

EXAFS studies of the formation mechanisms of metal clusters in micelles of surfactants

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Introduction

Colloidal dispersions of nanometer-sized platinum and gold clusters are of wide interest because of their specific functions which are different from those of either bulk metal solids or metal atoms. Surfactants are known to have the function to solubilize hydrophobic substances in aqueous solutions. The method to prepare colloidal dispersions of metal clusters in the hydrophobic field produced by the micelles of surfactants is important for the purpose of control of size and dispersity of the obtained metal clusters [1]. Colloidal dispersions of platinum and gold clusters could be prepared by photo-reduction of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$, respectively, in the presence of stabilizer such as polymers [2]. The aim of this study is the determination of the particle formation mechanisms in micelles of various surfactants as well as the change of average particle size in solution at the photo-reduction process.

Experimental

Platinum and gold colloids (0.66mM) were prepared from $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ by irradiation of 500W super-high-pressure mercury lamp in 100mM aqueous solution of surfactants (SDS: Sodium Dodecyl Sulfate, DTAC: Dodecyltrimethylammonium Chloride, PEG: Polyethylene Glycol Lauryl Ether) with benzoin, respectively. The reduced samples prepared in quartz cell at the designated duration of reduction were then poured into cells for EXAFS measurements.

Pt- L_3 and Au- L_3 edge EXAFS spectra were collected at the BL-7C and/or BL-12C. The EXAFS measurements of the metal colloids were carried out at room temperature in a fluorescence mode using a Lytle type detector to estimate their formation mechanism of colloids.

Results and discussion

Figure 1 shows the Pt- L_3 edge EXAFS Fourier transforms for 0.66mM Pt colloids stabilized by PEG after 5 hour's photo-reduction, comparing with that for Pt foil. The main peak is assigned to a Pt-Pt bond, which was determined to be 0.276 nm in distance by curve-fitting analysis. In the case of the Pt colloids stabilized by SDS and DTAC, Pt-Pt bond is mainly observed as shown in Table 1. Their coordination numbers (C.N.) and bond distances (R) obtained from the curve-fitting are listed.

On the other hand, the curve-fitting analysis of photo-reduced Au colloids stabilized by SDS, PEG, and DTAC was conducted with the model parameters extracted from the reference compounds of Au foil and $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ solid powder. As for any surfactants, the Au-Au bond distance values for Au colloids coincided with the value of 0.287 nm for Au foil, but the coordination numbers were in the range of 6.0 – 8.1, that were apparently smaller than that (C.N. = 12) of Au foil. Therefore, the Au colloids are strongly stabilized in micelles of surfactants in solution and they become very stable.

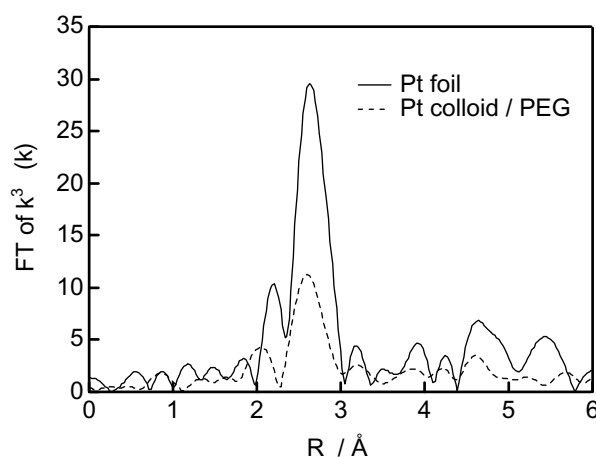


Fig.1 Fourier transforms of Pt- L_3 edge for Pt foil and Pt colloids.

Table 1. Curve-fitting results for Pt and Au colloids

Sample	Bond	R / Å	C.N.	$\sigma^2 / \text{Å}^2$	R factor
Pt / SDS100	Pt - Pt	2.76	5.5	1.23×10^{-3}	0.263
Pt / PEG100	Pt - Pt	2.76	6.4	1.28×10^{-3}	0.305
Pt / DTAC100	Pt - Pt	2.76	2.7	3.59×10^{-3}	0.314
	Pt - Cl	2.33	1.6	1.10×10^{-4}	
Au / SDS100	Au - Au	2.85	7.7	-1.68×10^{-3}	0.297
Au / PEG100	Au - Au	2.85	6.0	-2.83×10^{-3}	0.515
Au / DTAC100	Au - Au	2.87	8.1	-1.67×10^{-3}	0.216

References

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