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Structural and Optical Properties of ZnO Nano Particles Synthesised by Mixture of Fuel Approach in Solution Chemical Combustion

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Abstract. Zinc oxide has been used for many applications, for example optoelectronic devices, ceramics, catalysts, pigments, varistors and many other important applications. In this study, ZnO nanoparticles were synthesized by mixture of fuel approach in solution chemical combustion method. Mixtures of Urea and Zinc salts were mixed at room temperature resulting in spontaneous ignition because these are hypergolic materials resulting in production of ZnO nanopowder. The crystal structure and size of the synthesized powder were determined by X- ray diffractometer (XRD), which revealed that the synthesized ZnO nanopowder has the pure wurtzite structure having average crystallite size of 30nm. Morphological studies were carried out by scanning electron microscopy (SEM), Energy Dispersive X-ray analysis (EDAX) was carried out by Scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDAX), Optical studies were examined by FT-IR and UV-Visible absorption spectrum and the particle size was estimated from Nanoparticle size analyzer.

Introduction

Due to its excellent physical and chemical properties they are widely used in thermoelectric materials, field emission displays, photo catalysis, super hydrophobic coatings, information technology, bio- technology and environmental applications as future technologies [1-5]. Nanocrystalline ZnO with different particle morphologies and sizes were synthesised by several approaches, which includes thermal decomposition [6], chemical vapour deposition [7–10], sol–gel method [11], wet chemical synthesis [12], mechano-chemical [13], electro deposition [14], gas-phase reaction [15], hydrothermal synthesis [16]. It is essential to improve the synthesis techniques of ZnO nano-particles, since the generally used vapour methods as sol–gel method and CVD [17] are time consuming and expensive. As an alternative to these, Park et al. proposed and reported a novel SCM. They obtained ZnO nano-particles within 30 nm size, using different fuel and oxidizer combinations such as $[Zn(OH)_2]$ and glycine, $Zn(NO_3)_2 6H_2O$ and glycine dissolved in concentrated HNO_3 as starting materials. The Solid-state synthesis is standard method for synthesis of oxide powders, but having difficulties for producing fine particle distribution due to agglomeration problems at high temperatures. As compared to other oxide preparation techniques solution combustion method is a moderately low temperature synthesis route and produce more uniform particle distribution. This method, in recent times received great attention because of its simple and rapid preparation process, which results in homogeneous, fine and agglomeration free crystalline powders.

Material and Method:

ZnO nano-particles are synthesized by an amount of 20 g per batch according to Table 1 in this combustion method we are using analytic grade zinc nitrate $\{Zn(NO_3)_2 6H_2O\}$ as oxidizing agent and Urea $\{CO(NH_2)_2\}$ and ammonium acetate $(C_2H_7NO_2)$ are like fuel.

Table 1. Raw material characteristics

Raw materials	Formulation	Mol. weight(g/mol)	Purification	Physical state	Manufacturer
Ninc Nitrate	$Zn(NO_3)_2.6H_2O$	297.5114	99.5	Solid	Merck
Urea	$CO(NH_2)_2$	60.05526	99.5	Solid	Merck
Ammonium acetate	$C_2H_7NO_2$	77.0825	96	Solid	SDFIL

As per given table 2, zinc nitrate, Urea and ammonium acetate were mixed in 50 ml of distilled water in a glass beaker and heated on a hot plate ~100^0 C. As the distilled water evaporates, the ions of nitrate (NO_3-) react with the fuel, ignites spontaneously and intense heat is generated resulting in high temperature and high pressure. The spontaneous pressure led to deflagration resulting in the formation of ZnO nano-particles. The ZnO nano powder obtained was further characterized.

The fuel to oxidizer ratios were calculated by using this equation [18]

$$\varphi = \frac{n_1\{(1*4_c)+(1*-2_o)+(2*O_N)+(4*1_H)\}+n_2\{(2*4_C)+(7*1_H)+(1*O_N)+(2*-2_o)\}}{a\{(1*2_{Zn})+(2*0_N)+(6*-2_o)\}} \tag{1}$$

Where n_1 is the mole of fuel of urea and n_2 is the mole of fuel of ammonium acetate and a is mole of nitrate.

Table2. Preparation for 20gm sample of ZnO at at ψ=1

Sample Code	Urea%	ammonium acetate%	Urea weight (g)	Ammonium acetate weight (g)
U100A0	100	0	6.7285	0
U80A20	80	20	5.2333	1.0468
U60A40	60	40	4.0371	2.1425
U40A60	40	60	2.6914	2.8264
U20A80	20	80	1.3457	3.7685
U00A100	0	100	0	4.7107

Room temperature powder X-Ray diffraction (XRD) was carried out on the nono powder synthesized by SCM for crystallite size estimation and phase identification using X-R diffractometer (model Bruker D-8 Advance) with nickel filtered Cukα as radiation source (λ =1.54056A0 , 40 kV, Scan rate 10 /min, 200 ≤ 2θ ≤ 800). The shape and grain size of the synthesized ZnO powder and sintered specimen were evaluated using SEM (Hitachi, Model- S-3700N, Germany). Energy dispersive X-ray spectroscopy (EDAX) was carried out by Scanning electron microscopy (SEM) coupled with an energy dispersive X-ray spectroscopy (EDAX) unit. To determine the optical properties like FT-IR and energy band gap carried out by Shimadzu(Germany). The particle size measured by Nano particle size analyzer (SZ-100 Nanoparticle, Horiba, Germany).

Results and Discussion

X-Ray diffraction (XRD):

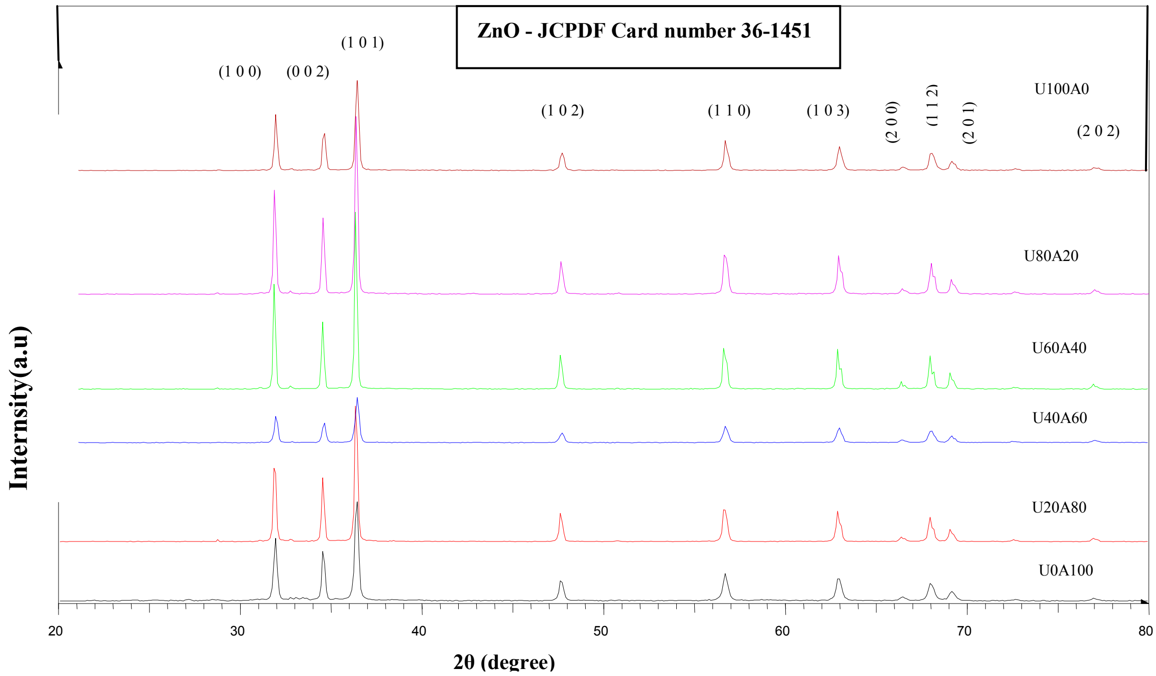


Fig 1. XRD diffraction patterns of ZnO powders synthesized using different fuel mixture ratios (U0A100, U20A80, U40A60, U60A40, U80A20, U100A0)

The XRD pattern of the ZnO nano-particles was recorded in diffraction angle range 20-80^0 and shown in Fig.1. The peaks are sharp which indicates their crystalline nature. The diffraction peaks are in conformity with the reported data and confirm ZnO with hexagonal phase. The spectrum shows an intense peak along (101) plane with other peaks of ZnO phase. No other peaks for any other impurities were observed. This confirms that the product obtained is phase pure. The mean values a= 3. 249 A^0, c=5. 206 A^0. The estimated c/a ratio of 1.60 indicated a good match with the literature reported value of 1.633 for an ideally close packed hexagonal structure. It is seen that crystallites grow is much faster in the (101) plane compared with the other planes. From the prominent diffraction peaks from crystal planes such as (1 0 0), (0 0 2) and (1 0 1) we can say that ZnO having hexagonal crystal system with Wurzite structure.

The crystallite size was estimated from Debey- Scherr's formula and was found to be 30nm. Hence, the crystallite dimensions have confirmed that the particles are of nano-size and the average crystalline size increases with urea concentration, from 26 nm to 40 nm. In fact, auto-combustion of Urea releases more energy than ammonium acetate, which can lead to rapid crystal growth. we calculated crystallite size by using Full width at hall maximum(FWHM) through Debye-Scherer formula.

$$t = \frac{0.96\lambda}{\beta Cos\theta} \qquad (2)$$

Where λ is the wavelength of incident X-ray, β is half width of diffracted peak and is diffracted angle and 't' is the size of the crystallite.

Fig1. shows the XRD patterns of synthesized powders obtained by different equivalence ratios. It can be observed that very intense single hexagonal ZnO phase with P63mc structure (JCPDS 36-1451) has been obtained. According to XRD patterns, the peak intensity of ZnO phase decreases with Urea content. This observation can be attributed to thermal decomposition of urea even at moderately low temperatures as compared to ammonium acetate.

Scanning Electron Microscopy (SEM) :

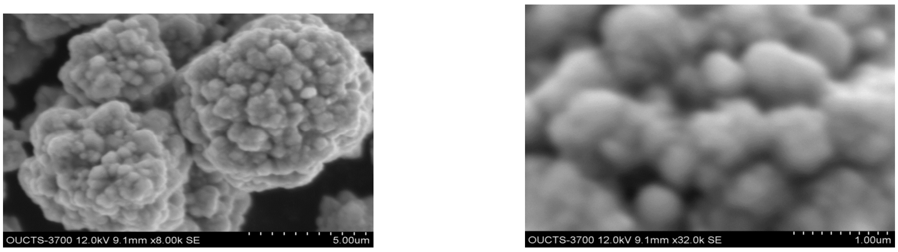
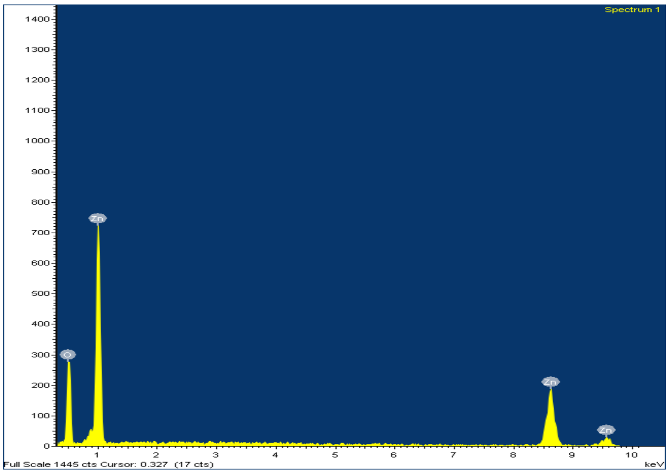


Fig 2. SEM images of ZnO nanopowder a) before calcinations 2 b) after calcinations

The surface morphology of ZnO nanopowder has been investigated by SEM and results are shown in Fig 2(a) and Fig 2(b) with different magnifications. The SEM shows that, the clusters of nano-particles like cauliflower. It was observed that nano structures resulting from the combustion reaction has porous morphology forming fuzzy network of nano-crystalline ZnO, and this may be due to the rapid release of gaseous by-products during the combustion process. At a higher magnification (shown in Fig 2(b) at 9.1mm.x32.ok SE), the agglomerated ZnO nano-particles consisting of tiny nano-particles of 30nm average size, and this agrees with XRD results.



Element	Weight%	Atomic%
O K	31.19	64.94
Zn K	68.81	35.06
Totals	100	100

Fig 3. EDAX spectrum of ZnO nanopowder

EDAX spectrum of ZnO nano-particles Energy Dispersive X-ray analysis (EDAX) was carried out by SEM with an EDAX unit. Fig 3. Shows the chemical compositional analysis of ZnO nano-particles is nearly in stoichimetriy.

Particle Size Analyser

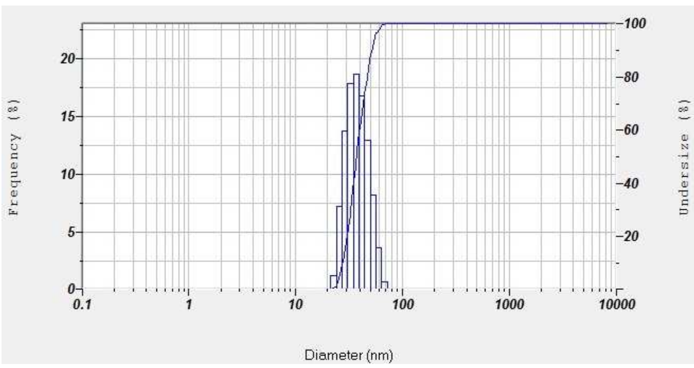


Fig 4. Particle size analyzer of ZnO solid solution

Particle Size Analyser The particle size of nano powders is done by particle size analyzer (Nano particle size analyzer SZ100). Fig 4 shows the distribution of particle size of ZnO nano powders. The size is estimated as 37.5nm from the graph. Fig 4. Particle size analyzer of ZnO solid solution.
Fourier transform infrared spectroscopy (FTIR). The FTIR spectrum of ZnO is shown in Figure 5. There is a broad band with very low intensity at 3493 cm−1 corresponding to the vibration mode of water OH group indicating the presence of small amount of water adsorbed on the ZnO nanocrystal surface. The band at 1628 cm−1 is due to the OH bending of water. A strong band at 500 cm−1 is attributed to the Zn-O stretching band.

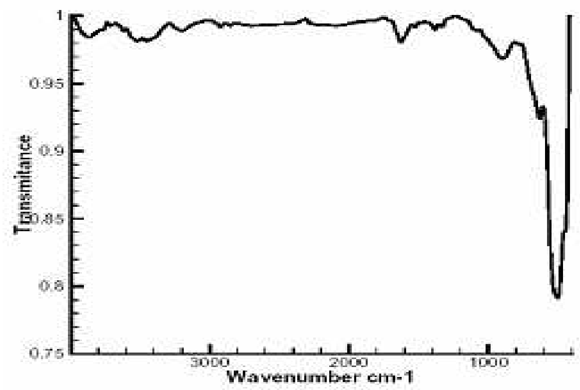


Fig 5: FT-IR spectrum of the ZnO nanopowder

UV-Visible obsorption spectrum

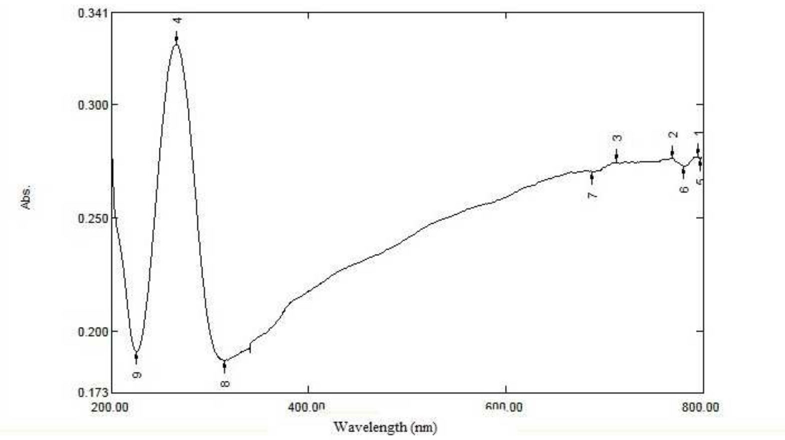


Fig 6:UV absorption spectrum for ZnO nanoparticles

Optical absorption spectrum of ZnO nano-particles prepared under aqueous conditions has been carried out .The UV visible spectra of nano-particles synthesized in aqueous media showed excitonic absorption peak at 292 nm which implies the lower particle size ZnO. The bandgap calculated from the UV cut-off is found to be 4.2 eV ZnO nano-particle. These band gap values blue shifted relative to the bulk zinc oxide of 3.37 eV

Conclusions

Conclusions We have successfully synthesized ZnO nanopowder via mixture of fuel approach in solution chemical combustion in the presence of different ratios of urea and ammonium acetate. It is observed that from the XRD analysis, the obtained crystallite size varies from 26 nm to 40 nm with urea content. Structural properties were examined by SEM, We observed the particles size in the range of 69.2nm to 95.7nm from SEM. The size is estimated as 37.5nm from Particle size analyzer. From UV absorption spectrum the energy bang gap was calculated as 4.2eV.

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