Synthesis and characterization of aggregated nano-cobalt particles by bottom up approach

Mohammad Hussain[1*], Kazi Haque[2], Syed Alam[2], Sheikh Islam[2]

[1]Saudi International Petrochemical Company (SIPCHEM), Al-Khobar, Saudi Arabia

[2]Shahjalal University of Science and Technology,Sylhet,Bangladesh

*Email of the corresponding author: mshussain@sipchem.com

Abstract

This paper reports a novel process for the synthesis of nano-sized cobalt particles by a bottom-up approach. Cobalt chloride has been reduced using hydrazine as the precursor, in a basic medium maintained at 70^0C. Other factors studied in this research were the combined effect of using an anionic surfactant – sodium dodecyl sulphate (SDS) and a cationic polymer-polyvinylpyrrolidone (PVP) in the formation of nano-sized agglomerated Co particles. Further particle size reduction (less than 5nm) was achieved by using this combination of SDS with PVP. These nano-aggregated cobalt particles were characterized by using high resolution electron microscopes HRSEM/HRTEM with EDX facilities. On the basis of electron microscopic observations a model is postulated: in the absence of SDS/PVP the cobalt atoms get aggregated and form a natural oxide layer around them, with time further aggregation occur they meet up with more Co particles. When both SDS and PVP are present, PVP is able to form a polymeric coating around the aggregated cobalt particles already oxidized and stops further agglomeration. The PVP-polymeric layer is able to hinder the formation of further agglomeration of Co atoms hence a dramatic reduction in the particle sizes are obtained.

Keywords: Bottom-up, SDS/PVP, Co particles, 5nm

1. Introduction

Ferromagnetic nanoparticles open a new field of science and technology because they are potential candidates for magnetic data storage. Ideally in these materials, each well-separated nanocrystal is expected to correspond to one bit of information (Lambeth et.al., 1996, T.Ogino et. al.1999). The preparation of nanosized materials and their characterization corresponds to the expectation of the 21stcentury to join up the macro, micro and nanotechnologies for the reason of the higher integration of the electronic components. Nanoparticles of various materials exhibit interesting and remarkable properties like optical, electric, magnetic and mechanical due to their quantum size resulting of quantum-size effects which differ from the bulk materials properties. This determines the world tendencies for the intensive development of methods for synthesis of nanostructural materials and their characterization (Kobayasi, 2001, Gussev, 2005).

Nano-structured materials can be produced by two different approaches, namely, “top down” and “bottom up” approach. The top down approach is the process of breaking down the bulk metals and subsequent stabilization of the resulting nano-sized metal particles of colloidal protecting agents (Hussain 2007, Hussain 2009, Hussain and Haque 2008). The bottom up approach on the other hand is the wet chemical nano-particle preparation, which relies on building nano-particles from the atom level of the metal. The interaction between polymers and surfactants in aqueous solutions has been very popular due to applications of mixed polymer-surfactant systems in various materials systems, such as detergents, hair care products, foams, emulsions, mineral oil recovery, and in gene-therapy DNA-lipid complexes.

Many different techniques have been used in the preparation of nano-sized particles, for example, the reduction of metal oxide salts (Kimijima andSugimoto, 2005), decomposition of carbonyls (E. Kauffeldt and T. Kauffeldt, 2006) and reduction in solutions by strong reducing agents (Hussain et. al. 2009). Reducing agents used include potassium borohydrides, sodium hypophosphite and hydrazine, which corresponds to the formation of metal borides (Petit et.al., 1993), metal phosphides (Zhang et.al. 1999, Scott and Geoffrey, 1998) and pure metals. In the recent past the use of surfactant-macromolecule clusters as template to prepare inorganic crystals become an area of much research interest (Scott and Geoffrey, 1998, Zheng et.al., 2002, Maria et.al., 2004.). It is now well-known that water-soluble non-ionic macromolecule, such as polyvinylpirrolidone (PVP) or polyethyleneoxide (PEO) interact strongly with anionic surfactant, such as sodium dodecyl sulphate (SDS), in aqueous solution (Maria et.al., 2004, Zana et.al., 1985). Above the critical association concentration (cac), surfactant aggregate on macromolecule chains in micellar structure, which is known as bound-micelle (Zana et.al. 1985).

The purpose of this research work was to study the effect of using SDS/PVP solution as a structure-directing agent in this chemical reduction process. The ultimate aim is to synthesize nano-sized MCrAlY(M= Ni or Co or Fe) alloy powders (less than 100nm in diameter) for high temperature applications in aerospace and power generation industries in bulk quantities. We report here a synthetic method of preparing nano-structured Co particles by bottom up approach, i.e. a wet chemical nano-particle preparation.

2. Experimental

2.1 Materials

Materials used in this research work were cobalt chloride analytical grade; sodium dodecyl sulphate (SDS, LOBA Chemie, India, 92%); polyvinylpyrrolidone (PVP Winlab, UK); hydrazine hydrate solution (LOBA Chemie, India, 80%); Sodium Carbonate (Sigma, 99%); de-ionized distilled water was used in the preparation of all the solutions. A thermostatically controlled hot plate with magnetic stirrer (Yellow Line) was used in this research work.

2.2 Synthesis of nanocobalt particles

The nano-sized cobalt particles were synthesized by dissolving 10g of $CoCl_2$ in a glass beaker containing 100mL of de-ionized water which was maintained at 40^0C. The pH of the cobalt chloride solution was then increased to 10.2 by adding concentrated sodium carbonate solution. 150mL of hydrazine was added to the solution slowly whilst stirring was on all the time. Temperature of the cobalt chloride solution was increased to 70^0C before adding the hydrazine to the $CoCl_2$ solution. At 70^0C as the reaction continues appearance of gray/black precipitates in the beaker meant that cobalt particles have started to form. This reaction is not instantaneous and can take several hours for the cobalt reduction to reach completion. Co particles were deposited at the bottom of the reaction vessel. The gray/black particles so formed were the aggregated nano-sized cobalt particles. The products were collected, centrifuged (4000 rpm), washed with distilled water and ethanol for three times, and finally desiccated at room temperature before characterization. Same experiment was carried out adding 20g/l of SDS and 20g/l of PVP to the cobalt chloride solution before adding hydrazine to study the effect of SDS/PVP on the morphology and size of the synthesized Co nanoparticles.

2.3 Characterization

The cobalt particles were characterized using a High Resolution Scanning Electron Microscope (HRSEM) FEI–NOVA 200Nanolab with EDAX and another High Resolution Transmission Electron Microscope (HRTEM) JEOL - JEM 2100F.

3. Results and Discussion:

Metal atoms are formed by transferring of electrons from a reducing agent (Red^{m-}) to the oxidized metallic species

$$M^{n+} + Red^{m-} \rightarrow M^0 + Ox^{m-n} \qquad (1)$$

where M^0 = metal atom produced by the gaining of electron from the reducing agent, Ox^{m-n} = species produced from the reducing agent after transferring electron to the metal ion, m and n are the charges. Transfer of electrons from the reducing agent to the metal ions mainly depends on the value of standard redox potential associated with the reaction ΔE^0 whichis direct measure of the free energy of the transformation according to the equation

$$\Delta G = - nF\Delta E^0 \qquad (2)$$

Where, n = Number of Faraday passed, F= 96500 coulomb, ΔE^0 = Change in standard electrode potential, ΔG is the change in free energy.

For the information about mechanism of the reduction reaction, the value of ΔE^0 is also an excellent predictor of the rate of the chemical reaction. Generally an increase in its value is associated with a more rapid generation of atoms in the liquid phase. E^0 of equation (3) in a basic medium is -0.73V and for the equation (4) is -1.16. So the value of ΔE^0 then becomes -0.73 - (-1.16) = +0.43V. The value of ΔE^0 for the reduction of Co^{2+} by hydrazine in a basic medium is +0.43V, hence the value of ΔG^0 (change in Gibbs free energy) would then be - 82990 (i.e. $\Delta G^0 = -2 \times 96500 \times 0.43$). According to the theory of thermodynamics, if value of ΔG^0 is negative then the reaction would take place. As the value ΔG^0 is negative so it is possible to reduce Co^{2+} ion by hydrazine in the basic medium. Co^{2+} ion can be reduced as follows:

$$Co^{2+} + 2e \rightarrow Co \qquad (3)$$

In a basic medium hydrazine acts as a very strong reducing agent

$$N_2H_4 + 4OH^- \rightarrow N_2 + 4H_2O + 4e^- \qquad (4)$$

So the overall reaction for the reduction of Co^{2+} by hydrazine in a basic medium is as follows:

$$Co^{2+} + N_2H_4 + OH^- \rightarrow Co + N_2 + H_2O \qquad (5)$$

In order to increase the pH to10.2 concentrated sodium carbonate solution was added to the $CoCl_2$ solution. However, as the sodium carbonate dissolves in water it forms NaOH which then react with $CoCl_2$ and form $Co(OH)_2$

$$Na_2CO_3 + H_2O = NaOH + H_2CO_3 \qquad (6)$$

$$NaOH + CoCl_2 = Co(OH)_2 + NaCl \qquad (7)$$

Hence, the Co^{2+} ionsfrom the compound $Co(OH)_2$ are reduced to Co atoms as shown in equation(5). Fig. 1 shows SEM image of a cobalt powder sample which was synthesized using hydrazine only without the addition of any SDS/PVP. The image shows the presence of a large number of spherical clusters of agglomerated particles. The sizes of the agglomerated spheres seem to vary between 100 to 200 µm in diameter. Fig. 2 shows SEM image of the same sample as shown in Fig. 1 but this time shown at a much higher magnification. At this higher magnification the spherical structure seems to have somewhat cauliflower-like structure, presence of much finer and spherical structure can be clearly observed residing inside the larger spherical structures. The size of these spherical embedded structures is apparently less than 1 µm in diameter. Figures 3 and 4 show SEM images of a cobalt powder sample synthesized by using hydrazine in the presence of SDS and PVP. Fig. 3 also shows structure which is similar to the particles shown in Fig. 1. However, this time the particles are observed to bevery well dispersed, agglomeration of particles has been greatly reduced. These particles are more uniformly dispersed with diameter of less than 30 µm. At a higher magnification, Fig. 4 shows that these spherical particles are also made up of much finer particles within the larger spherical objects as has been observed in Fig. 3.

Fig. 5 is the SEM/EDAX plot of Co nano powder sample which was synthesized using hydrazine only i.e. without any SDS or PVP. This plot shows two peaks, one for Co and the other one for oxygen. It is known from a studies carried out by the US General Accounting office in 1983 that the surface of cobalt is susceptible to oxidation at a variable rate, depending on such factors as temperature, humidity, and porosity. Furthermore in this experiment cobalt has been acquired in an aqueous form therefore this would make surface oxidation much likely.Therefore the presence of an oxide layer around the cobalt is expected. Fig. 6 is a SEM/EDAX plot of the Co sample powders synthesized by using hydrazine in the presence of both SDS and PVP. For cobalt, this plot shows exactly the same features as has been observed in Fig. 5, except that this time the peak of oxygen is much prominent and then there is a small peak showing the presence of carbon in the structures. In this reaction PVP, a carbon compound has been added along with SDS which was not present in the experimental results-plot shown in Fig. 5 hence the presence of carbon is expected to be present with these cobalt powders.

Figures 7 and 8 are the HRTEM images of Co sample powder synthesized by using hydrazine only and with SDS and PVP respectively. In Fig. 7 the TEM image shows that the particle size is around 10nm in diameter. Fig. 8 is the TEM image of the Co sample powder synthesized by using hydrazine in the presence of SDS and PVP. This image shows that the particle size is around 5 nm in diameter. These HRTEM images confirm that that the addition of SDS and PVP has been able to reduce the particle size of the cobalt powders quite considerably.

Fig. 9 shows a schematic diagram indicating that when only hydrazine is used for reducing the Co ions there is the possibility of Co atoms to become agglomerated from a few atoms forming clusters to a large number of atoms forming big clusters. However, in the absence of SDS/PVP a relatively small number of Co agglomerates and there remain possibility of forming oxide layers around them. These oxide layers around the clusters of Co particles are very thin (likely to be less than 2nm) hence they are attracted by other similar clusters of Co particles and continue to grow in size. At a certain point of time the agglomeration process stops and we observe a steady state spherical clusters of Co particles (figures 1 and 2), where we saw smaller particles were embedded within larger structures. Fig. 5 confirms that these Co particles become surrounded by an oxide layer. However, in case of the reduction processes where SDS/PVP was present, the growth or agglomeration process was hindered by the presence of PVP. Although the thickness of the polymer layer (C) around the Co particles are apparent from the HRTEM/HRSEM images but this is expected to be much thicker than the natural oxide layer which has been shown to be present in Fig. 5. Hence these much thicker polymer (C) layers which had formed around the agglomerated Co clusters were able to cushion the agglomerated Co clusters at a very early stage of the chemical reduction process from forming further agglomeration of the Co clusters. Hence the particle sizes in the reaction where SDS/PVP are present are able to produce much finer Co particles.

Here we use schematic diagrams (figures 11 and 12) to explain this hypothesis on the formation of Co nano-particles in the presence of hydrazine alone and in the reduction process where SDS/PVP was present. Fig. 9 shows the initial stages of the reduction reaction when Co atoms are formed. Most likely reaction is that as Co atoms are reduced in the solution - they are attracted to other similar Co atoms and form small clusters of Co atoms (Fig.10). It has been established from previous studies that Co do form oxide layers around them hence these smaller clusters are also likely to have an oxide layer around them. With time these smaller clusters of Co atoms aggregate further and form much larger clusters of Co atoms surrounded by an oxide layer (Fig.11). One of the possible reactions that could take place at this stage would be the formation of Co^+ and Cl^- ion particles this could as well be classed as an intermediate reaction from where further Co reduction would follow. Fig 13 shows the particle size distribution for the particles synthesized using hydrazine only. Result shows that the particle sizes vary from 1 to 8 nm but the average size is about 5 nm. Fig. 13 shows the particle size distribution for the particles that were synthesized using hydrazine with SDS and PVP. Result also shows that the particle sizes varied from 1 to 8 nm but the average size is less than 5 nm. SEM/HRTEM images confirm that by using SDS/PVP it has been possible to reduce the size of the Co particles quite significantly and it was in the range of 5nm in diameter.

4. Conclusion

Co particles have been synthesized by a bottom up approach. Spherical nano-structured cobalt particles with diameter less than 10 nm have been successfully synthesized by using hydrazine as the reducing agent. Dramatic reduction in the particle size was achieved by using a combination of SDS/PVP along with hydrazine. HRSEM/EDX characterization indicates that these spherical Co particles were covered by an oxide layer followed by an external C (polymer) layer surrounding the surface oxidized Co. These Co particles were as fine as 5nm in diameter–a hypothesis is postulated - this polymer layer is claimed to have stopped further agglomeration of the Co particles.

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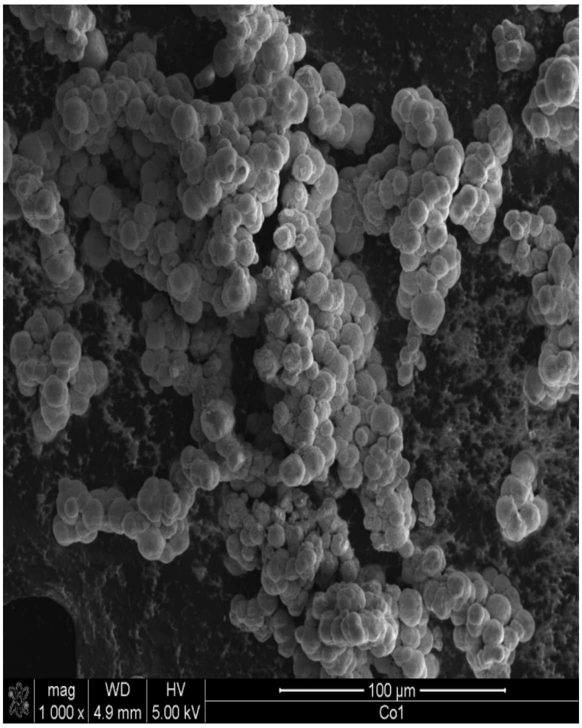


Figure 1. SEM image of Co particles synthesized using hydrazine only.

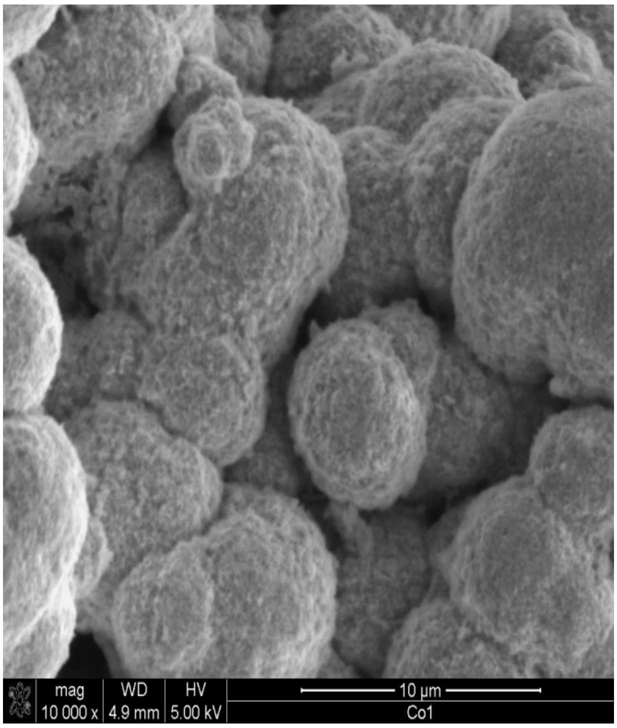


Figure 2. SEM image of Co particles synthesized using hydrazine only.

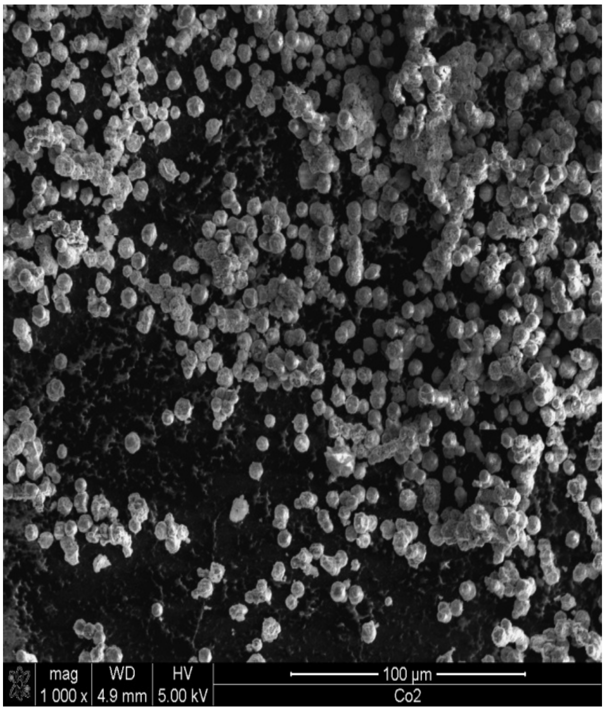


Figure 3. SEM image of Co particles synthesized using SDS/PVP with hydrazine.

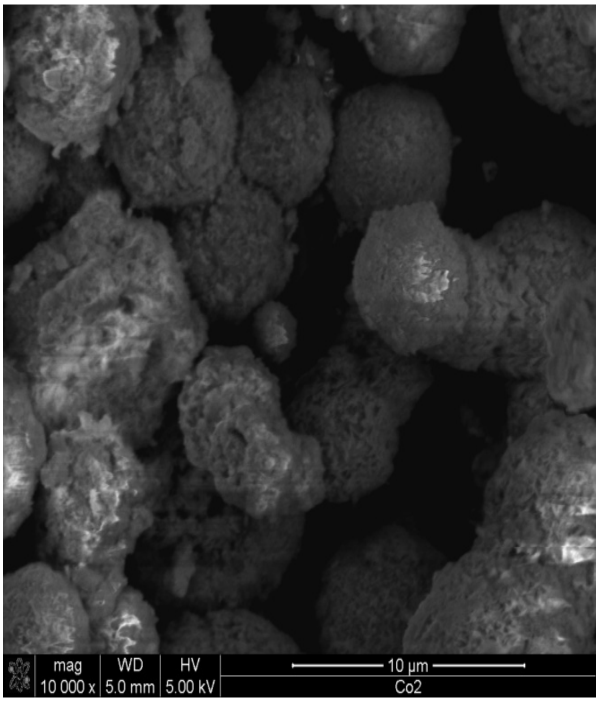
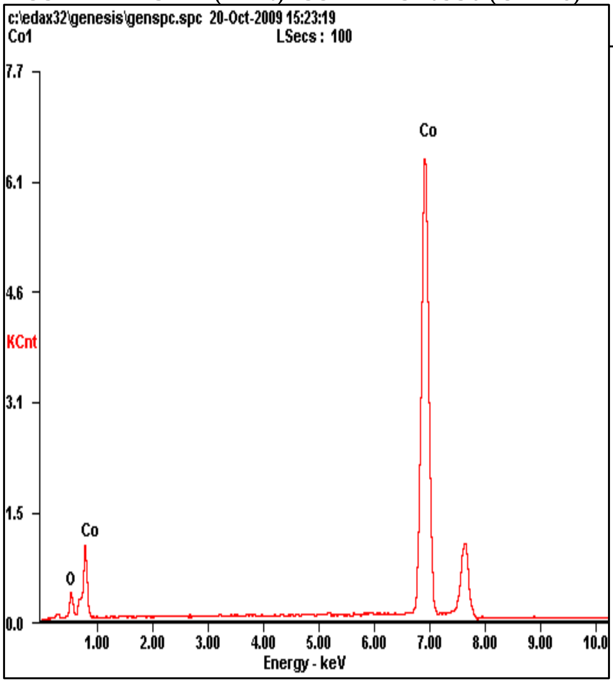


Figure 4. SEM image of Co particles synthesized using SDS/PVP with hydrazine.



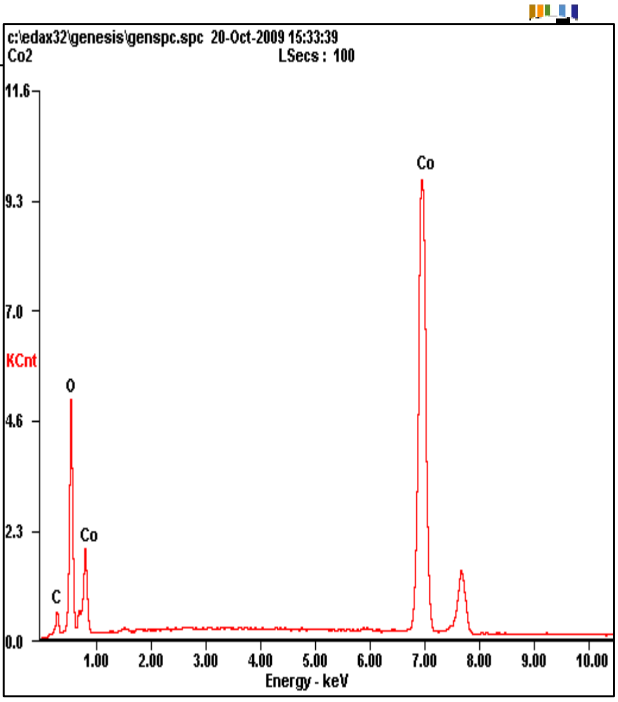
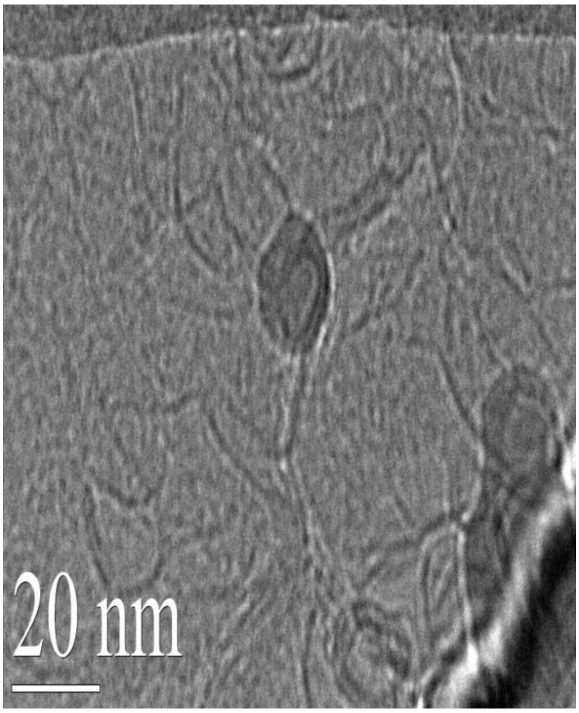


Figure 5. SEM/EDAX image of Co particles synthesized using hydrazine only.

Figure 6. SEM/EDAX image of Co particles synthesized using hydrazine with SDS/PVP.



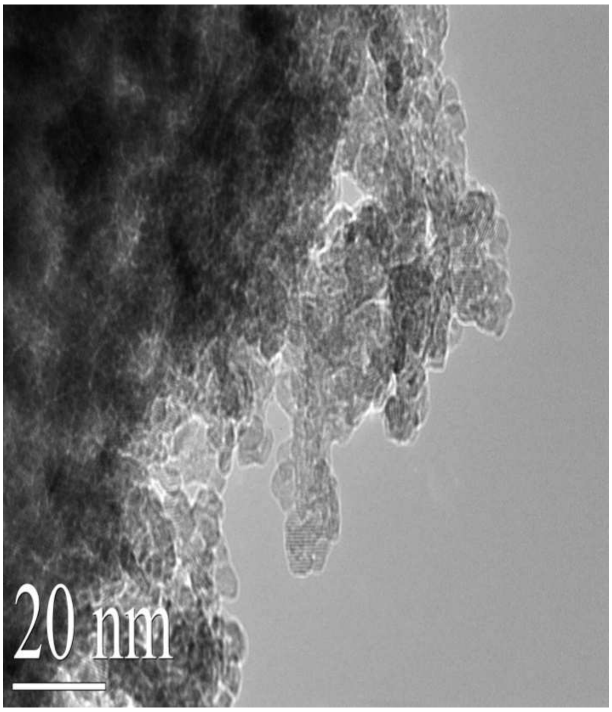


Fig.7. HRTEM image of Co particles synthesized using hydrazine only.

Figure 8. HRTEM image of Co particles synthesized using hydrazine with SDS/PVP.

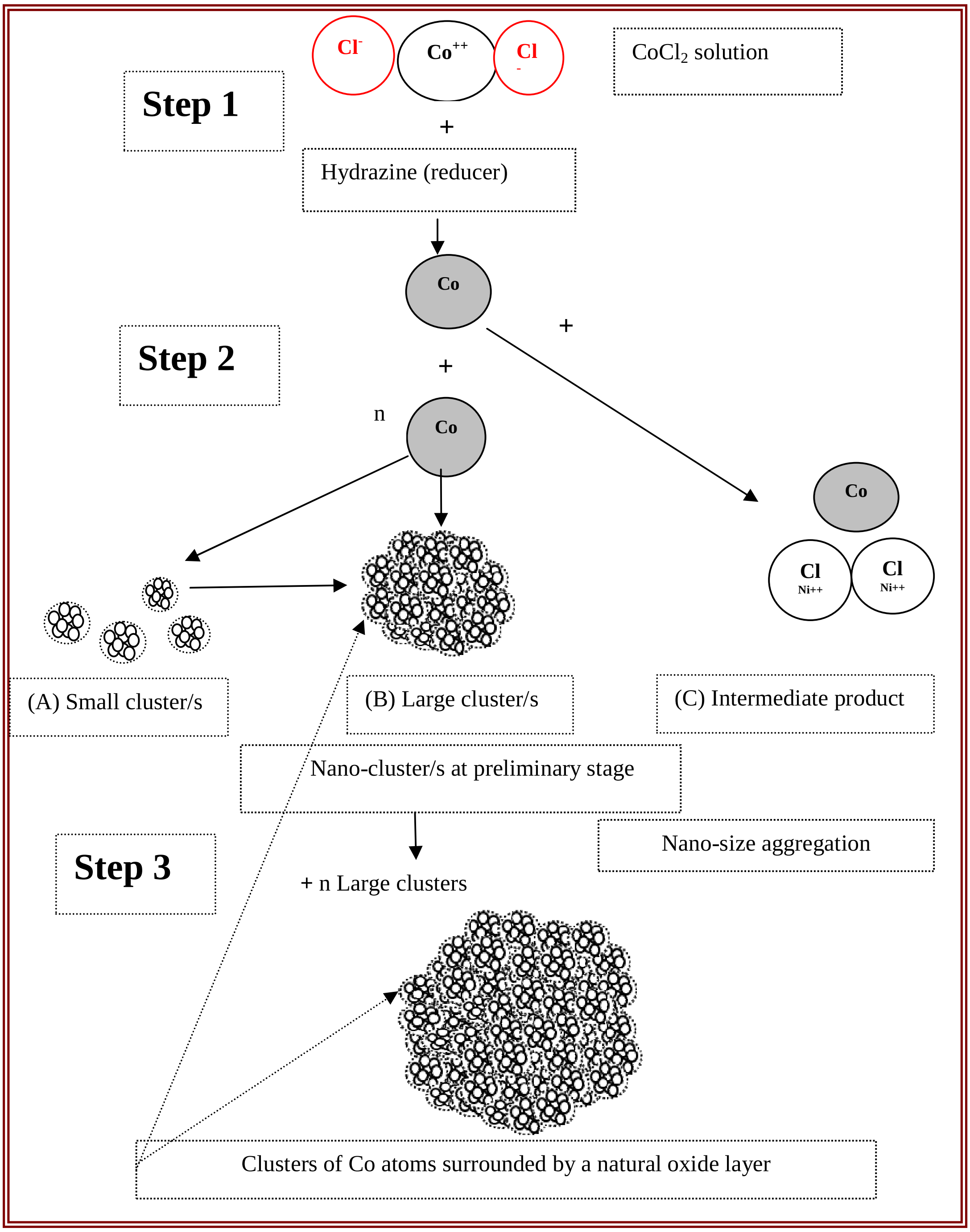


Figure 9. Schematic diagram showing the formation nano-clusters of Co in the absence of SDS/PVP

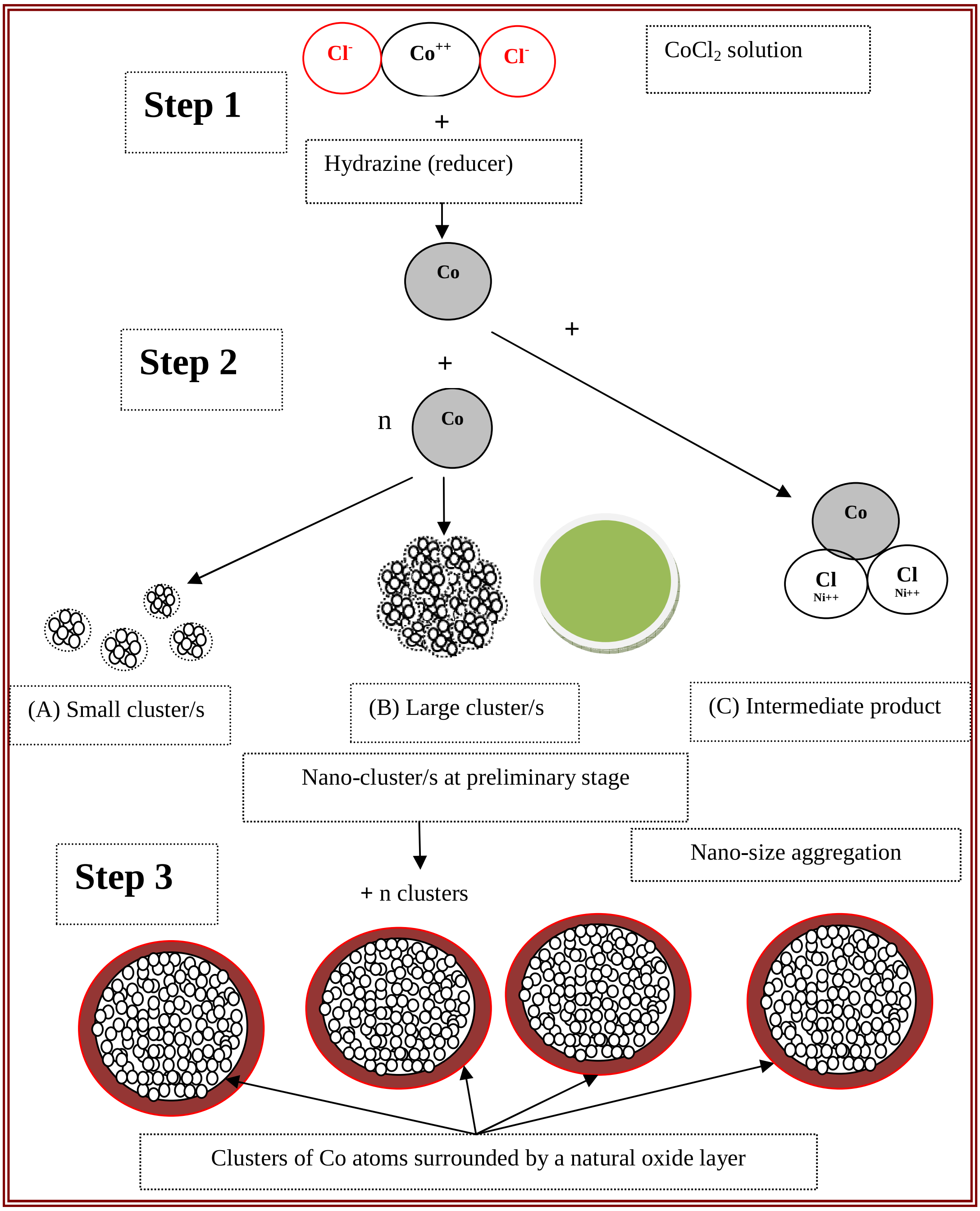
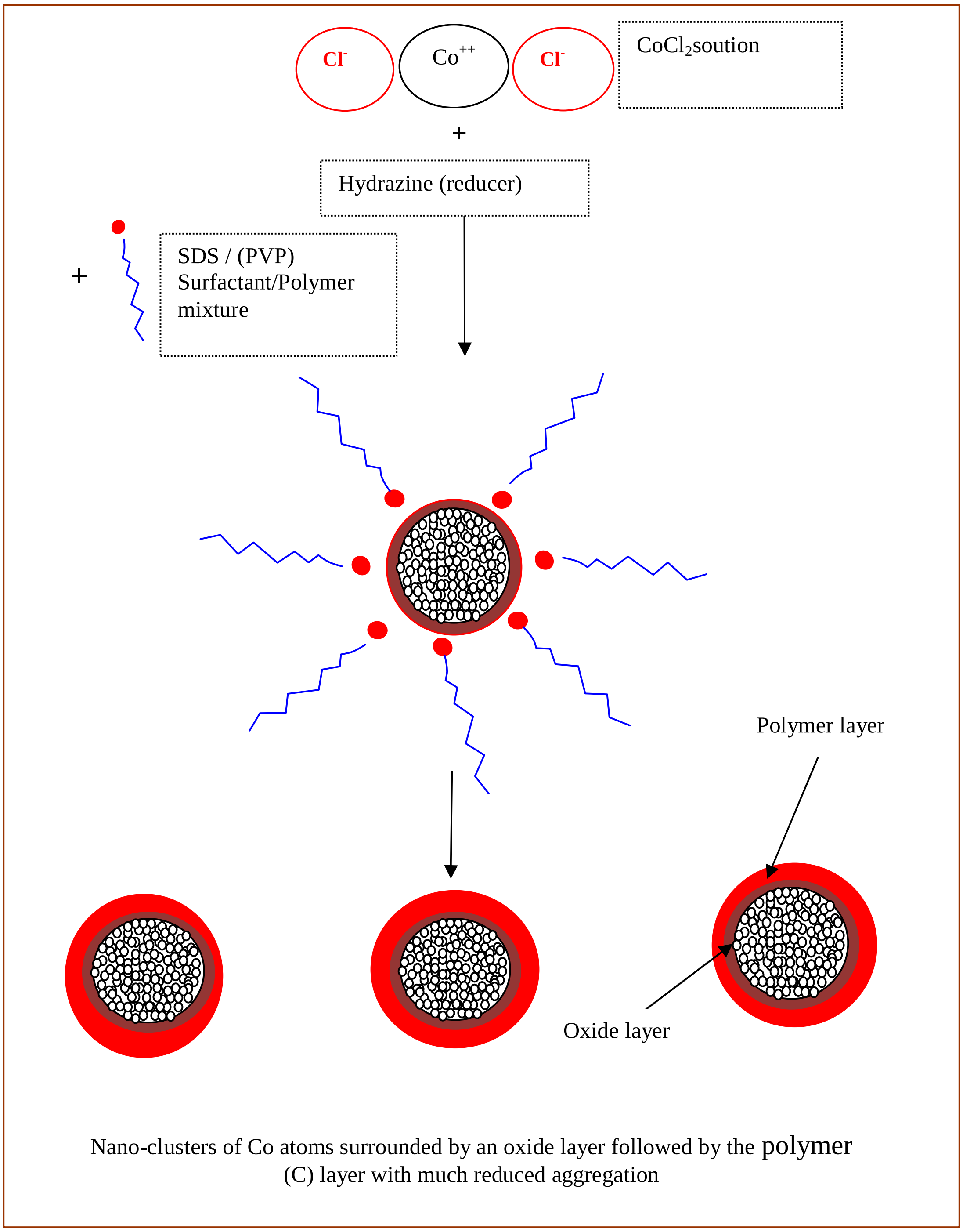
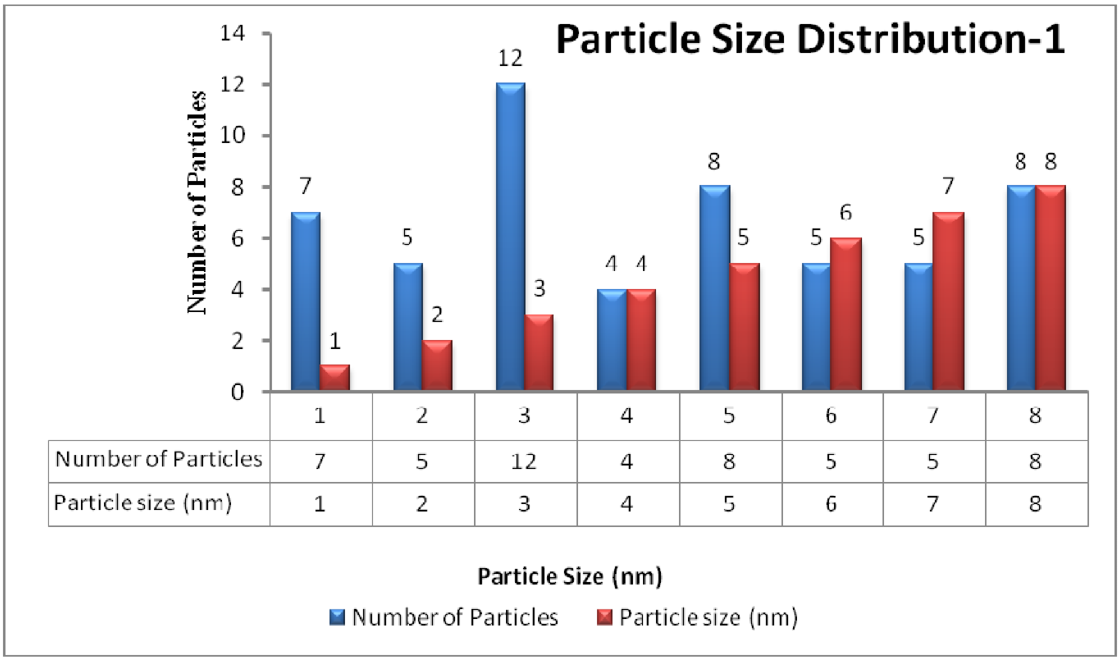


Figure 10. Schematic diagram showing the effect of using Surfactant/Polymer mixture during the formation of nano-crystalline Co particles



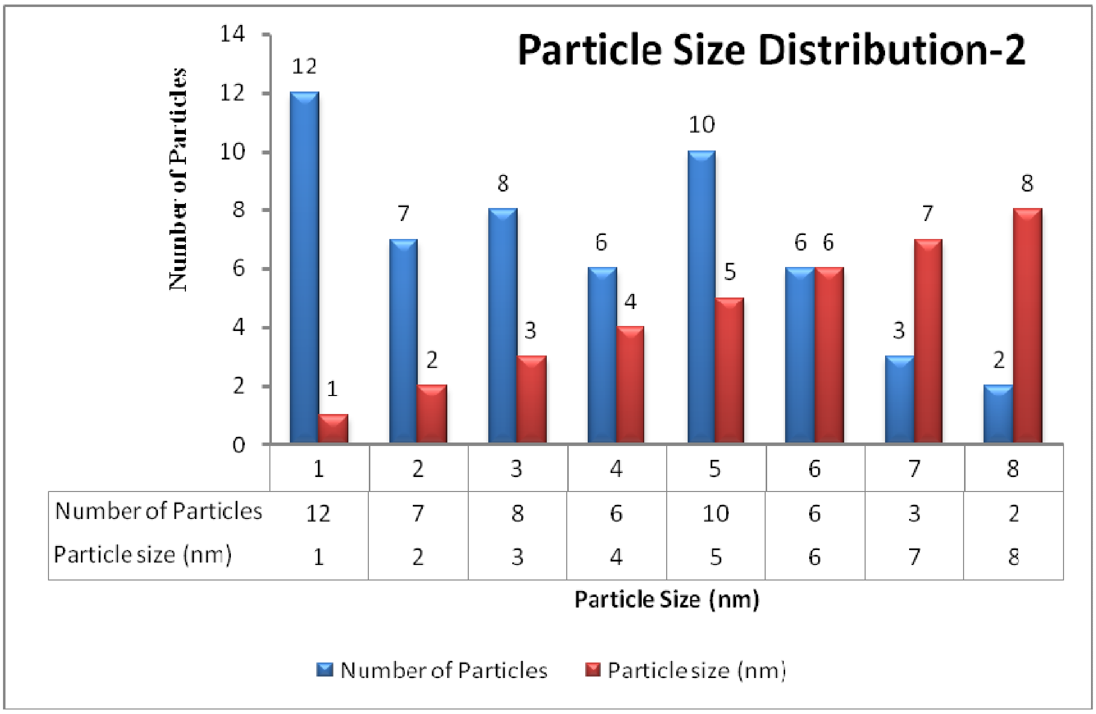
Nano-clusters of Co atoms surrounded by an oxide layer followed by the polymer (C) layer with much reduced aggregation

Figure 11. Schematic diagram showing the formation nano-clusters of Co surrounded by oxide layer followed by a polymeric (C) layer.



	1	2	3	4	5	6	7	8
Number of Particles	7	5	12	4	8	5	5	8
Particle size (nm)	1	2	3	4	5	6	7	8

Figure 12. Size distribution of Co particles synthesized using hydrazine



	1	2	3	4	5	6	7	8
Number of Particles	12	7	8	6	10	6	3	2
Particle size (nm)	1	2	3	4	5	6	7	8

Figure13. Size distribution of Co particles synthesized using hydrazine in the presence of SDS and PVP

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