Cobalt Ferrite Nanoparticles Prepared by Coprecipitation/Mechanochemical Treatment

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Cobalt ferrite ($CoFe_2O_4$) nanoparticles have been prepared by chemical coprecipitation, mechanical milling and subsequent thermal treatment. Sodium chloride was added as a diluent during mechanical milling to avoid agglomeration of the particles. Thermal treatment of the as-milled powder at 600 °C produces well-crystallized $CoFe_2O_4$ nanoparticles with an average crystal size of 22.5 nm. The mechanism of nanoparticle growth was discussed.

The preparation of cobalt ferrite ($CoFe_2O_4$) particles has been the subject of extensive investigation because of their wide range of applications.[1] The properties of $CoFe_2O_4$ are highly related to the particle size. It has been indicated that nanocrystalline $CoFe_2O_4$ is beneficial in promoting application properties.[2] Several techniques have been developed to prepare $CoFe_2O_4$ nanoparticles, including sol–gel process,[3] hydrothermal synthesis,[4] chemical coprecipitation method,[5] citrate precursor,[6] mechanical alloying,[7] combustion synthesis,[8] water-in-oil microemulsions,[9] and forced hydrolysis method.[10] But with each of above methods, nanosized $CoFe_2O_4$ powder is rather difficult to be obtained and often has a high degree of agglomeration.

Mechanochemical processing is a novel method for the production of nanosized materials.[11] The method has been widely applied to synthesize a variety of nanoparticles, including ZnS, CdS, $LiMn_2O_4$, SiO_2, and CeO_2.[12] Recently, a diluent, often the by-product of the reaction (NaCl), is added to the starting materials during the mechanochemical processing.[13] It can separate the nanoparticles, prevent their subsequent growth, the synthesized powder not being seriously agglomerated.[14] Removal of the salt matrix is usually carried out by simple washing. Mechanochemical technique is particularly suitable for mass production because it is a simple and inexpensive process.[15] In this paper, $CoFe_2O_4$ nanoparticles were synthesized by the combination of chemical coprecipitation and mechanochemical treatment.

The starting materials were AR-grade $CoCl_2 \cdot 6H_2O$, $FeCl_3 \cdot 6H_2O$, and NaOH with the molar ratio of 1:1:5. $CoCl_2 \cdot 6H_2O$ and $FeCl_3 \cdot 6H_2O$ were dissolved in hydrochloric acid to form acid solution, mixed with NaOH solution, and kept at 60 °C for 1 h to form the precipitates by a temperature-controlled reactor with a magnetic stirrer. Then, the coprecipitates were thoroughly washed with distilled water and dried at 75 °C for 2 h. The precursor thus prepared, NaCl and stainless steel ball of 2.5 mm in diameter were sealed in a 300-mL stainless vial with a ball-to-powder weight ratio of 10:1. The weight ratio of NaCl to precursor was 5:1. Mechanochemical milling was performed in a KM-10 type planetary mill for 4 h at 600 rpm. The as-milled powder was washed with distilled water to remove the diluent, and subsequently heat-treated at 600 °C for 2 h in air to produce the $CoFe_2O_4$ nanoparticles.

The structure of the sample was examined by X-ray diffraction (XRD) using a D/max-γA diffractometer (Cu Kα radiation, $\lambda = 0.154056$ nm). The morphologies of $CoFe_2O_4$ nanoparticles were observed by a JEM-200CX transmission electron microscope (TEM). The average crystal size (D) of the nanoparticle was calculated from diffraction peak half-widths according to Scherrer's equation.

Figure 1 shows the XRD patterns of (a) the coprecipitated precursor, (b) powder milled for 4 h and subsequently washed, and (c) powder after calcination at 600 °C for 2 h. After chemical coprecipitation of the starting materials, no peak was evident, and the coprecipitated product was amorphous. A new peak associated with $CoFe_2O_4$ was observed in the XRD pattern of the sample milled for 4 h and washed, it is deduced that the crystallization of $CoFe_2O_4$ is initiated in the coprecipitated powder and the crystallization degree can be accelerated by the mechanochemical milling. Calcination of the milled powder at 600 °C for 2 h promoted the crystallization of particles and consequently resulted in the formation of the well-crystallized $CoFe_2O_4$ nanoparticles. The calculated XRD crystal size of the nanoparticle was 22.5 nm. Our early experiments have indicated that the $CoFe_2O_4$ particles without mechanochemical treatment were extremely agglomerated and incompletely crystallized.

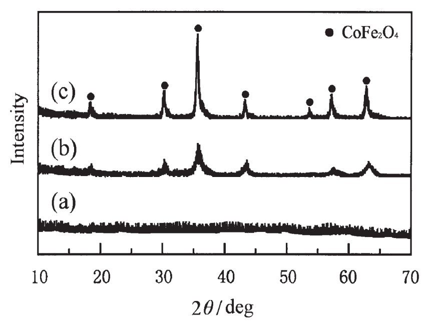

Figure 1. XRD patterns of (a) the precursor, (b) powder milled for 4 h and subsequently washed, (c) powder after calcination at 600 °C for 2 h.

Figure 2 shows the XRD patterns of the $CoFe_2O_4$ nanoparticles heat-treated at 600–800 °C. The intensities of the $CoFe_2O_4$ peaks increased with increasing the calcination temperature. Figure 3 shows the TEM image of the $CoFe_2O_4$ nanoparticles treated at 600 °C with uniform crystal size of about 30 nm in diameter, which is in good agreement with the XRD calculation. Both separated and moderately agglomerated particles seem to be present. The $CoFe_2O_4$ particles prepared without NaCl addition were also seriously agglomerated and monodispersive nanoparticles could not be obtained.

Figure 4 shows the size distribution of $CoFe_2O_4$ nanoparticles obtained from TEM image. It can be observed that most of

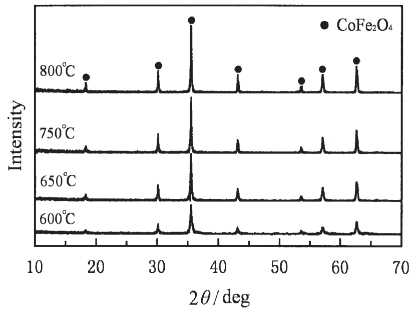

Figure 2. XRD patterns of the $CoFe_2O_4$ nanoparticles prepared at different calcination temperatures.

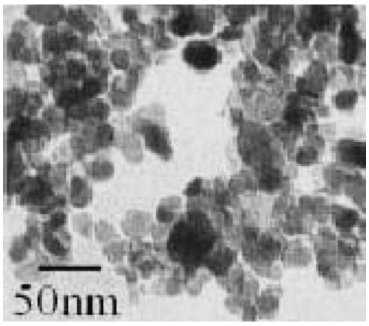

Figure 3. TEM micrograph of the $CoFe_2O_4$ nanoparticles (600 °C calcination).

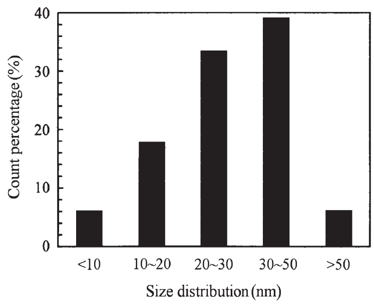

Figure 4. Size distribution of the $CoFe_2O_4$ nanoparticles from TEM image (600 °C calcination).

the particles are about 10–50 nm in diameter.

Straight line of ln D against $1/T$ is plotted in Figure 5 according to the Scott equation given below on the assumption that the nanocrystallites grow homogeneously,[16] which approximately describes the nanocrystallite growth during annealing:

$$D = C\exp(-E/RT) \quad (1)$$

where D is the XRD crystal size, C is a constant, E is the activation energy for nanocrystallite growth, R is the gas constant, and T is the absolute temperature. The activation energy calculated from the slope of the line is small as $E = 15.54\,\text{kJ/mol}$. It can be considered that the crystal grows primarily by means of an interfacial reaction.

In summary, well-crystallized cobalt ferrite ($CoFe_2O_4$) nanoparticles of about 30 nm in crystal size have been successfully synthesized by heating the as-milled powder after mechanochemically processing the coprecipitated precursor with NaCl as a diluent. Mechanical milling can greatly accelerate the crystallization of $CoFe_2O_4$ particles. The estimated value of the activation energy indicates that the nanocrystallite mainly grows by means of an interfacial reaction. Research on application of the $CoFe_2O_4$ nanoparticles is in progress. This novel route is also applicable for the synthesis of other functional nanoparticles.

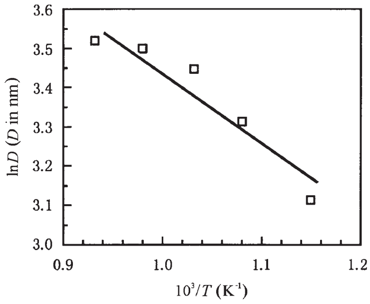

Figure 5. Plot of ln D against $1/T$ for the equation $D = C\exp(-E/RT)$.

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