

Preparation of Encapsulated Co Nanoparticles in Reversed Micelle and their Magnetic Properties

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Synthesis of encapsulated Co nanoparticles in DDAB/toluene reversed micelle solution and their magnetic properties were investigated. Co nanoparticles of about 1.3 nm particle size whose surface was covered with silica capsule of about 3.5 nm thickness, and of about 4.4 nm particle size whose surface was covered with silica capsule of about 2.2 nm thickness were obtained. The aggregation of capsules during drying was observed, since the active -OHs in silica capsule surface exists immediately after the hydrolysis. The surface modified with HMDS or TMCS was effective to yield isolated particles without the aggregation. Active -OHs of silica capsule surface is also inactivated by keeping in the liquid for 7 days without surface modification. The magnetization curves exhibit the superparamagnetic nature.

Key words: nanoparticle, encapsulate, reversed micelle, magnetic properties, Co

1. INTRODUCTION

Recently, magnetic nanoparticles with controlled size and composition, such as FePt nanoparticles for high density recording medium[1] and Co-Al-O granular thin films which shows tunneling magnetoresistance effect[2], have been a field of intense study. To synthesize nanoparticles, chemical methods, such as the polyol process[1] and the reversed micelle technique[3-6], can provide large amounts of final product using relatively simple apparatuses. Reversed micelles are nanometer size cages formed by dissolving surfactant molecules in an apolar organic solvent. These micelles can solubilize inorganic reagents, and various chemical reactions can be carried out inside the micelle cages to synthesize nanoparticles. A wide variety of nanoparticles, Pt, Rh[3], and Co[4,6], have been synthesized by this method.

Particles formed by the reversed micelle technique are usually well dispersed as colloids due to the surface coating of surfactant molecules. This good dispersiveness is suitable for the applications of magnetic fluid and self-assembled arrays[6,7]. However, the surfactant should be removed from the particle surface when the nanoparticles are utilized as powders. The nanoparticles without the surface coating tend to precipitate into large aggregations. It is necessary to improve the dispersiveness of nanoparticles without the surface coating of surfactant molecules for powder application.

The surface coating of nanoparticles can be considered to be a good protection against

aggregation[8]. Inorganic-SiO₂ is suitable as a surface coat material, because it has the relatively high thermal stability. Miyao et al. produced Pt nanoparticles supported on SiO₂ for metal catalysts by the hydrolysis of TEOS(tetraethoxysilane)[5], which was carried out in a reversed micelle solution of mono-dispersed Pt particles. It would be expected that the situation of water contained inside the reversed micelle cages would be important for the hydrolysis reaction of TEOS. By using that water, the encapsulated nanoparticles will be formed by reducing metal ions and then hydrolysis of TEOS in reversed micelles.

In this study, cobalt nanoparticles encapsulated in SiO₂ were prepared by two kinds of the reversed micelle in which the usage of the water differed, and their magnetic properties were investigated.

2. EXPERIMENTAL

The fundamental preparation method of the encapsulated Co nanoparticles was as follows: Co nanoparticles were synthesized in the binary system of DDAB/toluene, where DDAB (didodecyltrimethylammonium bromide) is a cationic surfactant. Sodium borohydride, NaBH₄, was used to reduce CoCl₂·6H₂O to obtain Co nanoparticles. To encapsulate Co nanoparticles, tetraethoxysilane (TEOS) was added into the dispersed solution of Co nanoparticles, and the hydrolysis of TEOS was carried out at 333 K for 72 hours. All the synthesis steps were carried out in N₂ to prevent the contamination of oxygen and water of the atmosphere during the reaction.

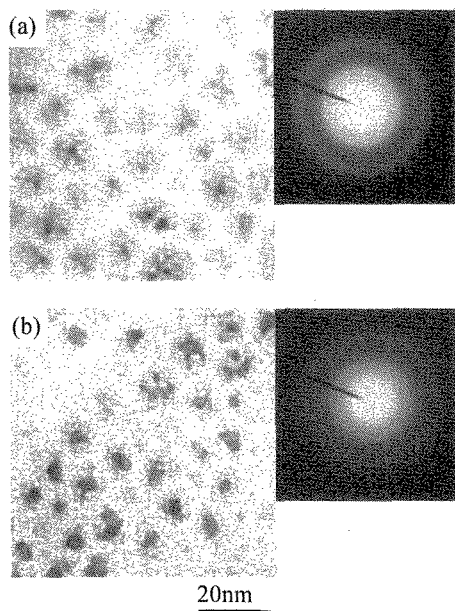


Fig.1 TEM images of encapsulated Co nanoparticles of (a) sample *A* and (b) sample *B* and selected area electron diffraction patterns.

Both the reduction of Co^{2+} and the hydrolysis of TEOS might be related to the water structure in the water pool of the micelle. In this study, the water necessary for both of reductive reaction and hydrolysis was added by two kinds of methods:

Sample *A*: Co nanoparticles was prepared in the system which retained sufficient water necessary for both reactions in the reversed micelle cages. 11 wt% DDAB solution in 10 ml of toluene was mixed with 0.06 ml of 3.3M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ aqueous solution. The solution was stirred vigorously. Then, NaBH_4 was dissolved in the solution by $[\text{BH}_4^-]:[\text{Co}^{2+}]=3:1$ and stirred vigorously. In approximately 2 min, the mixture turned from blue to black and formed stable colloids. After 30 minutes, TEOS was added into the dispersed solution of Co nanoparticles by $[\text{TEOS}]:[\text{H}_2\text{O}]=1:4$. The mixture was stirred at 333 K for 72 hours after stirring at room temperature for 3 hours.

Sample *B*: The second synthesis was done without water except for crystal water to reduce Co^{2+} in the reversed micelle cages. The water for the hydrolysis of TEOS was added after the reduction. The reversed micelles were prepared by mixing 10 ml of toluene, 1.24 g of DDAB, and 8×10^{-4} mol of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ followed by ultrasonic agitation. NaBH_4 was added in the solution by $[\text{BH}_4^-]:[\text{Co}^{2+}]=3:1$. In approximately 1 min, the mixture turned from blue to black and formed stable colloids. After 30 minutes, 0.06 ml distilled water was added and then TEOS was added by $[\text{TEOS}]:[\text{H}_2\text{O}]=1:4$. The mixture was magnetically stirred at 333 K for 72 hours after stirring at room

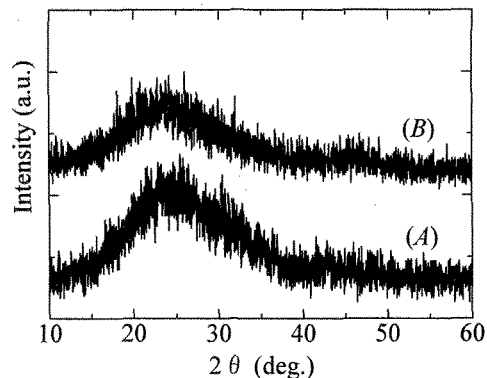


Fig.2 X-ray diagrams of sample *A* and sample *B*

temperature for 3 hours.

3.RESULTS AND DISCUSSION

3.1 Encapsulated Co nanoparticles

Particles were synthesized at different conditions of the water addition. Figure 1 shows the TEM images and the selected area electron diffraction patterns of the encapsulated Co nanoparticles prepared in the reversed micelles (a) with the additional water (sample *A*), and (b) without the water (sample *B*). Encapsulated and well isolated particles were obtained at each condition. The average diameters of the Co nanoparticles are about 1.3 nm and 4.4 nm for the sample *A* and *B*, respectively. The average thicknesses of the silica capsule are about 3.5 nm and 2.2 nm for the sample *A* and *B*, respectively. Only halo rings are observed in the electron beam diffractions for both samples.

Figure 2 shows the X-ray diffraction patterns of the sample *A* and *B*. Only broad diffraction peaks from amorphous silica are observed near $2\theta = 25^\circ$, but clear diffraction peak from the crystalline Co is not observed near $2\theta = 45^\circ$. In these as-prepared samples, clear evidence that the Co particles are crystalline has not been obtained. In the reduction of CoCl_2 by NaBH_4 , it was reported that amorphous Co metal or amorphous Co_2B were formed[9]. The existence of B which are formed in the reduction reaction may prevent the crystallization of Co in our samples.

Figures 3 shows the magnetic hysteresis curves at room temperature for the sample *A* and *B*. Because the Co particles are small and well isolated by silica capsule, the magnetization curves exhibit superparamagnetic nature, namely show nonhysteresis and unsaturation characteristics as indicate in Fig. 3.

3.2 Surface modification

One problem that exists in nanoparticle systems prepared inside the reversed micelle cage is that a large amount of excess surfactant always exists. To concentrate the encapsulated Co nanoparticles which

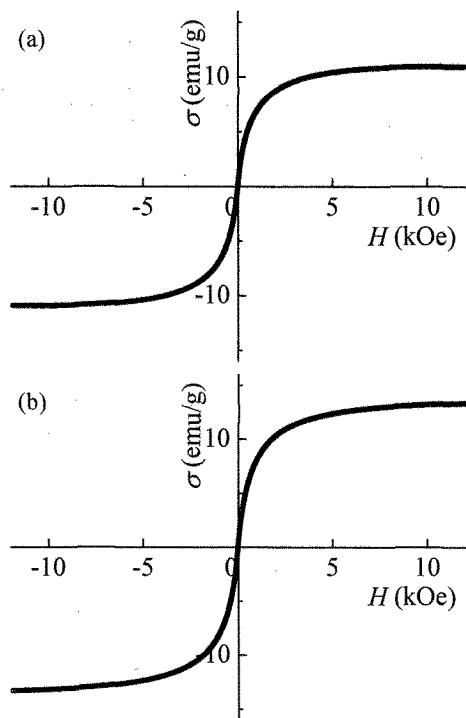


Fig.3 Magnetic hysteresis curves of (a) sample A and (b) sample B

removes the surfactant, ethanol was added to the colloidal solution. An alternative method is to wash the dried powder sample with excess ethanol. In the sample dried immediately after the hydrolysis of TEOS and washed in the ethanol, the black precipitate were separated from the solution after 12 hours. Figure 4 shows the TEM image of the precipitate of sample A. The Co nanoparticles are well separated from one another, indicating that they still are coated with a silica capsule. However, the large cluster in which the silica capsule combined to each other has been formed. It is considered that the combination of the silica capsule is caused by the condensation between -OHs in the capsule surface during drying.

In order to get encapsulated Co particle as an independent particle, it is necessary to eliminate the additional condensations between the surface -OHs of silica capsules. In this study, the surface -OH of silica capsules was modified with HMDS(hexamethyl-disilazane) or TMCS(trimethylchlorosilane) into non-reactive $-\text{CH}_3$ as shown in Fig. 5.

The surface modification with HMDS was carried out as following. HMDS was added to the solution after the hydrolysis of TEOS, and the mixture was stirred vigorously at 343 K for 48 hours. Another method of surface modification was carried out with TMCS. TMCS was added to the solution after the hydrolysis of TEOS. During the reaction, the solution was bubbled with He gas at room temperature for 48

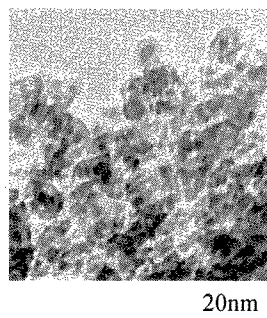


Fig.4 TEM image of the combination of capsules of sample A

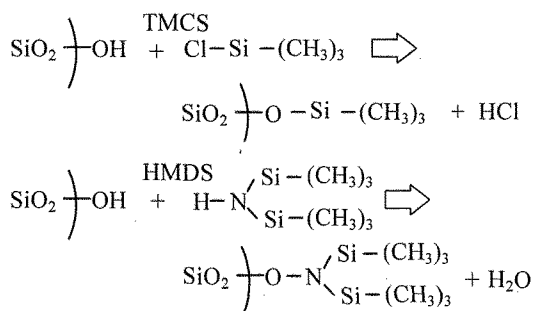


Fig.5 Illustration of surface modifications

hours in order to remove HCl which was created by the reaction. Only in the case of sample A, the mixture turned from black to blue within 10 seconds and the white lumps were precipitated. To remove the surfactant from the surface of the silica capsules, ethanol was added to the past, which remained after drying the solution. No precipitate was formed in both ethanol solutions.

Figure 6 shows the TEM images of the encapsulated Co nanoparticles after each surface modification. For the comparison, the TEM images of the particles which were kept in the liquid for 7 days at room temperature without surface modification were also shown in Figs.6 (a) and (b). In the particles modified with HDMS, the contour of the capsule of both sample A and sample B clarifies and individual particle has been isolated, as shown in Fig. 6(a) and (b) for sample A and sample B, respectively. Though attention is necessary for the ionization of Co by formed HCl, the contour of the capsule of sample B modified with TMCS also clarifies, and individual particle has been isolated as shown in Fig. 6(c). On the other hand, in the sample without modification in as of the liquid, the condensation of the capsule is not observed after 7 days, as shown in Fig. 6(d) and (e) for sample A and sample B, respectively. It is considered that keeping in the condition of the liquid changes surface -OH of silica capsules to the inactivation.

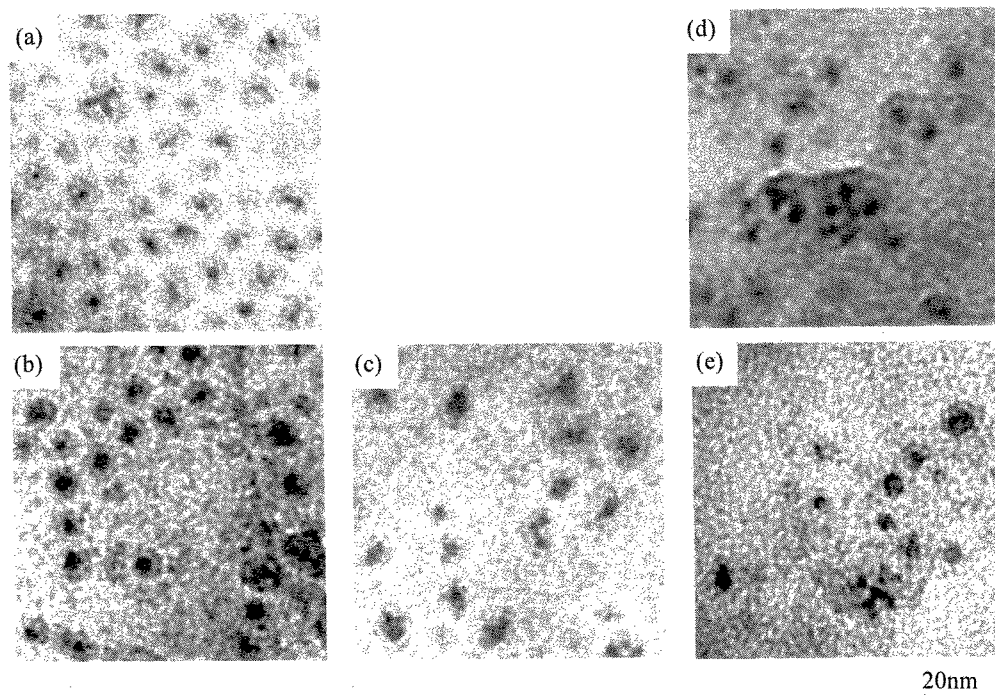


Fig.6 TEM images of encapsulated Co nanoparticles after the surface modification with HMDS of (a) sample A and (b) sample B, (c) with TMCS of sample B, without modification of (d) sample A and (e) sample B

Since the particles which were modified with HDMS or TMCS and which were kept in the condition of the liquid for 7 days without surface modification are not condensed, the sediment does not form in the ethanol solution. In order to get encapsulated Co nanoparticles which remove the surfactant, it will be necessary to examine the method by the magnetic separation using the magnetism of the particles.

4. CONCLUSION

Encapsulated Co nanoparticles have been synthesized with DDAB/toluene reversed micelle solution. Co nanoparticles of about 1.3 nm particle size that the surface was covered with silica capsule of about 3.5 nm thickness, and of about 4.4 nm particle size that the surface was covered with silica capsule of about 2.2 nm thickness were got. It was found that the hydrolysis of TEOS was selectively generated at the Co particle surface, even if the condition of the reaction water was changed. The aggregation of capsules during drying was observed, since the active -OH in silica capsule surface exists immediately after the hydrolysis. The surface modified with HMDS or TMCS was effective in order to get isolated particle without the aggregation. And, active -OHs of silica capsule surface also change to the inactivation by keeping in the liquid for 7 days without surface modification. The magnetization curves of the

encapsulated Co nanoparticles exhibit the superparamagnetic nature.

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