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Preparation and characterization of Co, Fe and Co-Fe magnetic nanoparticles

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This paper reports some results on the synthesis and characterization of cobalt, iron and cobalt-iron nanoparticles. The nanoparticles have been synthesised by polyol method and the obtained magnetic nanoparticles have a superparamagnetic behaviour. The morphology and size of the nanoparticles were studied by scanning electron microscopy (SEM) and dynamic light scattering (DLS). Compositional analysis of all the samples was conducted by EDS (energy dispersive X-ray analysis). The structure of the nanoparticles was examined by X-ray diffraction (XRD). Magnetic characteristics of the obtained nanoparticles were determined at room temperature by using a vibrating sample magnetometer (VSM), in an external magnetic field of 600 kA/m.

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Keywords: Cobalt nanoparticles, Iron nanoparticles, Cobalt-iron nanoparticles, Polyol process, Superparamagnetic behaviour

1. Introduction

The synthesis and investigation of magnetic properties of nanostructured magnetic materials present interest from both fundamental and technological point of view. Magnetic nanoparticles are used and are explored for use in fields as diverse as biology and data storage. In these applications, the ability to control particle size, shape, composition, and surface chemistry is critical in obtaining the desired magnetic properties. For biomedical applications the use of particles that present superparamagnetic behaviour at room temperature (no remanence along with a rapidly changing magnetic state) is preferred. In biomedicine, superparamagnetic particles are used for cell sorting and are explored for radiation treatment. Such particles are also being explored for use in drug delivery and gene therapy [1]. In magnetic data storage, the self-assembly of ferromagnetic particles is being explored for high-density magnetic media. The diverse range of applications has resulted in interest for nanoparticles with a wide range of magnetic properties. For example, the magnetic beads used in cell sorting are superparamagnetic in order to avoid aggregation; however, it is desirable that they have a relatively high magnetic moment so that they can be separated from the suspension at relatively low fields. In contrast, magnetic particles for magnetic recording should be ferromagnetic, with high saturation magnetization and high coercivity [2].

In this paper we reports some experimental results concerning the synthesis and magnetic properties of cobalt, iron and cobalt-iron nanoparticles obtained by a chemical method called the polyol process [3]. In the polyol process, the liquid polyol acts as the solvent of the metallic precursor, the reducing agent and in some cases as a complexing agent for metallic cations. The solution is heated to a given temperature reaching the boiling point of the polyol for less reducible metals.

2. Experimental details

Magnetic nanoparticles of Co, Fe and Co-Fe were prepared by refluxing an ethylene glycol solution containing their suspended sulphates. To obtain cobalt, iron and cobalt-iron nanoparticles we used cobalt sulphate heptahydrate and iron sulphate heptahydrate solutions in ethylene glycol having different molar concentrations: 0.07 M for obtaining Co nanoparticles, 0.07 M for obtaining Fe nanoparticles, 0.057 M $CoSO_4 \cdot 7H_2O$ and 0.014 M $FeSO_4 \cdot 7H_2O$ for obtaining $Co_{80}Fe_{20}$ nanoparticles, 0.04 M $CoSO_4 \cdot 7H_2O$ and 0.036 M $FeSO_4 \cdot 7H_2O$ for obtaining $Co_{50}Fe_{50}$ nanoparticles, and 0.014 M $CoSO_4 \cdot 7H_2O$ and 0.057 M $FeSO_4 \cdot 7H_2O$ for obtaining $Co_{20}Fe_{80}$ nanoparticles.

For the preparation of all magnetic nanoparticles, the pH of solutions was adjusted to 11 – 12 by addition of NaOH prior to reduction process. The sodium hydroxide was used to promote the reduction and to help control the particle size.

The refluxing temperature and the reaction time are specific for obtaining either nanoparticles type: 180˚C – 185˚C and 4 hours for Co nanoparticles, 190˚C – 195˚C and 4 hours for Fe nanoparticles, 180˚C – 185˚C and 4 hours for $Co_{80}Fe_{20}$ nanoparticles, 185˚C – 190˚C and 4 hours for $Co_{50}Fe_{50}$ nanoparticles and 190˚C – 195˚C and 190˚C – 195˚C and 4 hours for $Co_{20}Fe_{80}$ nanoparticles, respectively. In all cases, the solutions turned black within a few minutes of reaching refluxing temperature.

The metal-ethylene glycol mixtures were cooled to room temperature, filtered, and then the collected precipitates were dried in vacuum.

The morphology and size distribution of the magnetic nanoparticles were determined by scanning electron microscopy (SEM) (JEOL JSM-6390) and by dynamic light scattering (DLS) with a Microtrac Nanotrac 250 Particle Size Analyser. The structure of the nanoparticles was examined by X-ray diffraction (XRD) using Co Kα radiation (λ=1.7889 Å). Compositional analysis was conducted by EDS (energy dispersive spectrometry). Room temperature magnetic characteristics of the nanoparticles were determined by using a vibrating sample magnetometer (VSM) in an external field of 600 kA/m.

3. Results and discussion

3.1. Morphology and size of prepared magnetic nanoparticles

In Fig. 1 is shown a SEM micrograph of cobalt magnetic nanoparticles and in Fig. 2 is presented a SEM micrograph of iron nanoparticles.

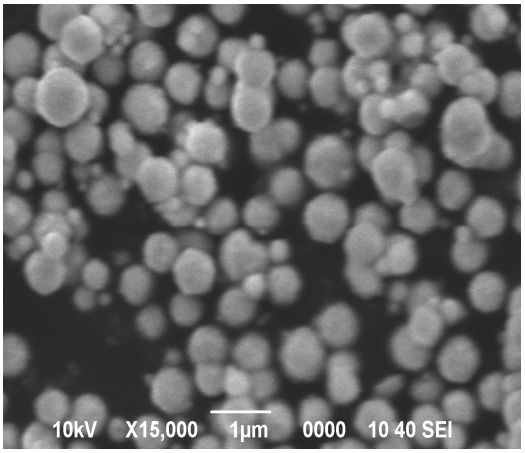


Fig. 1. SEM micrograph of Co nanoparticles

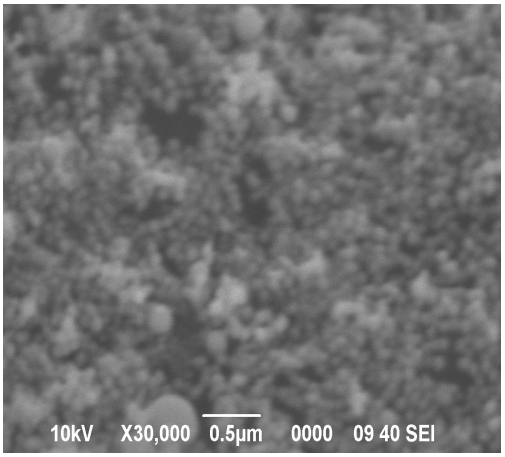
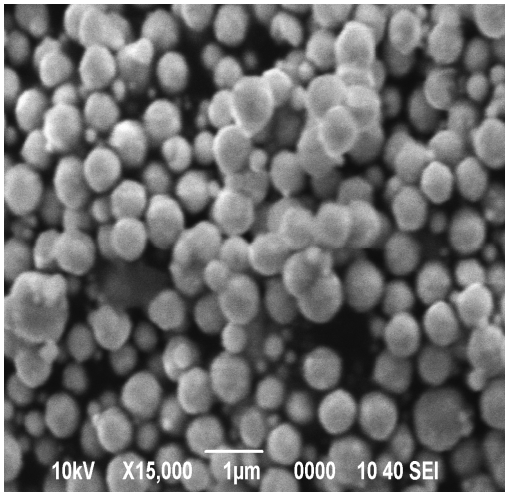
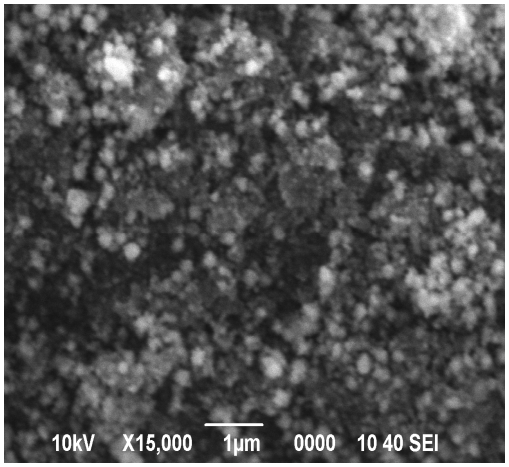


Fig. 2. SEM micrograph of Fe nanoparticles



a



b

Fig. 3. SEM micrograph of $Co_{80}Fe_{20}$ (a) and $Co_{50}Fe_{50}$ nanoparticles (b).

In Fig. 3 is presented a SEM micrograph of $Co_{80}Fe_{20}$ (a) and $Co_{50}Fe_{50}$ (b) nanoparticles.

The SEM micrographs presented in Fig. 1, Fig. 2 and Fig. 3, respectively, reveal that the shape of cobalt, iron and cobalt-iron nanoparticles is mostly spherical.

Due to the large surface to volume ratio and strong magnetic attraction forces, the magnetic nanoparticles tend to agglomerate in order to minimize the total surface energy of the system.

In Fig. 4 is presented the comparison plot of size distribution of cobalt, iron and cobalt-iron magnetic nanoparticles obtained by chemical reduction of metallic salts in ethylene glycol. It can be observed that the cobalt nanoparticles (Fig. 4) diameter varies between 300 and 600 nm. For iron nanoparticles were obtained spherical particles with mean diameter between 60 and 400 nm. For cobalt-iron nanoparticles the diameter varies between 80 and 500 nm.

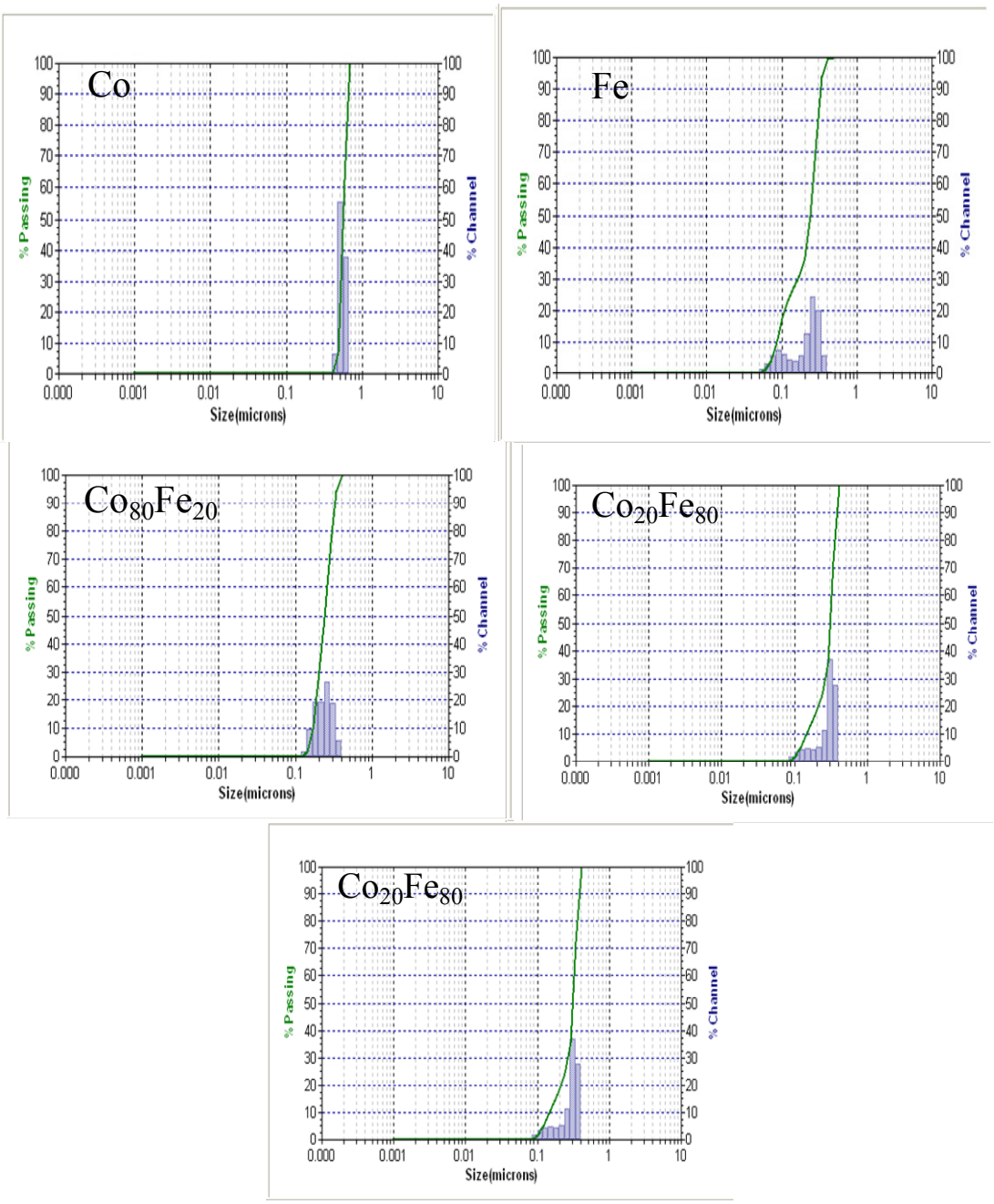


Fig. 4. Size distribution of cobalt, iron and cobalt-iron nanoparticles.

3.2. Structural features of the amorphous nanoparticles

The X-ray diffraction pattern of Co nanoparticles prepared by homogeneous nucleation (Fig. 5) shows the presence of sharp reflexes, corresponding to crystalline phases of Co (111), (200) and (220).

The X-ray diffraction pattern of iron nanoparticles (Fig. 5 b) shows the presence of sharp reflexes, corresponding to bcc Fe (110), (200) and (211), respectively.

Also, are presented the X-ray diffraction patterns of $Co_{20}Fe_{80}$ nanoparticles and for $Co_{80}Fe_{20}$ nanoparticles.

For Co-Fe nanoparticles one observes a crystallized structure, with sharp diffraction peaks corresponding to crystalline phases of Co-Fe (111), (200) and (220) for $Co_{80}Fe_{20}$ nanoparticles, and (110), (200) and (211) for $Co_{20}Fe_{80}$ nanoparticles, respectively.

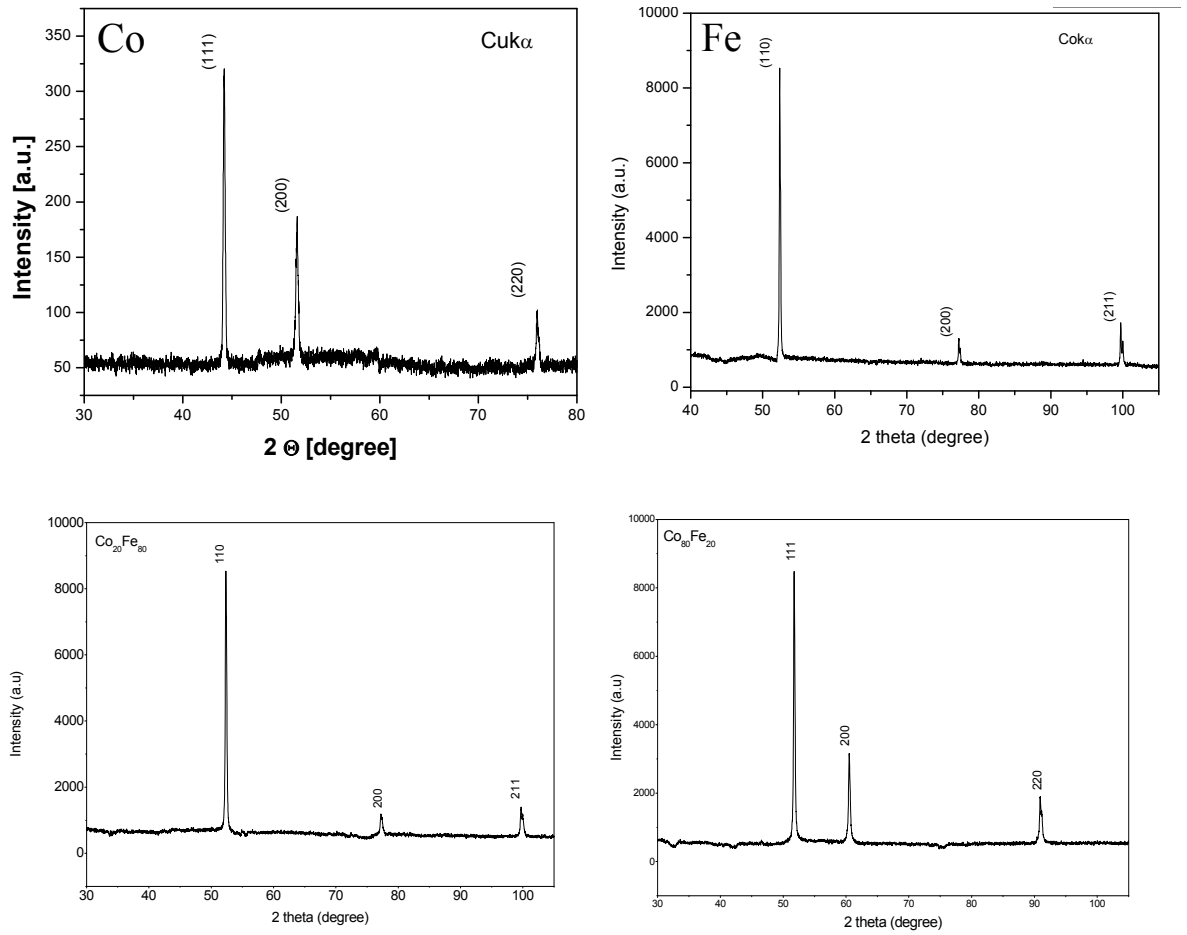


Fig. 5. X-ray diffraction patterns of Co, Fe, $Co_{20}Fe_{80}$ and $Co_{80}Fe_{20}$ nanoparticles.

3.3. Compositional analysis of magnetic nanoparticles

In Table I are presented the results of qualitative and quantitative analyses performed by EDS for $Co_{80}Fe_{20}$, $Co_{50}Fe_{50}$ and $Co_{20}Fe_{80}$ nanoparticles obtained by chemical reduction.

Table 1. Qualitative and quantitative analyses for Co-Fe nanoparticles.

Type	Qualitative analysis	Quantitative analysis (At. %)
$Co_{20}Fe_{80}$	Fe	76.46
	Co	23.54
$Co_{50}Fe_{50}$	Fe	48.84
	Co	51.16
$Co_{80}Fe_{20}$	Fe	17.97
	Co	82.03

3.4. Magnetic properties of cobalt, iron and cobalt-iron nanoparticles

In Fig. 6 are presented the hysterezis curves of cobalt nanoparticles prepared by polyol process and in Fig. 7 are presented the hysterezis curves of iron nanoparticles. From the hysterezis curves presented in Fig. 6 and Fig. 7 it can be observed that the cobalt and iron nanoparticles have a superparamagnetic behaviour.

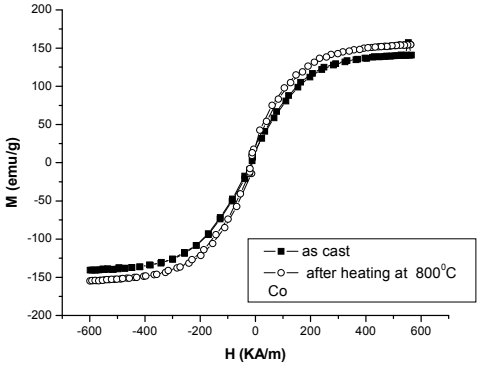


Fig. 6. Hysterezis curves of Co nanoparticles.

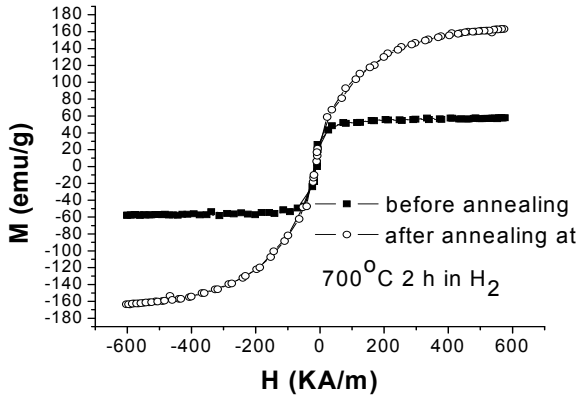


Fig. 7. Hysterezis curves of Fe nanoparticles.

The values of magnetization for cobalt nanoparticles varied between 135 and 140 emu/g for Co nanoparticles and between 60 and 160 emu/g for Fe nanoparticles, respectively.

In Fig. 8 a are shown the hysterezis curves of as-prepared Co-Fe nanoparticles and in Fig. 8 b are presented hysterezis curves of annealed Co-Fe nanoparticles. From the hysterezis curves presented in Fig. 8 a it can be observed that the Co-Fe nanoparticles have a superparamagnetic behaviour. The values of magnetization for Co-Fe nanoparticles varied between 120 emu/g for $Co_{80}Fe_{20}$, 60 emu/g for $Co_{50}Fe_{50}$ nanoparticles and 50 emu/g for $Co_{20}Fe_{80}$ nanoparticles.

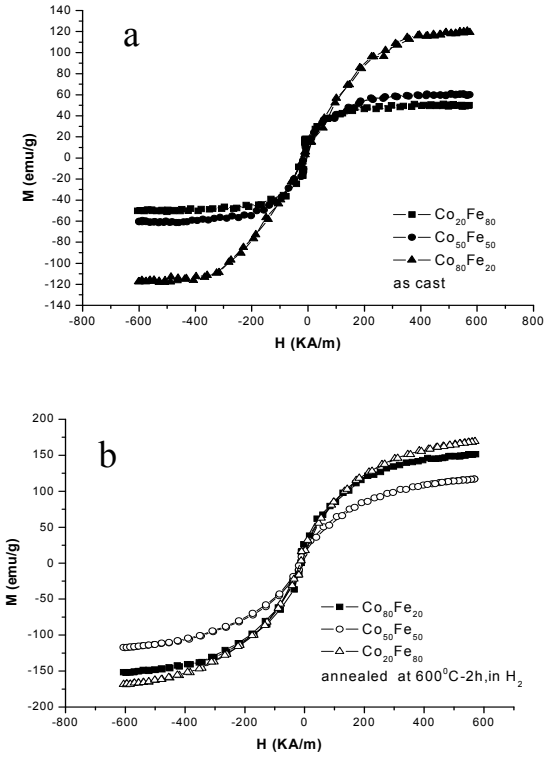


Fig. 8. Hysterezis curves of as-cast Co-Fe nanoparticles (a) and of annealed Co-Fe nanoparticles (b)

An improvement in magnetic properties (saturation magnetization and coercivity) of cobalt-iron nanoparticles occurs during heat treatments in hydrogen at temperature of 600°C, for 120 minutes, due to strain relaxation and of reduction of metallic oxides (Fig. 8 b).

The values of saturation magnetization were 150 emu/g for the $Co_{80}Fe_{20}$ annealed magnetic nanoparticles, 120 emu/g for $Co_{50}Fe_{50}$ annealed nanoparticles and for $Co_{20}Fe_{80}$ nanoparticles the value of saturation magnetization was 175emu/g.

4. Conclusions

The polyol process, which is known for providing monodisperse fine metal nanoparticles, afforded us the opportunity to synthesize ferromagnetic metal particles. The final particles have interesting morphological characteristics: an almost spherical shape, a narrow size distribution.

By control of the parameters of polyol process (molarity, pH, time and refluxing temperature of solutions), Co, Fe and Co-Fe nanoparticles with good magnetic properties and a superparamagnetic behaviour were obtained. Control of particle size and size dispersion requires careful control of the nucleation and growth steps in the process and elimination of aggregation during growth.

The resulting magnetic behaviour of the obtained Co, Fe and Co-Fe nanoparticles is rather complex, as it is strongly affected by the temperature - dependent interplay between finite size core effects, surface effects, and interface effects interactions. Such effects can complete, and the result of such competition is difficult to predict.

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