Syntheses and Characterization of Co/Fe₃O₄ Nanocomposites by Polyol Process

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ABSTRACT

Co, Fe₃O₄ and Co/Fe₃O₄ nanoparticles were synthesized by a polyol process in order to develop their new applications and improve chemical, magnetic properties. The synthesis involved a polyol process using Fe, Co acetylacetonate as precursors and 1-2 hexadecanediol as the polyol. The synthesized Fe₃O₄ and Co/Fe₃O₄ nanocomposite particles were monodispersed and self arrayed ranging in size of 8~10 and 10~25 nm, respectively. The Co nanoparticle has a crystallite size of 10~40 nm. The synthesized nanoparticles were characterized by their structural, morphological, compositional and magnetic properties using TEM-EDS, XRD, and PPMS techniques.

Key words : Nanocomposites, Nanoparticles, Co, Fe₃O₄, Polyol process

1. Introduction

Electrical, chemical, mechanical properties of nanoparticles play important roles in modern nanotechnologies. Also these nanoparticles have unique properties that make new applications possible.

There has been immense interest in the use of Co nanoparticles as monodomain magnets in areas such as magnetic recording media, MRI contrast agents, and environmental remediation.¹⁻³⁾ Unfortunately, the magnetic properties of Co particles decreases from oxidation in an ambient atmosphere.⁴⁾

Fe₃O₄ nanoparticles can also be utilized as monodomain magnets with no deterioration of their magnetic properties.¹⁻³⁾ However, the magnetic properties of these nanoparticles is not sufficiently strong enough for practical applications.

For these reasons, a new approach to the application of these materials is required.

Composites are the easiest and most effective way to overcome the above mentioned obstacles and these newly formed particles can be expected to exhibit some novel properties that maybe useful in other new applications.

The present study examines ways to maximize the benefits of some of the interesting properties of nanoparticles by creating composites.⁵⁻¹⁰⁾

Because the polyol process is simple and easy to conduct, it was used to prepare individual Fe₃O₄ and Co nanoparticles^{11,12)} in addition to the composite of the two.

The Co/Fe₃O₄ composite nanoparticles were prepared with the aim of utilizing the positive properties of each nanoparticle: the high magnetic properties of Co and the chemical stability of Fe₃O₄.

The structural, morphological, compositional and magnetic properties of Co, Fe₃O₄ and composite particles are characterized and discussed below.

2. Experimental

2.1. Synthesis of Fe₃O₄ nanoparticles

An iron acetylacetonate [Fe(acac)₃] (SIGMA ALDRICH, 99.9+%) was used as a precursor.

A 0.01 M solution of 1,2-hexadecanediol(HDD, SIGMA ALDRICH, 90%) was prepared in 20 ml absolute phenyl ether. Then, a clear red colored 0.002 M precursor solution was obtained by adding an appropriate quantity of Fe(acac)₃ powder to a 0.01 M HDD solution while stirring. Argon gas was flushed through the resulting solution after stirring.

To this solution, the surfactants, such as 0.006 M oleic acid (CANTO CHEM.) and 0.006 M oleylamine (WAKO) were added to improve the stability and avoid the agglomeration of the nanoparticles.

This mixture was heated at 200°C for 30 min and then for an additional 30 min at 265°C. The heated solution was allowed to cool at room temperature.

The resulting black solution was added to 20 ml ethanol. Additional 1-2 drops of oleic acid (0.05 ml) and oleylamine (0.05 ml) were added.

The solution was centrifuged for 10 min. Then 10 ml of hexane was added to the solution, and the resulting solution was again centrifuged for 10 min. This washing process was repeated and followed by size selection process.

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Fig. 1. XRD pattern of synthesized Fe₃O₄ nanoparticles by polyol process.

2.2. Synthesis of Co nanoparticles

The precursors used for synthesis of Co nanoparticles were cobalt acetylacetonate [Co(acac)₃] (SIGMA ALDRICH, 99.9+%), 1,2-hexadecanediol (SIGMA ALDRICH, 90%), oleic acid (CANTO CHEM.), oleylamine (WAKO) and phenyl ether.

A similar reaction procedure as that for Fe₃O₄ nanoparticles was followed, except for some reaction conditions, such as temperature, reaction time and molar ratio of the surfactant. This will be discussed further below.

2.3. Co/Fe₃O₄ nanocomposite

Again, a process similar to that used for the synthesis of the nanoparticles was followed for the synthesis of the Co/Fe₃O₄ nanocomposite. Synthesized Co nanoparticles were used as seeds and Fe as the precursor in a method described as seed mediated growth.¹³⁾

The amounts of Co nanoparticles was changed in order to get a more orderly arranged nanocomposite morphology.

To reduce the processing time of composite nanoparticles, Fe precursor was added to the just prepared Co nanoparticles (at 200°C without cooling to room temperature) and continued heating at same temperature to make Co-Fe₃O₄ composite.

After synthesizing all of the nanoparticles, they were characterized using X-ray diffraction (X'Pert APD system), Transmission Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy (TEM Tecnai 20-EDS Phoenix) and Physical Property Measurement System (PPMS).

3. Results and Discussion

3.1. Fe₃O₄ nanoparticles

Fig. 1 shows the XRD pattern of synthesized Fe₃O₄ nanoparticles in the diffraction angle range of 20~80°. The matching of 'd' values from the standard diffraction pattern confirms the phase pure formation of magnetite structure.

Fig. 2 shows a typical TEM image of as-synthesized magnetite nanoparticles, from which the size distribution and mor-

Fig. 2. TEM image of synthesized Fe₃O₄ nanoparticles by polyol process.

Fig. 3. Hysteresis loop of synthesized Fe₃O₄ nanoparticles by polyol process.

phology of the nanoparticles can be determined. The synthesized Fe₃O₄ nanoparticles were ranged in the size of 8~10 nm, and they are monodispersed and self arrayed.

Fig. 3 shows the hysteresis loop of magnetite nanoparticles which reveals the variation of magnetization with in the magnetic field. The single line hysteresis curve provides evidence for the characteristic superparamagnetism phenomenon. The saturation magnetization is 18 emu/g.

3.2. Co nanoparticles

Co nanoparticles showed different size distribution and morphology due to changes in the synthesis conditions.

The EDS study of synthesized Co nanoparticles as seen in Fig. 4 confirmed that no foreign entities are formed except Cu and C, which is due to the use of carbon coated Cu grid for recording the EDS spectrum.

Fig. 5 (a) shows TEM image of Co nanoparticles synthesized with reaction temperature of 200°C for 30 min after adding 0.006 M surfactant in stirring condition. No formation of particles was observed.

Fig. 4. TEM-EDS image of Co nanoparticles.

Fig. 5. TEM image of synthesized Co nanoparticles in different conditions; (a) use of 0.006 M surfactant, reaction temperature of 200°C for 30 min with stirring condition, (b) reaction temperature of 200°C for 30 min followed by 240°C for another 30 min, (c) with non stirring condition, (d) use of 0.002 M surfactant, (e) except hold process (directly heated to 240°C).

Image Fig. 5 (b) shows Co nanoparticles prepared with similar conditions as that of Fig. 5 (a), but the reaction temperature was held at 200°C for 30 min before carrying out the final reaction at 240°C for 30 min.

These Co nanoparticles were ranged in size of 10~40 nm. The morphology of Co nanoparticles prepared under other conditions (Fig. 5 (c) non stirring, Fig. 5 (d) 0.002 M surfactant, Fig. 5 (e) except hold process) agglomerated, and the

Fig. 6. Hysteresis loop of Co nanoparticles.

Fig. 7. XRD pattern of Co/Fe₃O₄ nanocomposites.

shape and size distribution of these particles is not certain.

The hysteresis loop of Co nanoparticles is shown in Fig. 6. These particles display superparamagnetism with a saturation magnetization of 73 emu/g, almost four times than that of Fe₃O₄ nanoparticles.

3.3. Co/Fe₃O₄ nanocomposite

Fig. 7 shows the XRD pattern of as-synthesized Co/Fe₃O₄ nanocomposite. The XRD pattern reveals the presence of only two materials, Co and magnetite.

Fig. 8 (a) shows the TEM image of Co/Fe₃O₄ nanocomposite synthesized by the addition of 0.04 g Co for seeding. The image shows well distributed particles that were ranged in size of 10~25 nm. The inset shows an image of the ring shaped diffraction caused by the formation of polycrystalline particles.

With an increase in Co seed from 0.04 to 0.12 g, there was a significant growth of particles with disordered morphology. A variety of irregular morphologies, such as spherical, hexagonal, and rod-like shape, are seen in Fig. 8 (b) and (c).

Fig. 9 shows TEM image of Co/Fe₃O₄ simultaneously synthesized using Co and Fe₃O₄ particles. The particle size dis-

Fig. 8. TEM image of Co/Fe₃O₄ composite with a different amount of Co nanoparticles; (a) Co 0.04 g, (b) Co 0.07 g, and (c) Co 0.12 g.

Fig. 9. TEM image of Co/Fe₃O₄ nanocomposites. (Co, Fe₃O₄ simultaneously synthesized)

tribution for these nanocomposite is different, and in part, seems like agglomeration.

Fig. 10 shows the EDS mapping images of Co/Fe₃O₄ nanocomposite and reveals more details of the distribution of Fe, Co, O elements.

The Co and Fe₃O₄ nanoparticles were distributed in similar amount at positions A and B. However, site C had the rectangular shaped Co element alone while the spherical shaped Fe₃O₄ was seen separately at site D.

The addition of a small amount of Co particles to the Fe precursor leads to uniform sized spherical nanocomposite particles. This is due to the controlled heterogeneous nucleation reaction.

Fig. 10. EDS mapping image of Co/Fe₃O₄ nanocomposites.

Fig. 11. Hysteresis loop of Co/Fe₃O₄ nanocomposites.

When this seeding amount is increased, more nucleation sites are available and there is no control over the growth of particles. This leads to agglomerated nanocomposite particles of different sizes.^{14,15)}

Hence, the excess amount of Co is responsible for an increase in the particle size of the Co/Fe₃O₄ composite.

Fig. 11 shows the hysteresis loop of Co/Fe₃O₄ nanocomposites. These nanocomposites also show the typical superparamagnetism behavior with saturation magnetization of 37.7 emu/g, which is almost twice than that of Fe₃O₄ and half than that of Co.

Thus, magnetic materials such as Co/Fe₃O₄ with good chemical stability and relatively high magnetic property when compared to a single Fe₃O₄ were found to be more effective in many applications.

These results suggest that Co/Fe₃O₄ nanocomposite are chemically stable and may have advantages in applications such as bio-sensor or as drug delivery materials over commonly used Fe₃O₄.^{16,17)}

4. Conclusion

Well-dispersed nanoparticles of Co, Fe₃O₄ and Co/Fe₃O₄ nanocomposites were successfully synthesized by Polyol process.

All synthesized particles showed the characteristic superparamagnetism behavior.

The size distribution and morphology of Co/Fe₃O₄ composite particles were affected by an increase in the amount of Co particles. Although Co/Fe₃O₄ nanocomposite has a lower saturation magnetization (half) than that of Co particles, its saturation magnetization level is superior (almost double) to that of Fe₃O₄ particles.

Moreover, Co/Fe₃O₄ is relatively chemically stable and hence may be useful in applications such as bio-sensor or as drug delivery materials.

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