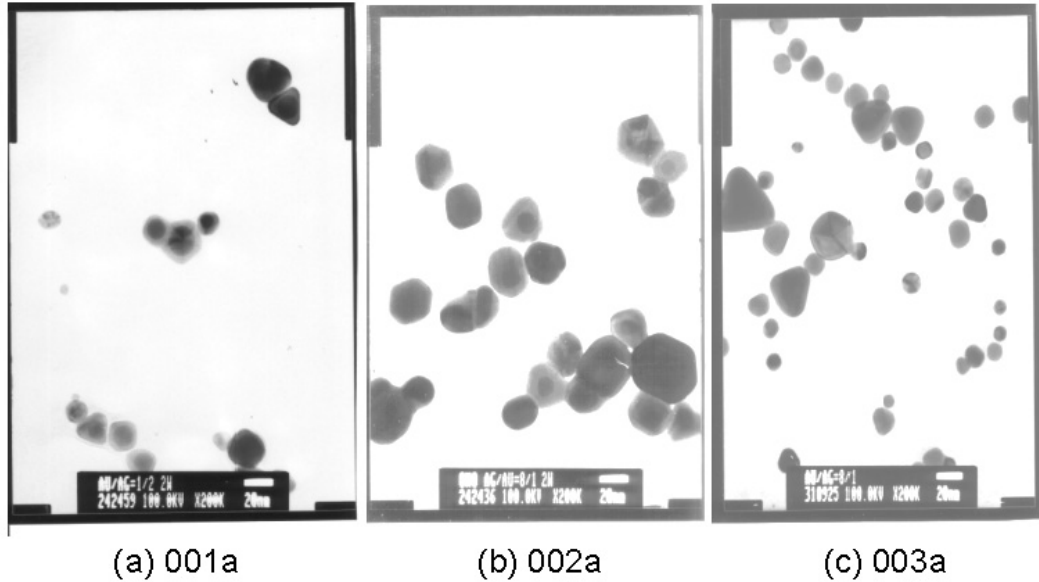


FIG. 1: TEM photographs for sample (a) 001a, (b) 002a and (c) 003a (Ag is shell and Au is core). The scale bars in the photograph are all 20 nm.

where r , N and σ are interatomic distance, coordination number and root-mean-square-relative displacement (RMSRD), respectively, for each atomic pair. Phase shift $\varphi(k)$, backscattering amplitude $f(k, r)$ and electron mean free path $\lambda(k)$ are obtained from FEFF6.01 calculation [7]. Actually the electron mean free path depends on the particle size when it is small as pointed out by Zhao and Monatno [8]. However, any general treatment of mean free path for various particle sizes has not been confirmed yet. So we apply the mean free path calculated from the FEFF code to all EXAFS data analyses for the present core/shell particles. From the standard sample (Ag and Au bulk foil), the edge shifts from the edge jump are determined to 3.6 eV for Ag K -edge and 13.48 eV for Au L_{III} -edge.

III. RESULTS

Figure 3 shows (a) $\chi(k)$ spectra (k -weighted) and (b) their Fourier transforms for Ag K -edge EXAFS for Ag-shell particles (bulk foil, 001a, 002a, 003a). The EXAFS for 001a and 002a are almost same as the bulk spectrum

(foil) but the amplitude for 003a is smaller than that for foil, 001a and 002a.

Figure 4 shows (a) $\chi(k)$ spectra (k -weighted) and (b) their Fourier transforms for Au L_{III} -edge EXAFS for Ag-shell and Au core particles (Au bulk foil, 001a, 002a, 003a). Both $k\chi(k)$ and their Fourier transform for the core structure of Au for 001a, 002a, and 003a are same as that for Au foil. For these core/shell particles, the diameters of the core Au are around 7.0 nm and these particles have same structures as that for the bulk Au (Foil).

Figure 5 shows (a) $\chi(k)$ spectra (k -weighted) and (b) their Fourier transforms for Au L_{III} -edge EXAFS for Au-shell and Ag-core particles (Au bulk foil, 001b, 002b, 003b). Both $k\chi(k)$ and their Fourier transforms for the shell structure of Au for 001b and 002b are same as that for Au foil. For these samples the Au shell thickness are estimated as 2.0 and 7.0 nm, respectively (see Table III).

On the other hand, $k\chi(k)$ and Fourier transform for 003b are different from the former two (001b, 002b): The amplitude of $k\chi(k)$ is smaller than former two (a) and the main peak shifts to smaller distance and another peak is appear at about 3.7 Å. This means that the Au shell structure for 003b sample differs from that for Au bulk,

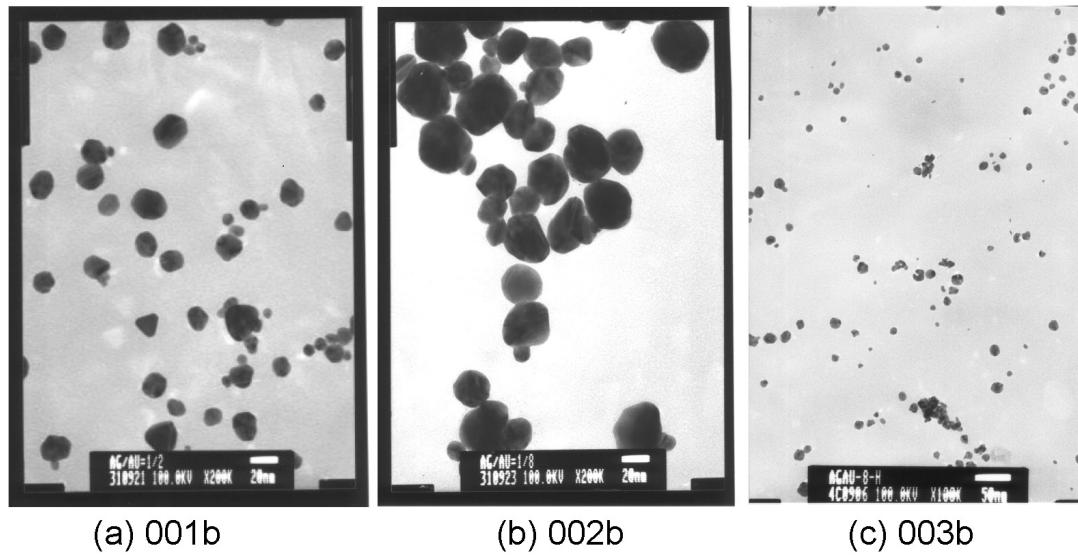


FIG. 2: TEM photographs for sample (a) 001b, (b) 002b and (c) 003b (Au is shell and Ag is core). The scales in the photos are 20 nm for (a), (b) and 50 nm for (c).

TABLE II: Example of Au/Ag core/shell TEM photograph and model obtained from the composition and average particle size estimated from TEM.

Sample	TEM	Model
001a Ag/Au=2/1 (3.1 nm : 6.9 nm)		
002a Ag/Au=8/1 (7.8 nm : 7.2 nm)		
003a Ag/Au=1/8 (0.3 nm : 7.2 nm)		

TABLE III: Example of Ag/Au core/shell TEM photograph and model obtained from the composition and average particle size estimated from TEM.

Sample	TEM	Model
001b Au/Ag=2/1 (2.0 nm : 4.5 nm)		
002b Au/Ag=8/1 (7.0 nm : 6.5 nm)		
003b Au/Ag=1/8 (0.18 nm : 4.32 nm)		

IV. DISCUSSION

001b and 002b. The Au shell thickness is about 0.2 nm (Table III). Similar change of the Fourier transform has been observed in the result reported by Shibata *et al.* [3]. They present the Au-Ag interaction in the interface between core and shell. It is strongly suggested that there are Au-Ag interaction between shell and core in addition to Au-Au in the shell in also present study.

In this section we first discuss about the structural parameters obtained from EXAFS one-shell curve-fitting procedure described in Section 2, where only homogeneous atomic pair as Au-Au or Ag-Ag are considered inside the shell and core.

Table IV shows the structural parameters obtained

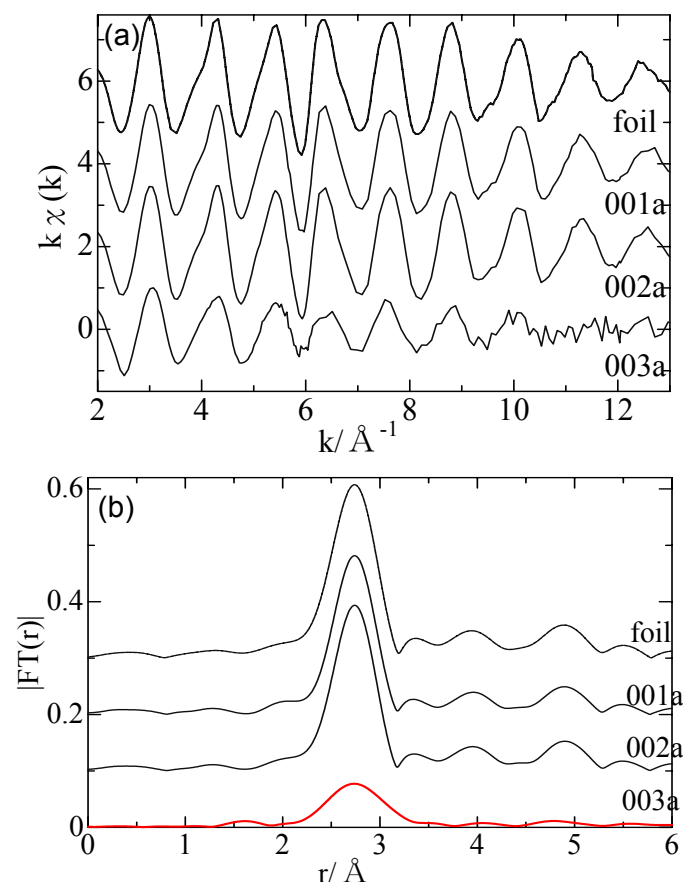


FIG. 3: (a) $k\chi(k)$ spectra and (b) their Fourier transforms of Ag K-edge EXAFS for 001a, 002a and 003a. For comparison the bulk Ag foil data is also shown (dash-dotted line).

from the present EXAFS for the Ag shell in the Au-core/Ag-shell samples. The error in the interatomic distance (r) is $\pm 0.010 \text{ \AA}$ and that in the coordination number (N) is ± 1.0 . Generally the effective coordination number (N) is reduced in the thin film or in fine particle systems because of surface effect [9]. T_{EXAFS} is calculated from the effective coordination number (N) using the equation presented by Crozier *et al.* [9]. In the present analyses the shell structure is assumed as infinite plane film [9, 10]. For these three samples (001a, 002a, 003a), the shell structure shows almost same values of inter atomic distances of Ag-Ag, RMSRD and third order cumulants C_3 except for the coordination number N . The N value for 003a sample (thinnest shell) is smallest and it is about 7.4. The shell thickness evaluated from N is also small, about 0.4 nm, for 003a. This means that the shell consists of almost 1 mono-layer (ML) Ag atoms. T_{TEM} is shell thickness estimated from the atomic composition and particle size obtained from TEM photograph described previously. It is pointed that the T_{EXAFS} (0.4) are almost same values as T_{TEM} (0.3).

Table V shows the structural parameters obtained from the present EXAFS for the Au core in the Au-core/Ag-shell samples. For this case, as expected from the EXAFS spectra shown in the previous section, the structural parameters of the shell for these three samples should be almost same. D_{EXAFS} is the core diameter calculated

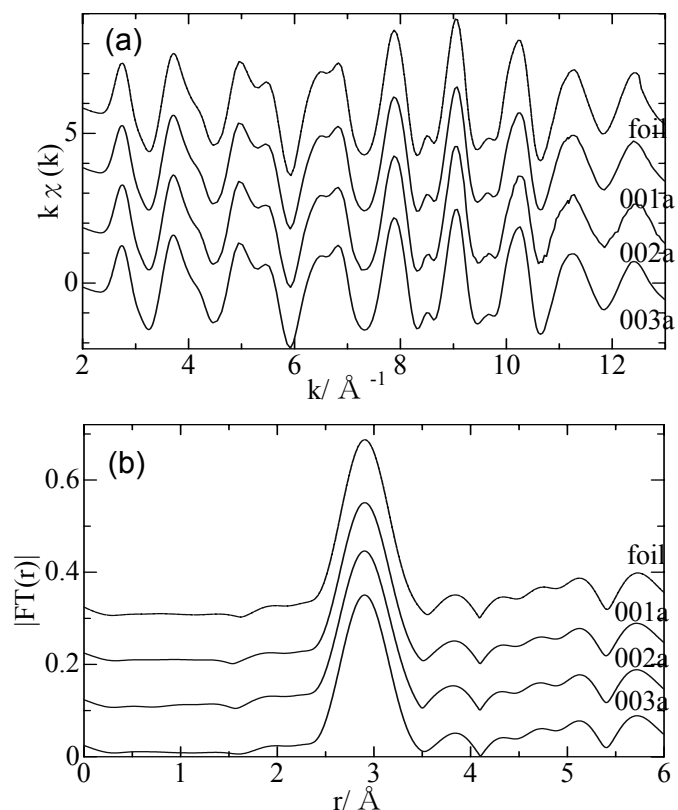


FIG. 4: (a) $k\chi(k)$ spectra and (b) their Fourier transforms of Au LIII-edge EXAFS for 001a, 002a and 003a. For comparison the bulk foil data is also shown (dash-dotted line).

from the same equation presented by Crozier [9]: in this case the core is assumed as cubic structure which volume is same as the core sphere. D_{TEM} is also obtained from atomic composition and particle size from TEM photograph. It is pointed out that D_{EXAFS} has same values of D_{TEM} except for 002a. This is because that for the large N which is close to 12 the error of D_{EXAFS} is large. The order of the D_{EXAFS} value can be same as D_{TEM} for 002a sample.

Table VI shows the structural parameters obtained from the present EXAFS for the Au shell in the Ag-core/Au-shell samples. The situation is similar to the discussion of Ag shell structure described in Table IV. The small value of N ($= 6.4$) for 003b results the small value of T_{EXAFS} ($= 0.6$). This means that the Au shell consists of 1 or 2 ML atoms in 003b sample. The error in T_{EXAFS} in comparison to T_{TEM} is larger for 001b and 002b than that for previous results in Tables IV and V. However T_{TEM} for 003b is smallest among these samples and the value of T_{TEM} ($= 0.2$) is same order as T_{EXAFS} ($= 0.6$).

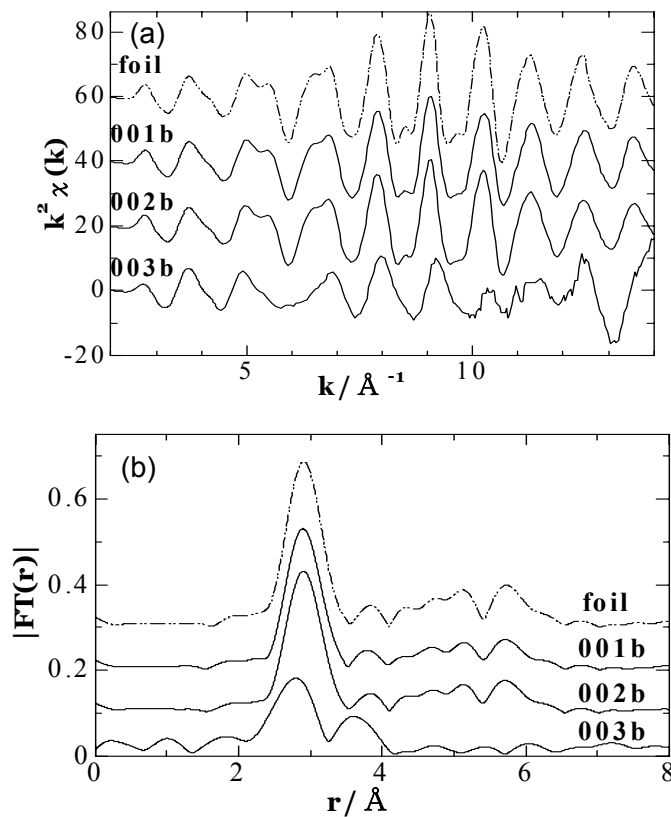
In above discussion we performed only one-shell curve-fitting. However, it is appeared that the shell of 003a and 003b samples consist 1 or 2 ML atoms. It is quite natural idea that there is another contribution from the interaction between core and shell. For example Ag-Au interaction can be observed in addition to Ag-Ag in the thin Ag-shell and Au-Ag interaction can be found other than Au-Au in the thin Au-shell. Actually Fourier trans-

TABLE IV: Structural parameters obtained from Ag- K EXAFS for the Ag shell in the Ag-shell/Au-core samples.

sample	$r/\text{\AA}$	N	$\sigma/\text{\AA}$	C_3 ($10^{-4}\text{\AA}^3$)	T_{EXAFS} (nm)	T_{TEM} (nm)
001a	2.883 ± 0.01	11.6 ± 1	0.097	5.6	2.7 ± 1	3.1
002a	2.883 ± 0.01	11.8 ± 1	0.098	5.9	4.6 ± 1	7.8
003a	2.888 ± 0.01	7.4 ± 1	0.11	5.1	0.4 ± 0.1	0.3

TABLE V: Structural parameters obtained from Au- L_{III} EXAFS for the Au core in the Ag-shell/Au-core samples.

sample	$r/\text{\AA}$	N	$\sigma/\text{\AA}$	C_3 ($10^{-4}\text{\AA}^3$)	D_{EXAFS} (nm)	D_{TEM} (nm)
001a	2.895 ± 0.01	11.5 ± 1	0.084	5.0	11.3 ± 3	13.8
002a	2.899 ± 0.01	11.0 ± 1	0.087	5.9	6.6 ± 2	14.4
003a	2.895 ± 0.01	11.6 ± 1	0.080	4.7	14.1 ± 2	14.4

FIG. 5: (a) $k\xi(k)$ spectra and (b) their Fourier transform of Au L_{III} -edge EXAFS for 001b, 002b and 003b. For comparison as bulk foil data is also shown.

form of Au shell in 003b suggests the existence of another Au-Ag interaction in the interface between core and shell as discussed in the previous section (see Fig. 5). We performed two-shell curve fitting for heterogeneous atomic pair, Au-Au and Au-Ag for Au shell, or Ag-Ag and Ag-Au for Ag-shell.

The structural parameters obtained from two-shell curve-fitting are listed in Table VII. In these parameters the absolute values of the coordination number N have slightly large error in comparison to interatomic distance r . We only focus on the ratio of N between homogeneous

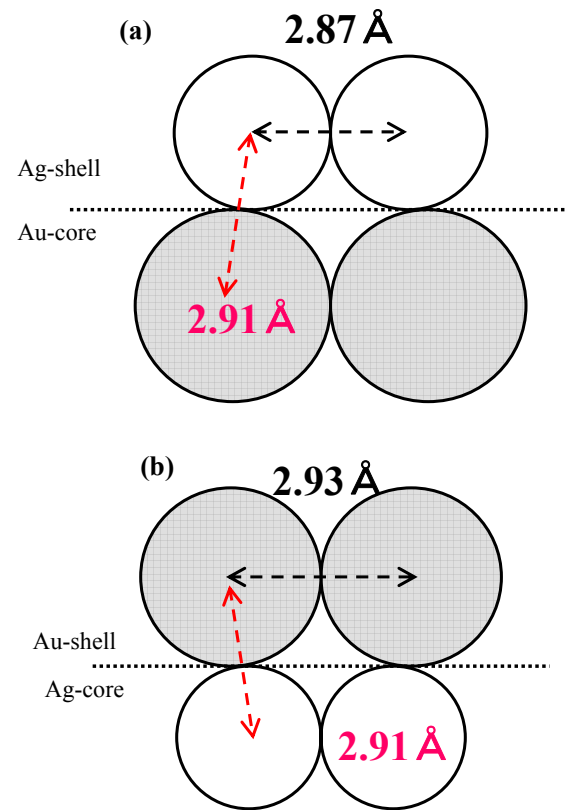


FIG. 6: Schematic models for interface between core and shell for the sample in which the shell is thinner (almost 1~2 ML) Ag/Au core/shell particle. (a) Ag-shell of 003a and (b) Au-shell of 003b.

and heterogeneous pair. The ratio of N for Ag-Ag/Ag-Au for 003a is about 1.5 and that of Au-Au/Au-Ag for 003b is 1.3. These values indicated the Ag-shell in 003a and Au-shell in 003b is 1~2 ML structure, which is consistent with the result previously discussed.

The result of the interatomic distance is more significant: That of Ag-Ag inside shell is 2.87 Å and Ag-Au of the interface between core and shell is 2.91 Å. On the other hand, the distance of Au-Au interaction inside thinner Au-shell is 2.93 Å and that of Au-Ag in the interface is 2.91 Å, which is same as Ag-Au distance in the

TABLE VI: Structural parameters obtained from Au- L_{III} EXAFS for the Au shell in the Au-shell/Ag-core samples.

sample	$r/\text{\AA}$	N	$\sigma/\text{\AA}$	C_3 ($10^{-4}\text{\AA}^3$)	T_{EXAFS} (nm)	T_{TEM} (nm)
001b	2.893 ± 0.01	10.8 ± 1	0.086	5.4	1.8 ± 1	2.0
002b	2.896 ± 0.01	10.6 ± 1	0.084	5.6	1.3 ± 1	7.0
003b	2.887 ± 0.01	6.4 ± 1	0.093	14.5	0.6 ± 1	0.2

TABLE VII: Structural parameters obtained from two-shell curve-fitting for 003a and 003b samples: thinner shell particles.

sample	Atomic pair	$r/\text{\AA}$	N	$\sigma/\text{\AA}$	C_3 ($10^{-4}\text{\AA}^3$)
003a	Ag-Ag	2.87 ± 0.01	6.9 ± 2	0.10	1.9
	Ag-Au	2.91 ± 0.01	4.7 ± 2	0.11	1.7
003b	Au-Au	2.93 ± 0.01	5.0 ± 2	0.061	4.9
	Au-Ag	2.91 ± 0.01	3.9 ± 2	0.061	4.9

interface. We suppose a certain interpretation of this phenomenon: a part of electron moves from Ag to Au atom through the interface between core and shell, and then the atomic radius for Ag decreases but that of Au increases. The atomic distances between interface, Ag-Au and Au-Ag are same (2.91 $\text{\AA}$) each other. A possible schematic model is shown in Fig. 6. Our preliminary study of optical absorption measurements for these core/shell particles shows that the absorption peak assigned from Au core at 380 nm shifts to lower wavelength, which supported by the model calculation when the electron density on Au atom increases [11]. This model is consistent with the present EXAFS result, but unfortunately the two-shell fitting has not so small errors for each parameter, we need more accurate measurements and analyses for these interesting

core/shell particle systems.

V. CONCLUSIONS

We measured Ag K - and Au L_{III} - edge EXAFS for Ag/Au core/shell particles. The structural parameters obtained from EXAFS analyses are discussed with that estimate from TEM photograph. The thickness of shell and diameter of core can be evaluated from the EXAFS results, which are almost consistent with the result from TEM. Two-shell fitting analysis indicates that the Ag-Ag distance decreases and Au-Au distances increase in the thinner shell. This suggests that the electrons transfer from Ag atom to Au atom at the interface between core and shell.

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