Int.J.Nano.Dim 1(1): 33-40, Summer 2010
ISSN: 2008-8868

Contents list available at **IJND**

International Journal of Nano Dimension

Journal homepage : **www.IJND.ir**

Synthesis and characterization of a Bi-Oxide nanoparticle ZnO/CuO by thermal decomposition of oxalate precursor method

M. Ghane [1], B. Sadeghi [2], A.R. Jafari [1,*], A.R. Paknejhad [3]

[1]*Department of Microbiology, Islamic Azad University Tonekabon Branch , Iran, Tonekabon, Iran*
[2] *Department of Chemistry, Islamic Azad University Tonekabon Branch , Iran, Tonekabon, Iran*
[3] *Department of Physics, Islamic Azad University Shabestar Branch, Iran*

Received: 15 April 2010 ; Accepted: 28 June 2010

Abstract

In the present work, we report the synthesis of binary nano metal oxides such as Zinc /Copper Oxide via novel dry synthetic methods such as thermal decomposition of oxalate precursor. The synthesis route involves facile solid-phase mechanochemical activation of a physical mixture of simple copper/zinc salts and oxalic acid, followed by calcination of the as-ground oxalate precursors at 450$^{\circ C}$. X-ray powder diffractometry (XRD), infrared spectroscopy (FTIR), and scanning electron microscopy (SEM) were used to the thermal spectroscopic, structural, morphological characterization and surface area determination of the product respectively . An average nanocrystallite size of 5.0 nm was obtained for Zn/Cu, as estimated by the Scherrer's equation.

Keywords: *Bi-Oxide, Zinc / Copper oxide, Nanoparticle, Thermal Decomposition of Oxalate Precursor Method, Chemical synthesis*

1. Introduction

The interest in nanomaterials has increased in recent years because of their unique physical and chemical properties [1]. The experimental conditions used in the preparation of these materials play an important role in the particle size of the product. For this reason, a great variety of experimental methods have been used in the production of nanoparticles, such as the sol–gel technique [2,3] , techniques that use liquid ammonia as solvent [4] and others. Bimetallic nanoparticles are of wide interest since they lead to many interesting size-dependent electrical, chemical, and optical properties. They are particularly important in the field of catalysis since they often exhibit better catalytic properties than their monometallic counterparts [5]. Shinde *et al* and Ghodake *et al*. have reported the oxalate precursor based precipitation method in order to

*Corresponding author: Ali Reza Jafari
Islamic Azad University, Tonekabon Branch
Tonekabon, Iran.
Tel +984517728020
Email Micro6190@Hotmail.com

prepare nanosized ferrites [6,7]. Rao *et al*. have reported an oxalate co-precipitation method for synthesis of ferrites using a mixture of water and alcohol as medium in order to avoid the precipitation of metal oxalates during synthesis [8].

ZnO is of significant importance due to its electronic and optical properties. It is a wide band gap (*Eg* _ 3.3 eV) metal oxide semiconductor with piezoelectric and optical properties in the UV range [9,24]. It crystallizes in the wurtzite structure and display spiezoelectric properties when its *c*-axis is oriented perpendicular to a substrate. For this reason, it is found in many electroacoustic applications such as sound sensors, SONAR emitters and detectors, and pressure transducers. ZnO is used as the clear top electrode in solar cells and has potential in the area of information storage as a piezoelectric memory device [9,24].

Copper oxide (CuO)/copper (II) oxide/cupric oxide is a semiconducting compound with a monoclinic structure. CuO has attracted particular attention because it is the simplest member of the family of copper compounds and exhibits a range of potentially useful physical properties such as high temperature superconductivity, electron correlation effects and spin dynamics [10,11]. As an important *p*-type semiconductor, CuO has found many diverse applications such as in gas sensors, catalysis, batteries, high temperature superconductors, solar energy conversion and field emission emitters. In the energy-saving area, energy transferring fluids filled with nano CuO particles can improve fluid viscosity and enhance thermal conductivity [12]. CuO crystal structures possess a narrowband gap, giving useful photocatalytic or photovoltaic properties as well as photoconductive functionalities [13]. Cu–Zn (brass) alloys have been used for coins and ornamental purposes since the beginning of metallurgy [14,15].

Cu–Zn based catalysts are well known to enhance both catalytic activity and selectivity in the synthesis of alcohols by hydrogenolysis of fatty acids [16]. A recent study showed that the formation of Cu–Zn alloys is a significant step in the methanol synthesis over Cu/ZnO catalysts [17]. Cu–Zn alloying has been well investigated in the bulk and several reports on the chemical reactions and phase transformations in this system have been published [18,19]. Few attempts to control the evolution of different phases during the synthesis of nanocrystalline Cu–Zn alloys by MA have been reported [20,21]. Nanocomposites of Cu–Zn particles have been prepared by condensing Zn vapor onto pre-formed Cu nanoparticles, which were prepared by the gas condensation technique [22,23]. The formation of the Zn layer was assumed to occur via a heterogeneous nucleation mechanism where the Cu nanoparticles acted as nuclei for the condensation of the Zn vapor [22]. The final nanoparticle composition revealed that Zn is present as ZnO as a result of the slow oxidation treatment to stabilize the double-layer nanoparticles [22].

In this work, we report the synthesis of intermetallic ZnO / CuO nanoparticles using by thermal decomposition of oxalate precursor method for the first time.

2. Materials and methods

All the chemical reagents used in our experiments were of analytical grad and were used as received without purification. The starting materials were: Copper nitrate (Merck), Oxalic acide (OA) (Merck), Zinc acetate (Merck), Ethanol (Merck). Zinc acetate and Copper nitrate were added to ethanol in a two neck flask giving a 0.3 M blue solution. The temperature was raised to 50 ^{oC} and after 30 min of continuous stirring, oxalic acid (OA) was rapidly added to the solution. The molar ratio Zn/Cu:OA was 1. The system was kept at 50 ^{oC} under reflux for 2 h and a blue

precipitate was obtained; then the resulting viscous gel was dried at 80 ^{oC} overnight. The dried Zinc/Copper oxalate was ground and calcined at 450 ^{oC} for 2 h. XRD patterns were recorded by a Bruker D8-Advance Diffractometer using Cu Kα radiation (λ=1.5406Å). Fourier transform infrared (FT-IR) spectra were recorded on a Bruker spectrophotometer in KBr pellets. Surface morphology of product was characterized by using a Cam Scan MV2300 scanning electronic microscopy (SEM) with an accelerating voltage of 30 kV.

2.1. Mechanism of thermal decomposition of AP

The thermal decomposition of AP (Thermal decomposition of ammonium perchlorate) is a complex process, which contains hundreds of chain reactions. AP has been extensively studied by YU Zongxue's group [25] and they proposed a mechanism for the decomposition of AP. At low temperature, the products of thermal decomposition of pure AP are NH_3, H_2O and a small amount of N_2O and O_2. During the high-temperature stage of AP decomposition, HCl, H_2O, N_2O, NH_3, Cl_2, NO, O_2, NO_2 and a small amount of ClO_2 are formed. Based on this mechanism we propose the following route for the decomposition of AP:

1. At low temperature:

$$NH_4ClO_4 \rightarrow NH_4^+ + ClO_4^-$$
$$NH_4^+ + ClO_4^- \rightarrow NH_3 + HClO_4$$
$$4HClO_4 \rightarrow 2ClO_3 + 2ClO + 3O_2 + 2H_2O$$
$$2NH_3 + 2O_2 \rightarrow N_2O + 3H_2O \leftrightarrow NH_4NO_3 + H_2O$$

2. At high temperature:

$$4HClO_4 \rightarrow 2Cl_2 + 5O_2 + 2ClO_2 + 2H_2O$$
$$2Cl_2 + 2H_2O \rightarrow 4HCl + O_2$$
$$2NH_3 + 2ClO_2 \rightarrow N_2O + Cl_2 + 3H_2O$$
$$N_2O + O_2 \rightarrow NO + NO_2$$

3. Results and discussion

Figure 1 displays a typical XRD pattern of the nano crystalline ZnO / CuO prepared with oxalate decomposition route. These results reveal that although the ZnO peaks are more evident, two phases (CuO and ZnO) co-exist. In this way, we propose that the oxide prepared corresponds to the (ICDD card no. 26-0571).

All its diffraction peaks can be readily indexed to a pure face-centered cubic (fcc) structure (space group: Fd3m [227]) of Zn / Cu normal spinel with lattice parameter a = 8.08370Å (ICDD card no. 42-1467). The average crystallite sizes (C.S) of the nanocrystals were calculated using the Debye-Scherer Equation from the major diffraction peaks.

$C.S = K.\lambda / \beta.\cos\theta$.

Int.J.Nano. Dim 1(1): 33-40, Summer 2010

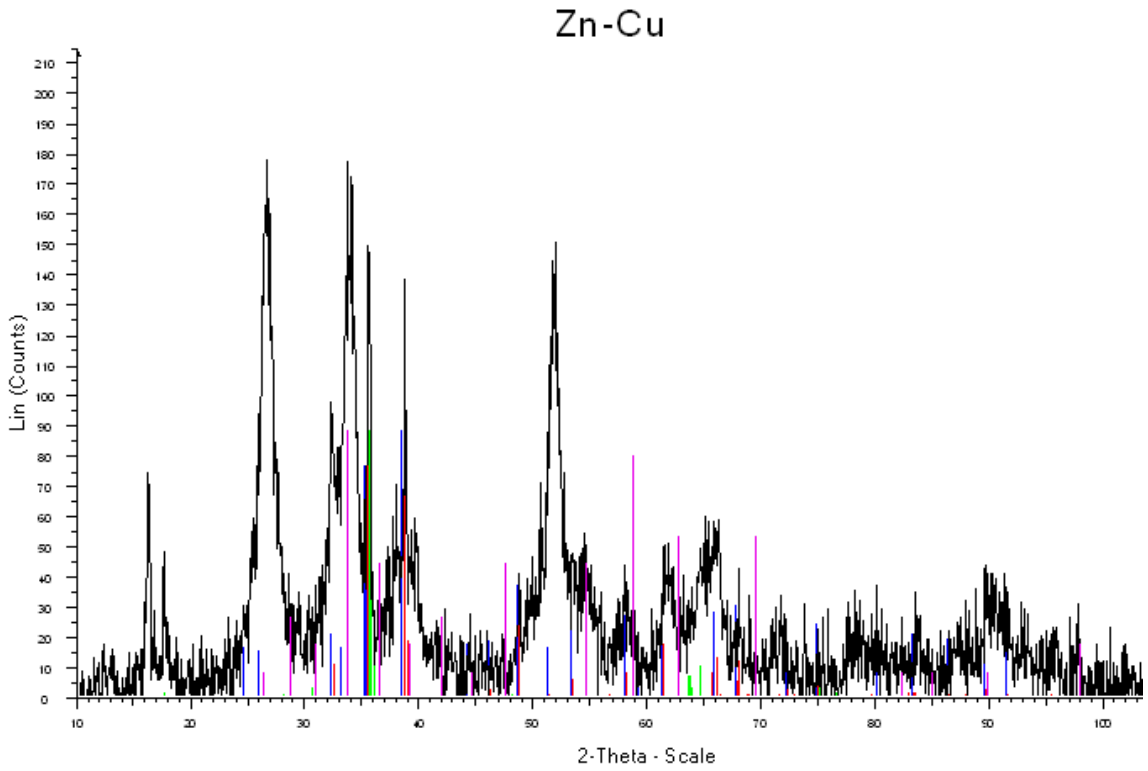

Fig.1. XRD spectra of the ZnO/CuO product obtained after calcination at 450 °C for 2 h

Where K is a constant equal to 0.9, λ is the wavelength of Cu Kα radiation, β is the full width at half maximum (FWHM) of the diffraction peak in radiant and θ is the Bragg angles of the main planes.

$CS = (0.9 \times 0.15418)/(0.0218 \times \cos 13.05) = 6.53$ nm

$CS = (0.9 \times 0.15418)/(0.0412 \times \cos 16.8) = 3.56$ nm

$(6.53 + 3.56) / 2 = 5.0$ nm

The average crystallite size of the Zn/Cu nanoparticle was 5.0 nm.

Figure 2 displays the FTIR spectra of the mixed oxide precursor and of the product powders obtained by calcination of the precursor in air at 450°C for 2 h. The shoulder at 3861 cm^{-1} is present in the spectrum of the product obtained at 450 °C, is evidence (O-H) water tensional tremble and concurrent, while such evidence of organics is visible in the spectrum of the product obtained at 450 °C. The absorptions at 2362 cm^{-1} present in the spectrum of the product obtained at

450$^{\circ C}$ have been assigned to (C-H) tensional. The shoulder at 1624 cm^{-1} is present in the spectrum evidence of (O-H) water tremble bendy and nonconcurrent. The shoulder at 1458 cm^{-1} is present in the spectrum evidence of (N-O) tremble. The shoulder at 1384 cm^{-1} is present in the spectrum evidence of (C-O) tremble and the shoulder at 986 cm^{-1} and 608 cm^{-1} are presents in the spectrum evidence of (O-C-O) tensional tremble and (M-O) tremble respectively.

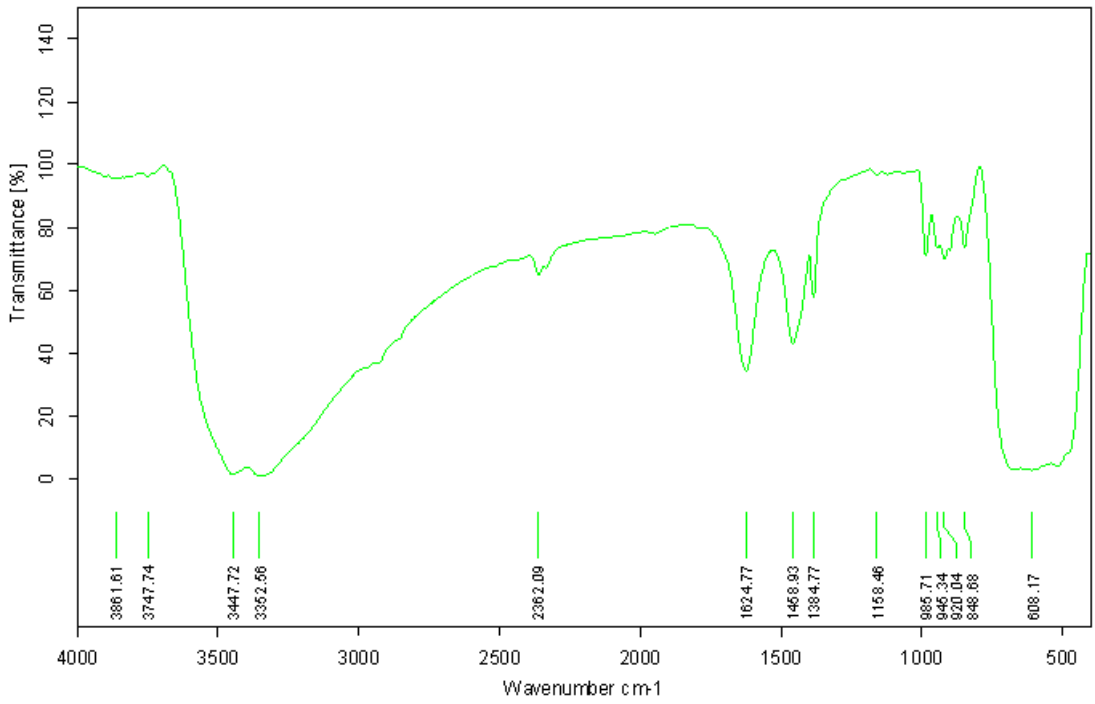

Fig.2. FTIR of ZnO/CuO products obtained after calcinations at 450 $^{\circ C}$ for 2 h

SEM micrographies of the mixed oxide samples are shown in Figure 3. It is only possible to observe clusters. This indicates that the particle diameter of these products is less than 10 nm, which agrees with the value estimated from XRD data.

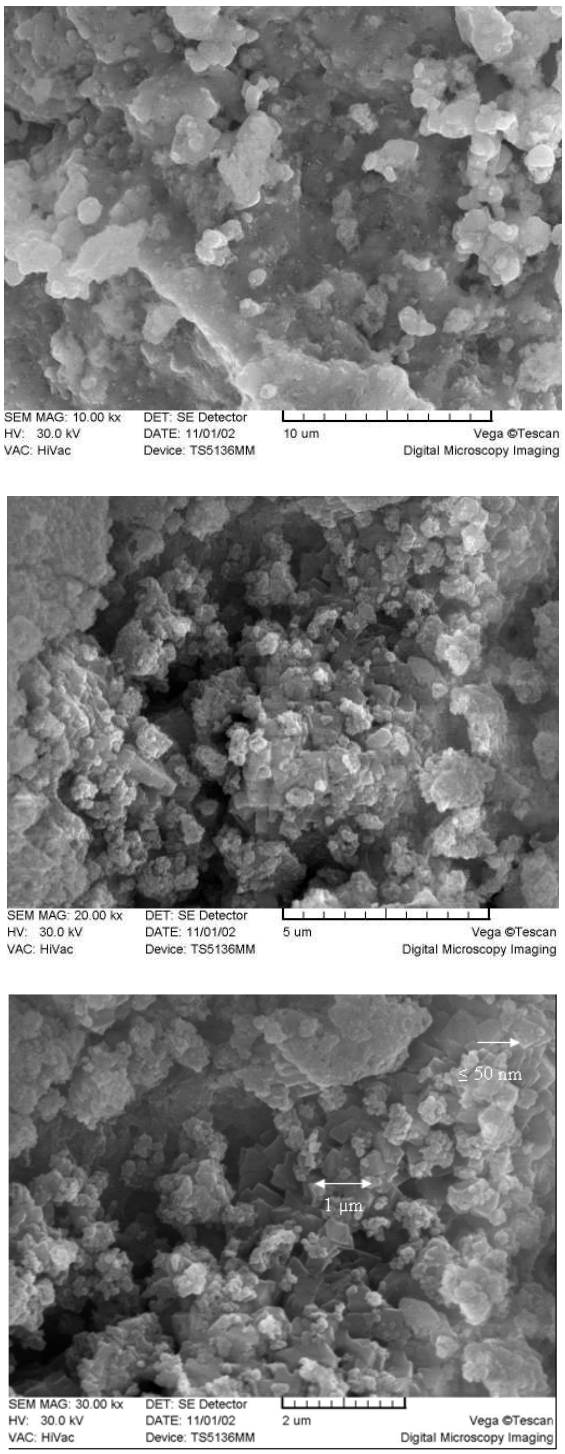

Fig.3. SEM micrographs of ZnO/CuO products obtained after calcinations at 450 $^{\circ}C$ for 2 h

4. Conclusion

In this work we synthesized binary nano metal oxide such as Copper/Zinc Oxide via different methods as thermal decomposition of oxalate precursor. The Zn/Cu systems have spinel phase in face centered cubic (fcc) crystallite structure. SEM and XRD data lead to the following particle diameters: <10nm for ZnO/CuO.

Acknowledgements

The financial and encouragement support provided by the Research vice Presidency of Tonekabon Branch, Islamic Azad University and Executive Director of Iran-Nanotechnology Organization (Govt. of Iran).

References

[1] Ball P., Li G., (1992), Nature. 355: 761-775.
[2] D.G. Lamas, G.E. Lascalea, N.E.Walsoe de Reca, (1998), Synthesis and characterization of nanocrystalline powders for partially stabilized zirconia ceramics .J. Eur. Ceram. Soc. 8:1217-1221.
[3] R.F. Juarez, D.G. Lamas, G.F. Lascalea, (2000), Synthesis of nanocrystalline zirconia powders for TZP ceramics by a nitrate–citrate combustion route N.F.Walsoe de Reca, J. Eur. Ceram. Soc. 2000;20, 133-139.
[4] L. Sun, Z. Zhang, Z.Wang, Z.Wu, H. Dang, (2005), Synthesis and characterization of CuO nanoparticles from liquid ammonia. Mater. Res. Bull. 40:1024-1031.
[5] N. Toshima, Y. Wang, (1993), Chem. Lett.1611-1625.
[6] Shinde T.J., Gadkari A.B., Vasambekar P.N., (2008), DC resistivity of Ni–Zn ferrites prepared by oxalate precipitation method. Mater. Chem. Phys. 111:87–91.
[7] Ghodake J.S., Kambale R.C., Kulkarni S.D., Sawant S.R., Suryavanshi S.S., (2006), Complex permeability studies of Ni–Co–Zn ferrites synthesized by an oxalate precursor method, Smart Mater. Struct. 2 doi:10.1088/0964-1726/18/12/125009.
[8] P.h. Tailhades, C. Villette, A. Rousset, G.U. Kulkarni, K.R. Kannan, C.N.R. Rao, M. Lenglet, Cation migration and coercivity in mixed copper–cobalt spinel ferrite powders, J. Solid State Chem. 1998;141,56-63.
[9] Hu, J.; Gordon, R. G., (1991), Solar Cells.30:437-444.
[10] Cava RJ., (1990), Structural chemistry and the local charge picture of copper oxide superconductors. Science. 247:656-62.
[11] Tranquada JM., Sternlieb BJ., Axe JD., Nakamura Y., Uchida S., (1995), Evidence for stripe correlations of spins and holes in copper oxide superconductors. Nature. 375-561.
[12] Kwak K., Kim C., (2005), Viscosity and thermal conductivity of copper oxide nanofluid dispersed in ethylene glycol. Korea–Australia Rheol J. 17:35-40.

[13] Xu JF JiW., Shen ZX., Tang SH., Ye XR., Jia DZ., (1999), Preparation and characterization of CuO nanocrystals. J Solid State Chem. 147:516-519.

[14] Sauthoff G., (1995), Intermetallics. Germany: VCH.

[15] Stoloff NS., Sikka VK., (1996), Physical metallurgy and processing of intermetallic compounds. New York: Thomson Publishing.

[16] Van de Scheur F, Brands D, Van der Linden B, Luttikhuis CO, Poels EK, Stall LH., (1994), Appl Catal A. 116-237.

[17] Harikumar KR., Santra AK., Rao CNR., (1996), A comparative study of the interaction of CO with Cu and Cu---Zn alloy clusters. Appl Surf Sci. 93-135.

[18] Gialanella S., Baro MD., Amils X., Surinach S., Yavari AR., (1997), Mater Sci Forum. 571-235.

[19] Cardellini F., Contini V., Mazzone G., Vittori M., (1993), Phase Transformations and chemical reactions in mechanically alloyed Cu---Zn powders Scr Metall Mater. 1993; 28,1035-1042.

[20] Pabi SK., Joardar J., Murty BS., (1996), Influence of Fe and Cr on the disordering behavior of mechanically alloyed NiAl J Mater Sci. 31:3207-3214.

[21] Pabi SK, Murty BS., (1998), Mater Sci Eng A.214-146.

[22] Oda M.,Hayashi C., Uyeda R., Tasaki A., (1997), Ultrafine particles: Exploratory science and technology. Westwood, NJ: Noyes Publications.133-144.

[23] Ohno T., (1997), J Jpn Soc Powder Metall.44:106-112.

[24] Mulligan Robert F., Iliadis Agis A., Kofinas P., (2003), Synthesis and Characterization of ZnO Nanostructures. Templated Using Diblock Copolymers; Journal of Applied Polymer Science. 1058-1061.

[25] Zongxue YU., Lifen C., Lude L., Xujie Y., Xin W.G, Chin J Catal., (2009), DSC/TG-MS Study on in Situ Catalytic Thermal Decomposition of Ammonium Perchlorate overCoC_2O_4 .30(1):19-23.