Int. J. Bio-Inorg. Hybr. Nanomater., Vol. 3, No. 3 (2014), 163-167

ISSN Print: 2251-8533
ISSN Online: 2322-4142

International Journal of Bio-Inorganic Hybrid Nanomaterials

Structural and Morphology Study of ZnO/CuO Powders Prepared by Combination of Sol-gel Auto Combustion and Ultrasonic Irradiation Methods with Different Fuels

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Received: 17 May 2014; Accepted: 21 July 2014

ABSTRACT

Nanocrystalline complex oxides have been synthesized by combination of sol–gel auto combustion and ultrasonic irradiation techniques using copper nitrate, zinc nitrate as metallic nitrates and glycine, urea and thiourea as fuels. Sol-gel combustion (combination of the chemical sol–gel process and the combustion process) as a proper synthesized technique is used to synthesize ZnO/CuO nanocomposites. This method is based on the gelling and further combustion of solution in aqueous phase which contain salts of the desired metals and fuels. Consequently, ZnO/CuO powders were prepared with molar ratio of nitrates to fuels 1:2. Combustion process is inexpensive since it does not involve intermediate decomposition and/or calcining steps. Combustion process ends, within 30 seconds for all systems.. Finally, the product powder was characterized by X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM).

Keyword: Nanocrystalline; Sol-gel auto combustion; Ultrasonic; ZnO/CuO; XRD; SEM.

1. INTRODUCTION

Nowadays, nanosized powders have gained a great interest among industries especially in electronic products, magnetic materials, optical applications, chemical industries, and environmental applications. In addition, nanosized powders plays a key role for producing structural ceramics inaugurate and thermal spray coatings. The large surface area and high sinterability are the main reasons for applying the nanosized powders used in the above mentioned industries [1].

The most usage of Zinc oxide (ZnO) nanostructural powder is due to its properties such as wide direct band gap, strong excitonic binding energy. Also, it is promising application for UV-laser with low threshold [2]. Moreover, there are other properties including field emission array [3, 4], surficial acoustic device [5] and transistor and biosensor (in nanoscale) [6] which make

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Zinc oxide (ZnO) a high value powder. For instance, ZnO has widely been utilized to degrade different organic dyes in wastewater due to the characteristics such as environmental stability, low cost and strong oxidizing power [7, 8].

Another nanostructural powder namely Copper (II) oxide (CuO) has special properties. The most remarkable properties which are interesting for industrial use are large Surface area to volume ratio, unique electronic and optical properties [9, 10].

CuO is mostly used to produce wide band gap semiconductors. It can improve the photocatalytic efficiency due to the having p-type with a narrow band gap [11-13]. In semiconductors production, the oxides of transition metals are important which leads the semiconductors to be a proper material to use in magnetic storage media, solar energy transformation and catalysis production.

There are various techniques which have been proposed for the preparation of nanophase materials, namely vapor deposition [14], ball milling technique [15], reversed micelles [16], Langmuir–Blodgett film [17] and self-assembled monolayers [18].

In this research for preparing of nanophase materials, the sol-gel auto combustion technique is suggested to use for the preparation of nanocomposite materials [19, 20]. However, a thermally induced anionic redox reaction takes place in sol-gel auto combustion technique. The energy from the exothermic reaction between oxidant and reductant can be high enough to form a desirable phase within a very short time [21, 22]. In addition, an important advantage of sol-gel process is to keep the composition homogeneous for obtaining pure and fine powders of materials [23].

The organic-inorganic hybrid materials possess interesting function through the incorporation of the important properties from both components [24-26]. The sonochemical methods have been presented to be very promising in the preparation of a variety of materials with nanometer dimensions, including nanochalcogenides [27, 28], metallic nanoparticles [29, 30] and nanosized metal oxides [31, 32]. These materials possess improved magnetic properties [33], energy storage capacities [34-36] and photocatalytic [37] and catalytic properties [38].

Synthesizing ZnO/CuO leads to produce a nano powder ceramic with interesting properties. Therefore, the aim of this research is to synthesize nanocrystalline ZnO/CuO by combination of sol-gel auto combustion and ultrasonic irradiation techniques.

2. EXPERIMENTAL METHODS

2.1 Materials and equipments

Zinc nitrate hexa hydrate ($Zn(NO_3)_3.6H_2O$, Merck), copper nitrate ($Cu(NO_3)_2$, Merck), glycine ($C_2H_5NO_2$, Merck), urea ($CO(NH_2)_2$, Merck), thiourea ($CS(NH_2)_2$, Merck) and NH_4OH (Merck, 25%) was obtained with analytical grade. All materials were used without further purification. All experimental investigations were made with deionized water.

ZnO/CuO powders were synthesized from sol-gel auto combustion by ultrasonic irradiation (Bandelin Electronic Company, Model RK100) methods. The phase identification of the burnt powder of ZnO/CuO is done using XRD (Model: XPERT-MPD, Philips with operated at 40 kV and 40 mA). The structural morphology is investigated using SEM (Phillips XL30 with 40 kV operating voltage).

2.2. Preparation of ZnO/CuO nanocrystals

In the first step, deionized water was prepared by dissolving $Zn(NO_3)_3$ $6H_2O$ and $Cu(NO_3)_2$. In the next step, the glycine, urea and thiourea (as fuel) were added to the prepared deionized water separately. Furthermore, the pH of the water needs to be neutralized by adding ammonia. This solution was left to evaporate at 90°C with continuous mechanical stirring, for 4 h, until a sticky gel was obtained. Increasing the temperature up to about 200°C led to the ignition of the gel. The combustion reactor which has been used, was made of sintered alumina that results show this reactor displays the highest combustion intensity. The dried gel was burnt in a self-propagating combustion manner until all gels are completely burnt out to form a loose powder. The spontaneous combustion lasted for about 10-20 s. Finally, the as burnt powder was calcined at 500°C for 3 h with a heating rate of 10°C/min to obtain ZnO/CuO nanoparticles. After that, the product was placed in ultrasonic irradiation bath at 25°C for 15 minutes. In this study, three samples were prepared

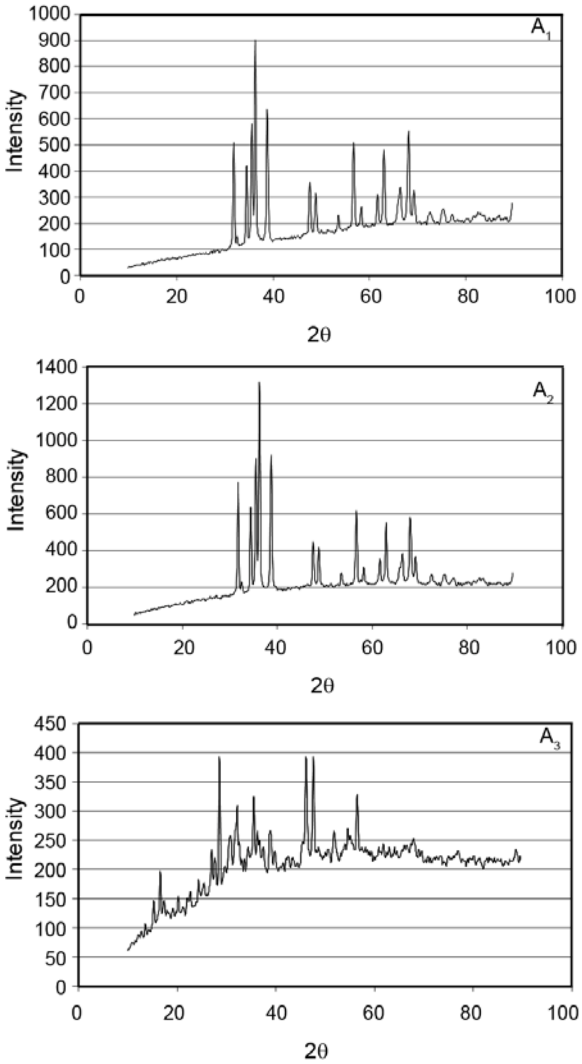

***Figure 1:** XRD patterns of the produced powders (A_1, A_2 and A_3).*

in molar ratio of nitrates to fuels 1: 2 with different fuels glycine, urea and thiourea which were called A_1, A_2 and A_3 respectively.

***Table 1:** Average particles size and crystallite percent for A_1, A_2 and A_3.*

Samples	Average particles size (nm)	Crystallite percent
A_1	47	67
A_2	59	41
A_3	47	72

3. RESULTS AND DISCUSION

The experimental observations showed that gels with the molar ratio 1:2 (nitrates: fuels), exhibit auto catalytic combustion behavior. When the gels were ignited, the combustion process rapidly propagated forward until all the gels were burnt out completely to form loose powders. The effects of ultrasound radiation on chemical reactions are due to the very high temperatures and pressures that develop during the sonochemical cavity collapse by acoustic cavitation.

XRD patterns of the produced powders (A_1, A_2 and A_3) from the fuel-nitrate precursors thermally treated at 500°C for 3 h are shown in Figure 1 and relevant data are collected in Table 1.

The average crystallite size of the powders was measured by X-ray line broadening technique employing the Scherrer equation:

$$D = \frac{0.9\lambda}{B\cos\theta} \tag{1}$$

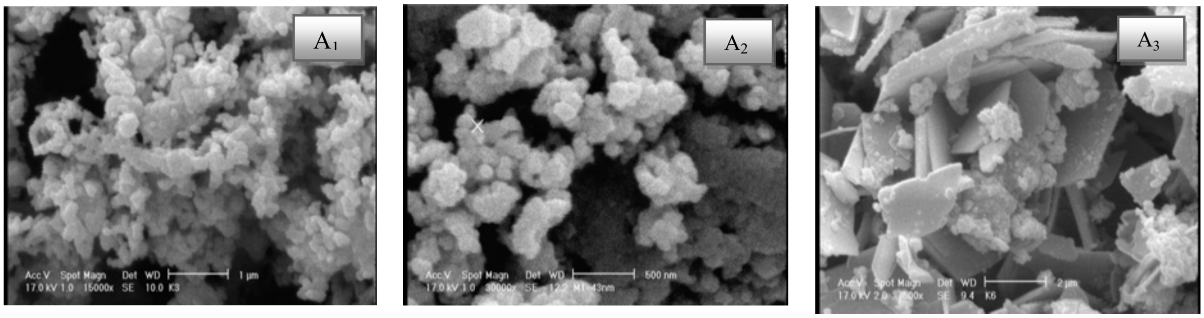

***Figure 2:** SEM images of ZnO/CuO nanoparticles with different fuels (A_1, A_2 and A_3).*

where D is the crystallite size, λ is the wavelength of X-ray radiation (0.15405 nm for Cu Kα), θ is the Bragg angle and β is the full width at half maximum (FWHM) of the most intense diffraction peak.

Composition of phases of all samples is consisting of CuO and ZnO. All of the diffraction peaks are confirmed the formation of CuO phase with monoclinic structure and ZnO phase with hexagonal structure. The structural morphology of the nanoparticles was investigated through SEM. Figure 2 shows the SEM images of ZnO/CuO nanoparticles with different fuels (A_1, A_2 and A_3).

4. CONCLUSIONS

Nanocrystalline ZnO/CuO was synthesized by a simple, general, one step sol-gel auto combustion method with different fuels. An interpretation based on the measurement of the adiabatic flame temperature and the amounts of gas evolved during reaction had been proposed for the nature of combustion. ZnO/CuO was prepared at molar ratio of nitrates to fuels 1:2. The treatment of precursor gel at low temperature removed all free water and most coordinated water as well as hydroxyl groups in gel, decreasing the formation of hydrogen bonds between adjacent particles and thus inhibiting the formation of hard agglomerates. Composition of phases of all samples is consisting of CuO and ZnO.

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