Asian Journal of Chemistry; Vol. 27, No. 9 (2015), 3407-3410

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2015.18865

# Synthesis and Characterization of Cobalt Nanoparticles Using Poly(vinyl pyrrolidone) and Sodium Dodecyl Sulphate

MD. AL-AMIN* and J. ALAM

Department of Chemistry, Shahjalal University of Science and Technology, Sylhet-3114, Bangladesh

*Corresponding author: E-mail: mdalaminchemsust@yahoo.com

*Received*: 19 November 2014; *Accepted*: 13 December 2014; *Published online*: 26 May 2015; AJC-17266

In this paper, cobalt nanoparticles were synthesized *via* wet chemical reduction method using hydrazine as reducing agent. The morphology of synthesized cobalt nanoparticles were studied with or without of poly(vinyl pyrrolidone) as well as an anionic surfactant sodium dodecyl sulphate. SEM with EDX facilities and TEM were employed to investigate the size of the nanostructures as well as the morphology of cobalt nanoparticles. The effect of poly(vinyl pyrrolidone) as well as an anionic surfactant-sodium dodecyl sulphate has been observed and found that it was potential candidate for tailoring the size of cobalt nanoparticles. Moreover, poly(vinyl pyrrolidone) were displayed a suitable coating agent for preventing agglomeration during synthesis of cobalt nanoparticles.

**Keywords: Cobalt Nanoparticles, Poly(vinyl pyrrolidone), Sodium dodecyl sulphate.**

## INTRODUCTION

Nanoparticles, zero-dimensional nanostructures, are generally classified according to their composition: metal oxides, noble metals, transition metals, magnetic metals, *etc*. These types of nanoparticles often exhibit exciting application in electrical, optical, magnetic, and chemical properties[1-4]. The synthesis of discrete magnetic nanoparticles with sizes ranging from 2 to 20 nm is of significant importance, because of their applications in magnetic storage devices[5-9]. Such type of magnetic nanoparticles could also find applications in magnetic resonance imaging, drug delivery and catalysis[1-2,8,10]. Cobalt is a well-known ferromagnetic material which is commonly used as an alloying element in permanent magnets[6-11]. Cobalt nanoparticles display a wide range of interesting size-dependent structural, electrical, magnetic, and catalytic properties. In particular, because of their large surface area, Co nanoparticles showed high chemical reactivity, which makes them suitable for catalysis[5-7,12-14]. The properties of nanoparticles are dependent on their size and shape. While the design of nanomaterials endowed with size dependant functions is gaining much importance, the synthetic strategies have matched their application needs, making a "made to order" relationship possible. It is also possible to control the size and the inner structure of the resulting nano-metals. 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[14]. The bottom up approach on the other hand is the wet chemical nanoparticle preparation, which relies on building nanoparticles from the atom level of the metal[12-17]. Cobalt nanoparticles in an aqueous medium are that they are highly unstable and undergo oxidation necessitating their use immediately after preparation[1-10]. To overcome the problem of oxidation, attempts have been made to synthesize these nanoparticles in an organic environment which is a suitable protective agent[15,16]. The materials covered in the current article are froth formation systems composed of isolated particles with nanometer-sized dimensions that are stabilized by surfactant molecules and a protecting agent in liquid media. An important component of metal salt reduction processes is the protective agent. Protective agents such as surfactants that form a layer of molecular membrane around the nanoparticles and polymers that provide steric hindrance between nanoparticles are added during the reaction to inhibit particle agglomeration and to control the particle growth[12]. Moreover, selection of the suitable protective agent for a particular reaction is a tedious task of trial-and-error, since the surface chemistry of the nanoparticles is complex due to their high surface energy and their tendency to accumulate surface charges. Thus, the interaction of the protective agent with the solvent and with the nanoparticles plus its properties, such as the solubility in the solvent, molecular weight and the amount needed for stabilization, must be taken into account when choosing the right protective agent. Thus, in some cases, agglomeration of nanoparticles still occurred even in the presence of protective agents[5-13,15-17]. One way to solve the problem is by the choice of a solvent that can also act as cleaning agent. In this study, preparation of Co nanoparticles was performed using Co salt reduction technique; a suitable protective agent poly(vinyl pyrrolidone) and a surfactant sodium dodecyl sulphate were used.

## EXPERIMENTAL

Sodium dodecyl sulphate (SDS, 92%), hydrazine sydrate solution (80 %) were received from LOBA Chemie, India. Poly(vinyl pyrrolidone) (PVP) was purchased from Winlab, UK. Sodium carbonate (99 %) was obtained from Guandgonjg Guanghua, China.

**Synthesis of cobalt nanoparticles:** The nano-sized cobalt particles were synthesized by dissolving 10 g of $CoCl_2$ in a glass beaker containing 100 mL of de-ionized water which was maintained at 40 °C. When the temperature raised at 70 °C the reaction occur and the black particles formed. 20 g/L of sodium dodecyl sulphate and 20 g/L of poly(vinyl pyrrolidone) were added to the solution. In order to study the effect of poly(vinyl pyrrolidone) and sodium dodecyl sulphate on the formation of nano-Co particles a cobalt solution was made without adding any sodium dodecyl sulphate and poly(vinyl pyrrolidone). The pH of the cobalt solution was then increased to 10.2 by adding concentrated sodium carbonate solution. 50 mL of hydrazine was added to the solution slowly while stirring was on all the time. The products were collected, centrifuged (4000 rpm), washed with distilled water and ethanol for three times and finally desiccated at room temperature before characterization. The froth also contained a fair amount of fine Co particles hence these particles were recovered by washing with acetone and water before drying. It has been observed that hydrazine used from a freshly opened bottle gives much faster reaction.

**Characterization of cobalt nanoparticles:** The cobalt particles were characterized by Scanning Electron Microscope (SEM) FEI-NOVA 200Nanolab with EDAX, and transmission electron microscope (TEM) JEOL-JEM 2100F.

## RESULTS AND DISCUSSION

Hydrazine is a normal reducer and its reductive ability varies according to the pH value of the solution. In acid medium, $\varphi^{o}_{N_2H_4}$ is 0.23V and $N_2H_4$ is easily oxidized to $NH_3$. In a basic medium, $\varphi^{o}_{N_2H_4}$ is -1.16V and it can be easily oxidized to $N_2$. At 25 °C, $\varphi^{o}_{/Co^{2+}/Co}$ is -0.28V, so it is possible to reduce cobalt ions in basic medium. The reaction equation between cobalt chloride and sodium carbonate in aqueous medium can be written as follows:

$$CoCl_2(aq) + Na_2CO_3\ (aq) \longrightarrow Co(OH)_2\ (s) + 2NaCl(aq) + CO_2\ (g) \quad (1)$$

Hydrazine is added to the solution containing cobalt carbonate at 60 °C to enhance the reaction rate. The reaction equation between cobalt and hydrazine is:

$$2Co^{2+} + N_2H_4 + 4OH^- \longrightarrow 2Co + N_2\uparrow + 4H_2O \quad (2)$$

Figs. 1 and 2 shows the SEM images of synthesized cobalt nano particles with and without sodium dodecyl sulphate and poly(vinyl pyrrolidone). SEM images show the morphology of the Co powders, very small spherical shaped objects clearly observed. According to the SEM images the monodispersed spherical particles are produced in the technique with surfactant and protecting agent. The protecting agent prevents agglomeration during nucleation.

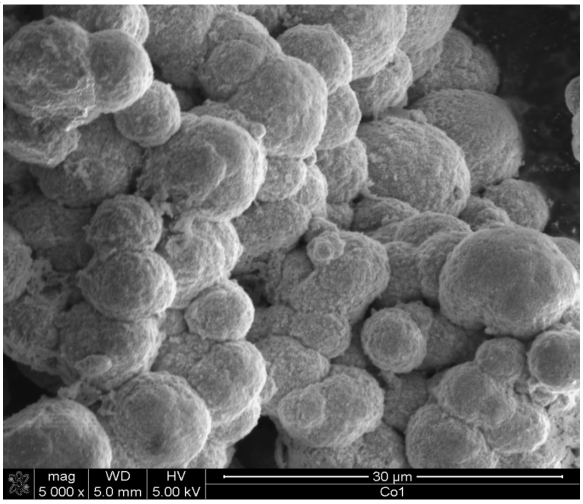


Fig. 1. SEM image of cobalt nanoparticles synthesized without sodium dodecyl sulphate and poly(vinyl pyrrolidone)

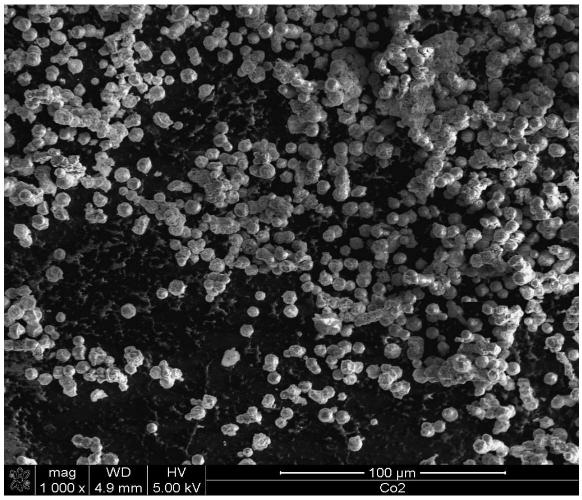


Fig. 2. SEM image of cobalt nanoparticles synthesized with sodium dodecyl sulphate and poly(vinyl pyrrolidone)

Figs. 3 and 4 shows the TEM images of synthesized cobalt nanoparticles with and without sodium dodecyl sulphate and poly(vinyl pyrrolidone) respectably. These indicate the presence of many small and spherical particles. The cobalt nano particles which synthesized in presence of SDS/PVP are smaller in diameter than those which are synthesized without presence of SDS/PVP. Due to the presence of surfactant and polymer the particles become finer and smaller in diameter (about 6 nm). Figs. 5 and 6 are SEM/EDAX plots of the Co powders synthesized at with/without poly(vinyl pyrrolidone) and sodium dodecyl sulphate respectively. Both figures show two clear peaks of Co. The oxygen and carbon peaks are

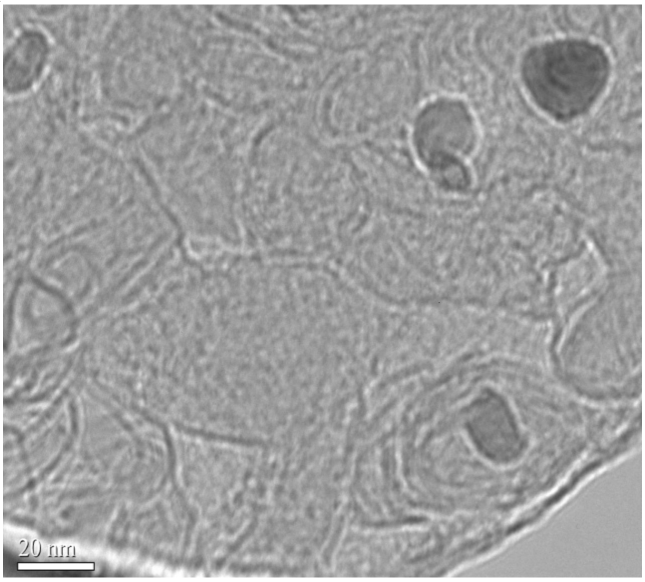


Fig. 3. TEM image of cobalt nanoparticles synthesized without sodium dodecyl sulphate and poly(vinyl pyrrolidone) (20nm)

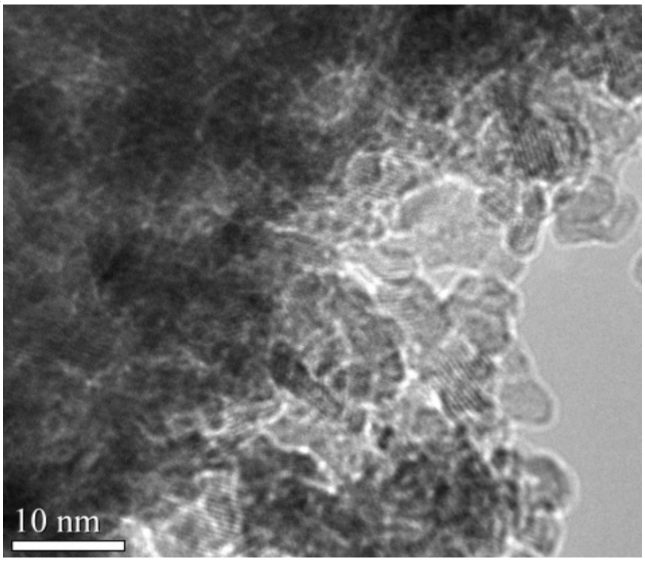


Fig. 4. TEM image of cobalt nanoparticles synthesized using sodium dodecyl sulphate and poly(vinyl pyrrolidone) (10 nm)

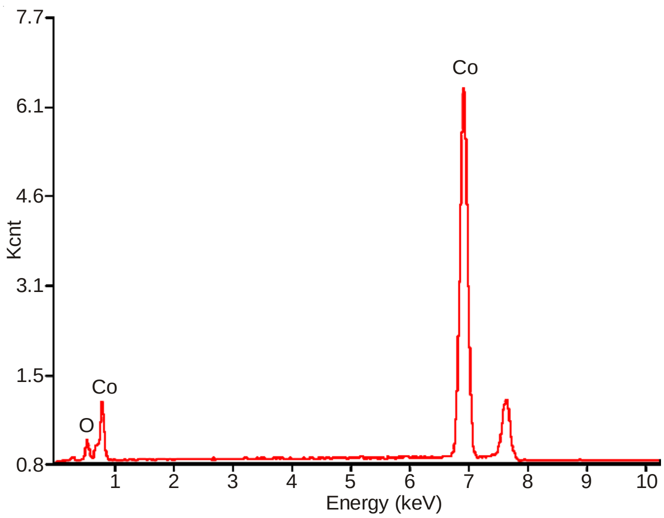


Fig. 5. SEM-EDAX image of cobalt nanoparticles synthesized without sodium dodecyl sulphate and poly(vinyl pyrrolidone)

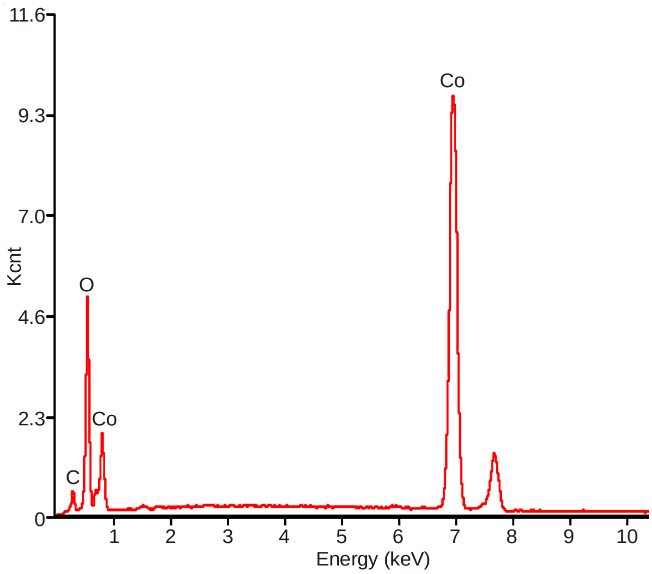


Fig. 6. SEM-EDAX image of cobalt nanoparticles synthesized without sodium dodecyl sulphate and poly(vinyl pyrrolidone)

negligible in Fig. 5. However, the oxygen level observed in Fig. 6 shows some prominence. The peak intensity of the Co sample synthesized by using a surfactant (sodium dodecyl sulphate) and a polymer [poly(vinyl pyrrolidone)] is larger than the peak intensity of Co particles synthesized without using sodium dodecyl sulphate and poly(vinyl pyrrolidone). Clearly the effect of using sodium dodecyl sulphate and poly(vinyl pyrrolidone) has resulted in the refinement of the cobalt particles. TEM images (Fig. 3) shows the presence of cobalt particles which are 20 nm in diameter where Fig. 4 shows the cobalt nano particles as finer as 10 nm in diameter. Cobalt crystals are magnetic at the same time nanosized particles are known to have very large surface areas, hence these synthesized nano-particles will also have very high surface energy. Consequently these fine cobalt crystals will be attracted towards each other and very quickly form aggregated cobalt particles in order to reduce their surface energies[10]. It is concluded that linear poly(vinyl pyrrolidone) molecule has template effect which means the newly synthesized cobalt crystals will be attracted by these poly(vinyl pyrrolidone) templates, with time the newly synthesized cobalt crystals will grow along the poly(vinyl pyrrolidone) chains, it may be the reason why these linear cobalt crystals formed are monodispersed spherical as observed in Figs. 2 and 4. The concept of surfactant micelle formation could help to deduce the most likely reaction mechanisms for the formation of nano-sized Co particles would be that these surfactant molecules (sodium dodecyl sulphate) will also have this template effect on the formation of cobalt particles. These surfactants reduce the interfacial tension between the newborn particles by adsorbing sodium dodecyl sulphate at the liquid-metal interface so formed[17]. However, poly(vinyl pyrrolidone) has a definite template effect on the formation and retention of the nanosized Co particles; spherical/monodispersed cobalt nano particles are formed due to template effects of poly(vinyl pyrrolidone) and sodium dodecyl sulphate. As the reaction temperature is increased even finer particles are produced with an increase in the rate of particle formation.

## Conclusion

In this paper, cobalt nanoparticles were prepared by wet chemical reduction method where hydrazine used as the reducing agent, poly(vinyl pyrrolidone) as the coating agent, and sodium dodecyl sulphate as the surfactant. The addition of poly(vinyl pyrrolidone) as well as sodium dodecyl sulphate has significantly reduced the size and dispersed of the cobalt nanoparticles so that these two types of chemical agents have shown their sustainability towards synthesis of cobalt nanoparticles. Although this research work has focused on effect of poly(vinyl pyrrolidone) and sodium dodecyl sulphate during synthesis of cobalt nanoparticles, there are some other possibilities to investigate the properties of cobalt nanoparticles by varying pH, temperature variations, other types of coating agents and surfactant.

## ACKNOWLEDGEMENTS

The authors thank Dr. Nur Uddin Ahamad for his assistance during the research period. Financial support was provided by Department of Chemistry, Shahjalal University of Science and Technology.

## REFERENCES

1. Y. Yu, A. Mendoza-Garcia, B. Ning and S. Sun, *Adv. Mater.*, **25**, 3090 (2013).
2. V.F. Puntes, K.M. Krishnan and A.P. Alivisatos, *Science*, **291**, 2115 (2001).
3. V. Skumryev, S. Stoyanov, Y. Zhang, G. Hadjipanayis, D. Givord and J. Nogu'es, *Nature*, **423**, 850 (2003).
4. B.K. Pandey, A.K. Shahi, R.K. Swarnkar and R. Gopal, *Sci. Adv. Mater.*, **4**, 537 (2012).
5. A.-H. Lu, E.L. Salabas and F. Schuth, *Angew. Chem. Int. Ed.*, **46**, 1222 (2007).
6. V.F. Puntes, K. Krishnan and A.P. Alivisatos, *Top. Catal.*, **19**, 145 (2002).
7. L. Guo, F. Liang, X.G. Wen, S. Yang, L. He, W. Zheng, C. Chen and Q. Zhong, *Adv. Funct. Mater.*, **17**, 425 (2007).
8. S.-H. Liu, H. Gao, E. Ye, M. Low, S.H. Lim, S.-Y. Zhang, X. Lieu, S. Tripathy, W. Tremel and M.-Y. Han, *Chem. Commun.*, **46**, 4749 (2010).
9. X. Wang, F. Yuan, P. Hu, L. Yu and L. Bai, *J. Phys. Chem. C*, **112**, 8773 (2008).
10. F. Cao, R. Deng, J. Tang, S. Song, Y. Lei and H. Zhang, *CrystEngComm*, **13**, 223 (2010).
11. Y. Song, H. Modrow, L.L. Henry, C.K. Saw, E.E. Doomes, V. Palshin, J. Hormes and C.S.S.R. Kumar, *Chem. Mater.*, **18**, 2817 (2006).
12. A. Dakhlaoui, L.S. Smiri, G. Babadjian, F. Schoenstein, P. Molini'e and N. Jouini, *J. Phys. Chem. C*, **112**, 14348 (2008).
13. D.D. Li, R.S. Thompson, G. Bergmann and J.G. Lu, *Adv. Mater.*, **20**, 4575 (2008).
14. A.-H. Lu, E.L. Salabas and F. Schuth, *Angew. Chem. Int. Ed.*, **46**, 1222 (2007).
15. Z.G. Wu, M. Munoz and O. Montero, *Adv. Powder Technol.*, **21**, 165 (2010).
16. K.A. Barnes, A. Karim, J.F. Douglas, A.I. Nakatani, H. Gruell and E.J. Amis, *Macromolecules*, **33**, 4177 (2000).
17. B.J. Kim, J. Bang, C.J. Hawker and E.J. Kramer, *Macromolecules*, **39**, 4108 (2006).