Journal of Korean Powder Metallurgy Institute
Vol. 14, No. 3, 2007

Synthesis of Multiferroic Nanocomposites by a Polyol Method

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(Received April 20, 2007; Accepted June 8, 2007)

Abstract The material design and synthesis are of important to modern science and technology. Here, we report the synthesis of multifunctional nanomaterials with different properties: ferroelectric $YMnO_3$ and multiferroic materials such as $CoFe_2O_4$-$YMnO_3$, Fe_3O_4-$YMnO_3$, $CoFe_2O_4$-$Cd_{0.85}Zn_{0.15}S$, and Fe_3O_4-$Cd_{0.85}Zn_{0.15}S$ nanocomposites by using a chemical synthesis process. These results provide a simple and convenient synthesis process to produce multifunctional nanocomposites.

Keywords : Multifunctional nanocrystals, Monodisperse, Nanomaterial, Ferromagnetic, Ferrimagnetic, Polyol method

1. Introduction

Nano scale materials have attracted huge interest due to their size-dependent properties and many important technological applications. These nanomaterials provide the possibility for enhanced functionality and multifunctional properties in contrast with their bulk counterparts. An important research trend in nanomaterials is the scale up from single component nanomaterials to composites nanomaterials with different shape, different properties, and different materials. These nanocomposites contain two or more functionalities and these can exhibit novel physical and chemical properties. Recently, there have been a few reports of design of heterostructure nanocomposite present; metal-metal composite (Au-Ag, and FePt-Ag)[1], metal-semiconductor (FePt-CdS, γ-Fe_2O_3-(ZnS, CdS, HgS), and Au-CdSe(S))[2-4], and metal-metal oxide (Au-Fe_3O_4, Ag-Fe_3O_4, FePt-MnO, FePt-Fe_3O_4, and Ag-$CoFe_2O_4$)[5-8]. The term multiferroism has been coined to describe materials in which two or all three of ferroelectricity, ferromagnetism, and ferroelasticity occur in the same phase. The coupling between ferromagnetism and ferroelectricity results in magnetostriction and the consequent application of piezomagnets as magnetomechanical actuators. There have been a number of reports on $BaTiO_3$-$CoFe_2O_4$ multiferroic composites[9] and related materials. Here, we reported synthesis process and variation of microstructure for ferroelectric $YMnO_3$ single material and $CoFe_2O_4$-$YMnO_3$, Fe_3O_4-$YMnO_3$, $CoFe_2O_4$-$Cd_{0.85}Zn_{0.15}S$, and Fe_3O_4-$Cd_{0.85}Zn_{0.15}S$ nanocomposites system by using a modified polyol method.

2. Experiments

All experiment was carried out using standard Schlenk techniques in an argon atmosphere. Monodispersed $YMnO_3$ nanoprticles were synthesized by a modified polyol method as reported Sun *et al*[10]. Yttrium acetylacetonate ($Y(C_5H_7O_2)_3 \cdot xH_2O$; 99.99%),

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manganese(II) acetylacetonate ($[CH_3COCH=C(O)CH_3]_2Mn$; 99.95%), oleic acid ($CH_3(CH_2)_7CH=CH(CH_2)_7CO_2H$; 90% tech.), oleylamine ($CH_3(CH_2)_7CH=CH(CH_2)_8NH_2$; 70%, tech.), octyl ether ($[CH_3(CH_2)_7]_2O$; 99%), 1,2-Hexanedecanediol($CH_3(CH_2)_{13}CH(OH)CH_2OH$; 90%, tech.), anhydrous ethyl alcohol, and hexane are purchased from Sigma-Aldrich. A typical experiment begins with mixing stoichiometric amounts of yttrium (0.1 mmol) and manganese (0.1 mmol), reducing reagent 1,2-hexanedecanediol (5 mmol), oleic acid (3 mmol), and oleylamine (3 mmol), in 10.0 ml of octyl ether solution at room temperature. The solution is then heated to reflux at 290°C and kept at this temperature for 30 min. Afterward, the heated mental is removed and the product solution is allowed to cool to room temperature. Under ambient conditions, EtOH (20 ml) was added to the mixture and a black material was precipitated and separated via centrifugation. The black product was dissolved in hexane (10 ml) in the presence of small amount of oleic acid and oleylamine precipitated with ethanol (20 ml) and separated via centrifugation (6,000 rpm, 20 min). The final product was redispersed into 10 ml of hexane.

The 3 nm $CoFe_2O_4$ and 6 nm Fe_3O_4 ferrimagnetic nanoparticles were synthesized by using a modified polyol method. A mixture of 0.1 mmol of Co(II)(acac)/or 0.1 mmol of Fe(acac), 0.2 mmol of Fe(III)(acac), and 3 mmol of 1,2- hexadecanediol was added to 250 ml three necked flask under the argon gas. Dioctyl ether (20 ml) was into the flask and the solutions stirred for 30 min at room temperature. The reaction flask was then heated to 100°C and kept for 15 min. The mixture was heated to 295°C and reflux at this temperature for 30 min. Finally, the reaction mixture was allowed to cool to room temperature and we obtained the ferromagnetic nanoparticles after above purification process. In order to synthesize $CoFe_2O_4$ (or Fe_3O_4)-$YMnO_3$ nanocomposite system, 3 nm $CoFe_2O_4$ (or 6 nm Fe_3O_4) in hexane were mixed with 2 mmol Y(acac), 2 mmol Mn(acac), 5 mmol oleic acid, 5 mmol oleylmine, 2 mmol 1,2-hexadecanediol and 10 ml benzyl ether under the argon gas. The mixture was first heated to 85°C to remove the hexane for 10 min. Then the mixture was heated to reflux (~260°C) for 1 h. The heat source was then removed and the dispersion was allowed to cool to room temperature. The black material was isolated for the purification and centrifugation. To synthesize the $CoFe_2O_4$ (or Fe_3O_4)-$Cd_{0.85}Zn_{0.15}S$ nanoparticle, 3nm $CoFe_2O_4$ (or 6nm Fe_3O_4) in hexane were mixed with Cd(acac) (0.85 mmol), Zn(0.15 mmol), Sulfur powder(1 mmol), 1,2-hexadecanediol (2 mmol), oleic acid (5 mmol), oleylamine (5 mmol) and benzyl ether (15 ml) were mixed and magnetically stirred under a flow of argon gas. The heating process was same as $YMnO_3$ composites. The crystalline structure of nanoparticles was measured using the X'pert x-ray diffractometer (PW1827) (Phillips) at room temperature with a CuKa radiation source at 40 kV and 30 mA. The dimension of nanoparticles was measured using JEM100CX II transmission electron microscopy (TEM; JEOL) imagnes at an operating voltage of 60 kV, using in house prepared copper grids (Cu, hexagon, 300 mesh). Samples for TEM analysis were prepared by drying a hexane dispersion of the nanoparticles on amorphous carbon coated copper grids. Analysis of images was carried out using ImagePro 4.1 software (MediaCybernetics). VSM measurements were carried out using a Waker HF 9H electromagnet with a Lakeshore 7300 controller and a Lakeshore 668 power supply.

3. Results and Discussions

The θ-2θ XRD pattern of $YMnO_3$ nanoparticles with a Y to Mn ratio of 1:1 indicated that the almost all peaks can be identified with the single hexagonal $YMnO_3$ phase (JCPDS 25-1079). Fig. 1 shows a typical low-magnification TEM image of $YMnO_3$ with different amount of metal(Y and Mn) and surfactant(oleic acid plus oleylamine) mole ratio. When the chemical reaction was performed in the presence

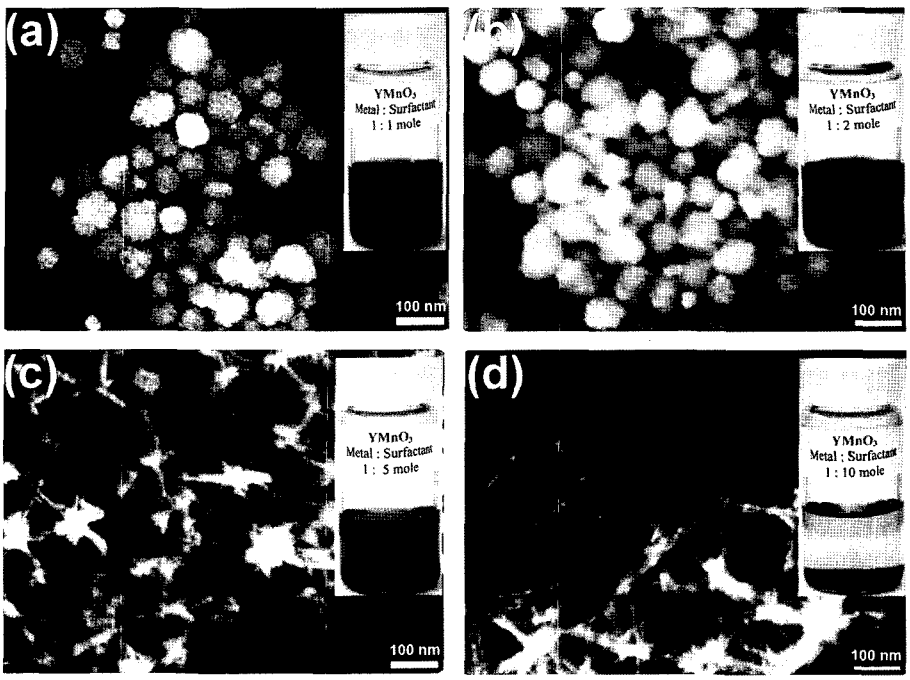

Fig. 1. Low magnification TEM images of $YMnO_3$ with metal (Y and Mn) and surfactant (Oleic acid and Oleylamine) mole ratio and 10 ml samples: (a) 1:1, (b) 1:2, (c) 1:5, (d) 1:10.

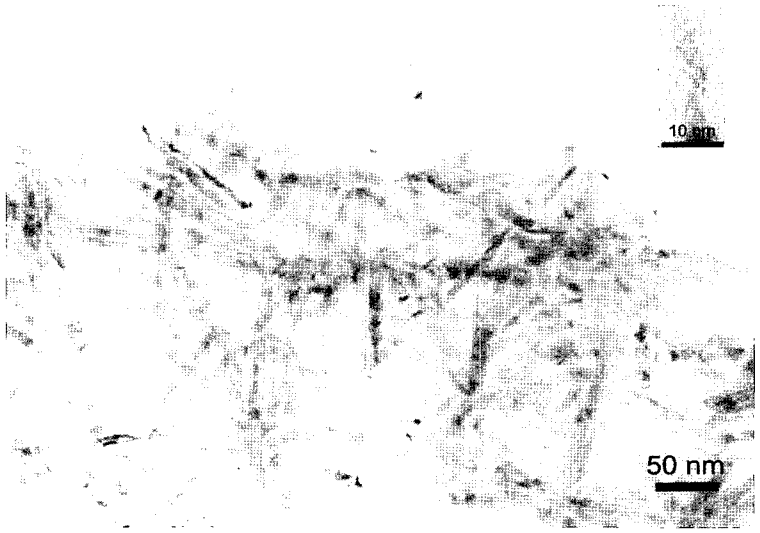

Fig. 2. HRTEM image of star-like $YMnO_3$ nanoparticles and the magnification.

of different metal and surfactant mole ratio, we can see the phase shape transition from spherical to star-like nanoparticles. An increase in the relative molar ratio of surfactant produced a star-like shape and the solution was more rapidly precipitated. D. Zitoun *et al*[11], X. Zhong *et al*[12], and T. Ould-Ely *et al*[13] reported a similar nanoparticle shape from Mn oxide and they explained in detail that the anisotropy of crystal structure was identified as a main driving force for the growth of anisotropic nanostructures.

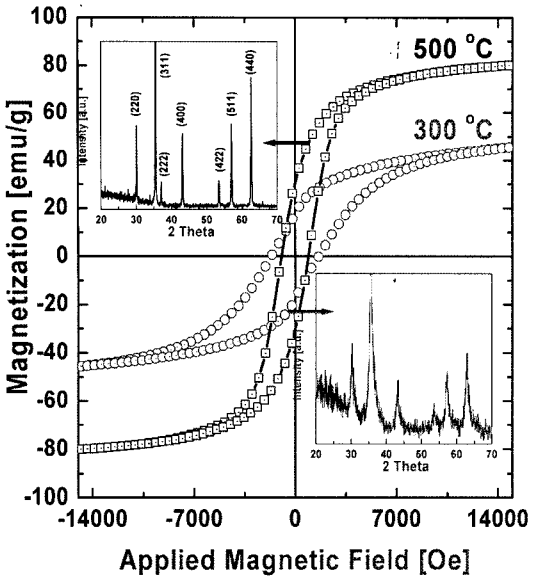

Fig. 3. Variation of magnetization with applied magnetic field for the $CoFe_2O_4$ nanoparticles at room temperatures and the inset shows the XRD patterns for with and without post annealing process.

Fig. 2 shows high resolution TEM (HRTEM) images of the star-like $YMnO_3$ nanoparticles. The HRTEM image shows that the well-defined lattice plane, and a higher magnification image shows a good crystallinity of layer-by layer growth orientation. Hence, we believe that under the control of the appropriate metal and surfactant molar ration, it is possible to form star-like $YMnO_3$ nanoparticles.

Fig. 3 shows the field-dependent magnetization of $CoFe_2O_4$ nanoparticles with and without post annealing at 500°C at room temperature, and the inset shows the powder XRD diffraction patterns. Large variations of the hysteresis curves were obtained after post annealing process. The magnetization value of the sample post-annealed at higher temperature (500°C) shows strongly enhanced ferromagnetic property against the case without post annealing. This could be attributed to preferential crystallization for post annealed samples as indicated by the XRD patterns. Typical X-ray diffraction patterns for the $CoFe_2O_4$ nanoparticles with and without post annealing are shown in figure 3. As seen in the fig-

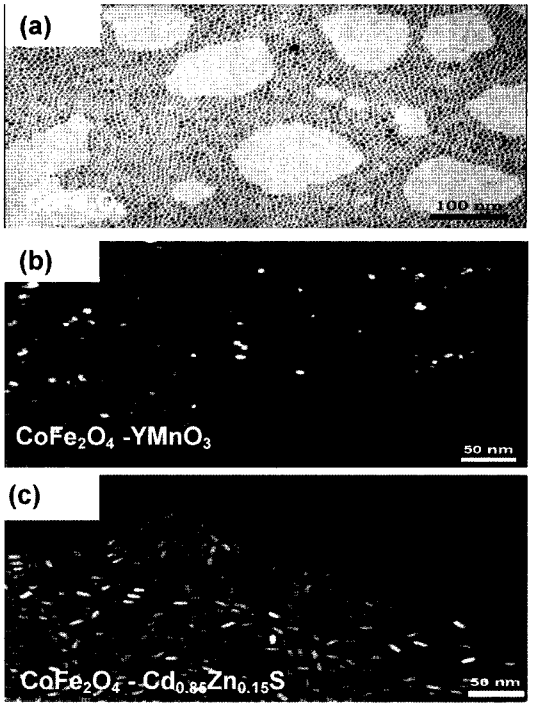

Fig. 4. TEM images of (a) single $CoFe_2O_4$; (b) $CoFe_2O_4$-$YMnO_3$; (c) $CoFe_2O_4$-$Cd_{0.85}Zn_{0.15}S$ composite nanoparticle system.

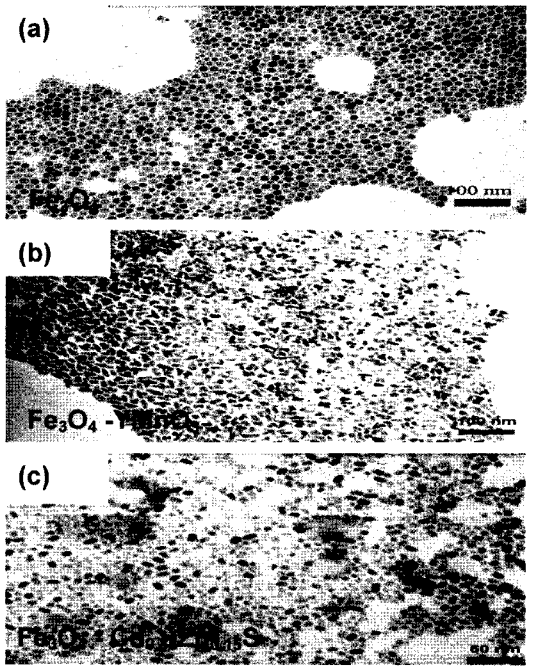

Fig. 5. TEM images of (a) single Fe_3O_4; (b) Fe_3O_4-$YMnO_3$; (c) Fe_3O_4-$Cd_{0.8}5Zn_{0.15}S$ composite nanoparticle system.

ure, the diffraction peaks were clearly broadened, which could be the result of the reduced particle size and a tendency of crystallization is increased with increasing annealing temperature. The XRD peaks can be indexed to (220), (311), (400), (422), (511), and (440) planes of a cubic unit cell, which corresponds to that of a $CoFe_2O_3$ structure (JCPDS. 22-1086).

In order to create multiferroic materials design with new shape, we synthesized $CoFe_2O_4$-$YMnO_3$/$Cd_{0.85}Zn_{0.15}S$, and Fe_3O_4-$YMnO_3$/$Cd_{0.85}Zn_{0.15}S$ nanocomposites by a modified polyol method. We selected $CoFe_2O_4$ and Fe_3O_4 as a magnetic phase, and $YMnO_3$ and $Cd_{0.85}Zn_{0.15}S$ as an electric phase.

Fig. 4 and 5 show low magnification TEM images of $CoFe_2O_4$- and Fe_3O_4-ferroelctric composite, respectively. Fig. 4(a) and 5(a) present the images of single $CoFe_2O_4$ and Fe_3O_4 nanoparicles, which have a spherical shape and an average particle diameter of 6 nm and 15 nm, respectively. The $CoFe_2O_4$-$YMnO_3$ (figure 4(b)) composites exhibit a larger size with a diameter of 10 nm and the produced $CoFe_2O_4$-$Cd_{0.85}Zn_{0.15}S$ (figure 4(c)) composite shows the bar shaped particles with dimensions of 14 nm× 7 nm. When synthesizing Fe_3O_4-$YMnO_3$ composite, the T and bar-shaped particles were produced (figure 5(b)). Figure 5(c) shows TEM image of Fe_3O_4-$Cd_{0.85}Zn_{0.15}S$ mixed with spherical and bar shaped composite nanoparticles.

4. Summary

We reported the synthesis of multiferroic $CoFe_2O_4$-$YMnO_3$, Fe_3O_4-$YMnO_3$, $CoFe_2O_4$-$Cd_{0.85}Zn_{0.15}S$, and Fe_3O_4-$Cd_{0.85}Zn_{0.15}S$ nanocomposites by a polyol method. We demonstrated a simple synthesis process with the investigation of magnetic properties and microstructure for nanocomposites. Through controlling the synthetic parameters, high-yield nanocomposites with different morphologies could be obtained.

Acknowledgements

This work was supported by the Korea Research Foundation Grant (214-C00036, 2005).

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