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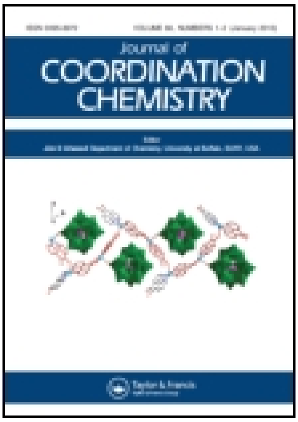

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Cobalt(III) ammine complexes as precursors in the synthesis of cobalt nanoparticles

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Cobalt nanoparticles have been prepared by the chemical reduction of $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5Cl]Cl_2$, and $[Co(NH_3)_5ONO]Cl_2$ in alcoholic solution. The reaction of these complexes with hydrazine as a reducing agent were carried out at 70 °C and pH = 10–12. The metallic nanoparticles were characterized by using X-ray powder diffraction, IR spectroscopy, scanning electron microscopy, and vibrating sample magnetometer. The synthesized cobalt nanoparticles have different morphologies and nanosheet distributions. The Co1 has a sheet thickness ranging from 15 to 40 nm and shows an aggregated dendrite structure. On the other hand, Co2 has a cactus like morphology with a nanosheet thickness ranging from 15 to 35 nm. The Co3 nanoparticles were pompon-like microspheres in shape and aggregated powders with a nanosheet thickness ranging from 10 to 45 nm. This work presents a novel approach for the preparation of metallic nanoparticles via metal complexes.

Keywords: Cobalt(III) complex; Chemical reduction; Cobalt nanoparticles; Magnetic materials

1. Introduction

Rapid and extensive developments of nanotechnology and nanoscience have created immense waves in the 21st century. In recent years, the preparation, characterization, and applications of nanosized materials have been interesting for many researchers in various fields, such as chemistry, physics, materials science, and biology [1]. Metallic particles that are prepared in nanoscale have outstanding properties. In metallic particles as the particle size decreases, the surface-to-volume ratio increase and all the properties depend on the surface-to-volume ratio changes. Thus, nanoparticles show many unusual chemical and physical properties compared to bulk. Ferromagnetic elements such as Fe, Co, and Ni have a wide range of application in catalysts, solar energy absorption, and magnetic recording. Among the above mentioned magnetic metals, cobalt has a maximum magnetization. The cobalt metal nanoparticles, due to their specific properties such as magnetism, thermal resistance, and chemical activity, have a wide range of applications including hard alloys, conducting paints, rechargeable batteries, chemical catalysts, optoelectronics, and magnetic recording media [2]. The preparation of metallic nanoparticles is the most desirable method in nanotechnology. In order to prepare nanosized metallic particles, ball milling

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electro-deposition, thermal plasma, the polyol process, chemical vapor deposition, the gas deposition method, radiolytic reduction, and the sonochemical method have been utilized [3, 4]. Chemical reduction is a frequently used method for the preparation of metallic powders. Among these methods, the chemical reduction of cobalt(II) compounds by a reducing agent in aqueous solution has been investigated [5, 6]. Hydrazine in alkaline aqueous solutions is a strong reducing agent. Depending on the influencing parameters such as oxidizing agent, pH, and temperature, the hydrazine reaction can be carried out in different pathways [7]. In preparation of cobalt nanoparticles, hydrazine reaction is highly desirable, because its byproducts are typically nitrogen gas and water [8]. Dinitrogen is produced in this reaction and helps to protect the metallic cobalt nanoparticles from oxidation. The formation of cobalt(II) hydrazine complex may be the starting compound in a redox reaction of hydrazine with a cobalt(II) ion. The extensive coordination chemistry of hydrazine is evidence for this type of reaction [7]. A great number of cobalt(III) coordination compounds are prepared by the oxidation cobalt(II) compound in the presence of a ligand. The chemistry of cobalt(III) coordination compounds is a wide area of inorganic chemistry and there has been a lot of research done on these compounds [9]. Cobalt(III) complexes have several features of reaction, the most important of which is the pattern of electron transfer [10]. In some cases, the ligand reacts as a reducing agent. Hydrazine is one of these compounds, therefore the preparation of cobalt(III) hydrazine complex has not yet been reported. On the other hand, the chemical reduction of cobalt(III) complex to metallic cobalt has not yet been reported. In this work, hydrazine as a chemical reducing agent is applied to the preparation of cobalt nanoparticles from $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5Cl]Cl_2$, and $[Co(NH_3)_5ONO]Cl_2$ complexes in alcoholic alkaline solution.

2. Experimental

2.1. *Starting materials*

All chemical reagents used in this experiment were pure grade and used without further purification. Cobalt chloride hexahydrate, hydrazine monohydrate solution, sodium hydroxide, ammonia solution, sodium nitrite, hydrochloric acid, hydrogen peroxide, activated carbon, and ethanol were purchased from Merck. The water used throughout this work was doubly distilled water. The preparation of hexaamminecobalt (III) chloride, pentaamminechlorocobalt(III) chloride, and pentaamminenitritocobalt(III) chloride were carry out according to the literature [11–13]. All reactions for the preparation of cobalt(III) complexes and cobalt nanoparticles were carried out under atmospheric conditions. The prepared cobalt nanoparticles were dried at room temperature in the form of powder.

2.2. *The preparation of cobalt metallic nanoparticle from hexaamminecobalt(III) chloride*

To 0.2 g (0.7 mmol) of hexaamminecobalt(III) chloride complex in a solution of water-ethanol (50:50), 3 mL of hydrazine hydrate and amount of NaOH was added at 70 °C. The resulting reaction mixture was stirred for two hours. The yellow solution turned to black and resulting cobalt particles were carefully decanted and washed repeatedly with doubly distilled water and acetone. The metallic powder was filtered and dried in oven at 80 °C for 24 h. The following reaction (equation 1) took take place at 70 °C in aqueous solution.

$$2[Co(NH_3)_6]Cl_3 + 3/2N_2H_4 + 6NaOH \rightarrow 2Co + 3/2N_2 \uparrow +6H_2O + 12NH_3 + 6NaCl \quad (1)$$

2.3. *Preparation of cobalt metallic nanoparticle from pentaamminechlorocobalt(III) chloride*

To 0.17 g (0.7 mmol) of pentaamminechlorocobalt(III) chloride complex in a solution of water-ethanol (50:50), 3 mL of hydrazine hydrate and amount of NaOH was added at 70 °C. The resulting reaction mixture was stirred for two hours. The purple red solution immediately turned black and therefore the rate of reduction of pentaamminechlorocobalt(III) complex to metallic cobalt is very much faster than that of hexaamminecobalt(III) chloride complex. The resulting black slurry was carefully decanted and washed repeatedly with doubly distilled water and acetone. The metallic powder thus obtained was filtered and dried in an oven at 80 °C for 24 h. The following reaction (equation 2) took place at 70 °C in aqueous solution.

$$2[Co(NH_3)_5Cl]Cl_2 + 3/2N_2H_4 + 6NaOH \rightarrow 2Co + 3/2N_2 \uparrow +6H_2O + 10NH_3 + 6NaCl \quad (2)$$

2.4. *Preparation of cobalt metallic nanoparticle from pentaamminenitritocobalt(III) chloride*

To 0.18 g (0.7 mmol) of pentaamminenitritocobalt(III) chloride complex in a solution of water- ethanol (50:50) 3 mL of hydrazine hydrate and amount of NaOH was added at 70 °C. The resulting reaction mixture was stirred for two hours. The pink solution immediately turned black and therefore the reaction rate for the reduction of pentaamminenitritocobalt(III) chloride complex to metallic cobalt is very much faster than that of hexaamminecobalt(III) chloride complex. The resulting black slurry was carefully decanted and washed repeatedly with doubly distilled water and acetone. Thus, the metallic powder obtained was filtered and dried in an oven at 80 °C for 24 h. The following reaction (equation 3) took place at 70 °C in aqueous solution.

$$2[Co(NH_3)_5ONO]Cl_2 + 3/2N_2H_4 + 6NaOH \rightarrow 2Co + 3/2N_2 \uparrow +6H_2O + 10NH_3 + 4NaCl + 2NaNO_2 \quad (3)$$

2.5. *Characterization of materials*

The cobalt complexes and cobalt powders were characterized by X-ray powder diffraction (XRD), infrared spectroscopy (IR), and vibrating sample magnetometery (VSM). XRD measurements were performed using a Philips X'pert pero MPD diffractometer with Cu Kα radiation in the range 2θ from 10 to 80 at room temperature. IR spectra were obtained as a KBr pellet in the range 4000–400 cm^{-1} using a Shimadzu FTIR spectrometer. The vibrating sample magnetometer (VSM, Maghnetic Daghigh Kavir Co) was used to evaluate the magnetic parameters.

3. Results and discussion

The chemical reduction reaction by hydrazine is the best method for controlling composition, size and shape of Co powders and also it is a simple procedure. The reaction of hydrazine as a strong reducing agent with oxidizing compounds results in destruction of the hydrazine molecule. In aqueous solution, hydrazine undergoes a 1-, 2-, or 4- electron oxidation and converts to a mixture of dinitrogen and ammonia, azide and ammonia, and/or only dinitrogen, respectively. In a basic medium, the 4-electron oxidation, E^{o}_{N2H4}, is –1.16V, and it can be easily oxidized to N_2. A major problem in the production of cobalt nanoparticles is their high reactivity towards oxidation by moist air. Nitrogen, which is produced by the oxidation of the hydrazine, would be provided an inert atmosphere for the protection of metallic cobalt. Aqueous solutions of simple inorganic cobalt salts contain the pink octahedral hexaaquacobalt(II) ion. The most common oxidation states of cobalt in aqueous solution, $[Co(H_2O)_6]^{2+}$ and $[Co(H_2O)_6]^{3+}$, are both known but the latter is a strong oxidizing agent in aqueous solution. It decomposes rapidly as the Co(III) oxidizes the water with evolution of oxygen. Consequently, in contrast to Co (II), Co(III) provides few simple salts, and those which do occur are unstable. Despite its high oxidation state, Co(III) complexes are usually air and light stable and relative inertness to ligand exchange that allows purification and facilitates studies of these complexes in solution. Complexes of Co(III) are easily prepared, from Co(II) precursors, they exhibit a huge variety of colors The golden yellow $[Co(NH_3)_6]^{3+}$ cation can be prepared by air oxidation of an ammoniacal solution of Co(II) in the presence of charcoal. The cobalt in aqueous solution has an E^{o} Co^{3+}/Co equal to +0.33 V at 25 °C, so it is possible to reduce cobalt(III) ions by hydrazine in a basic medium [14]. Octahedral cobalt(III) ammine complexes are stable. When a displacement of water molecules by ammonia takes place a cobalt complex is formed and E^{o} $Co[(NH_3)_6]^{3+}/Co$ is equal to the +0.24 V at 25 °C. Therefore, formation of hexaamminecobalt(III) causes stability of the Co^{3+} ion compared to the hexaaqua complex. The chemical properties of cobalt ions in aqueous solution are altered when they are combined with complexing agents. The effects of complexing agents were observed on some of the common properties of cobalt ions, such as color, reduction potential, and solubility. The formation of cobalt(III) complexes affects standard potentials, therefore the ability of formed complexes to accept an electron differs from that of the corresponding aqua ion. [7]. When Gibbs energy is positive, the reaction is not spontaneous and hydrazine will not reduce cobalt from the cobalt complex. By considering the half-cell reaction of the $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5Cl]Cl_2$, and $[Co(NH_3)_5ONO]Cl_2$ combined with the half-cell reaction of hydrazine in alkaline solution. The Gibbs energy is negative, therefore the cell reaction is spontaneous and hydrazine successfully will reduce cobalt metal from their complexes. In spite of cobalt(III) ammine complexes preparation being carried out at the beginning of the 20th century, the reduction of these complexes to metallic cobalt has not yet been reported in the literature. In preparation of cobalt metal powders, complexes such as $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5Cl]Cl_2$, and $[Co(NH_3)_5ONO]Cl_2$ as a suitable reagents are proposed. Such complexes are stable at ordinary to moderate temperatures depending on the type of the ligands. Preparation of metallic cobalt powders from cobalt(III) complexes offers several advantages. By changing the precursors it is possible to alter the purity and morphology of the obtained cobalt powders and the average particle size is decreased. In comparison with the method of preparing cobalt powders from cobalt(II) salts, the method of making cobalt powders via the reduction of cobalt(III) ammine complex precursors shows the advantages of using a smaller amount of hydrazine for complete reduction of cobalt(II) ions in solution, and the obtained cobalt particles show less agglomeration and better dispersibility. There are several influencing parameters on chemical reduction of cobalt metal due to complexing agents and the molecular structure of the complex. One of the most important parameters is the regulation and maintenance of the free cobalt(III) ion concentration, or activity of the cobalt complex dissociates to form a small quantity of free cobalt(III) ions. The rate of cobalt chemical reduction is proportional to the rate of the cobalt(III) complex dissociation to free cobalt(III) ion. Moreover, the average particle size of cobalt powders can be controlled from 10 to 45 nm by adjusting the reaction conditions. In this work, we present our experimental results on the preparation of cobalt nanoparticles with different shapes by using a wet chemical solution route. Using cobalt(III) complexs as reactants, cobalt nanoparticles of with different morphologies can be formed. The morphology and sizes of synthesized nanostructures of cobalt were studied by scanning electron microscopy (SEM). Quality characterization, crystallite size, and structural properties of nanoparticles were examined by X-ray powder diffraction.

3.1. *Analysis of crystalline phase*

According to the XRD patterns that have been reported in literature, $[Co(NH_3)_6]Cl_3$ crystallizes in the monoclinic system [15]. Both $[Co(NH_3)_5Cl]Cl_2$ and $[Co(NH_3)_5ONO]Cl_2$ crystallize in the orthorhombic system [16, 17]. During the reaction the cobalt(III) complexes were converted to metallic cobalt; thus, diffraction pattern peaks of complexes disappeared. The fundamental difference between crystalline and amorphous solids is due to their X-ray

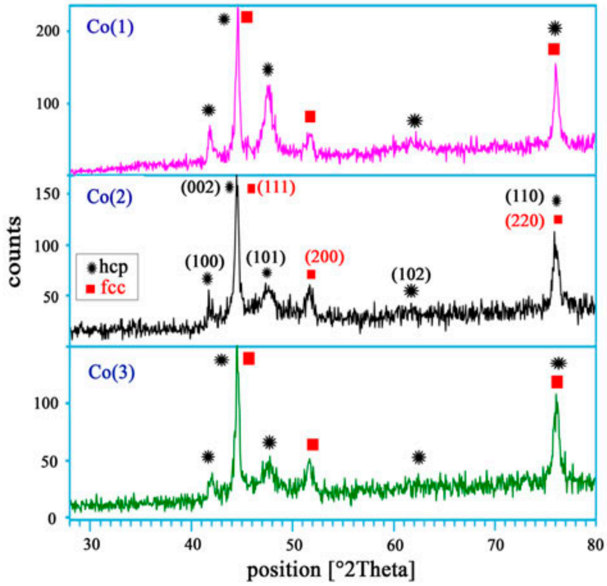

Figure 1. X-ray diffraction patterns show both phases, hcp, and fcc of metallic cobalt nanoparticles (Co1, Co2, Co3) which are produced from cobalt complexes $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5Cl]Cl_2$, and $[Co(NH_3)_5ONO]Cl_2$ respectively.

Table 1. Crystallite size and nanosheet size distribution in cobalt metal nanoparticle samples.

Cobalt metal nanoparticles	Crystallite size of cobalt	FWH	hkl	Particle nanosheet thickness
Co1	24.25 nm	0.3542	111	10-45 nm
Co2	24.25 nm	0.3542	111	15-40 nm
Co3	18.20 nm	0.4723	111	15-35 nm

diffraction patterns. However, poor crystallinity of the powder results in broad peaks in the X-ray pattern. There are different line broadening sources, such as crystallite size, lattice strain, anisotropic sample broadening, faulting, etc., tend to produce different effects on the line profiles. Here in the metallic cobalt pattern the background noise from fluoresced X-rays isincreased, which is most problematic in powder diffraction (figure 1). The choice of X-ray source in X-ray powder diffraction is dependent on the material that must be analyzed. Some atoms absorb incident X-rays and fluoresce by the absorption of X-rays, which decreases the diffracted signal, and also the fluoresced X-rays increase the background noise. When copper radiation is employed, the X-ray powder pattern of cobalt nanoparticles demonstrates the effect of fluorescence on the diffraction pattern [18]. The pattern of X-ray diffraction shows the crystalline structure of final products. All the diffraction peaks can be well indexed to the hexagonal and cubic phase of cobalt. Therefore the

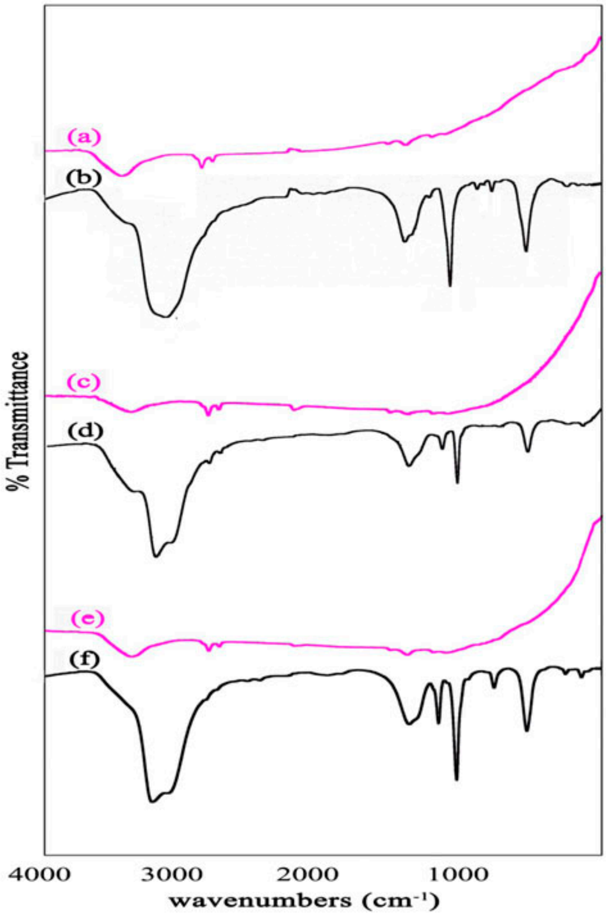

Figure 2. FTIR spectra of cobalt metal nanoparticle Co1 (a) and its precursor $[Co(NH_3)_6]Cl_3$ complex (b), cobalt metal nanoparticle Co2 (c) and its precursor $[Co(NH_3)_5Cl]Cl_2$ complex (d), cobalt metal nanoparticle Co3 (e) and its precursor $[Co(NH_3)_5ONO]Cl_2$ complex (f). The 1600–500 and 3500–2800 cm^{-1} region showing the position of the ligand stretch, and after the reaction the cobalt nanoparticles obtained from these complexes all the absorption bands have disappeared.

prepared cobalt consists of hcp and fcc (figure 1). Quantitative analysis by powder X-Ray diffraction is carried out by the Rietveld method. In these cases the complete profile of the theoretical diffractogram fits the experimental results very well. In most studies of the grain size of nanocrystalline materials, X-ray line-broadening analysis is used. The crystallite size is estimated from the full width at half maximum (FWHM) of the diffraction peaks by the Scherrer formula (table 1). The shape of the crystal depends on the shape of the unit cell, but it is not necessarily the same as that of the unit cell. The general rule relating morphology to growth velocity is that fast-growing faces disappear, slow-growing faces remain. Growth velocities are obtained by measuring the diameter of the crystal in different directions. The results show that cobalt complexes as a reactant have a fundamental effect on crystalline nucleation and morphology in cobalt metal. Depending on growth conditions, the same crystal species may show different morphology. The atomic order in crystalline solids indicates that small groups of atoms form a repetitive pattern. Thus, in describing crystalline structures, it is often convenient to subdivide the structure into small repeat entities called unit cells.

3.2. *Infrared spectra*

Vibration spectra of $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5Cl]Cl_2$, and $[Co(NH_3)_5ONO]Cl_2$ complexes have been studied extensively [19, 20]. Figure 2(a,d,e) shows the infrared spectra of hexaamminecobalt(III) chloride, pentaamminenitritocobalt(III) chloride, and

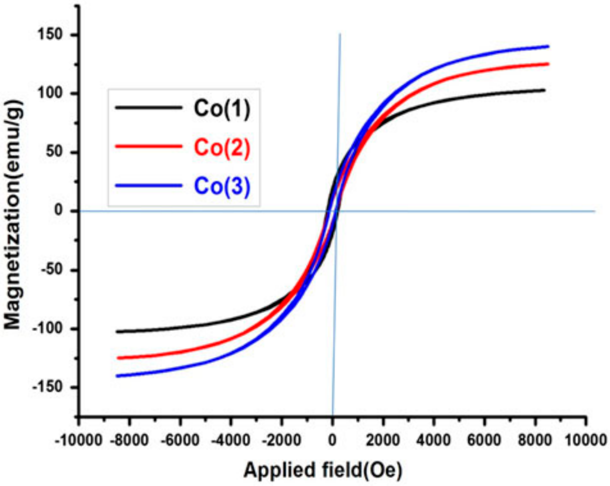

Figure 3. Magnetization curves and saturation magnetizations of cobalt nanoparticles (Co1 = 102.20, Co2 = 125.00 and Co3 = 135.00 emu/g, respectively).

Table 2. Cobalt metal nanoparticles magnetic parameter.

Cobalt metal nanoparticles	H_C (Oe)	H_R (emu/g)	M_S (emu/g)
Co1	204	19.4	102.20
Co2	123.5	9.3	139.00
Co3	125	10.4	125.00

pentaamminenitritocobalt(III) chloride in the 4000–400 cm^{-1} region. Vibration spectra of cobalt(III) amine complexes exhibit coordination sphere ligand vibrations. During the chemical reactions, complete destruction of cobalt(III) complexes occur and thus all spherical ligand vibration disappears. In the conversion of complexes into cobalt metal nanoparticles (Co1, Co2, and Co3), absorption bands due to the ligands group in complexes disappear and the cobalt metal has no absorption bands in the medium IR region. Metal nanoparticles have various unusual chemical and physical properties compared to bulk metals due to their large superficial area [21]. Therefore, the week absorption bands due to the water and organic-capped cobalt metallic nanoparticles are observed in the infrared spectrum (figure 2).

3.3. *Magnetic properties of molecular cobalt(III) complexes and cobalt metallic nanoparticles*

Ferromagnetic substances are strongly attracted to a magnetic field and have large positive field-dependent values of susceptibility. Cobalt metal has been known to be one of the important magnetic materials [22]. Cobalt nanoparticles were prepared from coordination compounds by chemical reduction. All of the cobalt(III) complexes such as $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5Cl]Cl_2$, and $[Co(NH_3)_5ONO]Cl_2$ are diamagnetic. The conversion of cobalt(III)

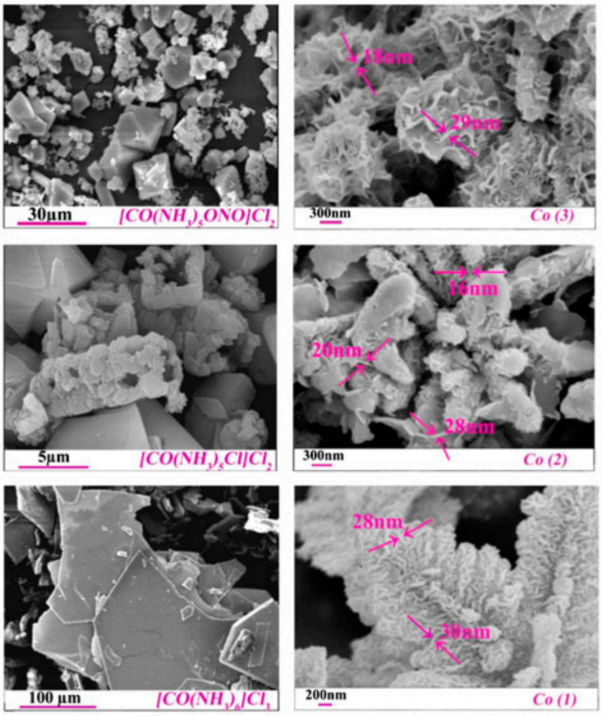

Figure 4. SEM image showing the morphology and nanosheet thickness of cobalt metal nanoparticles (right): Co1 has a dendritic crystal morphology; Co2 has an aggregated cactus-like morphology; Co3 has pompon-like microspheres. Cobalt(III) ammine complexes as precursor (left).

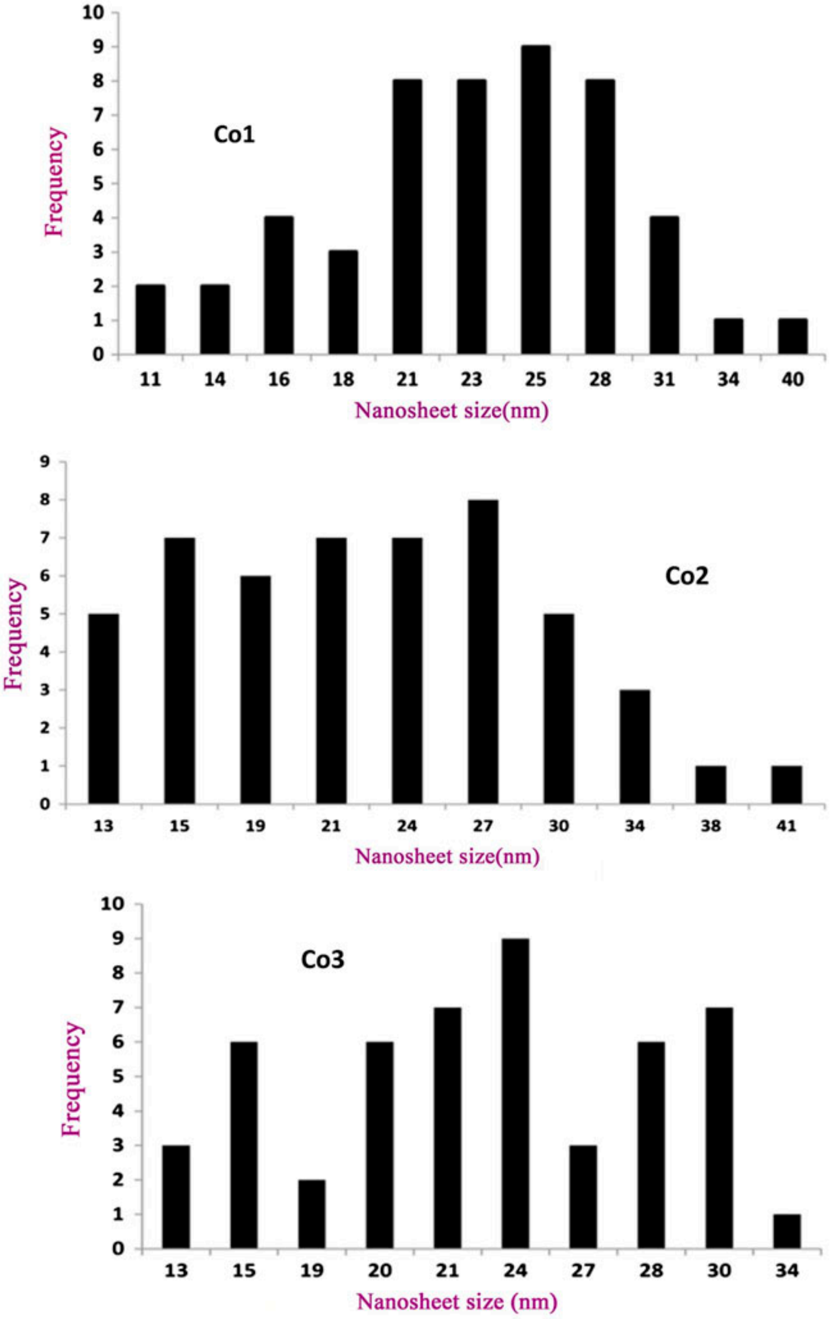

Figure 5. Histograms of nanosheet thickness distributions in cobalt nanoparticles (Co1, Co2, Co3), which are produced from $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5Cl]Cl_2$, and $[Co(NH_3)_5ONO]Cl_2$ respectively.

complexes into cobalt metal is accompanied by a change in magnetization. These molecular diamagnetic complexes are changed to ferromagnetic cobalt metallic nanoparticles (figure 3). The saturation magnetization (M_S) values of Co1, Co2, and Co3 are 102.20, 125.00, and 135.00 emu/g, respectively (table 2). Here the cobalt nanoparticles have a saturation magnetization less than that of the bulk cobalt. The M_S value of the bulk cobalt was about 160 emu/g at 300 K. It is reported in the literature that in magnetic nanoparticles, the magnetisation is often smaller than that of the bulk solid [23].

3.4. *Analysis of particle morphology and particle nanosheet thickness*

SEM provides valuable information regarding the structural arrangement, density, and geometric features of materials in solid state. Figure 4 shows SEM photographs of the reactants and products. The prepared cobalt particles have different morphology. The morphology of the cobalt nanoparticles depends on the complex structure as a reactant. Morphological analysis is concerned with particle characterization in the case of particle size, particle shape, and particle texture. According to the experimental conditions, the morphology of prepared cobalt can be controlled, whereas particle size and shape have a strong influence on the physical and chemical properties of particulate materials. We measured the 50 particle nanosheet of synthetic cobalt nanoparticles and investigated their frequencies as a function of nanosheet thickness in Co1, Co2, and Co3 (figure 5). The SEM micrograph of cobalt nanoparticles in Co1 shows an aggregated dendrite structure with sheet thickness ranging from 15 nm to 40 nm. The statistical analysis of histograms shows a narrow symmetrical nanosheet size distribution of Co1, whereas aggregated cactus-like nanaostructures consisting of nanosheet thickness ranging from 15 nm to 35 nm are observed in Co2. A polydisperse skew nanosheet size distribution is observed in Co2 (figure 5). The Co3 nanostructures have a pompon-like microsphere that consists of a nanosheet thickness ranging from 10 nm to 45 nm. The histogram of Co3 shows a polydisperse trimodal nanosheet size distribution. The statistical analyse show different morphologies and nanosheet thickness distributions in prepared metallic cobalt. These differences in nanoparticles may result from the changes in the coordination sphere of the complexes. In particular, the redox potentials of the cobalt(III) complexes are greatly modified by the changing of the coordination spheres. The mechanism of reaction during the electron transfer can be affected by the coordination sphere of the cobalt(III) complex. On the other hand, the rate of electron transfer depends on the mechanism of reaction. Therefore, the cobalt(III) precursors have a profound effect on both the physical and chemical properties of the metallic cobalt nanoparticles.

4. Conclusions

Fine cobalt powders with a different morphology were prepared from the reduction of cobalt ammine complexes in alcoholic alkaline solution. The phase and composition of complexes used as a precursor in this work, were highly dependent on the synthesis condition. The reduction of cobalt complexes into the metallic Co powder occurs via the dissociation of complexes and reduction by hydrazine in alkaline solution. The stability of metallic complexes depends on the interaction between the metal ion and ligands. The results show that when the ligands in complexes were changed from amine to chloro and nitrito, respectively, the crystallite size and morphology of cobalt metal nanoparticles are changed. When the metallic cobalt are produced from hexaamminecobalt(III) and pentaamminenitritocobalt(III), the particles have a narrow nanosheet thickness distribution. Whenever nanoparticles are produced by chemical reduction of pentaamminechlorocobalt(III) complex a broad nanosheet thickness distribution is observed in cobalt nanoparticles. The advantages of this work for preparing the metallic powders lie in the differences in narrow size distribution and morphology of the resulting powders. Therefore, it offers as an attractive method in preparation of metallic nanoparticles, because it is often towards the formation of the desired metallic nanoparticles.

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