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# Effect of PH on Cobalt Oxide Nano Particles Prepared by Co-Precipitation Method

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**ABSTRACT**

**Background:** This study has investigated the PH effect in obtaining cobalt oxide nano particles **Objective:** These particles are then characterized by SEM, EDX, UV, FTIR and XRD. In order to find the effects of PH, THE precipitation method has been used. The PH range is between 8 - 11. The PH has been controlled by PH meter and dropping of KOH. **Results:** The result shows that the PH 8-9 range is more homogenous in shape and structure and the more small crystalline sized particles have been achieved. **Conclusion:** In case of PH 8-9 the average particle size is 20-30 and in PH range of 10-11, its 40-50 nm respectively.



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## INTRODUCTION

Cobalt-based nanoparticles reside between the most promising materials for technological applications such as information storage, magnetic fluids and catalysts (Cao, Sergeev, 2005). Co is a well-known ferromagnetic material which is commonly used as an alloying element in permanent magnets. It exists in two forms: HCP (hexagonal close-packed) and FCC (face-centered cubic). HCP is the stable phase at room temperature, whereas FCC is stable at temperatures above 450 °C (Berger, D., 2007). In nano sized, Co particles display a wide range of interesting size-dependent structural, electrical, magnetic, and catalytic properties (Dinega and Bawendi,1999). In particular, because of their large surface area, Co nanoparticles showed high chemical reactivity, which makes them suitable for catalysis (Hyeon, T., 2001). If we want to have further applications of cobalt in different industries such as separation technology, information storage systems, catalysis, and biomedicine (Mary Donabelle L. Balela, 2008) require the nanoparticles to be discrete, identical in size and shape, and uniform in composition and crystal structure (Puntes, V.F., 2001). So the characterization should be done to have a broad knowledge of cobalt oxide nano particles. In this study the different factors have been investigated to see the effect of them on structure and morphology of cobalt oxide nano particles.

### *Experiments and Characterization:*

All the materials were bought from Sigma Aldrich and Acros organics. In order to have the optimized PH, first the experiment was done to see the effect of PH, and the PH control in the size and morphology of cobalt nano particles. 15 mmol cobalt salt Co $(NO_3)_2 \cdot 6H_2O$) was dissolved into deionized water containing dispersant polyethylene glycol (PEG), then excessive amount $NH_4OH$ was added with electromagnetic stirring at 50 ◦C to form $Co(OH)_2$ gel. The pH was monitored to 8−9-10-11 by dropping KOH. A certain volume of 40% $H_2O_2$ was dropped into the above suspension. Finally, these solutions were transferred into a centrifuge. Then they were put into an oven to be heated at 100◦ C then cooled to room temperature in air naturally. The black products were centrifuged and washed with deionized water and ethanol for five times, then dried in a vacuum oven at 80 ◦C for a day. In Figure 1-3 you can see the methods and procedures used.

### *Characterization:*

To study the obtained products, conventional characterization techniques will be applied, such as: X-ray diffraction (XRD), selected area electron diffraction (SAED), scanning electron microscopy (SEM), IR spectroscopy, UV-Vis.

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**Fig. 1:** Pink solution and stirring.


**Fig. 2:** Black precipitate, centrifuging

**Fig. 3:** Black powder (cobalt oxide nano particles).

## RESULTS AND DISCUSSION

***Effect of Ph:***

Figure 4 and figure 5 show the SEM image of $Co_3O_4$ synthesized by suspension of pH 8-9 in a co-precipitation reaction. Comparing them we will see, that nanocubic $Co_3O_4$ with the average particle size of 20 nm is formed when pH is 8−9, and when pH goes up to 10-11 some irregular $Co_3O_4$ including the grains that are recombined in the products can be seen. This fact has been shown in figure 7-8. This can be explained as the condensation reaction of Co $(OH)_2$ precursors is able to happen at higher pH value, agglomeration of the Nanoparticles occurs. The average sizes of Nanoparticles were calculated by DebyeScherrer's equation to be 20 and 30 nm at PH 8-9 and then 40 and 50 nm at PH 10-11respectively. In the particles of PH9-10 this fact can be found that in some areas distorted strings can be seen due to self alignment orientation that has happened and this can be attributed to the presence of weak interactions. However the crystalline $Co_3O_4$ Nanoparticles can be observed as crystals in some areas of the micrographs. The range of 8-9 PH makes more uniform and smaller Nanoparticles than the 10-11 PH. Large and agglomerated particles have been synthesized at higher PH since the nucleation rate is lower than particle growth rate. These results can be seen in the EDX spectrum shown in figure 7 and 9 and related tables of them the tables 1-3 showing the crystal and atomic weight percent. The more PH range make very high synthesis rate thus the produced cobalt sample will be non uniform and agglomerated. The obtained results shows that solution pH of 8-9 is a better one to synthesize uniform cobalt since at lower pH, condensation reaction was considerable so that the cobalt sample was completed agglomerated. At higher PHs 10-11, reduction rate of Co ions were fast so that obtained samples were agglomerated less and a bit without any nano rods (Kodama, R.H., 1999).

Identification was done out by comparing the diffraction patterns with the standard cards-ray diffraction pattern of the synthesized cobalt oxide. They were analyzed to investigate the phase structure and the crystallinity which is shown in the figure 10. The patterns shows sharp peaks relating to $Co_3O_4$ and according to standard $Co_3O_4$ XRD pattern (JCPDS, Joint Committee on Powder Diffraction Standards, card no. 43-1003), All the peaks of cobalt oxide can be indexed to cubic phase.

It shows a crystalline$Co_3O_4$ with small broadened profiles of all measured reflections. It shows a crystalline powder which has sharp and a kind of intense diffraction peak. There isn't any impurity peaks and this fact shows the final product synthesized is $Co_3O_4$ with nanocubic structure by co-precipitation. In addition to the facts mentioned the XRD patterns show crystalline phase and they are in agreement with reported values of Selected Area Electron Diffraction (SAED) diffraction pattern shows the presence of well-defined clear spot. However for the PH10-11 it has some broad diffraction lines which remind some inefficient crystallinity. Even if we look at the images of SEM we can see some spherical agglomeration with some pores. The XRD plot of the cobalt powder done at PH8-9 shows the presence of both HCP and FCC phases in it. And the allotropic transition from HCP to FCC phase is happened at PH change. The peak broadening at each reflection is also the indicative of formation of fine size cobalt powder.

When the PH lies in the range of 8-9, $Co_3O_4$ dominates the product in the XRD pattern. At PH10-11, a weak diffraction peak of CoO is observed. Small amount of cubic Co3O4 is found in the ones done by PH10-11. Based on Scherrer formula, the average particle sizes of $Co_3O_4$ in ph8-9 will be 20-30 nm and will be 40-50 for

PH 1—11. $Co_3O_4$ gave the large crystallite size because it contains 3 Co ions which has large radius. And the ones done by PH 10-11, the range is 40-50 nm .The crystallite sizes were calculated using XRD data based on Debye-Scherer equation as below:

$$d = \frac{0.89\,\lambda}{\beta \cos\theta}$$

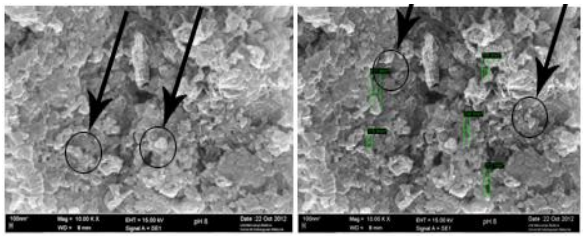
Where d, λ, θ and β are the crystallite size, X-ray wavelength (1.542 Å), Bragg diffraction angle and full width at the half maximum (FWHM) of the diffraction peak.After drying in an inert atmosphere the PH8-9 which is really close to each other; we will see the change of amorphous to the crystalline state.

This shows narrow particle size distribution in a well-defined particle size, purity of the phase and structure and the shape. A stretching frequency at 3361.2 cm−1 and a weak asymmetric band at 2919 cm−1 will prove the existence of OH− group due to the absorption of water by nano particle during sample preparation. The presence of two strong M–O stretching and bending frequencies at1481 cm−1 and 831 cm−1, shows phase purity of monodisperse one in the face centered cubic structure. The peaks at 1579 cm-1 and 1539 cm-1 correspond to $Co_3O_4$ asymmetric stretching vibrations. The peak at 3610 cm -1 corresponds to CoO bending vibrations at PH11.

The optical property of cobalt oxide nanoparticle has been done with high purity, and the crystallinity of the cobalt oxides were confirmed with the help of UV-visible absorption spectra by observing the absorption rate band at 210nm with a tail which is extended towards a longer wavelength and the reason for that, is their quantum size effects. In the extending tail there isn't any significant absorption peak in which the reason is quantum confinement effects in the energy gap. The absorption peak is a bit broad peak due to the particle size. Co3 O4 nanoparticle are considered as stable and this fact can be the result of symmetrical-polarity structure which depends on the weak interaction of VanderWaals forces within particle regime.

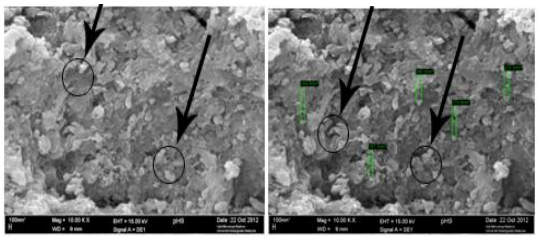
***Conclusion:***

It can be concluded that $Co_3O_4$ with the average particle size of 40 nm is formed when pH is 8−9, and when pH goes up to 10-11 irregular $Co_3O_4$ with grains are seen and the size is 30 in average. So PH has a great effect on the $Co_3O_4$ formation. So by Comparing all the results done it can be concluded that PH has a great effect on morphology and structure of cobalt oxide nano particles. The same conclusion can be seen in the work by You Ping *et al*. (2007).



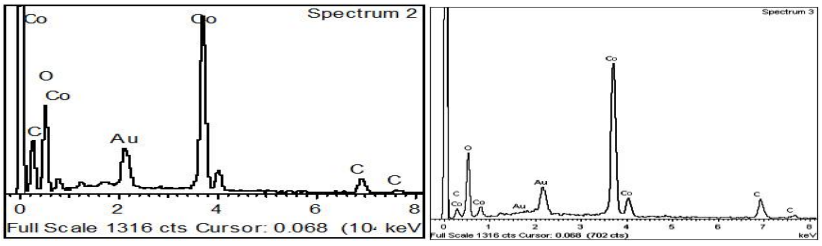
(a) (b)

**Fig. 4:** (a) PH 8 (b) PH 8



(c) (d)

**Fig. 5:** PH9(c) PH 9 (d).

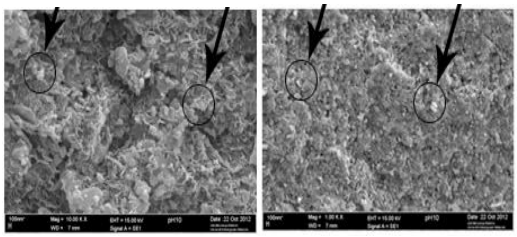



(e) (f)

**Fig. 6:** (e),(f) EDX analysis for the Nano particles done at PH 8 (e);PH and PH 9 (f).

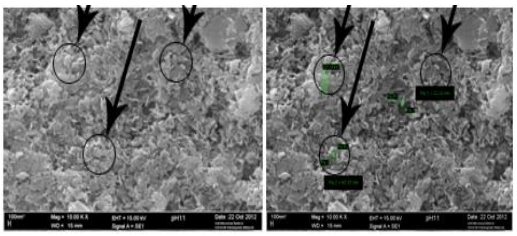
**Table 1:** EDX spectrum shown for PH8 and PH9 cobalt nano particles.

| Element | Weight%(PH8) | Atomic(PH8) | Weight%(PH9) | Atomic(PH9) |
|---|---|---|---|---|
| C K | 22.95 | 34.87 | 6.35 | 11.63 |
| OK | 45.73 | 5215 | 48.16 | 66.22 |
| CoK | 22.49 | 10.24 | 29.43 | 16.15 |
| NaK | 8.83 | 2.73 | 16.07 | 6.00 |
| Total | 100 | | 100 | |



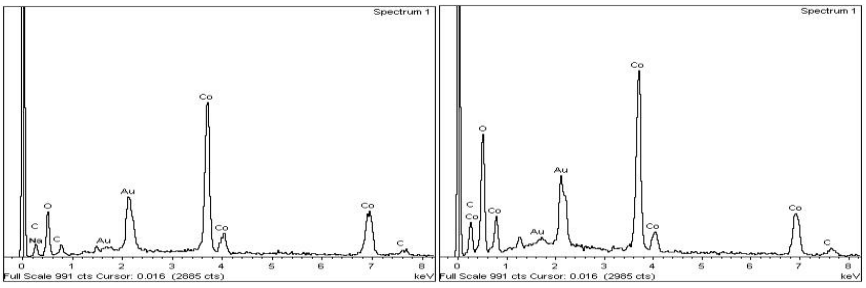
(g) (h)

**Fig. 7:** (g) PH 10 , (h) PH 10



(i) (j)

**Fig. 8:** (i) PH 11,( j) PH 11.




( k) (l)

**Fig. 9:** (k) ( l) EDX spectrum of cobalt oxide nano particles on the PH 10(k) on the right on PH 11.(l).

**Table 2:** EDX spectrum shown for PH10 and PH11 cobalt nano particles.

| Element | Weight%(PH10) | Atomic%(PH10) | Weight% (PH11) | Atomic%(PH11) |
|---|---|---|---|---|
| CK | 10.62 | 22.46 | 14.90 | 25.63 |
| OK | 29.14 | 46.29 | 43.97 | 56.77 |
| CoK | 26.05 | 16.51 | 19.30 | 9.95 |
| NaK | 34.20 | 14.74 | 21.83 | 7.65 |
| Total | 100 | | 100 | |

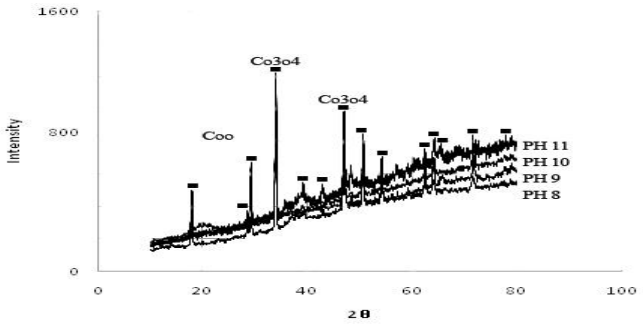



**Fig. 10:** The XRD patterns of cobalt oxide nano particles at different PHs.

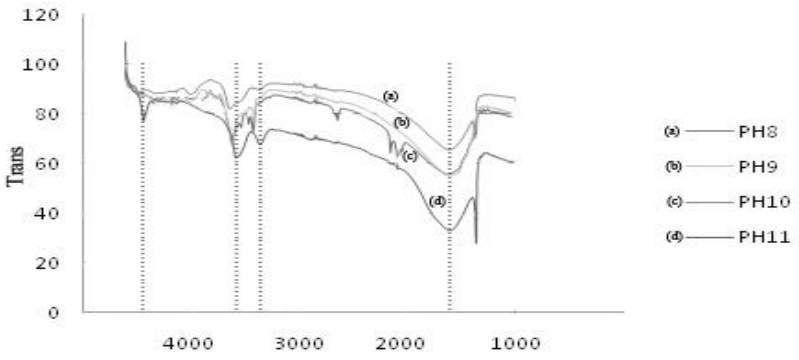



**Fig. 11:** FTIR Diagram shown for PH 8-11.

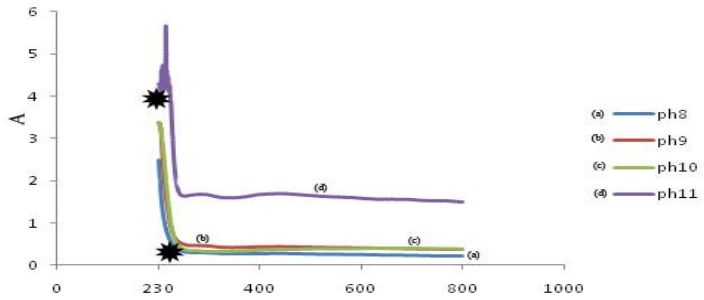



**Fig. 12:** (O) UV result of PH8, 9, 10, 11 from bottom to up.

**Table 3:** Crystalline size and particle size found by Scherer formula.

| PH | Crystallite Size (nm) | Particle Size (nm) |
|---|---|---|
| PH8 | 3.22 | 20 |
| PH9 | 3.25 | 30 |
| PH10 | 4.75 | 40 |
| PH11 | 4.89 | 50 |

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