

## EXAFS study for the formation of noble metal nanoparticles prepared from reverse micelles of metallosurfactants

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### Introduction

We have been studying the preparations and the formation of aggregates for the alkylethylenediamine metal complexes in aqueous organic solvent systems. These systems are utilized to create metal nanoparticles in high yields [1, 2]. In this study, we have prepared silver (Ag) nanoparticles by the chemical reduction of their alkylethylenediamine complexes in the microemulsion systems using a reducing agent such as NaBH<sub>4</sub>, and have estimated the average particle sizes of the Ag nanoparticles by means of EXAFS measurements. We have focused on the time-course in the interactions between the silver(0) and nitrogen of ligand on the surface of the silver(0) nanoparticles.

### Experimental

The amphiphilic bis(octylethylenediamine (= oct-en))silver nitrate, bis(dodecylethylenediamine (= dod-en))silver nitrate, and bis(hexadecylethylenediamine (= hexd-en))silver nitrate complexes were prepared by the reactions of oct-en, dod-en, and hexd-en ligands with silver nitrate in methanol, respectively. The microemulsion was prepared as the silver complex/heptane/water (water/metal complex molar ratio is in the range of 4-50) ternary system. The reduction of the metallosurfactants was performed by adding NaBH<sub>4</sub> aqueous solution to the microemulsion system and then by shaking the water/heptane phase.

EXAFS measurements of Ag-K edge of these metallosurfactant microemulsions were performed using polyethylene bag with 1 mm path length at room temperature in a transmission mode at BL-10B. The above obtained samples were sealed into polyethylene bags for measurements, and the metal concentration of [Ag] in these microemulsion systems is in the range of 0.1-0.8 (mol/L). In order to extract the backscattering amplitude and phase shift functions for the curve-fitting, the reference compounds (Ag foil and Ag(NH<sub>3</sub>)<sub>2</sub><sup>+</sup> solid compound) were used in this experiment.

### Results and Discussion

Table 1 shows the coordination numbers (C.N.) and bond distances (r) of the metallosurfactants of Ag(dod-en) microemulsion before and after the chemical reduction with NaBH<sub>4</sub> as well as Ag(oct-en) and Ag(hexd-en) complexes.

Table 1. Structural parameters from EXAFS analysis of the metallosurfactant of Ag(dod-en) microemulsion systems.

sample	bond	C.N.	r/Å
Ag(oct-en)	Ag-N	3.5	2.28
Ag(dod-en)	Ag-N	4.2	2.27
Ag(hexd-en)	Ag-N	2.3	2.21
Ag(dod-en)/heptane/H <sub>2</sub> O	Ag-N	2.4	2.20
Ag(dod-en)/heptane/H <sub>2</sub> O + NaBH <sub>4</sub>	Ag-Ag	2.6	2.86
	Ag-N	1.6	2.20
Ag(dod-en)/heptane/H <sub>2</sub> O+NaBH <sub>4</sub> (1day)	Ag-Ag	6.3	2.87
	Ag-N	0.8	2.19
Ag(dod-en)/heptane/H <sub>2</sub> O+NaBH <sub>4</sub> (1month)	Ag-Ag	5.9	2.87
	Ag-N	0.5	2.14

In the Fourier transforms of all the samples (not shown in this report), the peak around 1.8 nm assigned to the bond of Ag-N appears with the same height. The peak assigned to the bond of Ag-Ag appears immediately after the reduction, and their peak heights increase with increasing the duration of left under air. The particle diameters of the Ag nanoparticles (approximately 1.0-1.5 nm) estimated by the C.N. were significantly larger than those by the TEM observation and the difference is generally larger for the Ag(0) particles. It is characteristic that the Ag-Ag coordination number appreciably increases accompanying with the decrease in the Ag-N coordination number within 1 day after the reduction. The increase in the coordination number of Ag-Ag will mean the growth of the Ag(0) particles and the decrease in that of Ag-N will be the elimination of the Ag(0) coating ligands. The distances between the Ag-Ag and Ag-N bonds are nearly constant over 1 month, resulting in the stability of Ag nanoparticles encapsulated by the capping ligands of alkylethylenediamine.

### References

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