PREPARATION OF COBALT OXIDE/ZINC OXIDE NANOCOMPOSITE

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Abstract Cobalt Oxide/ Zinc Oxide nanocomposite was synthesized by dropwise addition of $Co(NO)_3.6H_2O$ and $Zn(NO_3)_2.4H_2O$ solutions to KOH solution at different temperatures followed by calcination at 300ºC for 4 h. The morphology and structure of nanoparticles and the influence of temperature on particle size were studied using scanning electron microscopy (SEM) and X-Ray Diffraction (XRD). Minimum particle size was obtained before calcination at 70ºC. In addition, the spherical, semispherical and flake-shaped nanoparticles were observed at ambient temperature. On the other hand, $Co(OH)_2$ was transformed to Co_3O_4, ZnO flakes were eliminated, and particle size changed during calcination. Synthesized samples at 50ºC and 70ºC showed an increase size after calcinations; however, elimination of flakes during calcination caused particle size reduction for synthesized sample at ambient temperature.

Keywords Natural Convection, Penalty Finite Element, Nusselt Number, Octagonal Enclosure, Rayleigh Number

چکیده در این مقاله، نانوپودرهای کامپوزیتی اکسید کبالت/ اکسید روی توسط افزودن قطره ای محلولهای نیترات کبالت آبدار و نیترات روی آبدار به محلول هیدروکسید پتاسیم در دماهای مختلف سنتز شده و کلسیناسیون آنها در دمای ۳۰۰ درجه سانتیگراد انجام شد. مورفولوژی و ساختار نمونه های بدست آمده به ترتیب توسط میکروسکپ الکترونی روبشی و تفرق اشعه ایکس بررسی شدند. مورفولوژی های بدست آمده کروی و نیمه کروی بوده و اشکال ورقه ای در دمای اتاق بدست آورده شدند. در این تحقیق، کاهش اندازه مواد بدست آمده با افزایش دما مورد بررسی قرار گرفت. در دمای ۷۰ درجه سانتیگراد، حداقل اندازه ذرات قبل از کلسیناسیون بدست آمد. پس از کلسیناسیون، هیدروکسید کبالت به اکسید کبالت تبدیل شده و ورقه ها نیز در تصاویر میکروسکپ الکترونی روبشی حذف شدند. اندازه ذرات نمونه ها بخاطر کلسیناسیون در دمای ۳۰۰ درجه سانتیگراد تغییر کردند. رشد نمونه های سنتز شده در دماهای ۵۰ و ۷۰ درجه سانتیگراد توسط کلسیناسیون مشاهده شد اما در نمونه سنتز شده در دمای اتاق، حذف ورقه ها باعث کاهش اندازه نانوذرات شد.

1. INTRODUCTION

In recent years, nanocomposites have been studied extensively due to their specific properties such as catalytic, optical, electrical, and magnetic properties, which are quite different from those for the bulk materials. Zinc oxide (ZnO), well known wide band gap semiconductors II-VI compound, has important applications such as chemical sensors, varistors, UV emitters, catalysts, transparent high power electronics, surface acoustic wave devices, piezo-electric transducers, etc [1]. Various methods have been reported for the synthesis of ZnO nanoparticles such as sol-gel[2], Chemical Bath Deposition (CBD)[3], sonochemcial synthesis[4], etc[5-6]. Among these various methods, CBD is an effective and simple method on account of its suitability for forming the new materials with different structures.

Cobalt oxides are important materials that find applications in different fields such as catalysis, various type of sensor, electrochemical, electrical,

and other opto-electronic devices [7]. Cobalt oxide is prepared by calcinations of $Co(OH)_2$ precursor synthesized by the chemical precipitation.

The main cobalt oxides are CoO and mixed Co(II) and Co(III) oxides ,Co_3O_4. When cobaltaus oxides are heated about 400-500 ˚C in oxygen, Co_3O_4 is readily obtained [8]. Co_3O_4 has typical spinel structure [9] and has various applications such as solid sensors, catalysts, electrode materials, magnetic materials, etc. In recent years, demands for monitoring of toxic and harmful gases have become more serious all over the world [10]. Various semiconductor gas sensors based on ZnO, SnO_2 and TiO_2 have been researched owing to their low costs and simple sensing method [11-13]. On the other hand, there still exist some disadvantages of them, for example, the poor sensitivity of SnO_2 and high working temperature of ZnO. In order to improve gas sensing properties of these sensors, many studies have been focused on novel metal catalysts such as Ag, Pt and Pd , materials doping, filming and oxides multiplicity (mixed oxides) [14].

Mixed oxide systems can be classified into top three categories: first category includes those that form distinct chemical compounds, such as $ZnCo_2O_4$ and $ZnSn_2O_4$. Into second category fall those mixed oxides that forms solid solutions, such as TiO_2-SnO_2. Finally, there are those systems that form neither compounds nor solid solutions, TiO_2/WO_3 [15].

In this paper, ZnO/ CoOH and ZnO/Co_3O_4 nanocomposites were synthesized by CBD method at different synthesis temperatures. X-Ray Diffraction (XRD), scanning electron microscopy (SEM), differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were used for characterization of synthesized nanocomposites.

2. EXPERMENTAL

2.1. Materials Cobalt nitrate-6-hydrate, $Co(NO)_3.6H_2O$, potassium hydroxide, KOH and zinc nitrate-4-hydrate, $Zn(NO_3)_2.4H_2O$ were purchased from Merck and used without further purification in this work. Distilled water was used for the preparation of aqueous solutions.

2.2. Synthesis $Zn(NO_3)_2.4H_2O$ (0.5M, 50ml) and $Co(NO_3).6H_2O$ (2M, 50ml) solutions were added dropwise to KOH aqueous solution within about 30 min under high stirring condition simultaneously. The reaction was allowed to proceed for additional 2 h at specific temperature at constant stirring condition. Synthesis conditions are listed in Table 1.

Then, the suspensions were centrifuged and were washed with distilled water and absolute methanol several times. Finally, the precipitates were collected and dried at 50 ºC for 24 h.

2.3. Calcination The synthesized $ZnO/Co(OH)_2$ nanocomposite was calcinated at 300ºC for 4 h in the air atmosphere.

2.4. Characterization The phase composition of nanoparticles was determined using X-ray diffraction (XRD) by a Philips (PW3710) X-ray diffractometer with copper Kα radiation (λ = 1.5418Å) and scan speed of 2˚/min. The 2θ range used in the measurement was from 20° to 70°. In addition, nanoparticles morphology was observed with an OXFORD Leo 440i Scanning electron microscope. The nanoparticles size was measured by Able Image Analyzer v3.6. Simultaneous differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed at argon atmosphere and at rate of 10 ˚C/min using a thermal analyzer system (model STA 1640).

3. RESULTS AND DISCUSSION

3.1. Synthesis of ZnO/ $Co(OH)_2$ nano-composites The XRD patterns of samples are shown in Fig. 1. The diffraction peaks could be indexed to ZnO and $Co(OH)_2$. It can be seen that (110) of ZnO is the major peak for sample I and II whereas (101) of $Co(OH)_2$ is the major peak for sample III. In addition, the peak intensity increases with increasing temperature, and $Co(OH)_2$ peaks intensities are higher than ZnO peaks intensities at higher temperatures.

The SEM images of synthesized nano-composites are shown in Fig. 2. It can be seen that the morphology of nano-composites are composed of spherical and semi-spherical nanoparticles as well

TABLE 1. Experimental conditions used for synthesis of nano- composite powders

Sample	*Temperature °C*	*Stirring time* ***(h.)***
I	25-35	2.5
II	65-75	2.5
III	85-95	2.5

as flake shaped crystallites. In addition, by increasing the sysnthesis temperature the particle size decreases and flake morphology is vanished [16].

Fig. 3 shows the influence of synthesis temperature on the nanoparticles size distribution. Maximum, minimum and **mean** size of nanoparticles were calculated by the image processing program, programmed with visual C++ at Materials Simulation Center of Materials and Energy Research Center (MERC).

The thermal behaviors of synthesized ZnO/ $Co(OH)_2$ nano-composites are shown in Fig. 4. In fact, because of the coexistence of ZnO and $Co(OH)_2$, no distinct $Co(OH)_2$ peaks can be detected in this figure. However, an endothermic tiny peak can be detected at about 284 $^{\circ}C$. Moreover, no ZnO peak (exothermic or endothermic) was observed in DTA curve at 280 $^{\circ}C$ indicating of no exothermic or endothermic transformations at this temperature. Indeed, DTA analysis has indicated that $Co(OH)_2$ converts to Co_3O_4 at about 280ºC [17].

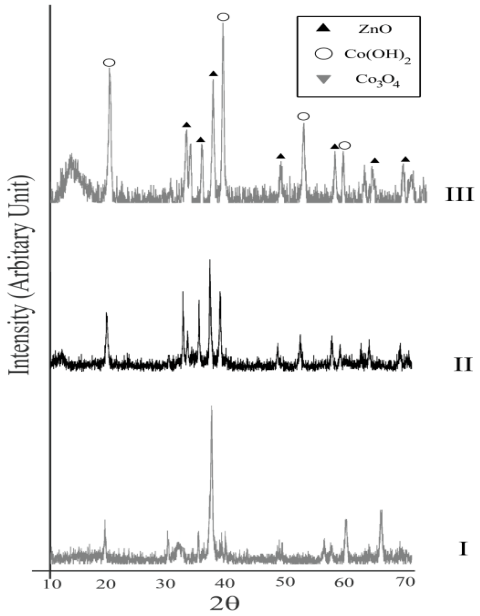

Figure 1. XRD pattern of samples

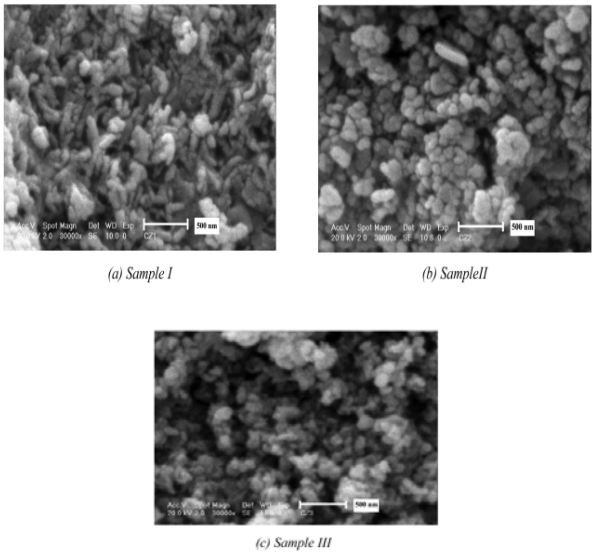

Figure 2. SEM images of synthesized samples

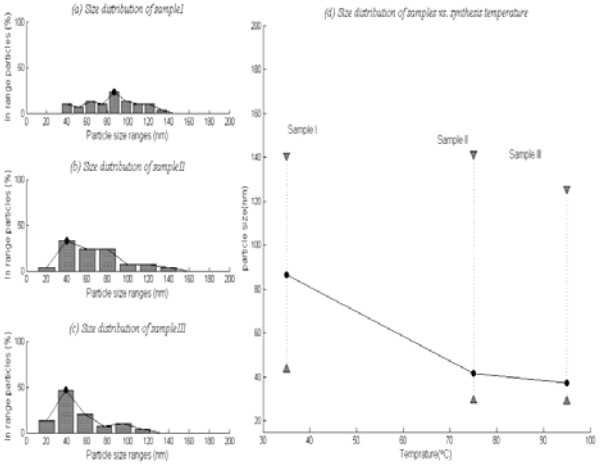

Figure 3. Histogram of particle size distribution

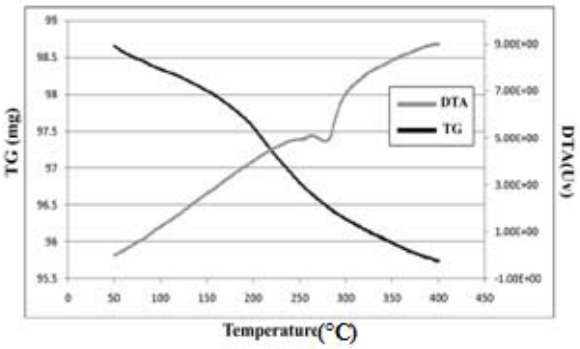

Figure 4. DTA/ TGA analysis of sample I.

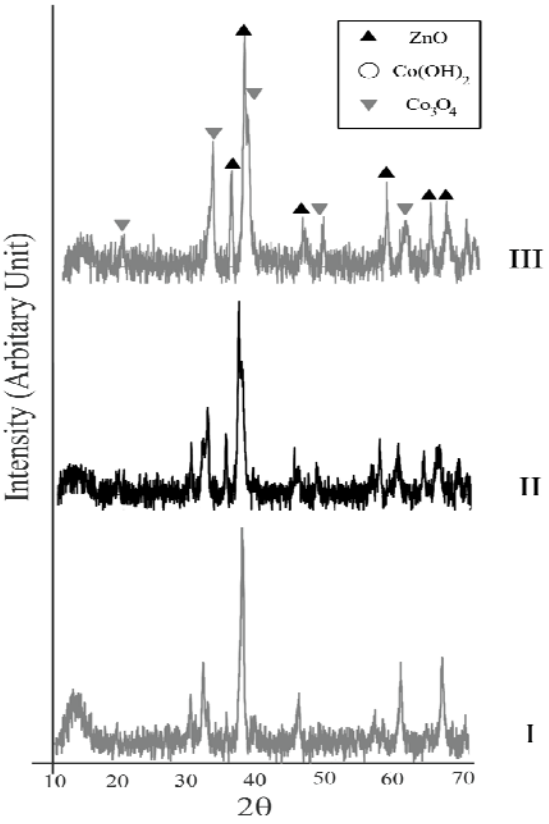

Figure 5. XRD patterns of samples after calcination in 300

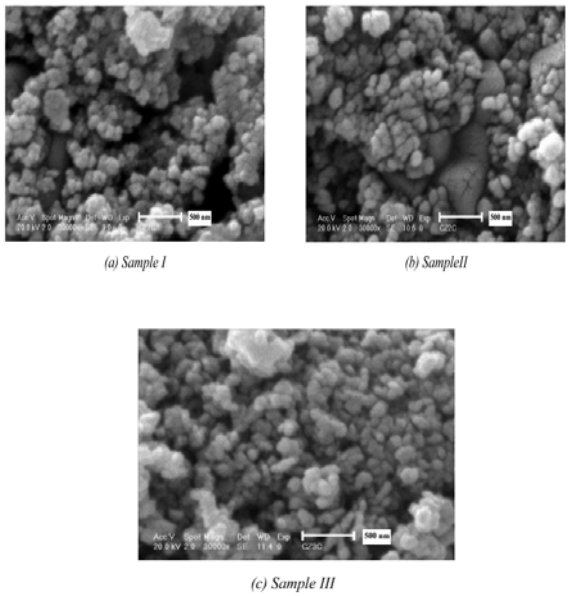

Figure 6. SEM images of samples after calcinations.

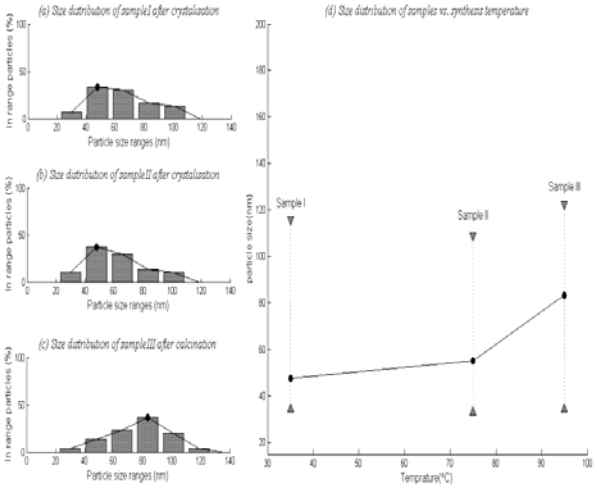

Figure 7. Histogram of particle size distribution after calcination

3.2. Calcination of samples at 300˚C.

Fig. 5 shows the XRD patterns of calcinated samples at 300 ˚C or 4 h. It was observed that calcination resulted in ZnO/Co_3O_4 nanocomposite formation. were formed and there was no trace of $Co(OH)_2$ peaks.

The SEM images of ZnO/Co_3O_4 nanocomposite are shown in Fig. 6. It can be seen that the calcination causes eliminating the flakes and ZnO/Co_3O_4 nanocomposites are composed of spherical and

semi-spherical nanoparticles. Maximum, minimum and **mean** size of calcinated samples were calculated by image processing program, programmed with visual C++ at Materials Simulation Center of Materials and Energy Research Center (MERC).

5. CONCLUSION

$ZnO/Co(OH)_2$ nanocomposite with different morphology was synthesized by Chemical Bath Deposition method. It was observed that by increasing the synthesis temperature the nanoparticle average size decreased and flake shaped ZnO vanished. In addition, calcination at 300 ˚C for 4 h resulted in transformation of $ZnO/Co(OH)_2$ nanocomposite to ZnO/Co_3O_4 nanocomposite. In addition, due to the absence of flakes and obtaining more uniform morphologies at upper synthesis temperatures, the average size of nanoaprticles for samples II and III increased after calcination. However, ZnO flakes changed to spherical nanoparticles and $Co(OH)_2$ transformed to Co_3O_4 during calcination which brought about particle size reduction.

6. REFERENCES

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