

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

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Introduction

Microemulsion systems composed of noble metallosurfactants can provide metal nanoparticles having uniform shapes and sizes [1, 2]. In this study, we have prepared silver and gold nanoparticles (Ag and Au nanoparticles) by the chemical reduction of their alkylethylenediamine complexes in the microemulsion systems using a reducing agent such as NaBH₄, and have estimated the average particle sizes of the Ag and Au nanoparticles by means of EXAFS measurements. We have tried to correlate the sizes of the nanoparticles with the structures of the original microemulsions by changing the alkyl-chain length of the original metal complexes and the solvent composition.

Experimental

The amphiphilic bis(dodecylethylenediamine (= dod-en))silver nitrate, bis(hexadecylethylenediamine (= hexd-en))silver nitrate, and bis(dod-en)gold chloride complexes were prepared by the reactions of dod-en and hexd-en ligands with the corresponding metal salts in methanol. The microemulsion was prepared as the silver complex/heptane/water (water/metal complex molar ratio is in the range of 4-50) or gold complex/methanol/diethylether ternary system. The reduction of the metallosurfactants was performed by adding NaBH₄ aqueous solution to the microemulsion system and then by shaking the water/heptane or water/diethylether phase.

EXAFS measurements of Ag-K or Au-L₃ edges of these metallosurfactant microemulsion systems were performed using the 10 mm path length cell with polyimide film windows at room temperature in a transmission mode at BL-10B. The above obtained samples were poured into cells for measurements, and the metal concentration of [Ag] in these microemulsion systems is in the range of 0.1-0.8 (mol/l). (3 mmol/l for [Au]) In order to extract the backscattering amplitude and phase shift functions for the curve-fitting, the reference compounds (Ag and Au foils and Ag(NH₃)₂⁺ solid compound) were used in this experiment.

Results and Discussion

Figure 1 shows the Fourier transforms of Ag K-edge EXAFS spectra for the metallosurfactant of Ag(dod-en) microemulsion before and after the reduction with NaBH₄.

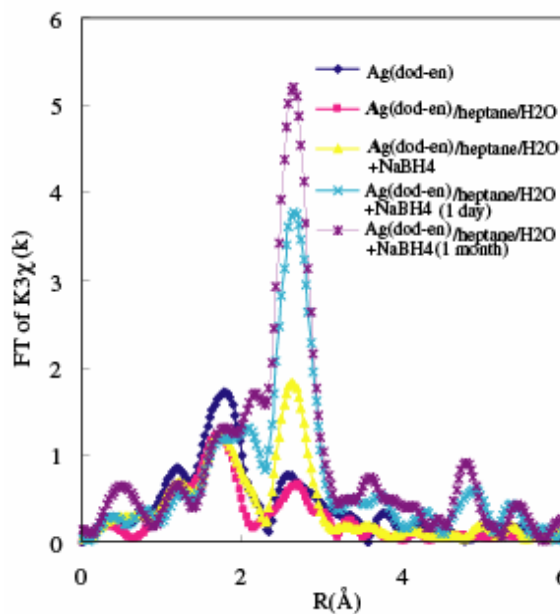


Fig. 1 Fourier transforms of EXAFS spectra for Ag-K edge of the metallosurfactant of Ag(dod-en) microemulsion systems.

In all the samples, 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 after the reduction, and their peak heights increase with increasing the duration of left under air. On the other hand, the sizes of the Ag nanoparticles estimated by the EXAFS study were significantly larger than those by the TEM observation and the difference is larger for the silver(0) particles than for the gold(0) particles. Therefore, the following characteristic features have been expected. 1) With increasing the water content, the size of the metal nanoparticles increases and the size distribution becomes larger. 2) The longer alkyl-chain length of the metallosurfactant results in the smaller size and smaller size-distribution of the metal nanoparticles. The detailed analysis is in progress.

References

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