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Synthesis of Cobalt Nanoparticles Prepared by Wet Chemical Reduction Method at Room Temperature

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ABSTRACT

A simple wet chemical route is followed to synthesize cobalt nanoparticles by the reduction of cobalt nitrate with sodium borohydride under various experimental conditions in an aqueous medium. It was found that variation in the concentration of Co^{2+} *solution changed the morphology of the products. Transmission Electron Microscopic studies of the prepared samples revealed that at a fixed concentration of* Co^{2+} *solution in the absence of any stabilising agent and surfactant, rod shaped cobalt nanoparticles along with some spherical nanoparticles are produced. TEM studies show that on increasing the concentration of cobalt (II) ions under the same experimental conditions, the clusters of cobalt are formed. TEM images also show that the addition of ascorbic acid initiates the formation of spherical cobalt nanoparticles while the addition of oleylamine (OAm) along with ascorbic acid stabilises these spherical cobalt nanoparticles.*

Keywords: Nanoparticles, Chemical reduction, Surfactant, Transmission electron microscopy, Aggregation.

INTRODUCTION

Metal nanoparticles [1] have attracted much attention of the researchers in nanoscience and nanotechnology over the past decade due to their unusual chemical and physical properties, such as catalytic activity [2], optical [3] and magnetic properties [4]. Their main application areas include catalyst [2], chemical and biological sensors [5], optoelectronics [6], photonic [7] and information devices [4] etc. Metal nanoparticles have potential applications in catalysis [8,9,10] because of their large surface to volume ratio. These nanoparticles of different shapes could catalyse the reaction with different efficiencies because nanocrystals of different shapes represent various facets. Till date various methods [11] have been used for the synthesis of nanoparticles including bottom up and top down approaches. The some common methods of the synthesis are wet chemical reduction [11], reverse micelles [12], electrochemical [13] and sol-gel methods [14]. Amongst these, the wet chemical reduction method has advantage over the others in easy control of the reaction process for the production of nanoparticles with controllable sizes and shapes. A challenge in nanotechnology is to tailor the optical, electronic and electrical properties of nanoparticles by controlling their size and shape [11].

The transition metal nanoparticles, especially the Fe, Co and Ni are considered to be very important for many technological applications as well as biological applications. Several reports [15, 16] are available for the production of cobalt nanoparticles of different shapes and sizes. Zurcher and co-workers [15] have synthesised cobalt nanorods through organomettalic precursor at 150°C. Significance of cobalt nanorods over the spherical cobalt nanoparticles is due to its magnetic anisotropy. It should be noted that the small spherical nanoparticles are supermagnetic at room temperature and can not be usable for many applications such as magnetic recording. This problem has been addressed by the Alivisatos [17] who initially demonstrated the importance of reaction conditions, in particular the concentration of the precursors and the molar ratio of reactants for preparing the CdSe nanocrystals of various shapes.

In this report, a wet chemical approach has been used to prepare rod shaped and spherical cobalt nanoparticles at room temperature. It is noteworthy that we have synthesised the cobalt nanorods in aqueous medium simply by changing the concentration of cobalt nitrate. Spherical cobalt nanoparticles have also been synthesised in the presence of complexing agent and surfactants. The complexing agent is used to control the rate of nucleation and surfactant is used to check the agglomeration of nanoparticles after the synthesis. Here the ascorbic acid is used as complexing agent and oleylamine (OAm) is used as the surfactant. As we know that the oleylamine [18] has been widely used for the synthesis of nanostructures.

MATERIALS AND METHODS

Materials: Cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, sodium borohydride ($NaBH_4$), oleylamine ($C_{18}H_{33}NH_2$), ascorbic acid ($C_8H_8O_6$) were purchased from Sigma-Aldrich and used as such without further purification for the synthesis of cobalt nanoparticles.

Preparation of the cobalt nanoparticles: The synthesis of nanoparticles at room temperature by a wet chemical route is a relatively simple procedure. Here, three different reaction procedures are followed for the synthesis of cobalt nanoparticles: (i) In the first reaction procedure 0.5 mL of 0.1 M cobalt nitrate (0.05 mmol) is added in 10 ml of 0.2 M NaOH to make solution alkaline. The resultant solution is stirred for one hour and then 10 mL of 0.1 M (1 mmol) $NaBH_4$ as a reducing agent is added drop wise with constant stirring. After the completion of the reaction, black precipitate is obtained. In a series of reactions the amount of cobalt nitrate is varied from 0.05 to 0.20 mmol in order to study the effect of concentration of cobalt nitrate on the size and morphology of its nanoparticles. (ii) In the second reaction procedure before adding the reducing agent, 10 mL of 0.1 M ascorbic acid is added and (iii) in the third reaction procedure, ascorbic acid and oleylamine (OAm) both are added before adding the reducing agent and after stirring for four hours, brown slurry is obtained. It should be noted that in this process mild heating is also required to form homogenous vesicles of OAm because it a hydrophobic surfactant.

Physiochemical characterisation of nanoparticles: The size and morphology for the prepared cobalt nanoparticles were determined by Transmission Electron Microscopy (TEM) on a MORGANI microscope at 200KV. Samples for TEM were prepared by drying a drop of nanoparticles solution on a polymer coated copper grid.

RESULTS AND DISCUSSION

Cobalt nanoparticles have been prepared in aqueous medium at room temperature by using sodium borohydride as the reducing agent. It should be mentioned that sodium borohydride reduces cobalt ions to metallic cobalt according to the following reactions [19, 20].

$$2Co(NO_3)_2 + 4NaBH_4 + 6H_2O \rightarrow Co_2B + 4NaNO_3 + 3B(OH)_2 + 11H_2 \quad (1)$$

$$4Co_2B + 3O_2 \rightarrow 8Co + 2B_2O_3 \quad (2)$$

If these two reagents are rapidly mixed and the product is handled under argon, the reduction of Co $(NO_3)_2$ (aq.) with $NaBH_4$ yields the Co_2B as the primary product. In the presence of O_2, a sacrificial reduction takes place, whereby boron is oxidised while cobalt is reduced, resulting in the conversion of Co_2B to Co(s).

In fact, Brown and his co-workers [21] previously pointed out the complexity of the chemistry, since the metals ions serve as catalysts for BH_4^- oxidation by water. Pileni et al [22, 23] also reported the synthesis of well defined and low size distribution of nanocrystals using reverse micelles and sodium borohydride as reducing agent, although they were smaller in size.

By the first reaction procedure as described in the preceding pages, spherical and rod shaped cobalt nanoparticles are obtained. The formation of rod shaped nanoparticles have been reported [24, 25] at elevated temperatures by hydrothermal/solvothermal process. The present report gives interesting results about the synthesis of rod shaped nanoparticles in the absence of ligand at room temperature. The TEM pictures clearly revealed (Figures 1&2) in the absence of any stabilising agent and surfactant; nanorods of cobalt along with some spherical cobalt nanoparticles are obtained. The size of synthesised nanorods is 8-10 nm in diameter and 30-50 nm in length.

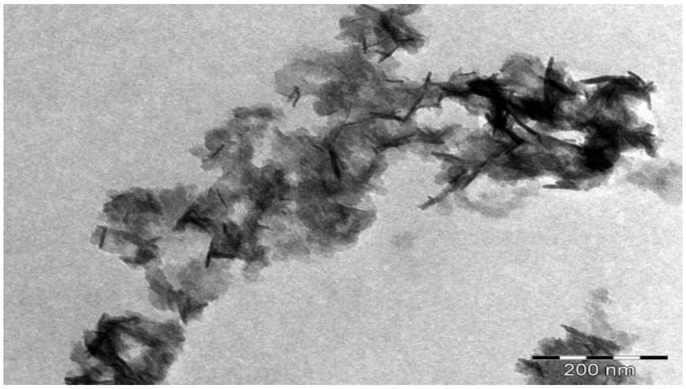

Figure 1: Nanorods of cobalt

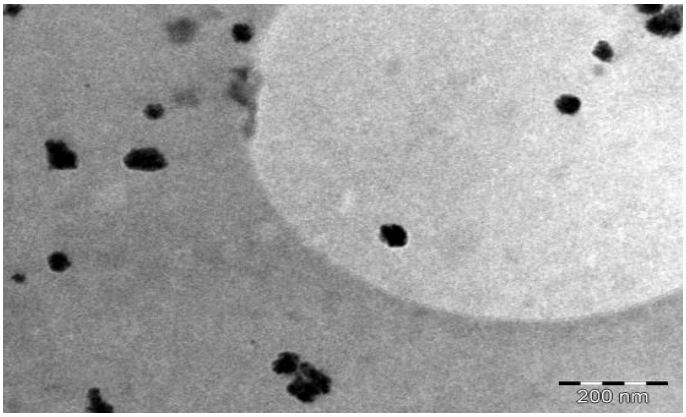

Figure 2. Spherical cobalt nanoparticles

Further, TEM studies show that on increasing the concentration of cobalt ions under the same experimental conditions, the clusters of cobalt are formed. At high concentration the rate of the growth of nanoparticle increases result in the formation of clusters of cobalt. In the next reaction process ascorbic acid is added as a stabilising agent which controls the rate of nucleation of the nanoparticles. The addition of ascorbic acid initiates the formation of spherical cobalt nanoparticles in the range of 30-50 nm, but the TEM image

(Figure. 3) clearly shows that the ascorbate ions behave as a poor stabilising agent, as a result spherical particles of cobalt coalesce with each other forming larger aggregation.

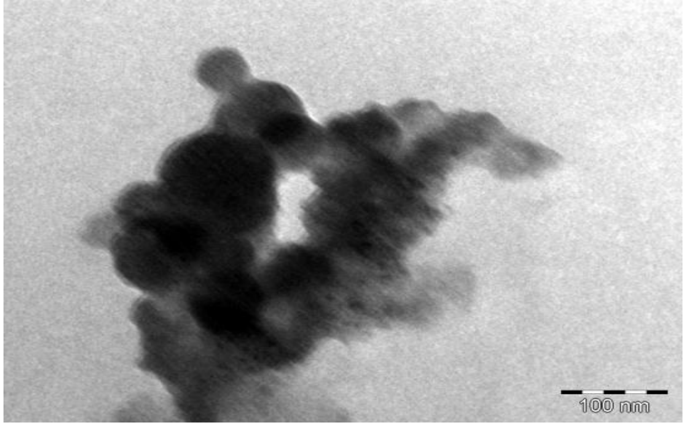

Figure 3: Cobalt nanoparticles in presence of ascorbic acid

TEM image (Figure. 4) shows that the addition of oleylamine as the surfactant with ascorbic acid produces nanoparticles of various size distributions varying from 40-70 nm. The surfactant oleylamine ($CH_3(CH_2)_7CH=CH(CH_2)_8NH_2$) has functional group —$NH_2$. It has $C_{18}H_{33}$ chain with a kink (C=C) at the ninth carbon. The —NH_2 group of oleylamine and hydroxy group of ascorbic acid coordinate to cobalt (II) ion due to donation of the lone pair of electrons by the amino nitrogen and hydroxyl oxygen atoms in to the partially empty d-orbitals of cobalt atoms [26].

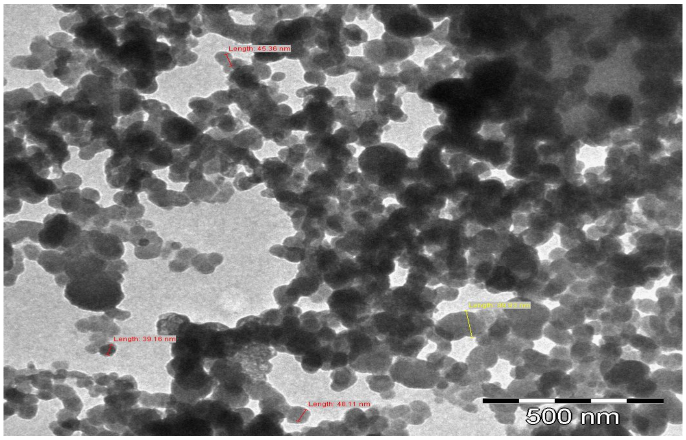

Figure 4: Cobalt nanoparticles in presence of ascorbic acid and oleylamine

Highlights:

- Cobalt nanoparticles have been synthesized at room temperature by wet chemical reduction method.
- Concentration of cobalt ions affects the size and morphology of the product.
- Rod shaped cobalt nanoparticles have been synthesized in the absence of any surfactants/ligands
- Ascorbic acid initiates the formation of spherical cobalt nanoparticles but the addition of Oleylamine along with ascorbic acid stabilizes the spherical cobalt nanoparticles.

CONCLUSIONS

Using the synthesis of cobalt nanoparticles as the model system, we have demonstrated the important role of the concentration of the Co^{2+} ions. The variation in the concentration of Co^{2+} changed the morphology of the products from nanorods to aggregated clusters of cobalt. Hence it clearly shows that the choice of concentration of precursor material affect the shape and size of cobalt nanoparticles. In addition to this the stabilising agent and surfactants also influence the shape and size of nanoparticles by altering the particle growth process. This study provides valuable information for controlling nanoparticle morphologies, which may possibly to generalize to other nanoparticle systems.

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