

Shape and Size control of Nano-crystals of Transition Metal Oxides

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Introduction

The strategy to manipulate the nanoscale building blocks via self-assembly and higher-ordered organization approaches into hierarchically complex architectures is a great challenge towards both material synthesis and advanced nanodevices. In this process, self-assembly driven by chemical or physical interactions enables primary building units to form versatile flexible shapes. In recent years, much attention has been paid particularly to the fabrication of hierarchically hollow structures including hollow spheres as well as polyhedrons by primary building unit self-assembly, because the materials with such hollow structures have broadly potential applications in catalysis and drug deliver and as artificial cell and light filler, etc. We could prepare hollow particles of CoOOH through a bubble template mechanism [1]. The obtained hollow structure exhibited a hierarchical structure comprised of single crystalline nanorods of CoOOH. Self-assembling process of nanorods around a bubble originated from H₂O₂ was the origin of the hierarchical structure. Hollow structures have broad applications in catalysis and drug delivery owing to their low density and large surface area.

Co₃O₄ is also a versatile material as oxidation catalysts. If hollow spheres of Co₃O₄ can be prepared, we can expect a high surface area and hence efficient catalytic reactions. In the present study various amino acids were adopted as template molecules in the oxidation process of cobalt chlorides in liquid phase by H₂O₂. Structural analyses were performed by TEM and EXAFS.

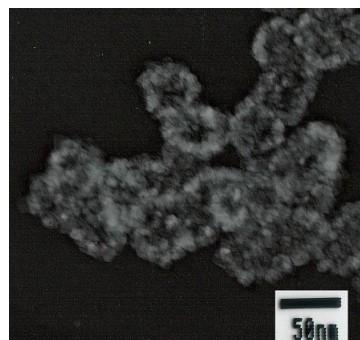
Experimental

Synthesis of nanocrystals were achieved in a teflon autoclave. TEM measurements were performed at ISSP, the University of Tokyo. Measurements of extended X-ray absorption fine structure (Co K-edge EXAFS) were carried out at the Photon Factory in the Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK-IMSS-PF). The measurements were made in a transmission mode. The EXAFS spectra were analyzed with the UWXAFS package.

Results and Discussion

We have succeeded in the synthesis of Co₃O₄ hollow spheres and the size control of hollow spheres by changing the ratio of cobalt to glycine (Figure 1). Co₃O₄ hollow spheres were prepared by the hydrothermal synthesis method: A 9 mL of solution containing N,N-

dimethylformamide(DMF), acetonitrile(MeCN), and water with the volume ratio of 1:1:1 was prepared in a 100 mL Teflon autoclave, and then 0.003 g of



Co(CH₃COO)₂ and 0.0075 g of glycine were added. After 2 mL of H₂O₂(30 %) was added, the reaction solution was kept at 150 °C for 20 h. Fig. 1 shows a TEM image for this hollow spheres.

Figure 1: The TEM image of hollow spheres. This image shows that the diameter of hollow sphere is about 50 nm.

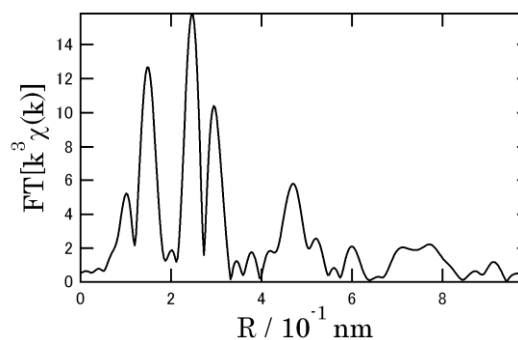


Figure 2: k^3 -weighted Co-K edge EXAFS Fourier transforms (absolute values) measured for Co₃O₄ hollow spheres

The x-ray diffraction (XRD) pattern for hollow sphere agreed well with that of Co₃O₄. TEM image shows that the walls are constructed by the aggregation of Co₃O₄ nanocrystals whose sizes are about 5 nm.

Figure 2 shows the Fourier transforms of the EXAFS of hollow spheres. Fitting analysis is performed including multiple scattering.

The mechanism for the formation of hollow spheres with glycine, catalytic activity of Co₃O₄ hollow spheres and the interaction between other doped metal elements and the hollow spheres are being examined.

Reference

- [1] J. Yang and T. Sasaki, Chem. Mater. 20, 2049 (2008).
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