XPS and Magnetic Properties of CoFe$_2$O$_4$ Nanoparticles Synthesized by a Polyacrylamide Gel Route

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Cobalt ferrite CoFe$_2$O$_4$ nanoparticles were prepared via a polyacrylamide gel route and were characterized by XRD, SEM, XPS and VSM. It is demonstrated that the sample (designated S1) prepared without using the cross-linking agent bis-acrylamide has an average grain size of 45 nm, while the sample (designated S2) prepared by introducing an amount of bis-acrylamide which is about 1.5 times the amount of acrylamide has an average grain size of 23 nm. The two kinds of particles are shaped like spheres. The cation distribution is determined, from Co 2p$_{3/2}$ and Fe 2p$_{3/2}$ XPS spectra, to be [Co$_{0.1}$Fe$_{0.9}$][Co$_{0.9}$Fe$_{1.1}$]O$_4$ for both the samples, where [Co$_{0.1}$Fe$_{0.9}$] and [Co$_{0.9}$Fe$_{1.1}$] represent cations in the tetrahedral and octahedral sites, respectively. Magnetic measurement reveals a saturation magnetization of 67.3 A·m$^2$·kg$^{-1}$ for sample S1 and 62.3 A·m$^2$·kg$^{-1}$ for sample S2, but a similar coercivity of about 87.5 kA·m$^{-1}$ for both the samples. [doi:10.2320/matertrans.M2012151]

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1. Introduction

Cobalt ferrite CoFe$_2$O$_4$ with a cubic spinel-type structure has been intensively studied in recent years due to its high magnetocrystalline anisotropy, saturation magnetization, magnetostriction, and coercivity at room temperature.$^{1-5}$ These outstanding properties make CoFe$_2$O$_4$ attractive for a wide variety of applications, such as magneto-optic recording medium, high density data storage device, stress sensor and microwave absorption.$^{3-6}$ The cationic distribution of cobalt ferrite can be described in terms of the chemical formula (Co$_{1-x}$Fe$_{x}$)[Co$_{1-x}$Fe$_{x}$]O$_4$, where (Co$_{1-x}$Fe$_{x}$) and [Co$_{1-x}$Fe$_{x}$] denote cations in the tetrahedral (A) and octahedral (B) sites, respectively. The variation of the cation distribution between A and B sites, which depends on the sample preparation process (especially the thermal history of the sample),$^{7}$ generally leads to different magnetic properties in cobalt ferrite.$^8$

Magnetic nanoparticles exhibit many unique properties like superparamagnetism compared to bulk materials, and are particularly used in the fields of biology and medicine. Due to their distinctive properties and special applications, magnetic nanoparticles have attracted a great deal of research interests recently. CoFe$_2$O$_4$ nanoparticles have been widely synthesized using various methods, such as sol–gel, microemulsion, chemical co-precipitation, hydrothermal synthesis and microwave synthesis.$^{9-15}$ Among these methods, the sol–gel route is very attractive, having the main advantage of easy control of chemical composition. Up to now, in the sol–gel synthesis of CoFe$_2$O$_4$ particles, the gel is built up by chemical and physical bonds between the chemical species. In this work, we introduce a different sol–gel route—polyacrylamide gel route—to prepare CoFe$_2$O$_4$ nanoparticles. In this method, the solution containing the required cations is gelled by the formation of polymer network polymerized from acrylamide/bis-acrylamide monomers. The formed polymer network, which provides a structural framework for the growth of particles, plays a role in controlling the particle size and morphology.

2. Experimental

In terms of the atomic ratio Fe : Co = 2 : 1, stoichiometric amounts of Fe(NO$_3$)$_3$·9H$_2$O and Co(NO$_3$)$_2$·6H$_2$O were dissolved into an aqueous nitric acid solution, where the total molarity of the Fe$^{3+}$ and Co$^{2+}$ cations was 1.5 mol·L$^{-1}$. Then to the solution were successively added ethylenediamine-tetraacetic acid (EDTA) (in the molar ratio 1.5 : 1 with respect to the cations), glucose (about 20 g in 100 ml) and acrylamide/bis-acrylamide monomers (in the molar ratio 9 : 1 with respect to the cations). Every step mentioned above was accompanied by constant magnetic stirring to make the solution transparent and uniform. The mixed solution was adjusted to a pH of ~2 with aqueous ammonia, and then heated at 80°C to initiate the polymerization reaction. A few minutes later a viscous polyacrylamide gel was formed. The gel was dried at 120°C for 24 h in a thermostat drier. The obtained xerogel was then calcined at 500°C for 3 h in a tube furnace to yield CoFe$_2$O$_4$ nanoparticles.

The phase purity of the as-prepared samples was checked by means of X-ray powder diffraction (XRD) with Cu $K\alpha$ radiation on a D8 Advance diffractometer. The particle morphology was investigated by a JSM-6701F field-emission scanning electron microscope (SEM). The electron binding energies for the elements were measured by X-ray photoelectron spectroscopy (XPS) on a PHI-5702 multifunctional X-ray photoelectron spectrometer. The magnetic properties of the samples were investigated using a vibrating sample magnetometer (VSM) at room temperature.

3. Results and Discussion

Figure 1 shows the XRD patterns of CoFe$_2$O$_4$ samples prepared separately without using the crosslinking agent bis-acrylamide (designated as sample S1) and by introducing a
small amount of bis-acrylamide which is about 1/5 times the amount of acrylamide (designated as sample S2). For both the samples, all diffraction peaks can be indexed to the cubic CoFe$_2$O$_4$ spinel phase without detectable impurities. The average grain size of the samples S1 and S2 is evaluated from the line broadening of the (311) peaks using Debye–Scherrer formula to be 45 and 23 nm, respectively.

Figure 2 shows the SEM images of the as-prepared CoFe$_2$O$_4$ samples. The particles appear to be heavily aggregated. The main reason leading to this phenomenon is due to the high surface activity and strong magnetism of CoFe$_2$O$_4$ nanoparticles, consequently making it difficult to disperse them uniformly at the SEM sample preparation. Despite their blurred edges due to the aggregation, the particles can be still well-seen to be shaped like spheres with a narrow diameter distribution. The average particle sizes of the samples S1 and S2 are centered around 45 and 25 nm, respectively. From the SEM and XRD results, it is demonstrated that the introduction of an appropriate amount of bis-acrylamide leads to the production of CoFe$_2$O$_4$ nanoparticles with a relatively smaller size.

In the present gel method, acrylamide/bis-acrylamide is polymerized to form a polymer network, which provides a structural framework to hold the precursor solution in place and for the growth of particles. Figure 3 schematically illustrates the polymerization reaction of acrylamide/bis-acrylamide and the formation of polymer network. Acrylamide monomer, terminating in an aminocarbonyl group (–CONH$_2$), is polymerized in a head-to-tail fashion into long polymeric chains without branching or interconnection. Bis-acrylamide consists of two acrylamide monomers linked through a methylene group (–CH$_2$–), and is regarded as an excellent crosslinking agent. When an amount of bis-acrylamide is introduced into the solution together with acrylamide, the growing polyacrylamide chains are expected to be crosslinked through the bis-acrylamide to form a complex web of interconnected loops and branches.$^{16}$ It has been shown that the crosslinking agent bis-acrylamide plays an important role in reducing the pore size of the gel matrix,$^{17}$ and this is why the introduction of an amount of bis-acrylamide leads to the production of smaller sized CoFe$_2$O$_4$ nanoparticles.

Figures 4–6 show the XPS spectra of Co 2$p_{3/2}$, Fe 2$p_{3/2}$ and O 1$s$, respectively. The XPS signals of the two CoFe$_2$O$_4$ samples are seen to be very similar. In Fig. 4, the Co 2$p_{3/2}$ XPS spectra are well fitted into three peaks situated on 779.8, 781.9 and 785.9 eV. The binding energies at 779.8 and 781.9 eV are assigned to Co$^{2+}$ ions in octahedral sites and tetrahedral sites, respectively. For both the samples, the ratio of Co$^{2+}$ ions in octahedral to tetrahedral sites is obtained, from the integrated intensity of the fitted peaks, to be about 3 : 2. The signal at 785.9 eV is characterized to be the satellite peak of Co 2$p_{3/2}$ main line.

In Fig. 5, the Fe 2$p_{3/2}$ main peak, shouldering with a satellite peak at 718.3 eV, is fitted into two signals positioned at 710.7 and 713.7 eV, indicating the existence of Fe species also in two different lattice sites. The binding energy at 710.7 eV arises from Fe$^{3+}$ ions in octahedral sites, while the binding energy at 713.7 eV is caused by Fe$^{2+}$ ions in tetrahedral sites. According to the integrated intensity of the fitted doublets, the distribution of Fe$^{3+}$ ions for both the samples is obtained to be about 70% in octahedral sites and about 30% in tetrahedral sites.

The O 1$s$ XPS signals shown in Fig. 6 are divided into three peaks at 529.6, 531.7 and 533.8 eV. The main peak at 529.6 eV is attributed to the contribution of the crystal lattice oxygen. However, the exact assignment of the higher binding energy peaks is rather complex and controversial as numerous factors like surface defects, contaminants, impurities, or chemisorbed oxygen species could result in the appearance of
the shoulder peaks.\textsuperscript{18,19} It is noted that the shoulder peaks in sample S2 appear more intense than those in sample S1, which suggests that they are caused mainly by the chemisorbed oxygen species, because the smaller sized nanoparticles generally exhibit a higher adsorption capability. Based on the above XPS results, the chemical formula of our cobalt ferrite nanoparticles can be expressed as $\text{(Co}_{0.4}\text{Fe}_{0.6})\text{[Co}_{0.6}\text{Fe}_{1.4}]\text{O}_4$.

Figure 7 shows the magnetic hysteresis loops of the CoFe$_2$O$_4$ samples measured at room temperature. The saturation magnetization ($M_s$), which is determined by extrapolating the plot of $M$ vs. $1/H$ using data at high magnetic fields, is observed to be 67.3 A·m$^2$·kg$^{-1}$ for sample S1 and 62.3 A·m$^2$·kg$^{-1}$ for sample S2. The slight decrease in $M_s$ for sample S2, compared to sample S1, can be explained by its relatively smaller particle size and hence...
the enhanced surface effects. For magnetic nanoparticles, various surface defects become appreciable, leading to a magnetically disordered (or magnetically dead) layer at the particle surface. The surface layer, which has no contribution to the magnetization, is expected to become more remarkable by reducing the particle size, consequently leading to the particle size-dependant $M_s$. In addition, the coercivities of the two samples appear to be very similar with a value of $87.5 \text{kA} \cdot \text{m}^{-1}$.

4. Conclusions

Two samples of CoFe$_2$O$_4$ nanoparticles separately with average grain size of 45 and 23 nm were prepared by a polyacrylamide gel route. The production of the smaller sized particles is ascribed to the introduction of the crosslinking agent bis-acrylamide in precursor solution. SEM observation shows that the as-prepared CoFe$_2$O$_4$ particles have nearly perfect spherical shapes. According to the XPS results, the cation distribution of the two samples can be described by the chemical formula $(\text{Co}_{0.4}\text{Fe}_{0.6})[(\text{Co}_{0.6}\text{Fe}_{1.4})\text{O}_4]$, where cations in parentheses and square brackets denote the occupation of the tetrahedral and octahedral sites, respectively. The saturation magnetization is obtained to be $67.3 \text{A} \cdot \text{m}^2\cdot\text{kg}^{-1}$ for the 45 nm sample and $62.3 \text{A} \cdot \text{m}^2\cdot\text{kg}^{-1}$ for the 23 nm sample, and the slight difference in magnetization can be attributed to the size-dependent surface effects. In addition, the two samples exhibit a similar coercivity of $87.5 \text{kA} \cdot \text{m}^{-1}$.

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