9A/2002G268

Local structure of anisotropic copper hydroxide nanoparticles

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Introduction

Because metal compound nanoparticles are expected to have unique electric, magnetic, and chemical properties different from bulk materials, much scientific attention has recently been paid to such a kind of materials. The microemulsion method is one of the most promising techniques to prepare nanoparticles. Nanoparticles synthesized with this method are protected by surfactants. Thanks to surfactant molecules, the nanoparticles often self-assemble to form a super-lattice structure.

Based on this method, we synthesized copper hydroxide ($Cu(OH)_2$) nanoparticles. They were characterized by transmission electron microscope (TEM), UV-vis absorption spectroscopy, and DC magnetization measurements. TEM images show that the copper hydroxide nanoparticles have a rectangular-plate-like shape with typical dimensions of 10x15x3 nm^3. The smaller copper hydroxide nanoparticles exhibits a red shift of a d-d transition in UV-vis absorption spectrum. We measured their magnetization by a superconducting quantum interference device (SQUID) and found a hysterisis curve in the field-dependent magnetization below 10 K, though the bulk shows an antiferromagnetic property. In this work, we investigated the local geometric structures of the copper hydroxide nanoparticles to correlate their structure with the magnetic properties.

Experimental

Sample preparation: Hexane solution of a surfactant (diisooctyl sodium sulfosuccinate (AOT)) were added to copper chloride aqueous solution. After stirred for 1.5 hours, NaOH aqueous solution was added into the solution. The reaction was carried out for 2.5 hours and then the reaction mixture was allowed to separate into two layers. The upper layer (hexane) contains copper hydroxide nanoparticles. By changing molar ratio of surfactant, the nanoparticle size was controlled.

XAFS measurements: Cu *K*-edge XAFS spectra were measured at 20 K with the transmission mode at BL-9A using a Si(111) double-crystal monochromator. Sample powders were dissolved in acetone and dropped onto a filter paper. A stack of the paper with an appropriate thickness was placed in front of the x-ray beam.

Results and Discussion

Figure 1 shows normalized Cu *K*-edge XANES spectra of the copper hydroxide nanoparticles (black) and the corresponding bulk (red). These spectra are almost identical, that means the local geometric and electronic structures of the nanoparticles are similar to those of bulk. Figure 2 shows Fourier transforms of Cu *K*-edge EXAFS spectra for the both samples. From curve-fitting analyses, we obtained the interatomic distance between the Cu and the nearest-neighbor oxygen (O1). The Cu-O1 distance in the nanoparticles is found to be longer by 0.04 Å than that in bulk. This result is consistent with the red shift observed in the UV-vis spectra of the nanoparticles, since the elongation of the Cu-O1 distance causes a weaker ligand field at Cu^{2+} sites. $Cu(OH)_2$ is a layered compound in which a quasi-2D network of $Cu(OH)_6$ distorted-octahedral unit is stacked with weak hydrogen-bond interlayer interactions. The anisotropic plate-like shape of the nanoparticles suggests a limited stacking along perpendicular to the 2D network. Such a limited stacking might induce the bond elongation and also the ferromagnetism observed at low temperatures. To get further structural information from polarization-dependence experiments, preparation of self-assembled superlattices of the nanoparticles is now underway.

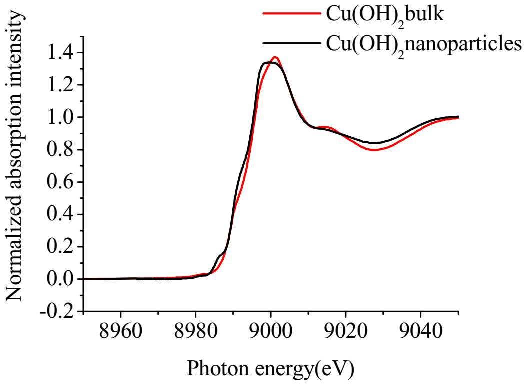

Fig.1. Cu *K*-edge XANES spectra for $Cu(OH)_2$ bulk and nanoparticles.

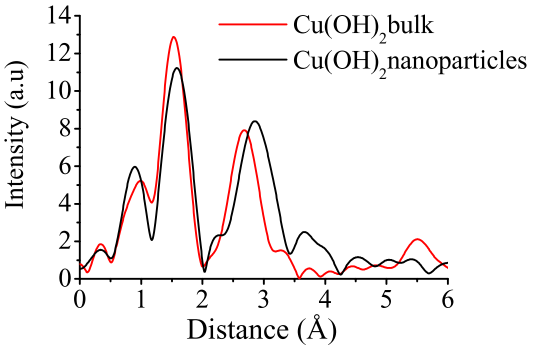

Fig.2. Fourier transforms of Cu *K*-edge EXAFS oscillations for $Cu(OH)_2$ bulk and nanoparticles.

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