FACILE SYNTHESIS OF FeCo NANOPARTICLES BY ONE-POT POLYOL PROCESS

K. Pratap,[a] Manam Sreenivasa Rao[b] and Mandava Venkata Basaveswara Rao[a]*

Keywords: Ferromagnetic, FeCo, nanoparticles, polyol, vibrating sample magnetometer

Ferromagnetic FeCo nanoparticles were prepared by a simple one-pot polyol process and followed by simple annealing treatment. The prepared ferromagnetic FeCo nanoparticles have a spherical shape and the size was controlled by the annealing temperature. Importantly, single FeCo phase was obtained at 400°C and these samples have spherical shape and size about 50 nm. While at a higher temperature (at 600°C) the nanoparticles have very lower aggregation and have higher coercivity. The prepared FeCo nanoparticle at low temperature with excellent magnetic properties is to be considered as a potential candidate for many applications.

* Corresponding Authors
E-Mail: professormandava@gmail.com
[a] Department of Chemistry, Krishna University, Machilipatnam, A.P, India
[b] Department of Chemistry, C. R. College, Chilakaluripet-522616, Andhra Pradesh, India

Introduction

High magnetization FeCo nanoparticles are to be considered as potential materials for the utilization in various biological applications such as hyperthermia, magnetic resonance imaging, targeted drug delivery, and other applications[1-4]. Many wet- chemical methods have been reported to prepare the synthesis of FeCo nanoparticles that includes sol-gel method[5], thermal decomposition[6], borohydride reduction[7], co-precipitation[8], chemical vapor deposition[9] and polyol process[4]. Among them the polyol process has many advantages over other methods because it is an eco-friendly, requires simple instrumentation and also a cost-effective route for the synthesis of magnetic nanoparticles[10]. Literature methods suffer from the limitations via prolonged reaction time, use of hazardous chemicals, undesirable oxide formation and complex synthesis setups[4,11]. Thus investigated on the polyol process to prepare the FeCo nanoparticles.

Many researchers reported the use of polyol to synthesize the FeCo nanoparticles. For example, Kodama et al. prepared the FeCo nanoparticles using polyol process[12]. Karipoth et al. prepared FeCo particles with different shapes by polyol method[13] and Huba et al. fabricated the FeCo spherical particles using polyol process[14]. However, the reported polyol processes and followed by high-temperature annealing to obtain FeCo nanoparticles. Unfortunately, the high-temperature annealing processes yielded nanoparticles that have very high aggregation and also challenging to suspend in water for many applications. In addition to that, the high-temperature annealing is an energy consuming process. Thus, it is worthy of consideration to propose a simple route with a low-temperature annealing process to prepare FeCo nanoparticles.

Since the polyol process is mostly affected by the alkali concentration and reaction temperature[4,13], herein, we used exact boiling temperature of polyol solution and high concentration alkali. Then, it is possible to get the FeCo nanoparticles at low-temperature annealing. Moreover, we investigated the possible annealing temperature to obtain pure phase FeCo and studied their magnetic properties.

Experimental

All reagents used in this investigation such as ferrous chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$), cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$), sodium hydroxide(NaOH), and ethylene glycol (EG) were obtained from Sigma-Aldrich Co. and are used without any further purification.

$FeCl_2 \cdot 4H_2O$, $CoCl_2 \cdot 6H_2O$ were suspended in ethylene glycol (EG) in a 1:1 stoichiometric ratio. The resultant solution was heated up to the boiling temperature of polyol (EG) to enhance reduction process and hydroxide ion concentration was regulated by adding NaOH (3 M) solution. It was kept for 2-hours under reflux condition then cooled down to room temperature with continuous stirring. After that, the solution was washed several times with ethanol and black colored nanoparticles were collected by magnetic separation. The wet sample was then dried in an oven at 60°C for 12 h. To get the crystalline particles, the as-synthesized particles were annealed at different annealing temperature (350,400 and 600° C) with a ramp rate of 5° C/min for 2-hours by passing pure hydrogen gas.

The nanoparticles morphology of the sample was observed by a Tecnai F-30 transmission electron microscope (TEM) operated at 300 kV. X-ray diffraction (XRD) data of the as-prepared powder samples were obtained in the 2θ range of 20-80° using a Bruker AXS D8 advanced diffractometer. Magnetization measurements of the representative samples were performed by using a vibrating sample magnetometer (VSM, Lakeshore 7304) at room temperature.

Results and discussion

Figure 1 shows the XRD patterns of the prepared samples at different annealing temperatures. All of the diffraction peaks for 400°C, 600°C annealed samples possessed the single phase of FeCo[2], but the 350°C sample has additional peak which is corresponds to maghemite peak along the FeCo peaks[4]. Thus the 400°C and 600°C is the suitable condition to obtain pure FeCo phase without additional phases.

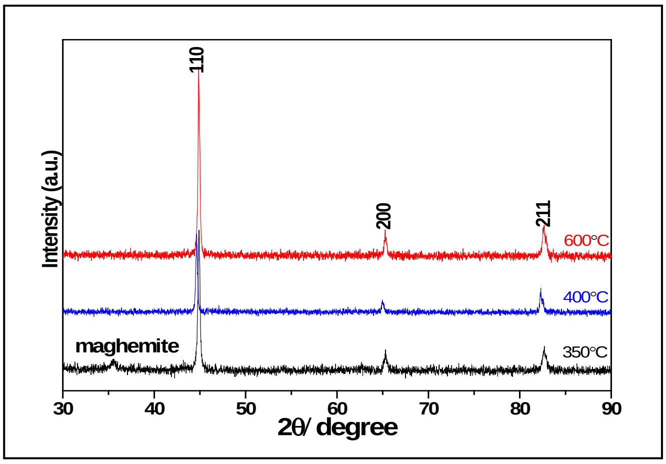

Figure 1. X-ray diffraction patterns of prepared samples.

The morphology of the prepared samples at 350°C was displayed in **Figure 2.** It shows that two kinds of particles were observed with different sizes. The reason for this could be that the annealing temperature was not enough to get a pure phase. It was also evident that in the XRD pattern for this sample and had two phases. Therefore, the mixture of phases was found at this annealing temperature and formed nanoparticles were aggregated and very small size of nanoparticles. While the single FeCo phase is obtained at the annealing temperature about 400°C, and 600°C. At the 400°C, the nanoparticles are in size of ~45 nm, as shown in **Figure 3**.

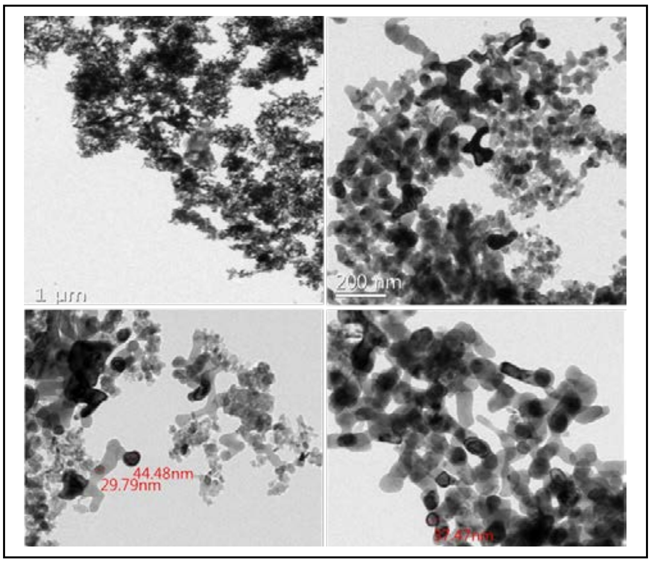

Figure 2. TEM images of FeCo nanoparticles prepared at 350° C

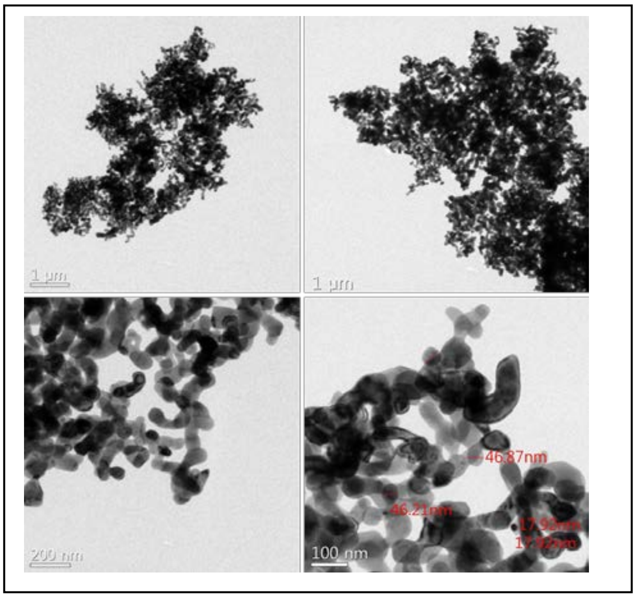

Figure 3. TEM images of FeCo nanoparticles prepared at 400° C.

Figure 4 shows the morphology of the nanoparticles prepared by annealing at 600°C. It demonstrated that the particles size is about ~90 nm and are little agglomerated and larger in size when compared to the other two samples which were annealed at a lower temperature. In addition to this, the FeCo nanoparticles are most stable owing to the thin oxide layer coating on the surface[13] so that it can be exploited for a wide variety of applications.

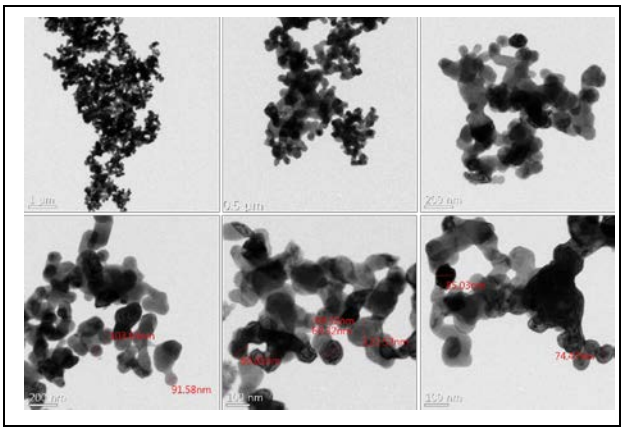

Figure 4. TEM images of FeCo nanoparticles prepared at 600° C

The magnetic hysteresis curves of FeCo nanoparticles were obtained by a VSM (Figure 5)at room temperature. **Figure 5**, indicated that the bigger FeCo nanoparticles (annealed at 600°C), shown the higher saturation magnetizations (Ms) value of 122 emu/g, than other samples, whereas samples annealed at 350, 400°C have the M_S values of 87, 109 emu/g, respectively as the particle gets smaller, the effective magnetic volume accounts for lower proportion and the Ms value decreases[15]. The coercivity (H_c) values are 101, 106 and 366 Oe for samples annealed at 350,400 and 600°C, respectively. It is found that both the M_s and H_c were higher for the sample annealed at 600°C and lower for 350°C due to the size of the FeCo nanoparticles. Therefore, the prepared FeCo nanoparticles are exhibiting the ferromagnetic nature with strong M_S values and are useful for many applications.

 DOI: http://dx.doi.org/10.17628/ecb.2019.8.150-152

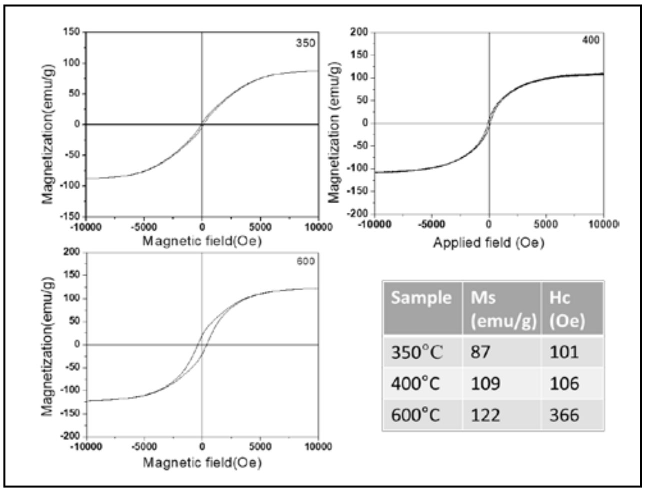

Figure 5. Magnetization curves of prepared samples and magnetic properties presented in table.

Conclusions

In summary, FeCo nanoparticles have been prepared through a one-pot polyol method via annealing process. The effect of the annealing temperature on the size and magnetic properties of FeCo samples was thoroughly explored. It is found that the annealing temperature plays a crucial role in controlling the size and magnetic properties of nanoparticles. The prepared FeCo particles at 600°C showed higher saturation magnetization, found air stable and are having many applications.

References

[1]Tang, Y. J., Parker. F. T., Harper. H., Berkowitz. A. E., Jiang. Q., Smith, D. J., Brand, M., Wang, F. $Co_{50}Fe_{50}$ fine particles for power frequency applications, *IEEE Trans. Magn.* 2004, *40(4)*, 2002-2004. DOI: **10.1109/TMAG.2004.832505**

[2]Abbas, M.., Nazrul, M., Rao, B. P., Ogawa, T., Takashi, M., and Kim, C. G., One-pot synthesis of high magnetization air-stable FeCo nanoparticles by modified polyol method, *Mater. Lett.* 2013, *91*, 326-329. DOI: 10.1016/j.matlet.2012.10.019

[3]Hütten, A., Sudfeld, D., Ennen I, Reiss, G., Hachmann, W., Heinzmann, U., Wojczykowski, K., Jutzi, P., Saikaly, W., and Thomas, G., New magnetic nanoparticles for biotechnology, *J. Biotechnol.* 2004, *112*, 47-63. DOI: 10.1016/j.jbiotec.2004.04.019

[4]Kuchi, R., Lee, K.-M., Lee, Y., Luong, C. H., Lee, K.-D., Park, B.-G., Jeong, J.-R. Synthesis of Highly Magnetic FeCo Nanoparticles Through a One Pot Polyol Process Using All Metal Chlorides Precursors with Precise Composition Tunability, *Nanosci. Nanotechnol. Lett.* 2015, *7*, 734–737. DOI: 10.1166/nnl.2015.2016

[5]Carta, D., Mountjoy, G., Gass, M., Casula, M. F. and Corrias, A., Structural characterization study of FeCo alloy nanoparticles in a highly porous aerogel silica matrix *J. Chem. Phys.* 2007, *127(20)*, 204705-204705-9. DOI: 10.1063/1.2799995

[6]Tzitzios, V., Basina, G., Niarchos, D., and Hadjipanayis, G., Synthesis of air-stable FeCo nanoparticles *J. Appl. Phys.* 2011, *109*, 07A313-07A313-3. DOI: doi.org/10.1063/1.3540387

[7]Kim, C. W., Kim, Y. H., Cha, H. G., Kwon, H. W., and Kang, Y. S., Synthesis and Characterization of Highly Magnetized Nanocrystalline $Co_{30}Fe_{70}$ Alloy by Chemical Reduction *J. Phys. Chem. B*, 2006, *110(48)*, 24418–24423. DOI: 10.1021/jp064440+

[8]Shin, S. J., Kim, Y. H., Kim, C. W., Cha, H. G., Kim, Y. J. and Kang, Y. S., Preparation of magnetic FeCo nanoparticles by coprecipitation route *Curr. Appl. Phys.* 2007, *7(4)*, 404-408. DOI: 10.1016/j.cap.2006.09.012

[9]Sun, C., Lee, J. S. H. and Zhang, M., Magnetic nanoparticles in MR imaging and drug delivery *Adv. Drug. Deliv. Rev.* 2008, *60(11)*, 1252-56. DOI: 10.1016/j.addr.2008.03.018

[10]Mendoza-Resendez, R., Luna, C., Barriga-Castro, E. D. and Serna, C. J., Control of crystallite orientation and size in Fe and FeCo nanoneedles *Nanotechnology* 2012, *23(22)*, 225601. DOI: 10.1088/0957-4484/23/22/225601

[11]Douvalis, A. P., Zboril, R., Bourlinos, A. B., Tucek J., Spyridi, S. and Bakas, T., A facile synthetic route toward air-stable magnetic nanoalloys with Fe-Ni/Fe-Co core and iron oxide shell. *J. Nanopart. Res.* 2012, *14(16)*, 1130. DOI: 10.1007/s11051-012-1130-z

[12]Kodama, D., Shinoda, K., Sato, K., Sato Y., Jeyadevan B., Tohji, K., Synthesis of Fe-Co Alloy Particles by Modified Polyol Process *IEEE Trans. Magn.* 2006, *42(10)*, 2796-2798. DOI: 10.1109/TMAG.2006.880072

[13]Karipoth, P., Thirumurugan, A. and Joseyphus, R. J., Synthesis and magnetic properties of flower-like FeCo particles through a one-pot polyol process *J. Colloid Interface Sci.* 2013, *404*, 49-55. DOI: 10.1016/j.jcis.2013.04.041

[14]Huba, Z. J., Carroll, K. J., Carpenter, E. E., Synthesis of high magnetization FeCo alloys prepared by a modified polyol process, *J. Appl. Phys.* 2011, *109*, 07B514. DOI: 10.1063/1.3544430

[15]Yang, H., Shen, L. C., Zhao, L. J., Song, L. Z., Zhao, J. Z., Wang, Z. C., Wang, L., Zhang, D., Magnetic properties of nanocrystalline $Li_{0.5}Fe_{2.1}Cr_{0.4}O_4$ ferrite *Mater. Lett.* 2003, *57*, 2455-2459. DOI: 10.1016/S0167-577X(02)01266-1

Received: 15.04.2019
Accepted: 26.05.2019.