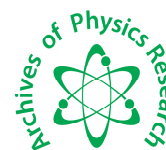




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Size and Shape Control Evaluation of Cobalt (Co) and Cobalt Ferrite (CoFe₂O₄) Magnetic Nanoparticles

S. Pauline¹ and A. Persis Amaliya²

¹Department of Physics, Loyola College, Chennai, India

²Department of Physics, Chevalier T.Thomas Elizabeth College for Woman, Chennai

ABSTRACT

This study focuses on the modulation of synthetic parameters in order to influence the size, structure, composition and arrangement of cobalt nanoparticles. The synthetic procedure followed is the hydrothermal chemical route. The role of cobalt precursors and different capping ligands (EG, PVP, HH) on the Co, CoFe₂O₄ was investigated. The reaction conditions are also responsible for the final product composition. The prepared nano particles of different morphology were analyzed through SEM.

INTRODUCTION

Ferrite nano-particles have shown a growing interest in recent years due to their specific magnetic and electrical properties. They have potential applications in high-density magnetic recording devices especially those with high coercivity [1-2], electronic devices and medicine [3]. One of the most recent applications studied is to be used in the complete decomposition of CO₂ [4]. This decomposition has significantly improved by developing ultra fine ferrite particles with high surface area as a catalyst [5]. Biasi et al [6] have developed nanocrystalline particles of cobalt ferrite (CoFe₂O₄) by a combustion wave method using iron nitrate (Fe(NO₃)₃·9H₂O) cobalt nitrate (Co(NO₃)₂·6H₂O) and glycine (C₂H₅NO₂). The average particle size, determined by means of X-ray diffraction, was found to depend on the glycine–nitrate ratio and varied between 2.7 and 17 nm. In their proposed work glycine –nitrate influence the size of the particles. In order to investigate the effect of degree of crystallinity and mean crystallite size of CoFe₂O₄ nanocrystals on the magnetic properties, a series of CoFe₂O₄ samples with different degree of crystallinity and mean crystallite size were produced by varying the subsequent calcination temperatures.

Compared to magnetic iron oxide particles, cobalt (Co) nanoparticles have been a subject of intensive research because of its high magnetocrystalline anisotropy (7×10^6 erg/cm³) and large estimated critical size for single domains (approx. 70 nm) [7]. Monodisperse magnetic nanoparticles, like cobalt are used in Information data storage and sensor [8-9]. The significance of using magnetic metal nanoparticles, e.g., Co, Fe, FeCo, or FePt is manifold: firstly, they can be prepared with a narrow size distribution whereas the direct synthesis of iron oxides often results in rather broad particles size distributions. For numerous biomedical applications monodisperse particles are required. Secondly, magnetic metal nanoparticles exhibit a high saturation magnetization, e.g., the saturation magnetization Ms of bulk cobalt is 162 Am²/kg. Moreover, based on the higher magnetization, Co nanoparticles exhibit a higher specific loss power than the iron oxide ones, which makes them interesting as potential candidates for applications in hyperthermia (770 W/g for a Co magnetic fluid in kerosene at 400 kHz, 10 kA/m) [10].

In addition, the synthesis of magnetic metal nanoparticles is typically performed in organic media and, thus, phase transfer of the as-prepared particles into the aqueous phase is important for biomedical application. Besides, the potential toxicity for in vivo applications of Co nanoparticles has to be explored. On the other hand, using magnetic metal nanoparticles, only small amounts of particles would be required due to the excellent magnetic characteristics, minimizing potential side effects.

A variety of methods for the preparation of cobalt colloid dispersions has been reported [8-11]. The most common are the reduction of a cobalt salt and the thermal decomposition of cobalt carbonyl. Depending upon the synthetic route, Cobalt (Co) nanoparticles are observed in at least three crystallographic phases: typical for bulk Co hcp, ϵ -Co cubic, or multiply twinned fcc-based icosahedral. The final product structure has been influenced by the Conditions for synthesis reactions. Methods for the synthesis and magnetic properties of cobalt nanoparticles' different structures have been described in detail in a review [12]. Ultraviolet irradiation of a cobalt (II) acetate solution has also been used to synthesize Co NPs which have certain morphologies depending upon the experimental parameters [13]. For any particular application there is an optimal size of NPs. For instance, biomedical applications require NPs with a size comparable to bio-molecules [14] and indeed, very small NPs are desirable for labeling cellular organelles. In addition, very small NPs are also more rapidly transported across the endothelium and it, therefore, may be easier to get a large number of smaller NPs to a specific target than a small number of larger NPs but with the overall mass of magnetic material being the same. A novel approach for the synthesis of Co NPs less than 5 nm in diameter, using laser pulses to stimulate the rapid decomposition of cobalt carbonyl in a solution of stabilizers was reported in a review [15].

The aim of this work is to examine the effect of different parameters in the self arrangement, the product yield, and the morphology of cobalt and cobalt ferrite nanoparticles. The role of the cobalt precursor, the surfactants such as Ethylene glycol (EG), Hydrazine hydrate (HH), Polyvinylpyrrolidone (PVP), synthesis temperature and the presence of different capping ligand with subsequent calcinations temperature are emphasized. The final products is cooled to room temperature, centrifuged and washed with ethanol to remove any non-reacted compounds and excessive solvent.

MATERIALS AND METHODS

2. Experimental Procedure

The materials used in the synthesis of Co were procured from Merck 98% purity and were used without any purification. The cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), hydrazine hydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) and Polyvinylpyrrolidone (PVP- $\text{C}_6\text{H}_9\text{NO}$)_n were used in the preparation of nanocrystalline Co. A step wise synthesis procedure of Co nanoparticles is shown in figure 1.

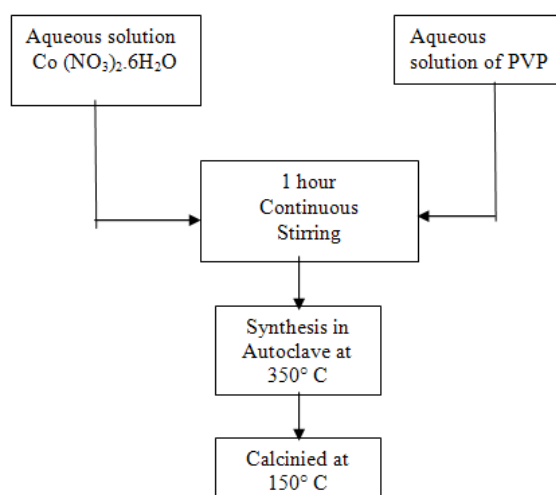


Figure.1 Flow chart showing the PVP assisted hydrothermal synthesis of Co

In the typical synthesis, 2.9103 g of cobalt nitrate was dissolved in 20 ml of milli-Q water and PVP was dissolved in 20 ml of milli-Q water. Both solutions were mixed together with continuous stirring. After stirring for 1 hour, the prepared solution was transferred into a Teflon coated autoclave and heated at 350°C for 5 hours. After the hydrothermal reaction time, autoclave was cooled to room temperature naturally. The as prepared powder sample was annealed at 150°C temperature for 5 hours. To synthesize hydrazine hydrate (HH) capped Co nanoparticles, cobalt nitrate solution is mixed with 10 ml of HH and the above procedure is followed. The author [16] is already described the synthesis of CoFe_2O_4 nanoparticles by hydrothermal synthesis method in the presence of Ethylene Glycolic (EG) acid.

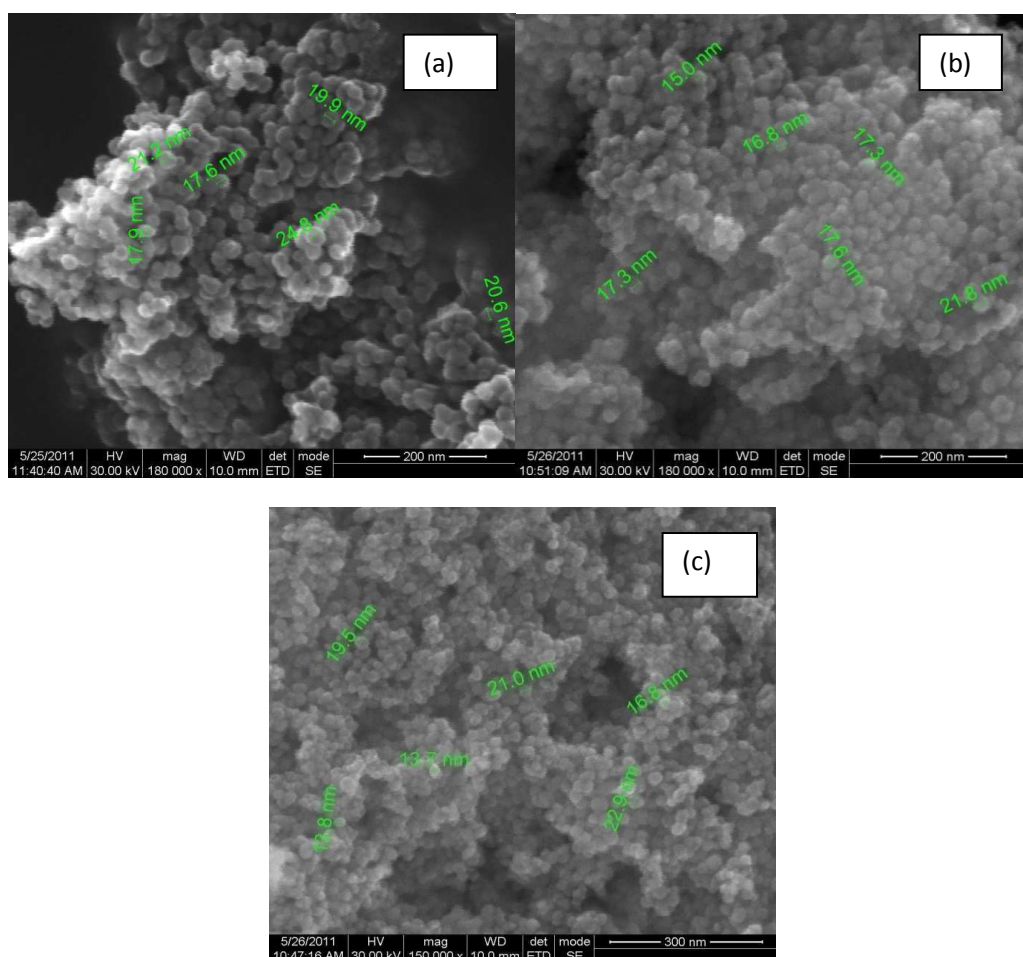


Figure 2. SEM photograph of CoFe_2O_4 nanoparticles calcinated at a) 300 °C b) 400 °C c) 500 °C

RESULTS AND DISCUSSION

3.1 Morphological behavior of CoFe_2O_4

The structural morphology of nanoparticles was investigated through SEM. Figures 2 (a-c) show the SEM images of CoFe_2O_4 nanoparticles. The SEM images show that the CoFe_2O_4 nanoparticles prepared by hydrothermal method have uniform, monodispers spherical structure morphology with a narrow size distribution of particles. The uniform spherical morphology of nanoparticles was obtained in the temperature range of 300-500 °C. The sizes of the obtained nanoparticles are 22 nm, 19 nm and 17 nm which are calcined at 300 °C, 400 °C and 500 °C respectively. When the annealing temperature increases, the particles size decreases simultaneously. From the morphology it is interesting to note that when temperature increases the shape does not change but affects only the radius of the nanoparticles. In this experiment, the Ethylene Glycolic (EG) acid was used for getting spherical shape nanoparticles. The temperature and EG plays important role in getting spherical shape morphology of the

nanoparticles and reduction in the particle size. The obtained results at various temperatures agree with the nucleation theory. At subcritical conditions, reaction takes place to produce monomers during the heating period. Subsequently, the reaction gradually precedes to increases the concentration of monomer in the reaction and nucleation occurred when the monomer concentration went beyond the saturation point [17]. As a result, the crystals grow with increasing temperature and the solubility of metal oxides gradually decreases and drops to an extremely low level at the critical temperature. Particles formed at lower temperature could dissolve again to re-crystallize at constant temperature (390 °C).

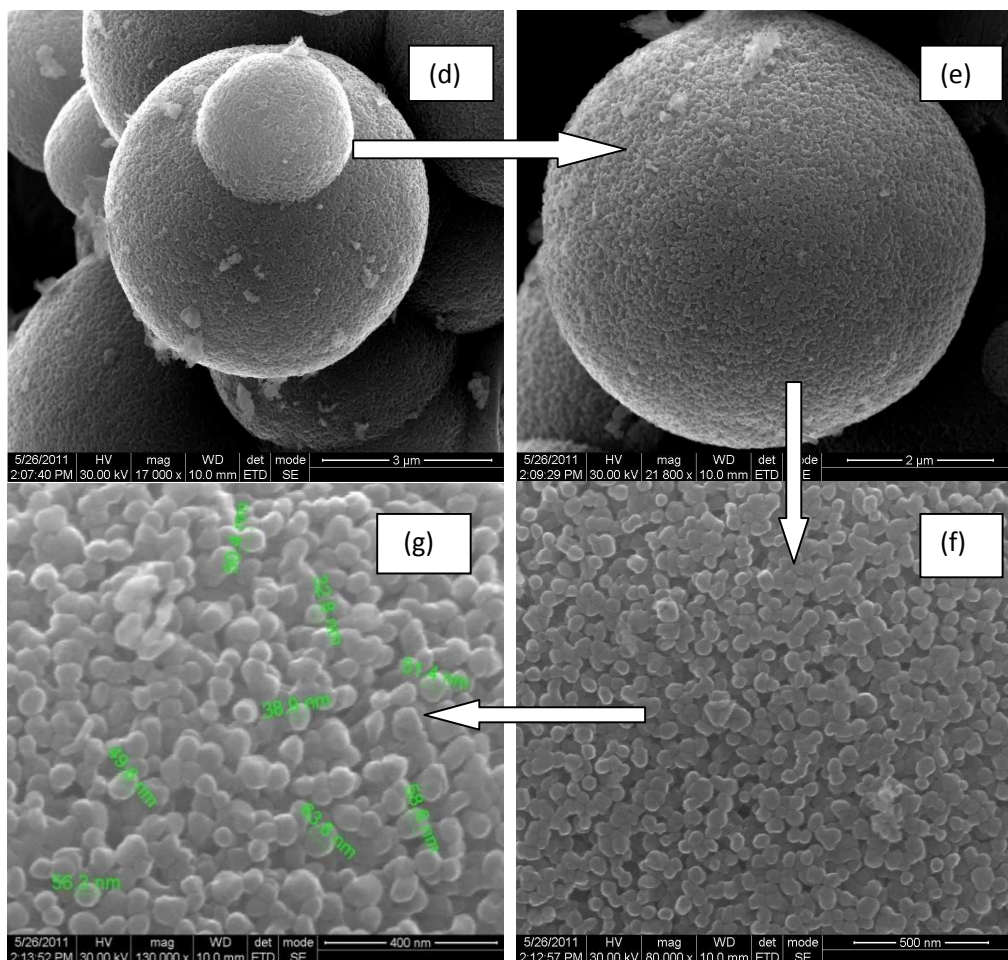


Figure 3. SEM micrograph of PVP capped Co nanospheres

3.2 Morphological behavior of Co nanoparticles

The SEM image of Co nanoparticles with water as a solvent and polyvinylpyrrolidone (PVP) as capping reagent is shown in Figure.2 d-g. The solvothermal temperature along with the capping agent can influence the nanoparticle size and shape. The average size of the as grown monospherical nanosphere is 35 nm. At the lower temperature around 200 °C only irregular nanospheres of large diameter are formed. A close observation of the SEM image of the present case suggests that poly microspheres (Fig 2 d,e) containing Co nanoparticles are obtained and they all are agglomeration free spheres, this could be attributed to the relatively high reaction temperature the sample is synthesized at 350 °C for 5hrs, and annealed at 150 °C for 5 hrs.

It reveals that PVP played an important role in controlling the size and mono-dispersion of the Co nanocrystals in this process. The absence of agglomerates is attributed to the role played by PVP. In the formation process of the Co architectural structure, the capping agent PVP is absorbed onto the different planes of the incipient. Co nuclei and it not only prevents the particles from agglomeration, but also influences the growth of these planes [18].

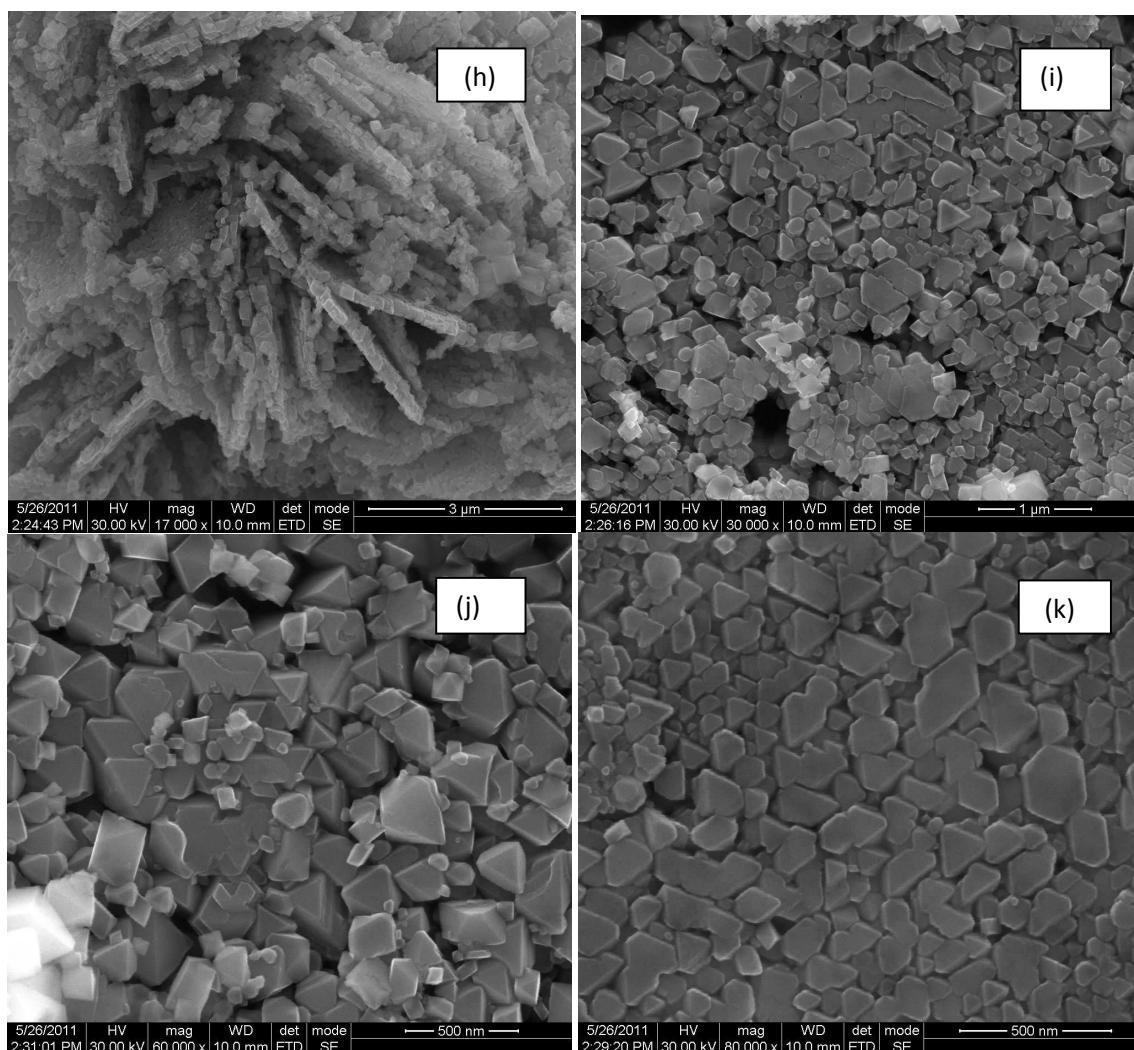


Figure 4. SEM photograph of HH capped Co triangular nanoparticles

The ability to control the chemical surface in nanocrystalline is essential to the fabrication of nanodevices. However, compared to the study of their bulk properties, the chemistry of the surfaces of magnetic nanocrystals is still at a primitive stage. Two main issues arise in the fabrication of a nanostructured material by manipulation of nanocrystals with derivatized surfaces: the chemical reactivity at the interface between the nanocrystals and a distinct material, usually an organic matrix; assembly methods to produce organized nanostructures using passivated nanocrystals as the building blocks. Obviously both approaches require derivatization techniques at the particles surface. Figure 4 h-k shows the ideal images of triangular Co nanoparticles obtained using Hydrazine hydrate (HH) as a capping ligand or surface modifiers. The influence of hydrazine hydrate controls the morphology of triangular Co.

In the hydrothermal chemical route method, hydrazine hydrate was used as both reducing and templating agent, and their presence were found to favors the formation of wall-like structure. It is observed from the SEM images (Fig.4 j and k) that the Co nanotriangular synthesized in this work are in good shape with less pronounced stacking faults occurred. One dimensional (1D) nanostructures, (nanorods, nanowires, nanobelts and nanotubes, nanotriangular) have recently attracted substantial research interest because of their unusual optical and electronic properties and potential applications in nanodevices[19]. The top view of microwalls can be seen in the figure 4 h which are orderly arranged. The microwalls contain triangular nanoparticles. These triangular nanoparticles are very smooth.

Each nanoparticle has occupied a space along the microwall without any agglomeration. From our research view we suggest that these different types of morphology are very useful while making nano building blocks.

CONCLUSION

In this work a simple process for the synthesis of Co nanoparticles by hydrothermal method is described, SEM image shows the formation of monodisperse microspheres containing spherical Co nanoparticles and microwalls containing triangular Co nanoparticles. They can be used to construct bulk nanostructures. The formation of monodisperse CoFe_2O_4 nanoparticles is also confirmed. The particles size decreases with the increase in annealing temperature. Further the SEM results reveal that EG, PVP and HH plays important role in getting spherical and triangular morphology and reduction in particles size. The synthesized nanoparticles can be used in several technological applications such as soft magnets, low loss materials at higher frequencies and magnetic fluids.

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