RESEARCH ARTICLE

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# Cobalt Nanoparticles by Prudent Chemical Method and It's Characterization

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## ABSTRACT

For the synthesis of Cobalt Nanoparticles (CoNPs), the prudent wet phase reduction process was applied by employing urea as an effective oxidizing agent. The requirement of analogous precipitation of executed synthesis method was fulfilled by taking advantage of sufficiently slow hydrolysis of urea in water at an acceptable temperature. The experiment was carried out by mixing cobalt nitrate and urea (1:2) in distilled water. The reaction mass was then subjected to 400ÚC temperature in muffle furnace by intermittent shaking. The product formed i.e. cobalt oxide was cooled and crushed to get powder which was then reduced at 800°C in presence of inert gas i.e. hydrogen. Newly formed nanoparticles (i.e. nano catalyst) were analyzed and characterized for surface morphology using different analytical tools like X-ray powder diffractometer (XRPD), Fourier Transform Infra-red spectroscopy (FTIR), Scanning Electron Microscopy (SEM) and Nitrogen adsorption by BET. The extension of study was done to evaluate the effect of change in reduction temperature on characteristic properties of CoNPs.

***Keywords*:** Cobalt nanoparticles, Scanning Electron Microscopy, Urea decomposition, wet phase reduction.

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## INTRODUCTION

The segment of science which was christened as 'Nanotechnology' deals the in-house manufacturing and improvement of nanoparticles. In nanotechnology, a particle is defined as a small object that behaves as a whole unit with respect to its transport and properties [1]. Different metals such as zinc, gold, magnesium, silver, titanium, copper are used to obtain metal based nanoparticles of all these metals, Cobalt is proven to be the first catalyst made from non-precious metal with properties closely resembling with those of platinum [2].

Cobalt serves as a model system for the macroscopic magnetic response since it's low to moderate crystal anisotropy allows the effects of size, shape, internal crystal structure and surface anisotropy to be observed in a single system [3][4]. Cobalt is one of the most important ferromagnetic metals due to its three metastable phases with different crystallographic structures, namely the hexagonal closed pack (hcp) phase, the face-centered cubic (fcc) phase, and the epsilon phase [5][6]. Synthesizing metallic nanoparticles following wet-chemistry route is a powerful way of obtaining a reproducible macroscopic amount of homogeneous sample [7]. Several wet-chemical methods have been developed to synthesize cobalt crystals with different morphologies, for example pyrolysis, solvothermal and hydrothermal decomposition, microfluidic synthesis, modified polyol processes and

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template-based methods [8]–[10]. The basic object of this research work is to execute the co-precipitation phenomena for the synthesis of cobalt oxide nanoparticles (CoONPs). Co-precipitation is recognized as efficient, economical and simple method for in-house manufacturing of cobalt nanoparticles by the reduction of cobalt oxide in presence of hydrogen gas environment.

Newly formed CoONPs and CoNPs were evaluated by FTIR, XRPD, nitrogen adsorption by BET and SEM tools.

## MATERIALS AND METHODS

### Materials used in research work

| | |
|---|---|
| Cobalt Nitrate Hexahydrate | : ACS Grade |
| Urea | : AR Grade |
| Water | : Demineralized |

### Experimental

**Synthesis of CoONPs:** Accurately weighed and transferred about 20g. of cobalt nitrate hexahydrate and 40g.of urea in 500 ml glass beaker so that to achieve blend in the molecular ratio of 1:2. Laboratory grade demineralized water was added to the content and the blend was shaken to develop uniform solution. In proposed synthetic experiment, urea performed the role of booster. Later the beaker was kept in muffle furnace and heated at 400°C for 3.0 hours. An intermittent shaking was applied to the reaction mass so that to ensure the synthesis of oxide form of cobalt from entire mixture. After intended interval of heating i.e. 3.0 hours, the beaker was removed from furnace and cooled to laboratory temperature and later the obtained product was slowly crushed using spatula to get powder (CoONPs).

**Reduction of CoONPs to CoNPs:** Representation of schematic diagram of split tube furnace (Make: Lenton) is shown as Figure 1. Approximately 500mg of CoONPs were taken into two quartz boats, quartz boat (A) and quartz tube (B) and inserted into one meter long furnace tube which was maintained under inert gas atmosphere i.e. hydrogen throughout the experiment (for 2.0Hrs). The quartz boats were heated upto 700°C and 800°C in two different sets of experiments using electric coils (C). Hydrogen gas cylinder (D) was connected to the instrument as shown schematic representation.

After reduction phenomena, CoONPs were converted to CoNPs. The furnace was allowed to cool at laboratory temperature and the samples were collected from furnace, powdered it and stored in glass bottle.

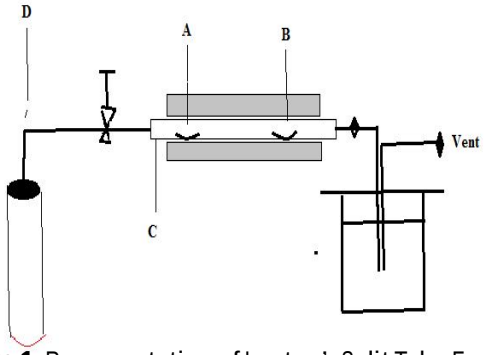


**Figure 1:** Representation of Lenton's Split Tube Furnace

### Characterization Tools

The evaluation of CoONPs and CONPs was conducted by hydraulic die press KBr pellet method using Perkin Elmer Spectrum One model. The collection of diffractions was done by using Panalytical's X'pert Pro model with a cathode and copper anode material set at 45kV/40mA voltage. The measurement of surface area was done by using single point, low temperature nitrogen adsorption based on BET principle (Make: Smart Instruments Co. Pvt. Ltd.; Model: Smartsorb 92/93). The regeneration of samples was done at 150°C for about 2.0 hours before analysis. The evaluation of surface morphology was performed using scanning electron microscopy designed by Philips having model SEM 505.

## RESULTS AND DISCUSSIONS

From the results it is observed that, the co-precipitation method can be applied for qualitative and quantitative synthesis of CoNPs. Figure 2 shows FTIR spectrum of as grown CoONPs. Figure 3 and Figure 4 respectively shows CoNPs obtained after reduction of CoONPs at 700°C and 800°C. In Figure 2, the band at 650 $cm^{-1}$ indicate the $Co^{2+}$-O vibration of the cobalt-oxygen bond in tetrahedral hole whereas the band at 558 $cm^{-1}$ relates $Co^{3+}$-O vibration in the octahedral hole [12]. Figure 3 and Figure 4 indicates the lacking of characteristic bands pertaining to CoONPs. This ensures the alterations at molecular level by means of sacrificing various oxides while reduction experiments. But an improvement in the FTIR transmittance of CoNPs reduced at 800°C as compared to CoNPs reduced at 700 °C was observed. This further proves the formation of desired CoNPs at elevated temperatures.

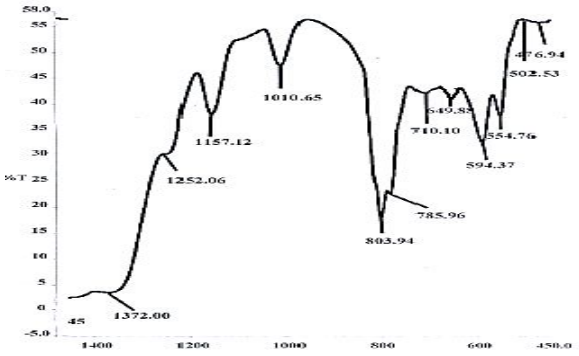


**Figure 2:** FTIR Spectrum of CoONPs

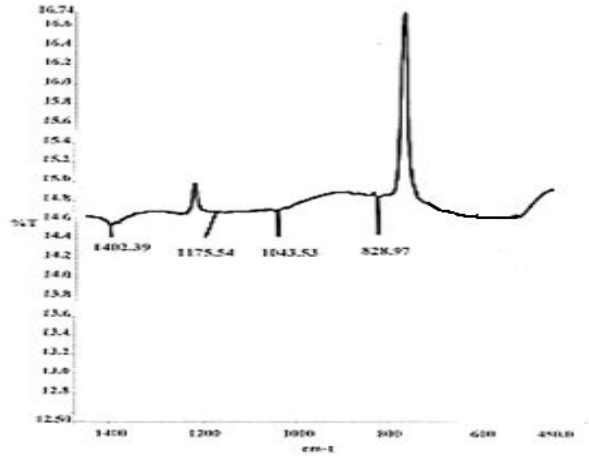


**Figure 3:** FTIR Spectrum of CoNPs obtained at 700°C

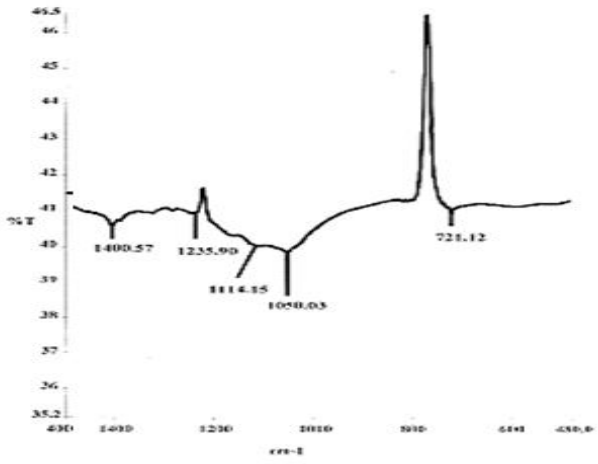


**Figure 4:** IR Spectrum of CoNPs obtained at 800°C

Table-1 indicates the comparison of bands obtained in FTIR spectra of as grown CoONPs and in CoNPs collected at 700°C and 800°C.

**Table-1:** Distinguished FTIR Bands in CoONPs and CoNPs:

| Characteristic FTIR Bands | CoONPs | CoNPs reduced at 700°C | CoNPs reduced at 800°C |
|---|---|---|---|
| $Co^{3+}$-O vibration in octahedral hole | 558 $cm^{-1}$ | Absent | Absent |
| $Co^{2+}$-O vibration in tetrahedral | 650 $cm^{-1}$ | Absent | Absent |

Figure 5 exhibits XRD pattern of as grown CoONPs The diffraction signals obtained at about 31.2°, 37.4°, 59.6°, and 65.5° in the XRD profile are assigned to the standard diffraction peak of CoONPs (PDF.43-1003) [13]. This confirms formation of CoONPsnanoparticles.

Figure 6 and Figure 7 respectively shows the XRD profile of CONPs obtained at 700°C and 800°C.

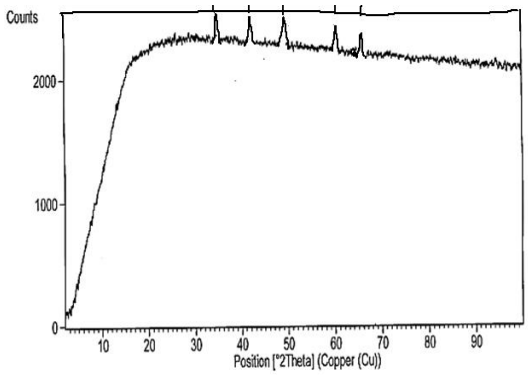


**Figure 5:** XRD Pattern of CoONPs

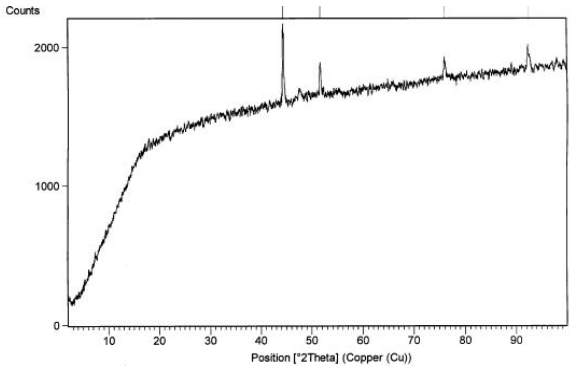


**Figure 6:** XRD Pattern of CoNPs obtained at 700°C

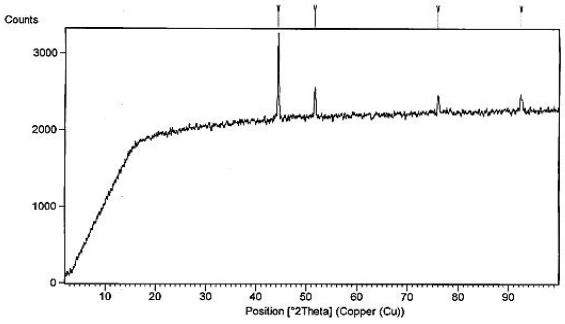


**Figure 6:** : XRD Profile of CoNPs obtained at 800°C

From Figure 7 and Figure 8 it is observed that, the characteristic 2- theta reflections obtained in XRD profile of CoONPs are absent in XRD patterns of CoNPs reduced at 700°C and 800°C. The interesting features of obtained XRD profiles are the diffraction peaks at 2-theta about 44.9°, 52.4°, 77.4° and 92.5°. With reference to JCPDS #73, the obtained 2θ peaks are benchmarking for cobalt nanoparticles. The intensity of 2-theta peaks was greater in the XRD pattern of nanoparticles obtained at 800°C unlike the peak intensity of nanoparticles obtained at 700°C.

The crystallite size of reduced CoONPs is calculated by Debye Scherrer equation as below,

$$\tau = \frac{K\lambda}{\Delta(2\theta)\cos\theta}$$

where, $\tau$ = the average size of the orderly arranged crystalline counterpart;

$\lambda$= X-ray wavelength

K = shape factor with a value close to unity;

$\Delta$ (2$\theta$) = line broadening at half the maximum intensity (FWHM);

$\theta$ = the Bragg angle.

**Table-2:** Comparison of XRD Intensity Counts and Average Crystallite Size

| 2θ (°) | CoNPs obtained at 700°C | | CoNPS obtained at 800°C | |
|---|---|---|---|---|
| | Intensity Counts (cts) | Average Crystallite Size (nm) | Intensity Counts (cts) | Average Crystallite Size (nm) |
| 44.9 | 375 | 24 | 650 | 35 |
| 52.4 | 190 | | 307 | |
| 77.4 | 127 | | 250 | |
| 92.5 | 152 | | 209 | |

Table-2 indicates that, the relative intensities of 2θ peaks in XRD diffractogram of CoNPs collected at 700°C are lesser than the relative intensities of 2θ peaks in XRD diffractogram of CoNPs formed at 800°C. It proves generation of crystallinity in CoNPs with elevated temperatures. The mean crystallite size of CoNPs obtained at 700°C is lower than mean crystallite size of catalyst obtained at 800°C. It reveals that, increasing reduction temperatures has impact on the crystallite size of the CoNPs [14].

The specific surface area (SSA) of CoONPs is determined as 4.65m$^2$/g whereas the specific surface areas of CoNPs obtained at 700°C and 800°C were respectively calculated as 12.15m$^2$/g and 16.54m$^2$/g. The increase in specific surface area from CoONPs to CoNPs indicates the development of nanosized particles during reduction phenomena. Further, the difference in the specific surface area at two reduction temperatures clearly indicates the impact of reduction temperature on the surface area of cobalt nanoparticles [11].

Table-3 indicates the comparative values of specific surface areas obtained at oxide stage and after reduction of oxide.

**Table-3:** Comparative Specific Surface Area of CoONPs and CoNPs

| CoONPs (m$^2$/g) | CoNPs obtained at 700°C (m$^2$/g) | CoNPs obtained at 800°C (m$^2$/g) |
|---|---|---|
| 4.65 | 12.15 | 16.54 |

Figure 8 (a) and (b) shows pictures of gathered from SEM of CoNPs obtained respectively at 700°C and 800°C reduction temperatures.

The image of CoNPs formed at 800°C presents significant clarity unlike the image of CoNPs obtained at 700°C. There observed agglomeration in the image of the CoNPs obtained at 700°C. The CoNPs reduced at 800°C sized between 26nm to 37nm.

This assessment supports our prediction that, the increased reduction temperature ended-up into desired CoNPs.

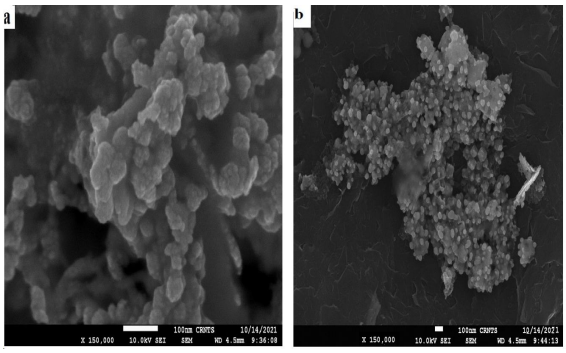


**Figure 8:** (a) SEM of CoNPs obtained at 700°C and (b) SEM of CoNPs obtained at 800°C

## CONCLUSION

Wet phase co-precipitation method for the synthesis of CoNPs is practically simple and cost-effective. The reduction of CoONPs to CoNPs at higher temperature in hydrogen gas atmosphere is novel approach. The

increase in FTIR transmittance of CoNPs obtained at 800ÚC comparatively with CoNPs obtained at 700°C confirms the development of desired CoNPs at increased temperature.

On comparison of crystallite size, the CoNPs obtained at 700°C had lower crystallite size than that of CoNPs obtained at 800°C. This focuses on the effect of elevated reduction temperatures on the average crystallite size of CoNPs.

From all above experimental evaluation it has been concluded that better quality crystallite size of cobalt nanoparticles along with higher specific surface area are obtained at elevated reduction temperature.

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