Electronic state and local Structure of Mn oxide nanoparticle synthesized by microemulsion method

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Introduction

It is expected that metal nanoparticles have special properties, which are different from those of bulk. But it was difficult to keep them such a small size. Recently, the microemulsion method has been developed, and nanoparticles protected by surfactants can be obtained in a stable state. Products are often self-assembled and form a super-lattice structure called nanocrystal [1].

Using this method, we synthesized Mn oxide nanoparticles with different sizes, which are expected theoretically to be ferromagnets. Ferromagnetic nanoparticles have been studied as attractive materials for new memory devices.

In this work, we measured and analyzed Mn *K*-edge XAFS spectra of Mn oxide nanoparticles, and these results were compared with those of SQUID.

Experimental

Xylene and a surfactant (sodium dodecylbenzene-surfonate) were added to 0.1 mol/l $MnCl_2$ aqueous solution. Then 0.1 mol/l NaOH aqueous solution was added and was stirred, and Mn oxide nanoparticles was obtained from an organic phase. In the microemulsion method, the size of nanoparticles is controlled by the molar ratio of a surfactant (Fig. 1). Smaller nanoparticles were obtained with larger amount of surfactants as shown by peak broadening of powder x-ray diffraction, but they are too small to measure x-ray diffraction peaks quantitatively.

Mn *K*-edge XAFS spectra were measured at 16-18 K in the conventional transmission mode at BL-9A using a Si(111) double-crystal monochromator. Incident and transmitted x-ray intensities were detected with ionization chambers filled with N_2 100%. Sample powders were diluted by BN and pressed into disks.

Results and Discussion

Fig. 2 shows Mn *K*-edge XANES spectra. Compared with reference compounds, it was found that Mn oxidation number increases as the nanoparticle size reduces. It is explained that oxidation of Mn^{2+} takes place more significantly for smaller nanoparticles, due to larger surface areas.

Fig. 3 shows Fourier transforms of Mn *K*-edge EXAFS spectra. They indicate that the small clusters consist of MnO_2 while the large one predominantly consists of Mn_3O_4. This result is consistent with that of XANES. The Fourier transform peak contributed from a higher coordination shell (3.1Å) disappears as decreasing the cluster size probably due to static disordering in the small clusters.

Though magnetization measured by SQUID also supports particle size dependence, we couldn't observe ferromagnetism for small-sized samples. Because Mn_3O_4 and MnO_2 are a ferrimagnet and an antiferromagnet respectively, the size-dependent difference in magnetization is caused by different oxidation.

References

[1] J.S.Yin et al., Phys. Rev. Lett. 79, 2570 (1997).

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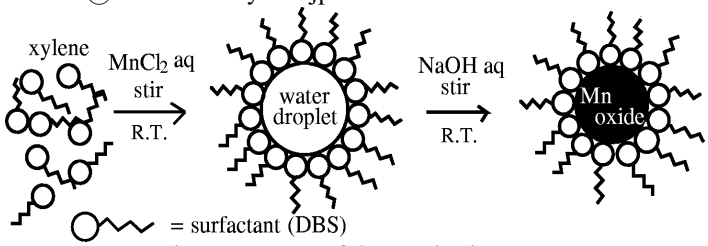

Fig. 1. Process of the synthesis

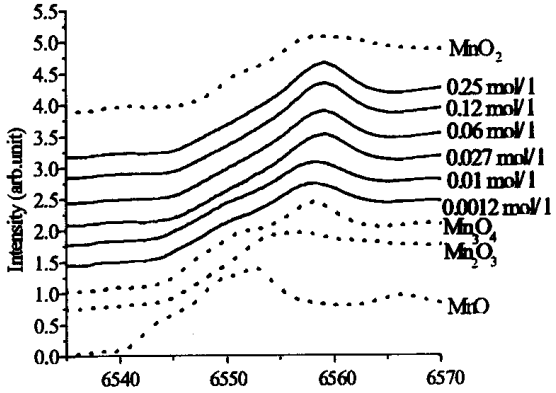

Fig. 2. Mn *K*-edge XANES

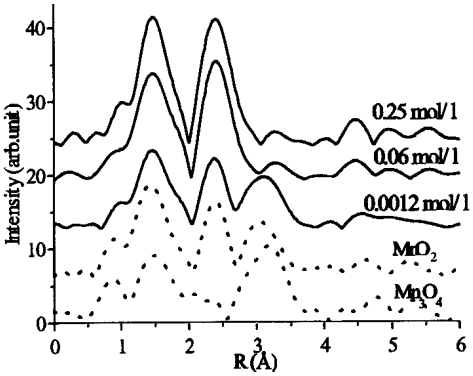

Fig. 3. Fourier transforms of the EXAFS spectra
(The density of surfactant is shown in each figure)