

Extended Abstract

# Colloidal Aqueous Synthesis of Cobalt-doped ZnO Nanoparticles with MSA as Stabilizing Agent

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**Abstract:** Zinc oxide (ZnO) is an n-type II-VI semiconductor material that has gained prominence in recent decades due to the possibility of applications in the most diverse scientific areas, such as photonics, optoelectronics, magnetism, and biological systems. In this context, the scientific community seeks alternative synthetic methodologies to those already established in the literature, emphasizing the use of organic solvents, which are increasingly efficient, low-cost, and easy to reproduce. Thus, the present work proposed a method of colloidal aqueous synthesis, using different precursors of zinc and cobalt salts in a molar fraction according to the expression,  $Zn_{1-x}Co_xO$  ( $x = 0.05, 0.075, 0.10$ ), and mercaptosuccinic acid (MSA) as a stabilizing agent. The results confirmed the formation of cobalt-doped ZnO nanoparticles from X-ray diffractometry characterization. To evaluate their properties, studies of compositional analysis and size distribution of ZnO nanoparticles using characterization techniques such as inductively coupled plasma spectroscopy (ICP) and transmission electron microscopy (TEM) are being carried out to obtain even more promising results in this field.

**Keywords:** ZnO nanoparticles; cobalt doping; colloidal synthesis.

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## 1. Introduction

Zinc oxide (ZnO) is an intrinsic binary n-type semiconductor material that belongs to class II-VI, has a bandgap of about 3.37 eV, and excitonic binding energy of 60 meV. This semiconductor is considered a good host network for doping elements, such as transition metals (MTs), which have an ionic radius comparable to  $Zn^{2+}$  and are highly soluble [1].

Doping with transition metals promotes the insertion of discrete energy levels in the bandgap, allowing the occurrence of lower energy electronic transitions and tuning the spectral region profiles associated with them. Doping also improves the mobility of charge carriers (electrons and holes), the appearance of donor and acceptor defects, conductivity as well as different optical and magnetic properties. These characteristics open up the possibilities of application of pure and doped ZnO in several fields of nanotechnology, such as optoelectronic devices, LEDs [1], diluted magnetic semiconductors (DMS), photonics [1], and in nanomedicine [2]. Therefore, this material has been attracting the attention of the scientific community in recent decades due to its potential applications.

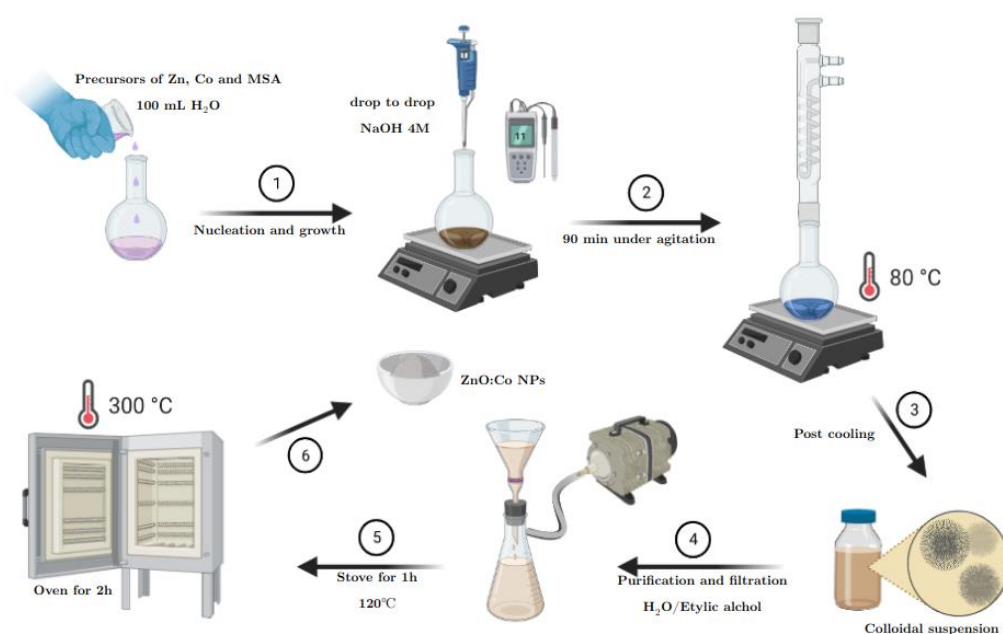
These materials have been mainly prepared by wet methods such as sol-gel, solvothermal, hydrothermal, and coprecipitation [2]. Many of them use organic solvents and high temperatures. Since the properties of interest are generally related to the morphology and size of the nanoparticles, which can be modulated from synthetic parameters, the preparation of ZnO nanocrystals, with dimensions lower than 100 nm, in water is still a challenge. In this context, we aimed to develop an alternative synthetic procedure to obtain ZnO nanocrystals in water. For this, we used the colloidal synthesis methodology, followed by a heat treatment. Thus, this manuscript presents the preparation of pure ZnO and ZnO:Co NPs via colloidal chemistry in an aqueous medium using mercaptosuccinic acid (MSA) as a surface stabilizing agent.

## 2. Materials and Methods

Colloidal synthesis of pure and Co-doped ZnO was carried out using as zinc source, zinc chloride ( $\text{ZnCl}_2$ ) or zinc nitrate hexahydrate [ $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ], and as cobalt source, cobalt chloride hexahydrate ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ) or cobalt nitrate hexahydrate [ $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ], mercaptosuccinic acid (MSA) as the stabilizing agent, and sodium hydroxide (NaOH) as precipitant agent for pH control. The molar ratio between Zn and Co was utilized according to the expression,  $\text{Zn}_{1-x}\text{Co}_x\text{O}$  ( $x = 0.05, 0.075, 0.10$ )[5], and the molar ratio between Zn:MSA was 1:4[6].

Initially, 0.004 mol of zinc precursor and 0.016 mol of MSA were added to a two-neck synthesis flask and solubilized in 50 mL of double-distilled water. For the system containing the dopant, the same procedure was followed with the addition of the cobalt precursor according to the Zn:Co molar ratio. Then, under stirring, the pH of the solution was adjusted to 11 with a  $4 \text{ mol}\cdot\text{L}^{-1}$  solution of NaOH. Subsequently, the sample was heated and stirred for 90 min at a temperature of  $80 \text{ }^\circ\text{C}$ .

Thus, the colloidal suspensions obtained were frozen to aid the destabilization of the colloidal system. Then, after thawing, isopropyl alcohol was added to the suspensions to force precipitation. The precipitate was washed with ethyl alcohol and distilled water, filtered using a vacuum pump and a sintered plate filter, dried in an oven for 1 h at  $120 \text{ }^\circ\text{C}$ , and calcined in a muffle furnace for 2 h at  $300 \text{ }^\circ\text{C}$ . Schematic representation of the synthetic procedure is shown in Figure 1. Finally all samples obtained were analyzed with an X-Ray Diffractometer SmartLab of the brand Rigaku.



**Figure 1.** Schematic representation of synthetic procedure for the aqueous colloidal synthesis of cobalt-doped ZnO nanoparticles using MSA as stabilizing agent.

### 3. Results and Discussion

X-ray diffraction patterns of  $\text{Zn}_{1-x}\text{Co}_x\text{O}$  ( $x = 0.05, 0.075, 0.10$ ) NPs synthesized using MSA as stabilizing agent and chloride salts as precursors of Zn and Co are shown in Figure 2a. The XRD profiles are well-matched with standard data (ICSD-13950), corresponding to the structure of hexagonal wurtzite, similar to the ZnS. For the  $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ , an uncommon peak was observed around  $45^\circ$  that can be attributed to some secondary phase, such as Co clusters or cobalt oxides, which present characteristic peaks between  $40$  and  $47^\circ$ [7], or other impurities of the samples. In order to study the effect of Co doping, a careful analysis of the position of XRD peaks was carried out, especially the prominent (100), (002), and (101) peaks that are shifted toward a lower  $2\theta$ , as shown in Figure 2b.

In Co-doped ZnO was also observed a decrease in the diffraction peak intensities with increasing the Co concentration. This can indicate that the dopant  $\text{Co}^{2+}$  ions (ionic radius:  $0.58 \text{ \AA}$ ) entered in the inner lattice of  $\text{Zn}^{2+}$  ions (ionic radius:  $60 \text{ \AA}$ )[8] more efficiently with the increase of doping amount. Since the ionic radius of  $\text{Co}^{2+}$  is close to that of  $\text{Zn}^{2+}$ , the changes in the FWHM are in accordance with the crystallite size, according to the Debye–Scherrer’s Equation.

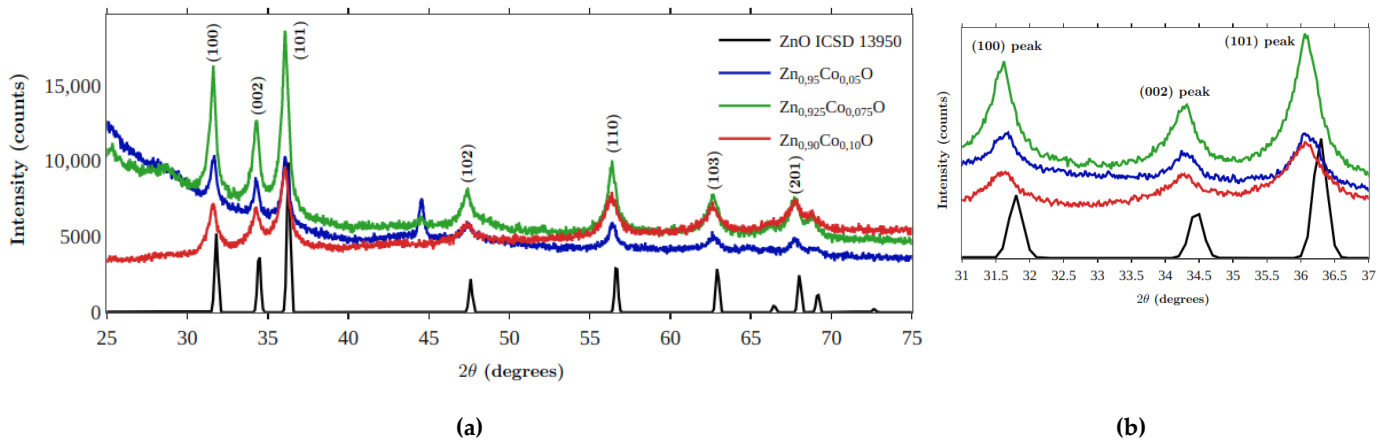


Figure 2. Structural analysis of Co-doped ZnO NPs using chloride as counterion: (a) Powder X-Ray diffraction patterns of  $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ ,  $\text{Zn}_{0.925}\text{Co}_{0.075}\text{O}$  and  $\text{Zn}_{0.90}\text{Co}_{0.10}\text{O}$ ; (b) (100), (002) and (101) peak shifting toward lower  $2\theta$  value.

Apparently, the average crystal size decreases for Co-doped ZnO NPs with the increase of concentration of dopant (Table 1). The reduction in the crystal size is mainly due to the distortion in the host ZnO lattice by the foreign impurities of  $\text{Co}^{2+}$  that decrease the nucleation and subsequent growth rate of ZnO NPs [5]. Furthermore, the surface stabilizing agent (MSA) also has an importance in the nucleation process because of the possibility of a higher control in the size of the particles retarding the growth process.

**Table 1.** Crystal size and microstrain of Co-doped ZnO Nanoparticles using chloride as counterion.

Theoric concentration of Co ( $x$ )	Average crystal size (nm)	Microstrain $\times 10^{-3} \text{ lines}^{-2}/\text{m}^4$
0.050	20	1.577
0.075	14	1.812
0.100	16	1.991

Figure 3a shows the structural analysis of Co-doped ZnO NPs synthesized using nitrate salts as precursors for Zn and Co. The diffractogram shows that all peaks are according to the standard data, corresponding also to the hexagonal wurtzite structure. Differently from Figure 2a, there were no observed peaks of a secondary phase. The Table

2 illustrates the same trend of the Co-doped ZnO NPs with chloride precursors, in which the increase of the concentration of doping (Co) in synthesis leads to a decrease in average size crystal and the increase in microstrain in the crystal lattice.

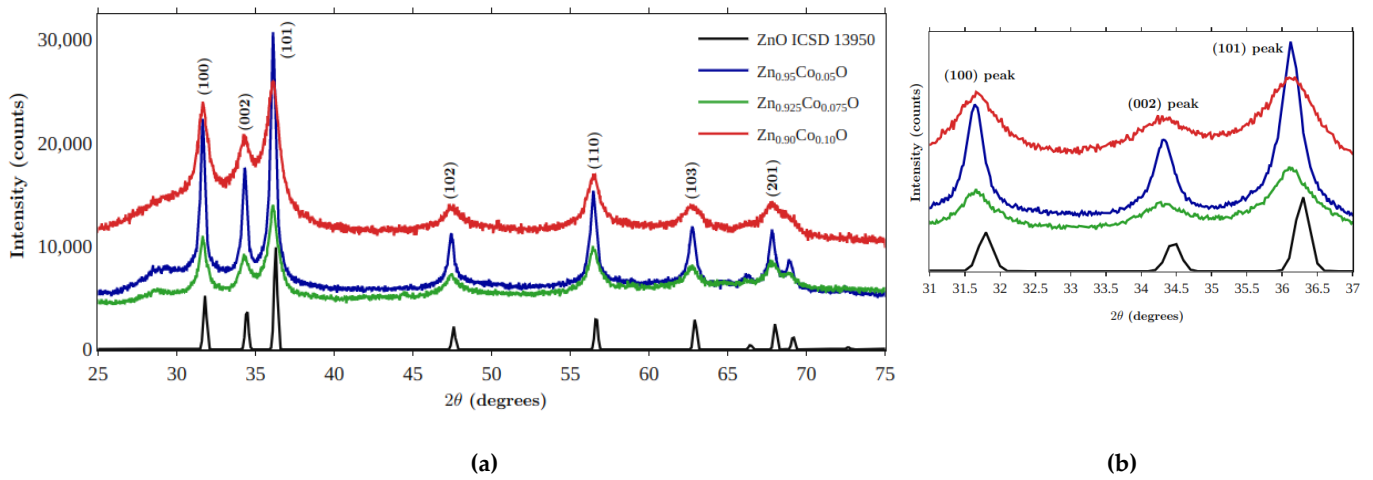


Figure 3. Structural analysis of Co-doped ZnO NPs using nitride as counterion: (a) Powder X-Ray diffraction patterns of  $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ ,  $\text{Zn}_{0.925}\text{Co}_{0.075}\text{O}$  and  $\text{Zn}_{0.90}\text{Co}_{0.10}\text{O}$ ; (b) (100), (002) and (101) peak shifting toward lower  $2\theta$  value.

**Table 2.** Crystal size and Microstrain of Co-doped ZnO Nanoparticles using nitrate as counterion.

Theoric concentration of Co (x)	Crystal size average (nm)	Microstrain $\times 10^{-3} \text{ lines}^{-2}/\text{m}^4$
0.050	17	1.521
0.075	12	2.334
0.100	10	2.954

Another parameter to analyze is the microstrain suffered by the ZnO network due to the insertion of  $\text{Co}^{2+}$  ions (Table 1 and 2). The substitution of  $\text{Co}^{2+}$  in an interstitial position would affect the concentration of the interstitial Zn, oxygen, and Zn vacancies. The observation of small changes of  $2\theta$  values in diffraction peaks and the peak broadening (Figures 2b and 3b) is due to the increase of microstrain[9], and the line broadening may be due to the size and microstrain[10] of nanoparticles. The slight change observed in the diffraction peaks indicates that the incorporation of  $\text{Co}^{2+}$  ions into the ZnO lattice causes minimal changes in the crystal lattice. Nevertheless, with increasing the dopant concentration, the microstrain also increases, which indicates that more Co was incorporated into the ZnO host network, causing major compaction of the crystal lattice due to the replacement of Zn by Co.

In terms of the counterion used, stoichiometrically, we have a molar ratio of 1:2 Zn:counterion for  $\text{M}^{2+}:\text{Cl}^-$  and  $\text{M}^{2+}:\text{NO}_3^-$  where  $\text{M} = \text{Zn}$  or  $\text{Co}$ . It was observed that there was a slower precipitation of the system containing nitrate than with chloride as the counterion. One of the explanations may be related to the high colloidal stability of the system containing nitrate as a counterion due to morphological aspects of the nanoparticles obtained or to the fact that nitrate ions may interact with surface ligands (MSA) via hydrogen bonds, that increase the charge concentration negative around the ligand and consequently the colloidal stability of the suspension.

The availability of these ions for the processes of nucleation and growth of NPs is one of the determining factors of the average size of nanoparticles. Comparing the enthalpy and Gibbs energy of formation of ions in aqueous media under temperature and pressure normal conditions, we have that nitrate has a more exothermic enthalpy than chloride, -

207.4 kJ/mol and -167.2 kJ/mol, respectively, and the Gibbs energy corresponds to the exergonic processes, -131.2 kJ/mol to  $\text{Cl}^-$  and -111.3 kJ/mol to  $\text{NO}_3^-$  [11].

Therefore, it is plausible that the nitrate interacts for a longer time with the constituents species of the colloidal suspension, favoring morphological changes and interactions between ligand-counterions that can reflect in the smaller average size observed for nanoparticles based on nitrate salts.

#### 4. Conclusions

$\text{Zn}_{1-x}\text{Co}_x\text{O}$  NPs were successfully prepared by a colloidal aqueous synthesis method utilizing MSA as a surface stabilizing agent. The hexagonal (wurtzite) crystalline structure was identified for doped ZnO through XRD analysis and confirmed the probable incorporation of the  $\text{Co}^{2+}$  ions into the ZnO matrix. Using nitrate salt precursors, it was not observed the existence of CoO (Co cluster) peaks. However, the presence of a probable CoO phase for  $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$  NPs with chloride salts as precursors was observed. The crystal size average for Co-doped ZnO NPs showed that with the increase of concentration of Co the size of the crystal decreases while the microstrain of the host crystal lattice of ZnO increases due to the probable substitution of Zn by Co in the network.

As perspectives of this work, additional measurements of transmission electron microscopy (TEM) and scanning electron microscopy (SEM), X-ray photoluminescence spectroscopy (XPS), active surface measurements (BET) will be carried out for a better characterization in terms of compositional analysis, size distribution and morphology of the nanoparticles to evaluate their future application potential.

In addition, more established methods in the literature, such as synthesis via coprecipitation, will be used as a comparative basis to evaluate the most promising properties via colloidal synthesis, whose presence of the surface stabilizing agent has a crucial impact on the nucleation and growth processes, resulting in smaller nanoparticles.

Finally, it is also important to highlight that the synthetic procedure developed in this work is practical, reproducible, and environment-friendly, allowing the preparation in aqueous medium of doped ZnO nanocrystals.

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