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One-pot synthesis of Fe-Co nanospheres by modified polyol process and their structural, magnetic studies

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Abstract. Fe-Co nanoparticles stabilized by polyvinylpyrrolidone (PVP) have been prepared using modified polyol process. When 5 mmol of PVP was used, aggregated nanoparticles with irregular shapes were resulted; whereas on increasing the PVP concentration to 10 mmol, highly spherical nanoparticles were obtained. In the present work, the influence of non-ionic stabilizer viz. PVP on the synthesis of spherical nanoparticles and their structural, macromagnetic properties have been reported.

1. Introduction

Synthesis of magnetic nanoparticles is of vast interest because of their applications such as ultrahigh density data storage [1], magnetic resonance imaging [2], ferrofluids [3], magnetic hyperthermia treatment [4] and drug delivery [5]. Synthesizing magnetic nanoparticles with narrow size distribution is a significant task for most of the applications. A variety of chemical methods such as co-precipitation [6], thermal decomposition [7], polyol process [8,9] and sonochemical synthesis [10] are reported for synthesizing nanoparticles. Among all the methods, polyol process has been demonstrated as an excellent choice for synthesizing highly crystalline and monodispersed magnetic nanoparticles, as firstly reported by Micheal Figlarz et al. [11]. Among all the binary transition metal alloys, Fe-Co alloys are well known to possess a unique combination of high saturation magnetization, high Curie temperature, low magnetocrystalline anisotropy and good strength. They are ideally suited for applications requiring high flux densities [12]. The saturation magnetization of Fe₇₂Co₂₈ is 242 emu/g [13,14]. Synthesis of Fe-Co nanoparticles by polyol process is successful in controlling the size and morphology [8]. Fe-Co nanoparticles with a variety of morphologies such as spherical [8], dice [9], microcages [15], hollow spheres [16] and acicular [17] have been synthesized through chemical methods. When compared to other chemical synthesis techniques, polyol process is the best one for fine tuning the morphology of the synthesized nanoparticles [18]. Synthesizing spherical nanoparticles is a subject of intense interest for various technologically important soft magnetic applications, since the morphology is also one of the deciding parameters of coercivity [19]. Moreover, spherical particles do not introduce shape anisotropy. To avoid conflicts due to the shapes in the magnetic properties, we have synthesized spherical nanoparticles. We followed the method reported by Daisuke Kodama et al. [9]. They have reported the synthesis of Fe-Co nanocubes by varying refluxing temperature from

403 K to 470 K and they were able to synthesize nanocubes at 403 K. We modified the synthesis process performing the reaction at 470 K but varying the stabilizer concentration which had resulted in Fe-Co nanospheres. Then, structural and macromagnetic properties of as-synthesized Fe-Co nanospheres have been studied.

2. Experimental

Nanoparticles of Fe-Co were synthesized by the modified polyol process [9]. All the chemicals were obtained from commercial sources with ultra purity and used without further purification. Iron chloride tetrahydrate was procured from M/S Fluka and cobalt acetate tetrahydrate and other reagents were procured from M/S Merck chemicals, India. In a typical synthesis, 5 mmol of iron chloride tetrahydrate, 5 mmol of cobalt acetate tetrahydrate, 0.4 mol of sodium hydroxide and polyvinylpyrrolidone (PVP) were dissolved in 1 litre of ethylene glycol and purged with 99.99 % pure nitrogen gas (N₂ gas) for two hours. The solution was refluxed at boiling point for two hours under the nitrogen atmosphere. The formation of Fe-Co nanoparticles was witnessed by the colour change from dark red to black. The solution was cooled to room temperature and flocculent viz. ethanol was added to precipitate, and the supernatant was discarded. Using a strong magnet synthesized Fe-Co nanoparticles were separated. The resultant Fe-Co nanoparticles were washed thrice with ethanol and acetone to remove the reaction by-products and allowed to dry at ambient atmosphere. The above synthesis was performed using different PVP concentrations of 5 mmol, 10 mmol and the as-synthesized samples were named as S1 and S2 respectively. The typical reaction mechanism for the formation of Fe-Co nanoparticles is [20,21]:



3. Results and Discussion

The main issue in synthesizing iron based metallic nanoparticles is oxidation. During the synthesis, the presence of trace amount of oxygen would aid the formation of ferrites [22]. Hence, in the present synthesis, the precursor solution was degassed with N₂ gas for two hours to eliminate the dissolved molecular oxygen and the whole reaction was carried out under nitrogen atmosphere. When the precursors were refluxed at boiling point the colour of the solution changed from dark to black which indicated the formation of Fe-Co nanoparticles. The colour of the synthesized nanoparticles may give a hint about the formation of Fe-Co nanoparticles. The oxide counterpart of Fe-Co is CoFe₂O₄, having a dark brown colour that was not evidenced during the synthesis [22,23]. We ended with black powder. X-ray diffraction (XRD) pattern of as-synthesized Fe-Co nanoparticles is shown in Figure 1(a) which apparently confirms the formation of disordered bcc phase, the peak can be easily assigned to (110) plane reflection of bcc Fe-Co alloy (JCPDS card number 44-1433). The composition of the as-synthesized nanoparticles was measured by atomic absorption spectroscopy (AAS) and was found to be 42.2% of iron and 57.7% of cobalt. The iron content in the resultant nanoparticles is always less than the charged [24]. For both the samples S1 and S2 iron and cobalt content is almost same. The functionalization of PVP was studied with Fourier transform infrared spectroscopy (FT-IR). As it can be seen from Figure 1(b), all the vibrations of the PVP are clearly noticed in both the samples (S1 and S2), confirming the functionalization of PVP over Fe-Co nanoparticles [25]. The slight deviation in the vibrations is due to the interaction of PVP molecules with the alloy nanoparticles and the observed vibrations are listed in table 1. Figure 2(a) and Figure 2(b) shows the agglomerated Fe-Co nanoparticles and spherical nanoparticles. Morphology and dimensions of the as-synthesized nanoparticles strongly depend on reaction conditions such as temperature, concentration of precursors, and the molar ratio between the repeating unit of stabilizer and precursors [26]. In the present work, for the synthesis of both the samples S1 and S2, all the conditions were constant except the stabilizer concentration. When 5 mmol of stabilizer was used, more surface of the nanoparticles is exposed to the solvent resulting in agglomeration to reduce the total surface area and the energy of the coated

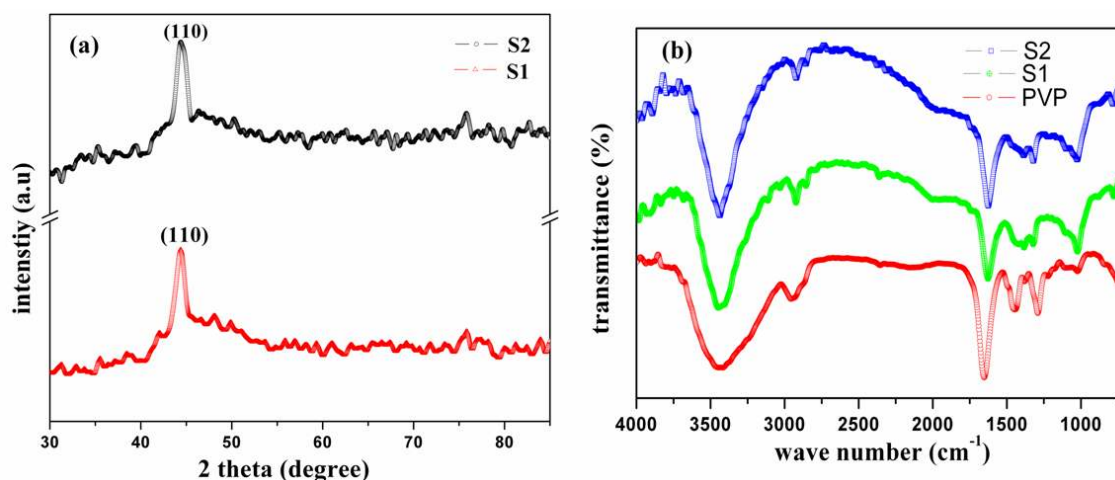


Figure 1 (a). XRD pattern of Fe-Co nanoparticles functionalized with PVP (S1 and S2)

Figure 1 (b). FT-IR spectrum of PVP functionalized Fe-Co nanoparticles (S1 and S2)

surface. The strength of this process is proportional to the amount of the stabilizer with respect to any given amount of non-coated material. A larger amount of the stabilizer (10 mmol), allows for coating a larger surface, which becomes inactive and thus limits agglomeration [19]. If the synthesized nanoparticles are magnetic, the magnetic dipolar interactions also tend to agglomerate, which is possible because the particles are mobile in the reaction medium. The other possible reason for obtaining spherical shape at 10 mmol of PVP concentration could be the reaction time employed (two hours), as it is obvious that all the nucleated nanoparticles will transform into thermodynamically stable spherical shape, when they are heated for sufficiently longer time [18, 19, 27]. In total, the reaction temperature and higher concentration of stabilizer (10 mmol) facilitated the synthesis of spherical nanoparticles.

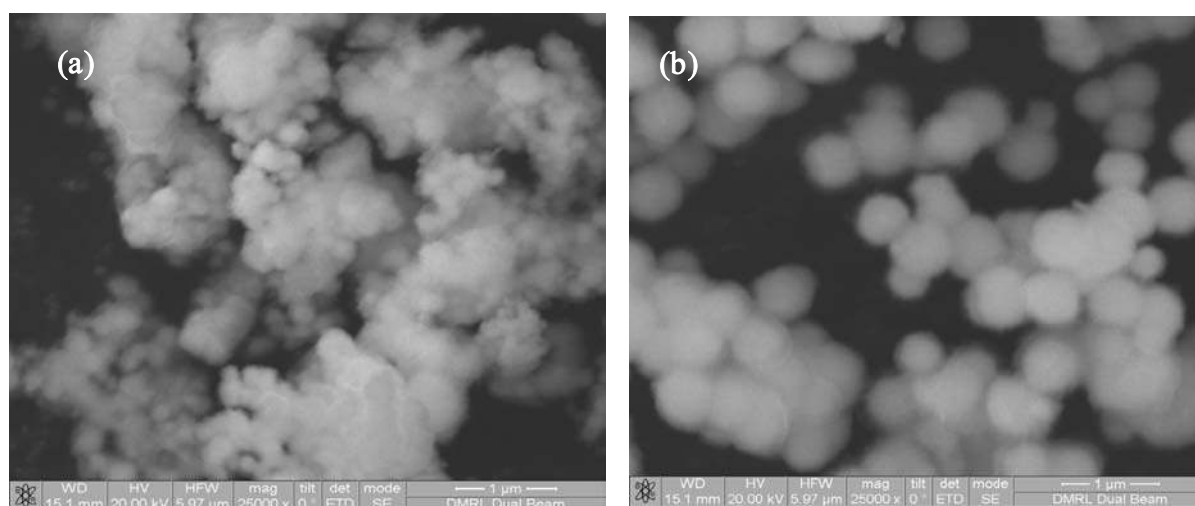


Figure 2. Scanning electron micrograph of Fe-Co nanoparticles (a) S1 and (b) S2

Table 1. FT-IR Bond vibration of the samples S1 and S2

Wave number (cm ⁻¹)	Bond vibration
3454	O-H
2940	C-H
1660	C=O
1482	PVP bond
1457	absorption
1280	N→H-O complex

Table 2. Macromagnetic properties of the samples S1 and S2

Parameter	S1	S2
Coercivity (Oe)	93.4	158.4
Saturation magnetization Ms (emu/g)	141.8	104.9
Magnetic remanence (Mr) (emu/g)	0.099	0.140
Squareness (Mr/Ms)	0.041	0.077

The magnetic hysteresis measurements were carried out at room temperature in vibrating sample magnetometer (VSM) and the hysteresis loop is shown in Figure 3(a). The region highlighted in Figure 3(a) is magnified and shown as Figure 3(b) to demonstrate the ferromagnetic nature of S1 and S2. The macromagnetic properties of the samples are listed in table 2. In the present study, coercivity values have been determined as 93.4 and 158.4 Oe for the samples S1 and S2 respectively. The increase in coercivity in S2 may be due to the size dependent property of the synthesized nanoparticles. By increasing the stabilizer concentration, the coercivity increases by 65 Oe. It is well known that in single domain particles, the coercivity tends to reduce with reduction in the particle size [25]; when the particle size is reduced less than 10 nm, it apparently falls on the super paramagnetic limit [29,30].

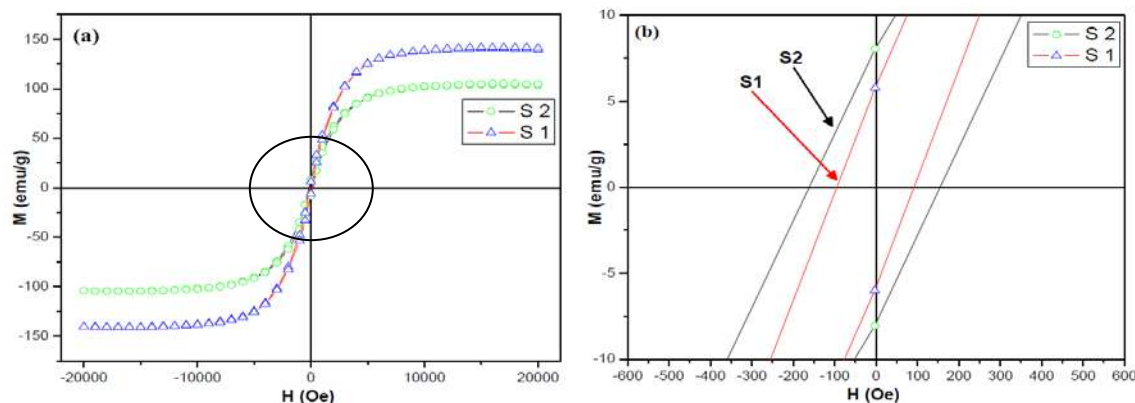


Figure 3. (a) Hysteresis loops of Fe-Co nanoparticles (S1 and S2). (b) Magnified hysteresis loop of S1 and S2

The observed saturation magnetization values for the samples S1 and S2 are 141.8 and 104.9 emu/g respectively. These values are significantly reduced as compared to that of their bulk values Fe₅₀Co₅₀ (211 emu/g) [15]. The reasons for the reduction of saturation magnetization are decrease in iron content in the samples i.e. Fe_{42.2}Co_{57.7} than charged in the reaction Fe₅₀Co₅₀, lack of crystallinity of the as-synthesized nanoparticles (disordered bcc phase) and the stabilizer masking. Annealing the samples in inert atmosphere can greatly enhance the saturation magnetization. Currently we are exploring the possible route to synthesize colloidal Fe-Co nanoparticles for sophisticated soft magnetic applications.

4. Conclusions

In summary, Fe-Co nanospheres have been synthesized using modified polyol process and their structural, macromagnetic properties have been studied. The X-ray diffraction pattern confirms the formation of disordered bcc phase; FT-IR studies show the functionalization of PVP on Fe-Co

nanospheres. The increased PVP concentration from 5 mmol to 10 mmol effectively yields spherical nanoparticles, which may be due to the larger amount of PVP molecules which efficiently stabilizes the nucleated nanoparticles. Adversely, the increased concentration of PVP also contributes to decrease the saturation magnetization from 141.8 to 104.9 emu/g, other probable reason for the reduction in saturation magnetization may be the lack of crystallinity and the compositional effects of the synthesized nanoparticles. But the major advantage of increased PVP concentration is that agglomeration is reduced and spherical nanoparticles are formed.

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