Protective Agent-Free Synthesis of Colloidal Cobalt Nanoparticles

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Abstract: *Herein, we report a facile low-temperature (80˚C) synthesis route for colloidal cobalt (Co) nanoparticles by Co^{2+} reduction using hydrazine (N_2H_4) in a basic solution of ethylene glycol (EG). The colloidal particles were spherical and monodispersed, with mean diameter ranging from 2–7 nm increasing with the Co chloride concentration. However, precipitation of the nanoparticles resulted in weakly agglomerated spherical Co structures of submicron size. X-ray diffraction (XRD) of the precipitated powder revealed hexagonal close-packed-Co (hcp-Co). But since the major peaks of hcp and face-centered cubic-Co (fcc-Co) are overlapping, the presence of fcc-Co cannot be ruled out. Besides precursor concentration, it was found that pH, reaction temperature, and molar ratio of N_2H_4 to Co^{2+} also influence the reduction rate. An alkaline medium, elevated temperature (80˚C) and high molar ratio of N_2H_4 to Co^{2+} promoted the formation of colloidal Co nanoparticles. Nonetheless, when the molar ratio of N_2H_4 to Co^{2+} was greater than 12, the mean particle size remained almost constant.*

Keywords: cobalt, nanoparticles, protective-agent, hydrazine, ethylene glycol

1.   INTRODUCTION

Extensive study on the synthesis and properties of Co nanoparticles has been carried out in the past years due to its unique size-dependent chemical, electrical, catalytic and magnetic properties[1–3] that have both scientific and technological importance because of their plentiful applications in the field of magnetic recording, ferrofluids, catalysis, and biomedicine.[1–8] Therefore, several physical and chemical processes have already been exploited in order to produce Co nanoparticles within the said size range.[9–10] By far, wet chemical methods such as thermal decomposition of metal-containing compounds, sonochemical treatment, solvothermal method, metal salt reduction, reverse micelles, and polyol method are the most promising owing to the ease and directness of these synthetic routes and to the simplicity of the experimental set-up needed.[1–14] Recently, Li and Liao prepared around 2 nm monosized colloidal

Co nanoparticles by an organic colloid technique using sodium formate and sodium citrate as reductant and complexing agent, respectively.[15] However, the use of a relatively high processing temperature (180˚C) and a long reaction time (8 h) make the method less attractive for large-scale synthesis. Su et al.[16] also reported the formation of colloidal Co nanoparticles with sizes in the range of 6–10 nm by high-temperature reduction of Co chloride with superhydride in the presence of oleic acid and triphenylphosphine. Similarly, the high reaction temperature (210˚C) and the use of environmental unfriendly reagent such as triphenylphosphine are the main disadvantages.

Over the last decade, N_2H_4 has been used as reducing agent for the preparation of Co and other metallic nanoparticles[17] because it is facile, cheap, and the product usually does not contain any chemical contamination from the reducing agent.[5,7,18–19] As an example, Gibson and Putzer used N_2H_4 to reduce Co chloride in an alkaline-aqueous system by employing ultrasound energy.[7] Furthermore, Chen and Wang reported the formation of Ni-Ag core-shell nanoparticles by first generating Ni nanoparticles through the reduction of Ni^{2+} with N_2H_4 and followed by coating of the as-prepared Ni nanoparticles with Ag by introducing $AgNO_3$ in the reaction system.[20]

In this paper, we described a simpler and faster method of producing colloidal Co nanoparticles by the reduction of Co chloride in a basic EG with N_2H_4.[12,20] Synthesis was conducted by heating the solution to 80˚C for one hour in a closed vessel with stirring. EG was employed as both solvent and protective agent,[12] which greatly simplified the process. It is known that protective agents such surfactants and polymer stabilizers, though control the morphology of the nanoparticles[1] and hinder oxidation and agglomeration, are not easy to be removed by simple washing and may cause contamination of the final product.[12] To avoid complication, a suitable solvent such as EG that can also act as a protective agent was employed to avoid the addition of an extra protective agent. Furthermore, a moderately high precursor concentration (30–90 mM) was used in this study in order to evaluate the potential of the process for up-scale production. The colloidal Co nanoparticles were investigated in a transmission electron microscope (TEM), field-emission scanning electron microscope (FE-SEM), XRD and energy dispersive X-ray spectrometer (EDX).

2.   EXPERIMENTAL DETAILS

2.1   Materials

All materials used throughout this work were analytical grade. No further purification was performed. Cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$), N_2H_4 and EG were products of Merck Darmstadt. Sodium hydroxide (NaOH) was supplied by Systerm.

2.2   Preparation of Colloidal Co Nanoparticles

The synthetic procedure can be described as follows: a mixture of $CoCl_2 \cdot 6H_2O$ (1 mmol) in 20 ml EG was prepared followed by the addition of an aqueous solution of NaOH (2 mmol) to obtain an alkaline solution prior to reduction. Next, an appropriate amount of N_2H_4 (50 mmol) was added slowly to the metal solution for reduction to occur. The solution was then heated to 80°C continuously. After one hour, the colloidal Co nanoparticles were produced. Stirring at 420 rpm was done continuously throughout the process.

Heating the colloidal solution for an extended period (1–5 h) caused the precipitation of the Co nanoparticles. The particles were allowed to settle at the bottom of the reactor while the supernatant solution was removed from the top. The discarded solution was immediately replaced with ethanol. This washing process was repeated until the pH of the solution changed to 7.[7] This suggests that excess N_2H_4, sodium and chloride ions were no longer present in the solution. The obtained powders were then dried at room temperature and under vacuum for about one hour to prevent oxidation. After drying, the precipitated particles were stored in sample vials and placed in vacuum dessicators to prevent oxidation.
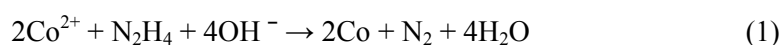
2.3   Characterization of Colloidal Co Nanoparticles

The morphology of the colloidal Co nanoparticles was examined under a CM 12 Philips TEM running at 80 kV and a Zeiss Supra 50 VP FE-SEM. Sample for TEM was prepared by diluting the colloidal solution with ethanol followed by ultrasonication for 5 min.[12] A drop of the sample was then taken, placed on a copper (Cu) grid, and dried in air. The phases present in the powdered samples were identified by using D5000 Siemens XRD with Cu-Kα (λ = 1.5405Å) radiation. Semi-quantitative analyses of the composition of the sample were performed in an EDX.

3.   RESULTS AND DISCUSSION

3.1   Formation and Characterization of Colloidal Co Nanoparticles

Colloidal Co nanoparticles were prepared by the reduction of Co chloride with N_2H_4 in EG. An elevated temperature and a basic solution played significant roles in enhancing the reduction rate. From initial results, no visible reaction was observed within one hour when synthesis was performed below 80°C, as well as when the pH was less than 10. This can be explained by the very slow reduction of Co ions by N_2H_4 at these conditions. It is known that N_2H_4 is considered as a mild reducing agent at room to moderate temperatures, but its reducing ability can be improved in an alkaline medium.[11–13] The overall reaction can be expressed as:

$$2Co^{2+} + N_2H_4 + 4OH^- \rightarrow 2Co + N_2 + 4H_2O \qquad (1)$$

In theory, Equation (1) is thermodynamically feasible and very exothermic.[7] However, it is still kinetically slow.[7,21] Furthermore, side reactions, for example, the decomposition of N_2H_4 to hydrogen and nitrogen gases, and the disproportionation of N_2H_4 to ammonia and nitrogen gases, may also occur and may compete with Co^{2+} for N_2H_4.[11,22] This can lead to less N_2H_4 available for reducing Co ions, hence, slower the reaction rate.

To avoid the lack of N_2H_4, excess amounts must be used.[22] From Equation (1), it can be observed that the equilibrium molar ratio of N_2H_4 to Co^{2+} is equal to 0.5. However, the ratio experimented was purposely much larger than 0.5 to accelerate the reaction. It was also observed from earlier experiments that the reaction will not be completed within one hour when the ratio of N_2H_4 to Co^{2+} is less than 10. Therefore, higher molar ratio of N_2H_4 to Co^{2+} is preferred.[12–13,20]

As shown in Figure 1(a), the synthesized colloidal Co nanoparticles were spherical and well-dispersed. The calculated average diameter was 4.1 ± 1.1 nm suggesting that the colloidal nanoparticles were rather monodispersed with narrow size distribution as seen in Figure 1(b). This can be the effect of the alkalinity of the reaction solution since it was found that formation of monodispersed nanoparticles by homogeneous nucleation is easier at this condition. In an alkaline medium, a large concentration of hydroxyl ions keeps the Co ions in its active state of $Co(OH)_4^{2-}$, which then promotes the reaction. Thus, to narrow down the size distribution of the particles in the solution, an alkaline environment during reduction is required.
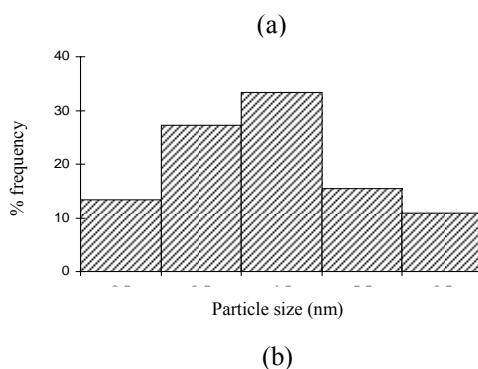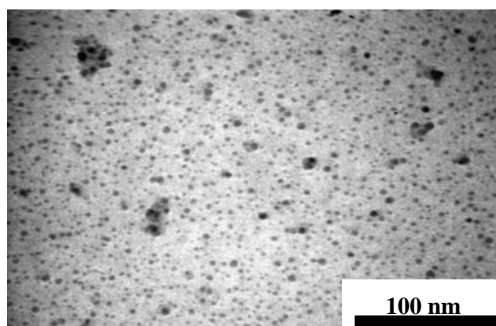
(a)

(b)

Figure 1:   (a) Typical TEM image and (b) size distribution of colloidal Co nanoparticles. $CoCl_2 = 40$ mM; $N_2H_4 = 5$ M.

Meanwhile, the unagglomerated state of the colloidal Co nanoparticles could only mean that the EG efficiently acted as both solvent and protective agent. Moreover, it has been found that EG can be adsorbed on the surface of the colloidal particles via the interaction of the hydroxyl group with the metal nuclei.[12,20] Thus, no additional protective was needed to prevent the agglomeration of the synthesized colloidal Co nanoparticles.

In other works, the use of a mixture of different protective agents like tricotylphosphine oxide, triphenylphosphine, lauric acid and oleic acid not only hinders particle agglomeration, but also tailors the shape of the nanoparticles.[1,3,8] Nonetheless, it was found that in the presence of a single protective agent, sphere is the most probable shape for the nanoparticles since it represents a minimal surface and consequently a minimal surface energy.[2,8] Thus, the spherical shape of the synthesized colloidal Co nanoparticles can be attributed to the influence of the surface energy in arranging the surface structure of the nanoparticles in order to minimize its value.[2] Furthermore, it also possible that the EG molecules surrounding the Co nuclei prevented further diffusion of zero-valent Co atoms

during the growth period leading to a diffusion-controlled growth, which also favors the formation of spherical shape nanoparticles.[10]

On the other hand, continuous heating of the colloidal nanoparticles led to their growth and precipitation from the solution. The precipitated Co nanoparticles were then examined under FE-SEM, where they were found to be in the form of large spheres of submicron size (0.1–1 µm) as shown in Figure 2. This indicates that Ostwald ripening probably occurred during the precipitation of the colloidal Co nanoparticles by extended heating. Therefore, bigger secondary particles were formed from the agglomeration of smaller colloidal nanoparticles.

Figure 3 shows the XRD of the precipitated Co nanoparticles. All peaks were attributed to hcp-Co, which were indexed as the reflections of (100), (002), (101), (102), (110), (112), and (004) planes at around 41.8°, 44.4°, 47.6°, 63°, 75.9°, 92.6°, and 99°, respectively. Nevertheless, the presence of fcc-Co cannot be ruled out since fcc-Co has 2θ peaks at 44.5°, 75.8°, and 92.6°, which might have overlapped with the hcp-Co peaks. Reference ICDD cards were 05-0727 for hcp-Co and 15-806 for fcc-Co. It is known that hcp and fcc are the stable phases of Co; hcp is stable at temperatures below 425°C and above this temperature is the fcc regime. However, both phases can co-exist at room temperature when the particles are very small.[8] This supports the possibility of a mixed hcp and fcc phases in the samples. On the other hand, the lower intensities of the peaks, as well as the absence of other diffraction peaks could be due to lattice
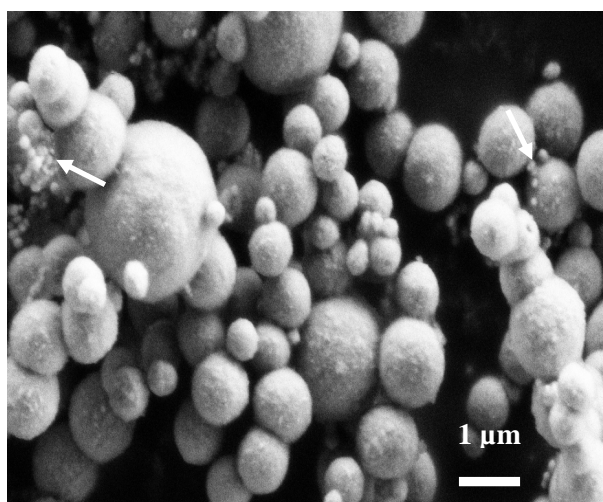

Figure 2: FE-SEM of precipitated colloidal Co nanoparticles showing Co spheres of submicron in size indicating agglomeration of nanoparticles. Arrows point to smaller Co particles attached to larger ones.

imperfections such as stacking faults and twin planes observed in the colloidal Co nanoparticles under the TEM.[23] This led to the collapse of periodicity along some directions and consequently to the poor crystallinity of the sample.
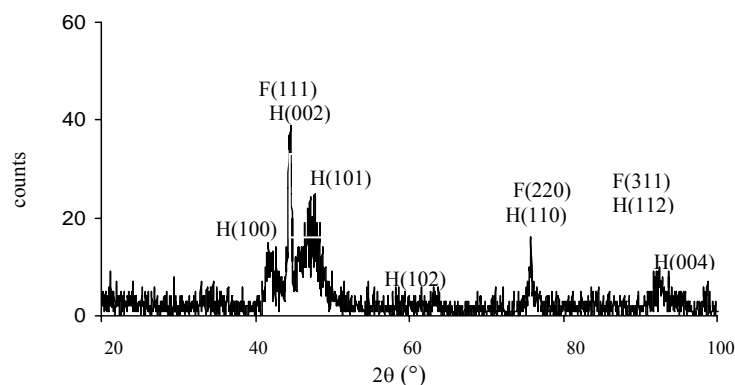

Figure 3: XRD pattern of precipitated colloidal Co nanoparticles. H = HCP; F = FCC.

Meanwhile, no peaks related to Co alkoxide, oxide, or hydroxide was identified from the XRD pattern. It is possible that the impurities were also in nanoscale, too thin to be detected and amorphous. Hence, their detection by XRD would be impossible. Additionally, Joseyphus et al.[24] demonstrated that Co alkoxide formation from Co chloride heated in EG only occurred at about 200°C and after around 20 min of heating. Since the reaction temperature was kept to 80°C in the current work, formation of Co alkoxide was not feasible. Furthermore, semi-quantitative analysis by EDX revealed that the precipitate is almost pure Co (98.53%), while the rest are C and O. The contained C and O were presumed to be from residual organic material such as ethanol and EG. Furthermore, the precipitated Co nanoparticles were observed to react strongly to a permanent magnet indicating its metallic character, which confirms the XRD and EDX results.

3.2   Effects of N_2H_4 and Co Chloride Concentration on the Colloidal Co Nanoparticles

Optimization of process parameters for the fabrication of colloidal Co nanoparticles was done by investigating the effects of the molar ratio of N_2H_4 to Co^{2+} (R) and the precursor concentration on the reduction rate and particle size. In Figure 4(a), it was observed that the mean diameter of the colloidal Co nanoparticles did not significantly change when R > 12. On the other hand, a 40% increase in size was observed when R is equal to 10. This can be explained as the effect of reduction rate on nucleation of the nanoparticles.[12–13,20] Accordingly, there is a required number of atoms to produce a stable nucleus, and

before a nucleus forms, collisions between atoms are necessary.[10,12–13,20] Therefore, a high concentration of N_2H_4 enhanced the reduction rate, which increased the concentration of Co atoms. As a consequence, more Co nuclei were generated and smaller colloidal nanoparticles were produced.[10,12–13,20] However, with increasing molar ratio (R > 12), it is possible that the number of Co nuclei created was almost constant due to the inherent limitation of the process. Thus, even with higher amounts of N_2H_4, an almost equal number of nuclei grew at the same rate that resulted to colloidal Co nanoparticles having nearly identical diameters.[10,12–13,20] On the other hand, at a low value of R (< 12), the reduction rate was too slow due to the low concentration of N_2H_4, thus, only a few Co ions were reduced to Co atoms. In turn, the number of nuclei formed in the solution was decreased and larger colloidal Co nanorparticles were produced.[10,12–13,20]

In the case of increasing precursor concentration, it was found that the formation of Co nanoparticles was very slow at low concentrations of Co chloride (< 30 mM) even with a large amount of N_2H_4 (R = 50). At Co chloride concentration ranging from 30–90 mM, the reaction finished within one hour and the colloidal nanoparticles grew bigger with increasing precursor concentration as presented in Figure 4(b). It was also noted that even at a concentration of 90 mM,
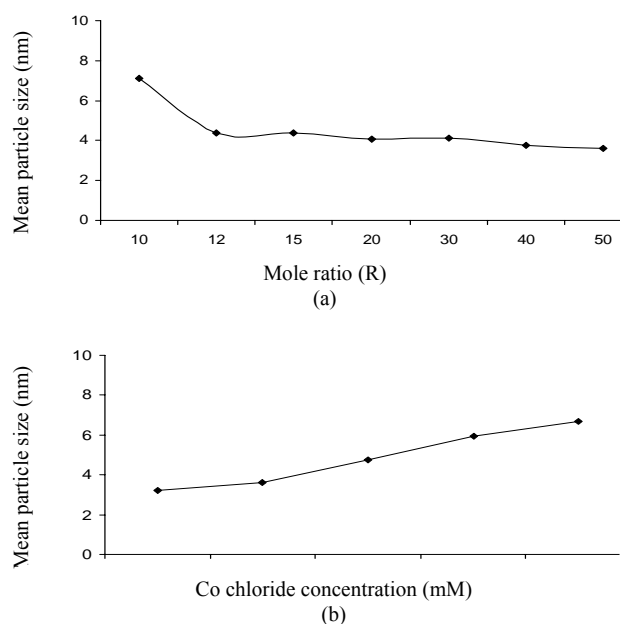

Figure 4 :(a) Effect of N_2H_4 to Co^{2+} molar ratio on the mean particle size of colloidal Co nanoparticles; Co^{2+} = 40 mM, N_2H_4 = 1–10 M and (b) Effect of precursor concentration on the mean particle size of colloidal Co nanoparticles; R = 50.

the average particle size was approximately 6 nm. This is important for future attempts of large-scale production of Co nanoparticles. However, some degree of weak agglomeration was observed at this concentration. But with the use of ultrasound energy, the nanoparticles can still be re-dispersed.

On the other hand, at very high Co chloride concentrations (> 90 mM), immediate precipitation of large nanoparticles was observed. This phenomenon is attributed to the immediate supersaturation of the solution with Co atoms and the very fast growth rate of the nanoparticles.[10] Thus, synthesis of colloidal Co was limited to concentration below 90 mM to better control the size of the Co nanoparticles.

From the results, it was found that an optimum precursor concentration is a balance among several factors such as rate of reduction, mean particle size and size distribution. A low precursor concentration, thus a slow reduction rate, can result to smaller particle size with good distribution. On the other hand, a fast reaction can be induced by higher precursor concentration. Then again, large particle size with possible agglomeration can be obtained. In this study, 40 mM was found to be the optimum amount of precursor (particles approximately 4 nm).

4.   CONCLUSION

Colloidal Co nanoparticles were successfully synthesized by reducing Co chloride in a basic solution of EG using N_2H_4. The colloidal Co nanoparticles were spherical and monodispersed with mean diameters ranging from 2–7 nm. It was also found that pH, temperature, molar ratio of N_2H_4 to Co^{2+}, and precursor concentration influenced the reduction rate, thus affecting the size, distribution, and degree of agglomeration of the colloidal nanoparticles. High pH, elevated temperature (80˚C), a large amount of N_2H_4 (R), and a relatively high Co chloride concentration resulted in faster reduction rate. At a Co chloride concentration of 40 mM, the average particle diameter approached a constant value with increasing N_2H_4 concentration (R > 12), while at a constant value of R, the mean particle size increased with increasing Co chloride concentration. Precipitated Co particles of about 0.1–1μm were found to be hcp-Co, but fcc-Co possibly co-exists as well.

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