One Step Rapid Synthesis of Nano-Crystalline ZnO by Microwave-Assisted Solution Combustion Method

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ABSTRACT

In this study nano-crystalline ZnO particles were synthesized by microwave-assisted solution combustion method. Zinc nitrate and urea were used as oxidizer and fuel, respectively. The effect of fuel to oxidizer (F/O) ratio on ZnO powder properties was investigated by using different urea/nitrate ratios. X-ray diffractometer, scanning electron microscopy and fourier transform infra-red were used in powders characterization. The results showed that under microwave radiation the pure ZnO phase was formed after combustion reaction with different F/O ratios. The crystallite size was calculated in the range of 28-32 nm using Scherrer's equation. The result has shown that F/O ratio variation influenced the particle morphology from pyramid structure to partially sintered spherical. Prog. Color Colorants Coat. 3(2010), 19-25. © Institute for Color Science and Technology.

1. Introduction

Zinc oxide has a wide band gap, large exciton binding energy and low threshold power for optical pumping, therefore, it is a very fast and efficient phosphor [1-4]. Zinc oxide is also a wide gap semiconductor material that has been studied extensively [5]. It has high exiting bonding energy (60 meV), which can result in less trapping of carriers and higher luminescence efficiencies [6, 7]. In recent years, nano materials have been extensively studied because of their interesting physical and chemical properties compared to their counterpart bulk materials [8]. Various methods have been employed by several workers to synthesize ZnO nano/micro crystals such as solvothermal, hydrothermal, self assembly and sol-gel [9-13].

Solution combustion synthesis is an exothermic redox reaction between metal nitrates (oxidizer agents) and an appropriate fuel (a reducing agent) and had been successfully used to synthesize nano-crystalline metal oxides [14]. This method is convenient in process, simple in experimental device and time saving. Solution combustion synthesis process involves an aqueous mixture containing suitable metal salts which are the precursors of the final desired oxide and a proper sacrificial organic fuel which acts as reagent reducer. Generally, hydrate nitrates are preferred to other salts since their good water solubility allowing them to obtain a highly homogeneous solution.

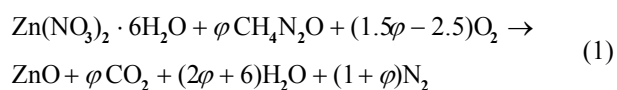*Corresponding author: rasouli@icrc.ac.ir

Recently a novel technique called 'microwave-assisted combustion synthesis' was used to synthesize oxide materials. Microwave heating can be more advantageous than conventional heating because of short processing time and volumetric heating [15]. The microwave heating process is fundamentally different from other heating processes because heat is generated internally within the material instead of originating from external heating sources.

In a combustion method the fuel to oxidizer (F/O) ratio can play a critical role either in influencing reaction or at flame temperature. In fact, the flame temperature of the reaction is controlled by varying the fuel to oxidizer ratio.

In this study the microwave irritation was used for preparation of nano-crystalline ZnO sample. This process involves a self-sustained reaction in homogeneous solution of zinc nitrates as an oxidizer and urea as fuel, the effect of the fuel to oxidizer ratio has been investigated. X-ray diffractometer, scanning electron microscopy and Fourier transform infra-red were used in powders characterization.

2. Experimental

All the raw materials in this research were analytical grade. $Zn(NO_3)_2.6H_2O$ (Merck, Germany), as an oxidizer and urea (Merck, Germany) as a fuel were used. Stoichiometric equation of ZnO synthesis can be presented as below:

$$Zn(NO_3)_2 \cdot 6H_2O + \varphi CH_4N_2O + (1.5\varphi - 2.5)O_2 \rightarrow$$
$$ZnO + \varphi CO_2 + (2\varphi + 6)H_2O + (1 + \varphi)N_2 \qquad (1)$$

Where the value $\varphi=0.93$ represents equivalent ratio (the ratio at which the oxygen content of oxidizer can be completely reacted to oxidize or consume fuel completely).

Fuel to oxidizer (F/O) ratio can be dictated as rich ($\varphi>1$) and fuel lean ($\varphi<1$). Four F/O ratios; 0.25φ (high fuel lean), 0.75φ (fuel lean), 1φ (stoichiometric) and 1.2φ (fuel rich) were selected to investigate the effect of the F/O ratio on the ZnO formation.

Metal nitrate and urea were added to deionized water in a beaker. The obtained solution was heated on hotplate to 80-90 $\overset{\circ}{C}$ until the excess water was removed and a highly viscous precursor gel was obtained. The beaker vessel was transferred into microwave oven (Samsung, Korea, 900 W, 2.45 GHz frequency) to complete the combustion reaction. It is noteworthy to mention that all experiments were performed in maximum power of microwave for 50 seconds.

A D-500 (Siemens, Karlsruhe, Germany) diffracto-meter was used for XRD analysis. Morphology analysis was performed using scanning electron microscopy (SEM, LEO 1455VP Oxford, UK). The FT-IR spectra of the gel and dried powder were given by FT-IR (Spectrum one, FT-IR spectrometer, Perkin-Elmer).

3. Results and discussion

The precursor solutions containing nitrate–urea transformed into viscous liquids upon heating. Then by spontaneously igniting the viscous liquid changed to a foamy and voluminous mass. The exothermic heat generated in this combustion process is governed by a thermally induced redox reaction involving urea and nitrate in the precursor, where the nitrate anions act as oxidizer and the urea act as reducing agent.

Figure 1 presents the effect of the F/O ratio on the as-synthesized ZnO powders by the XRD patterns. Results show that the main phase characterized in different samples was hexagonal ZnO at peaks 31.7, 34.4, 36.2, 47.5, 56.6, 62.9 and 67.9 (2-theta degree) from which are consistent with the Joint Committee on Powder Diffraction Standards (JCPDS) 5-664. As the obtained patterns show the formation of crystallite ZnO phase is insensitive to F/O ratio variation. Even high fuel lean combustion has led directly to the appropriate ZnO phase. No attributeable peak to other phases was observed. Therefore, the synthesis of the single phase zinc oxide can be concluded. For the stoichiometric and fuel rich samples the formation of huge amount of heat which are generated by urea-nitrate reaction can lead to the single phase ZnO. For the fuel lean samples, formation of pure ZnO can be due to the growth mechanism [16-17]. In fact, the lowest combustion energy in fuel lean samples can be correlated to interface growth, comes from a mismatch of atomic positions on the interface.

The apparent crystallite size using Scherrer's equation can be calculated as follows:

$$d = \frac{k\lambda}{\beta \cos\theta} \qquad (2)$$

where k is the shape factor (close to unity), λ is the x-ray wavelength (typically 1.54 Å), β is the line broadening at half the maximum intensity (FWHM) (in radians), and θ is the Bragg's angle.
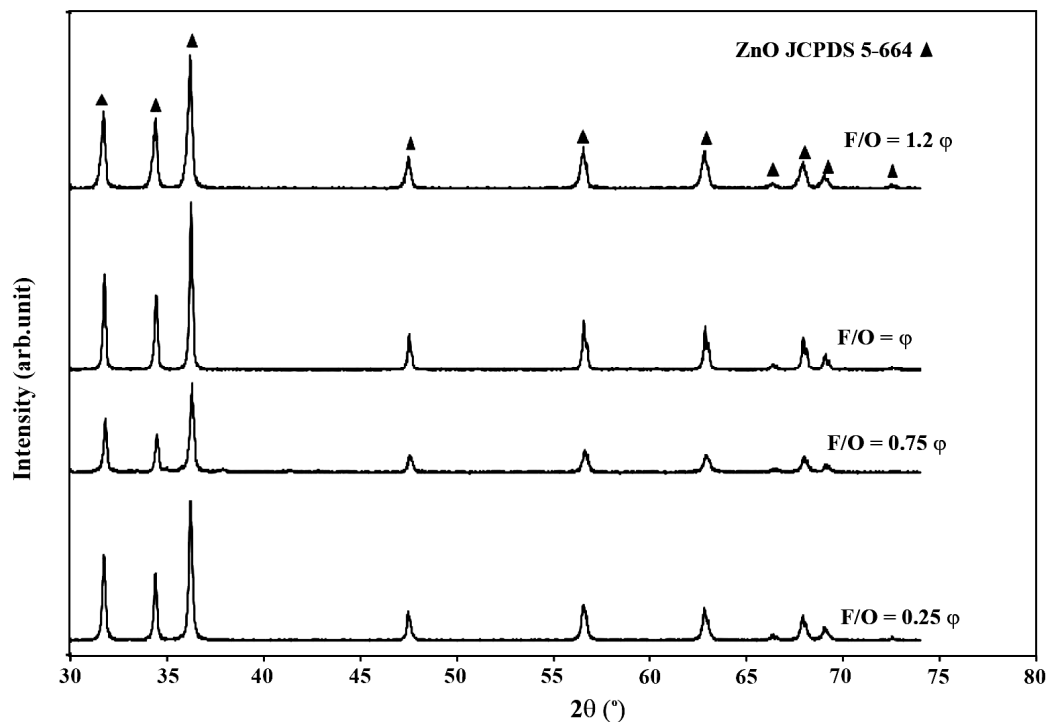
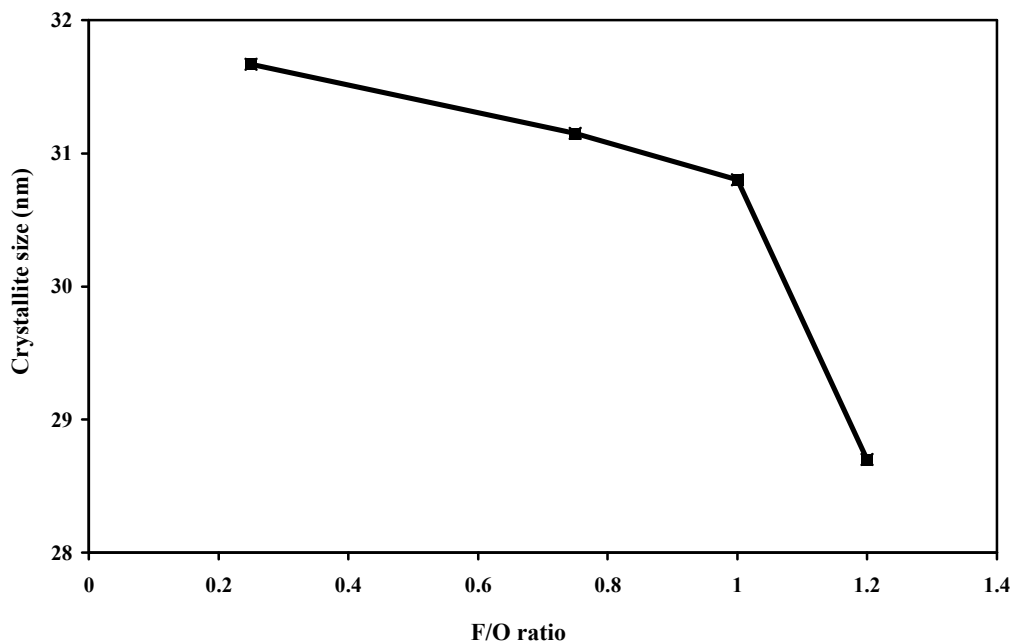**Figure 1:** XRD pattern of the as-prepared ZnO by different F/O ratios.

Figure 2: The trend on crystallite size of the as-prepared ZnO by different F/O ratios.

The average crystallite size obtained using equation 2, is shown in Figure 2. Crystallite size is a measure of the size of coherently diffracting domains and is not generally the same as particle size due to polycrystalline aggregates. From Figure 2 a systematic decrease in average crystallite size is observed when F/O ratio increases from high fuel lean to fuel rich. Sharma *et al.* showed that fuel lean synthesis condition can lead to large crystallite sizes which can be related to increase of crystal growth rate by interface growth [18].
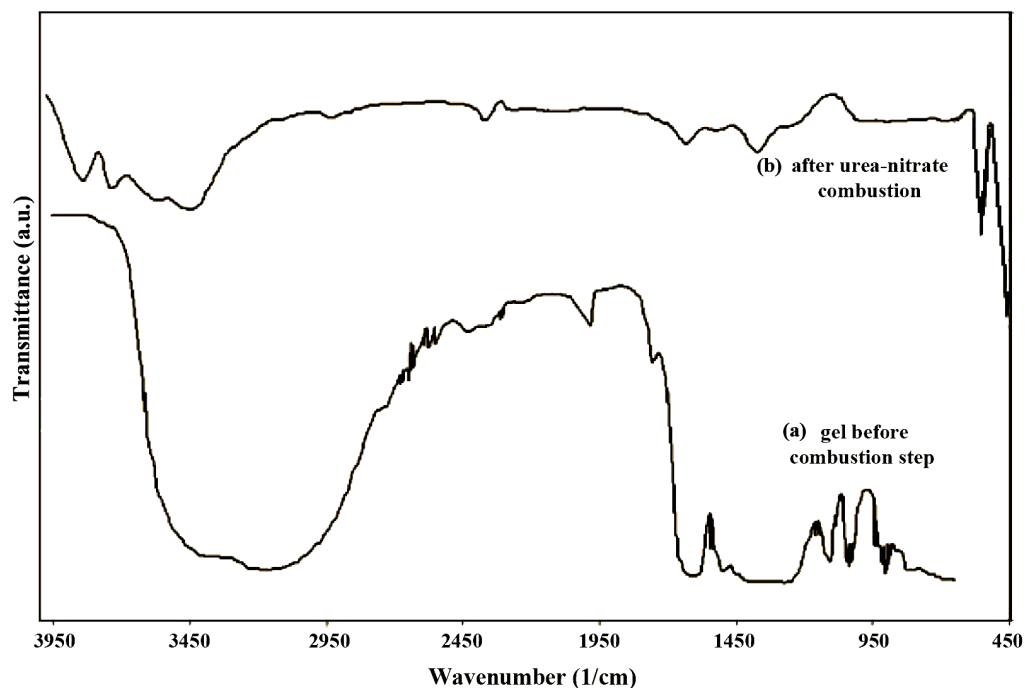
Figure 3: FT-IR spectra of the gel and the as-synthesized ZnO powder with stoichiometric F/O ratio.

Fourier transform infra-red (FT-IR) in KBr matrix was used for investigation of the chemical and structural changes that occur during combustion. Figures 3 (a, b) show the FT-IR spectra of the prepared gel and as-synthesized powder (stoichiometric F/O ratio), respectively, in the range of 450-4000 cm^{-1}. The gel (Figure. 3(a)) showed the characteristic bands around 3400, 3160, 1600 and 1380 cm^{-1} corresponding to the O-H group, N-H, carboxyl group and NO_3^- ion, respectively. In Figure 3(b) a strong band at 540 cm^{-1} is observed which can be attributed to the asymmetric stretching mode of the tetrahedral ZnO_4 group present in the Wurtzite ZnO structure. This is consistent with the results reported by others [19, 20].

Morphological and structural properties of the samples were investigated using scanning electron microscopy The results in Figures 4(a-d) show that the high fuel lean (F/O=0.25φ) sample yield the hexagonal pyramids which were regrouped in the form of the flower like clusters. As F/O ratio increases to moderate fuel lean the hexagonal pyramid form has developed as quasi-platelet structures. Above F/O=0.75φ the quasi-spherulitic polycrystalline aggregates were formed.

Previous works have demonstrated that the overall growth process under the influence of changing F/O contents can be interpreted in terms of 2-D nucleation growth model [16, 17]. They have showed that the important factor for changes in the morphology of ZnO crystal is a critical value for 2-D nucleation growth model. Consequently, various growth forms can be obtained depending on whether the driving force is smaller or longer than this critical value. In Figure 4(a) for the low value of F/O the boundary plane of ZnO takes a non-crystallographic irregular form thereby attaining cyclic twin-like structures.

This can be correlated to low interface energy which have led to an inter-growth connection between two individuals of the same crystal species, hence increasing the probability for twining [18]. For F/O=0.75 φ, semi-spherulitic morphology evolves, while few hexagonal pyramids are also visible (Figure 4(b)). When F/O ratio increases to stoichiometric amount and more, the crystallites scatter in all directions probably due to the evolution of large amount of heat generated by fuel. On the other hand, the sinterability tendency has increased to form the partially sintered agglomerates as show in Figures 4(c) and 4(d). This tendency is due to an increase in surface area and surface energy, which is a driving force for sintering during combustion process [21].

(a)

1μm EHT = 10.00 kV WD = 5 mm Mag = 10.00 K X Signal A = SE1
Institute for Colorants, Paints & Coatings (ICPC)

(b)

1μm EHT = 10.00 kV WD = 5 mm Mag = 10.00 K X Signal A = SE1
Institute for Colorants, Paints & Coatings (ICPC)

(c)

1μm EHT = 10.00 kV WD = 5 mm Mag = 10.00 K X Signal A = SE1
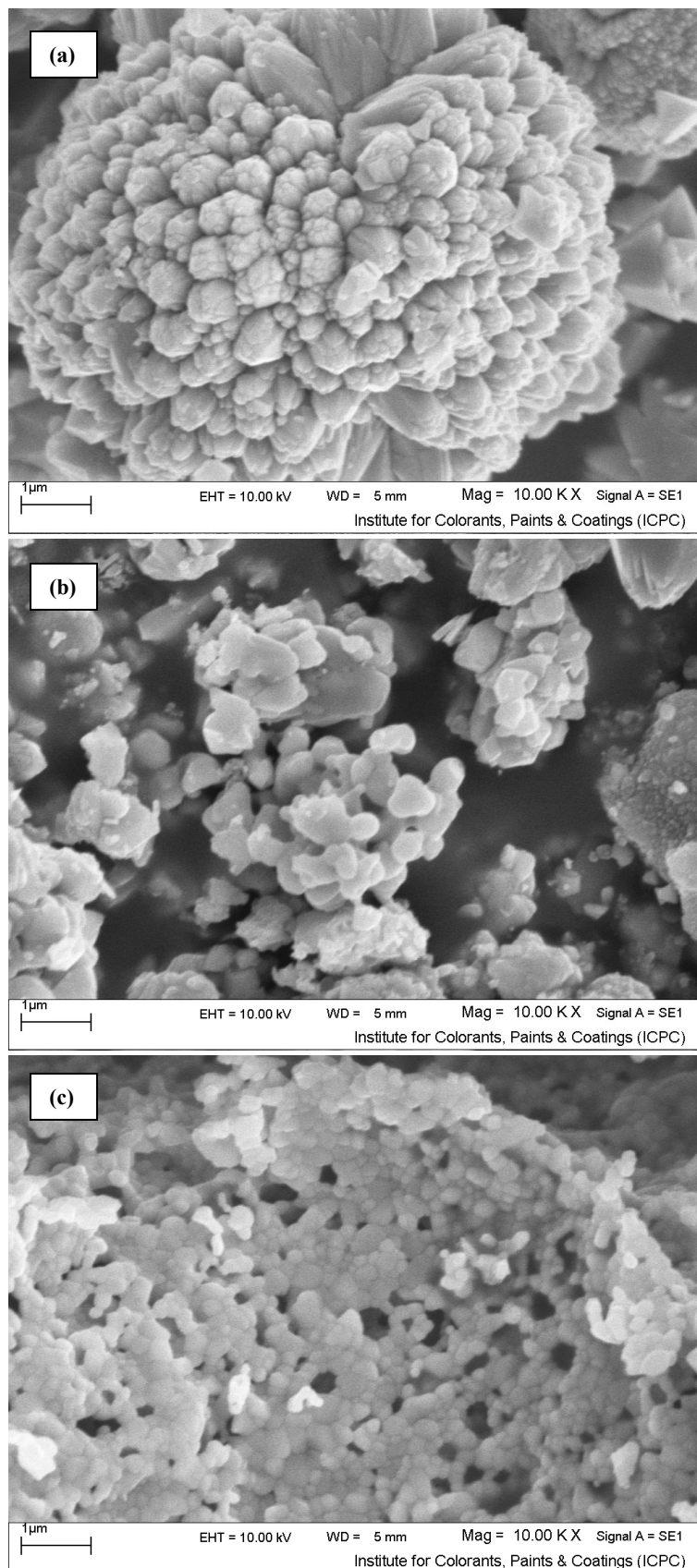Institute for Colorants, Paints & Coatings (ICPC)

Figure 4: SEM images of ZnO powders prepared by different F/O ratios; a) F/O=0.25φ, b) 0.75φ, c) φ and d) 1.2φ.
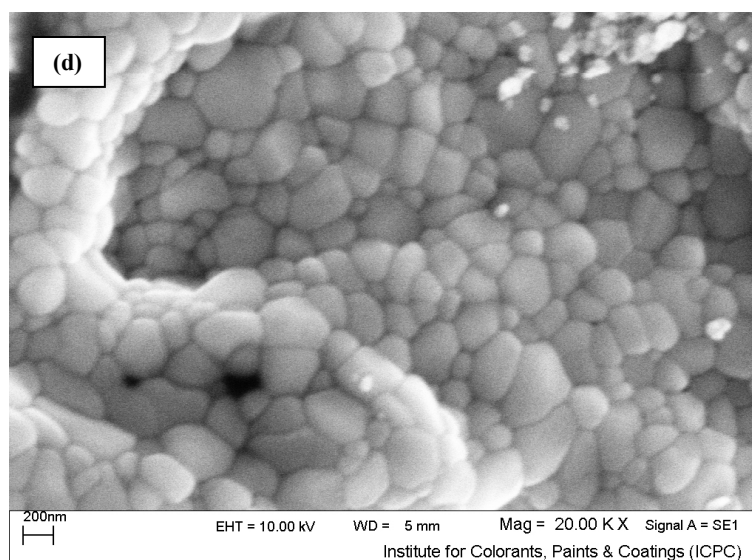
Figure 4: continued.

From the XRD patterns the crystallite size was calculated in the range of 28-32 nm whereas the SEM images show particles with mean particle size between 0.2 to 1 μm. In fact, the Scherrer formula provides a lower bound on the particle size because of the contributions of a variety of factors to the width of a diffraction peak besides particle size; such as inhomogeneous strain and instrumental effects. If these contributions to the width are non-zero, then the particle size can be larger than that predicted by the Scherrer formula [22].

4. Conclusions

Microwave-assisted solution combustion method was used for preparation of nano-crystalline ZnO powder.

The effects of fuel to oxidizer ratio on powder properties have been investigated at different urea/nitrate ratios. X-ray diffractometer results demonstrated that the formation of crystallite ZnO phase is insensitive to F/O variation. No calcinations step was needed to obtain pure ZnO phase for all F/O ratio. The crystallite size was calculated using the Sherer's formula and was in the range of 28-32 nm. The SEM micrographs have revealed that the morphology of the particles have been influenced by F/O variations. It can change from pyramid structure to partially sintered spherical form from high fuel lean to fuel rich powder.

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