Nano-scale Control of Magnetic Materials by Means of Soft Chemistry

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In these decades, the control of morphology and structure in nm scale of functional materials has been studied in many fields in order to realize fascinating materials for the application to future devices. Among the synthesis methods of such nm controlled materials, soft chemical process, *i.e.*, materials synthesis at ambient temperature in solution leads to a possibility to regulate the physical properties and functions. In the field of magnetic materials, the regulated structure and morphology are issues to be concerned to satisfy adequate properties.

In this paper, two typical synthesis of nm range controlled magnetic materials prepared using micelles formation phenomena will be introduced. One is the synthesis utilization of micelles as template and the other is the one utilization of inside of reverse micelles as the regulated space of the reaction.

Utilization of micelle formation of surfactant in solution is one of the interesting phenomena for the synthesis of nm range regulated materials. Above the critical micelle concentration (CMC), surfactant molecules in a solution assemble to form micelles and the size and morphology of micelles are determined by the molecular structure, concentration, etc.

The utilization of difference of the hydrophilic/hydrophobic properties separated by the surfactant layer is the key factor to synthesize nm range controlled structure and morphology using micelles. Inside the micelles surrounded by water is hydrophobic and hydrophobic molecules can be dissolved inside the micelles. The reverse micelle, which can be formed in oleophilic solvent with surfactant and the hydrophilic group of the surfactant associates inside the micelles, can incorporate hydrophilic solute inside the micelles.

1. Mesoporous metals prepared with lyotropic liquid crystal as template

Many mesoporous materials with variable compositions and morphologies have extensively been investigated.1) The specific features of regular pore arrangement, homogeneous mesopore size, and high surface area make those materials very promising for various applications.2) Mesoporous metals are also promising materials due to their high surface area, ordered regulated structure, and the feature of metal. Mesoporous metals were prepared by reduction of metal ions in the presence of lyotropic liquid crystals made with nonionic surfactants. 3) We revealed that combining the use of lyotropic liquid crystal and electroless deposition of metal enables a highly ordered mesoporous structure.4)

The aqueous solution containing surfactant, Ni^{2+} and Co^{2+} was prepared to form lyotropic liquid crystal. In order to reduce the metallic ions into metals, combination of reducing agents was proposed to realize the highly ordered meso-structure. The selection of reducing agents based on their chemical properties both in water and on the metallic surface enabled to form the metal phase incorporating the micelles existed in the lyotropic liquid crystal. The resultant powders were rinsed with alcohol to remove the surfactant. The samples obtained with this procedure were Ni and NiCo alloys with highly ordered mesoporous structures, as confirmed by elemental analysis, TEM(Fig. 1), HR-SEM, N_2 adsorption isotherm, and XRD analysis.

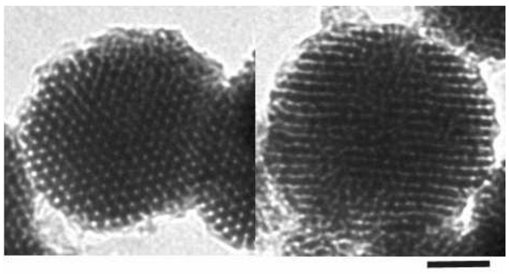

Figure 1. TEM image of 2D-hexagonal channels of highly ordered mesoporous Ni particles. (Scale bar: 50 nm)

2. nm-sized iron oxide particles synthesized inside the reverse micelles

For the synthesis of nanoparticles, a method by using a water-in-oil microemulsion including a reverse micellar system has been used widely. As a novel approach for the preparation of iron-oxide nanoparticles, we report the method via successive reduction–oxidation of Fe^{2+} or Fe^{3+} ions in reverse micelles.5) Two heptane solution of sodium bis(2-ethylhexyl)sulfosuccinate (AOT) were prepared separately. An aqueous solution of Fe^{2+} was added to one solution, while an aqueous solution of $NaBH_4$ to the other in order to give the molar ratio of $W = [H_2O]/[AOT] = 11$ for both the solution, in which a diameter of water pool is expected to be 6 nm. The mixing of these solutions brought about the formation of intermediate metallic state and the spontaneous oxidation successively. The formation of gamma-Fe_2O_3 nanoparticles with diameter of ~4 nm was revealed by XRD pattern (Fig. 2).

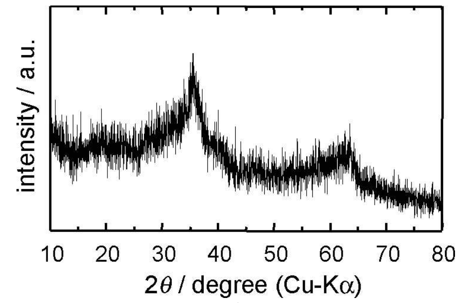

Figure 2. XRD pattern of the sample prepared via successive reduction–oxidation in reverse micelles.

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