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Chapter

Structural and Luminescence Properties of ZnO Nanoparticles Synthesized by Mixture of Fuel Approach in Solution Combustion Method

Trilok K. Pathak and H.C. Swart

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 combustion method. Mixtures of urea, glycine and citric acid were mixed at room temperature with Zinc nitrates as fuels resulting in spontaneous ignition 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 crystallite size 26–40 nm. Optical studies of nanomaterial were examined by FTIR and UV-Visible absorption spectrum. The luminescence studies also investigated in the visible region 360–800 nm with excitation 325 nm laser. These nanomaterials may be used in solid-state lightening devices.

Keywords: ZnO NPs, X-ray diffraction, bandgap, luminescence

1. Introduction

Nanoscale ZnO powder has attracted great attention due to its excellent physical and chemical properties they are widely used in nanoscale devices such as nanogenerators [1], ultraviolet photodetectors [2], gas sensors [3], solar cells [4], field emission displays [5], electrical and optical devices [6, 7], photocatalysis [8, 9], medical [10] and environmental applications [11]. These nanomaterials have novel electronic, structural and thermal properties which have potential interest in basic and applied research. ZnO is a wide bandgap ($E_g = 3.37 \text{ eV}$) semiconductor some basic properties listed in **Table 1** [12].

Semiconductor nanocrystals or nanoparticles may have superior optical and antibacterial properties than bulk crystals due to quantum confinement effects and the large surface to volume ratio. The synthesis and properties of ZnO nanostructure such as nanowires [13], nanotubes [14], nanorods [15] and nanoparticles [16] have been reported. The nanoparticles have great significance

Property	Measured value			
Crystal structure	Hexagonal, wurtzite			
Molecular weight	Zn:65.38, O:16 and ZnO:81.38			
Lattice constant	a = 3.246 Å, c = 5.207 Å			
Density	5.67 g/cm ³ or 4.21×10^{19} ZnO molecules/mm ³			
Cohesive energy	E_{coh} = 1.89 eV			
Melting point	T _m = 2250 K			
Heat of fusion	4470 cal/mole			
Thermal conductivity	25 W/mK at 20°C			
Bandgap at RT	3.37 eV			
Refractive index	2.008			
Electron and hole effective mass	$m_e^* = 0.28, m_h^* = 0.59$			
Dielectric constant	$\varepsilon_{\rm o}$ = 8.75, ε_{∞} = 3.75			
Exciton binding energy	E _b = 60 meV			

Table 1.

Basic properties of ZnO [12].

as three dimensional confined systems bridging the gap between bulk materials and molecular compounds. A variety of techniques have been employed for the synthesis of ZnO nanoparticles such as sol-gel synthesis [17], the hydrothermal method [18], the solution combustion method [19] and solid state reactions [20]. Among these, the combustion technique is noteworthy as a fast method to synthesize nanocrystalline materials in as-synthesized form with large surface area without the further need of heat treatment. Nanocrystalline oxides are produced through the redox reaction between an oxidizer containing the metal precursor and anorganic fuel at a moderately low initiation temperature of around 350–600°C within a few minutes [21]. The main advantage of this method is that the high temperature of the exothermic reaction assures high purity and well crystallized powder. In combustion synthesis, the type of fuel and the fuel to oxidizer ratio (F/O) play critical roles in influencing the nature of combustion reaction and the flame temperature. Selection of a suitable fuel and the F/O ratio influences the combustion process and the properties of the product. The F/O ratio of unity is known to produce highest exothermicity with complete combustion. An arbitrary ratio of fuel to oxidizer (F/O—1) sometimes leads to formation of intermediate phases raw materials in the final product [22]. In this regard, various fuels have been tested to synthesize nanocrystalline ZnO. Sousa et al. [23] used metallic nitrate and urea to synthesis ZnO nanopowder with a size about 400–500 nm for various applications. Hwang et al. [24] worked on ZnO nanopowder synthesized by a combustion method with glycine as a fuel and metal nitrate mixed in a stoichiometric ratio.

In the present work, we report the synthesis of nanocrystalline ZnO powders by combustion technique using new, eco-friendly and cost-effective organic fuels as urea, glycine and citric acid. The effect of fuel in different ratio of two fuels combinations on the properties of the final product has been studied. The structure and luminescence properties of ZnO nanoparticles are also being studied in this work.

2. Experimental

2.1 Preparation of ZnO nanoparticles

Synthesis of ZnO NPs the different materials were used such as zinc nitrate, urea, glycine, and citric acid. **Table 2** shows the characteristic of the raw materials. The chemical reaction used in synthesis of ZnO powder are given in **Table 3**.

The zinc nitrate hexahydrate and fuel were dissolved in 5 ml of double distilled water and stirred thoroughly to obtain a transparent solution, which was placed inside a preheated muffle furnace at 600°C to initiate the combustion process. Within a short time the mixture ignited with a flame and the rapid evolution of enormous amounts of gases produced a voluminous foamy product (ash). This was ground using an agate pestle and mortar to produce the final powder, without any additional heat treatment. The fuels used in this synthesis have different combination of fuels and shown in Table 4.

The synthesis process of ZnO NPs is illustrated in Figure 1.

Raw materials	Formulation	Molecular weight (g/mol)	Manufacturer
Zinc nitrate	Zn(NO ₃) ₂ .6H ₂ O	297.49	Sigma Aldrich
Urea	NH ₂ CONH ₂	60.06	Sigma Aldrich
Glycine	NH ₂ .CH ₂ .COOH	75.06	Sigma Aldrich
Citric acid	C ₆ H ₈ O ₇ .H ₂ O	210.14	Sigma Aldrich

Table 2.

Characteristics of raw material.

Fuel	Combustion reaction
Urea	$3\text{Zn}(\text{NO}_3)_2 + 5\text{CO}(\text{NH}_2)_2 \rightarrow 3\text{ZnO} + 5\text{CO}_2 + 10\text{H}_2\text{O} + 8\text{N}_2$
Glycine	$Zn(NO_3)_2 + 2CH_2(NH_2)(COOH) + 2O_2 \rightarrow ZnO + 4CO_2 + 5H_2O + 2N_2$
Citric acid	$Zn(NO_3)_2 + C_3H_5O(COOH)_3 + 2O_2 \rightarrow ZnO + 6CO_2 + 4H_2O + N_2$

Table 3.

Table 3.					
Chemical reaction	n in combustion syn	thesis of ZnO using	g different fuels [25].		

Sample name		Fuels contents (%)			
	Urea	Glycine	Citric acid		
UC1	75		25		
UC2	50	_	50		
UC3	25	_	75		
UG1	75	25	_		
UG2	50	50	_		
UG3	25	75	_		

Table 4.

Sample name with respect to used fuels in different combination of fuels.



Figure 1. *Systematic diagram of ZnO synthesized by the combustion method.*

2.2 Characterization method

The prepared ZnO-NPs were characterized by X-ray diffraction (XRD) using advanced Bruker D8 diffractometer with Cu K_{α} radiation was carried out to check up the crystal structure. The bond characteristics studies using FTIR-8400S. The Optical transmittance spectra were collected using a UV-Vis-IR spectrophotometer (Perkin Elmer, lambda 950). The photoluminescence (PL) data was recorded using 325 nm He-Cd laser system.

3. Results and discussion

3.1 X-ray diffraction pattern

The XRD patterns of the ZnO powders synthesized using mixed fuels is depicted in **Figure 2a** and **b** and are typical of ZnO powders having the hexagonal wurtzite structure (JCPDS 01-036-1451). This indicates that the ZnO was formed directly by the self-propagating high temperature exothermic combustion reaction initiated at moderate temperature. The crystallize size varied from 30 to 70 nm with different fuels contents. UC2 and UG3 show the wurtzite ZnO structure without any impurity peak in the XRD pattern. All three fuels resulted in nanocrystalline powders, but the crystallite size varied significantly with the type of fuel. The effect of the type of fuel, and the F/O ratio in the case of urea, on the properties of the final product also has been studied in our previous research article [25].

3.2 Fourier transform infrared spectroscopy (FTIR)

The FTIR spectrum of ZnO is shown in **Figure 3**. The broad band with very low intensity at 3466 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 during synthesis. A strong band at 482–455 cm⁻¹ is attributed to the Zn-O stretching band. The bond related to C=O and other are shown in **Table 5**.

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3.3 UV-Visible absorption spectrum

The UV-Vis reflectance spectra of the ZnO nanomaterial synthesized using different fuels are shown in the inset of **Figure 4a** and **b**, and the corresponding absorbance spectra are calculated using the Kubelka-Munk function [26]:

$$K = \frac{(1-R)^2}{2R}$$
(1)

where K is the reflectance transformed according to Kubelka-Munk, h is Planck constant, *v* is the light frequency, and R is reflectance (%). The relevant increase in the absorption at wavelengths less than 400 nm can be assigned to the optical band-gap absorption of ZnO due to changes in their morphologies, particle size and surface microstructures or the quantum confinement effect [27, 28]. The absorption edges are change with fuels as taken to synthesis ZnO. ZnO has a direct transition



Figure 2. *XRD pattern: (a) ZnO with mixed fuel (urea + citric acid) and (b) ZnO with mixed fuel (urea + glycine).*





Functional group			Waven	umber (cm ⁻¹)		
	ZC1	ZC2	ZC3	ZG1	ZG2	ZG3
Stretching vibration of Zn-O	482	482–555	482	482	482–547	482–547
Bending mode of carbonate	823–910		863	839	815	831
Stretching vibration of C-O	1031		1025	1001	1098	
C-H in plane bending vibration	1163	_	_	_	_	
Bending vibration of –CH ₂	1374		1349	1382	1382	1374
C=O band	1536	1582	1585	1544	1625	1617
Carboxyl group	1925			1917	1917	1917
Existence of CO ₂	2428		_	2201–2355	2363	_
O-H stretching of water	3466	3441	3473	3466	3466	3457

Table 5.

Chemical boding characteristics of synthesized ZnO with mixed fuels.



Absorbance spectra with reflectance insect: (a) ZnO with mixed fuel (urea + citric acid) and (b) ZnO with mixed fuel (urea + glycine).

and the corresponding bandgaps for different mixed fuels shown in **Figure 5a** and **b** respectively are calculated from a Tauc plot of $(\alpha h\nu)^2$ versus the photon energy $(h\nu)$. These bandgap values blue shifted little 3.08 to 3.2 eV relative to the zinc oxide nanomaterial.

3.4 Photoluminescence study

The photoluminescence properties of semiconductor materials undergo change when their size gets down to nanometer scale known as the quantum size effects. The photoluminescence originates from the recombination of surface states. **Figure 6a** and **b** shows the photoluminescence spectra of ZnO powder synthesis by different fuels with excitation wavelength of 325 nm at room temperature. The spectra exhibits two emission peaks, One is located at around 384 nm (UV region)

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Figure 5. Energy bandgap: (a) ZnO with mixed fuel (urea + citric acid) and (b) ZnO with mixed fuel (urea + glycine).



Figure 6.

PL spectra (a) ZnO with mixed fuel (Urea + Citric acid) (b) ZnO with mixed fuel (urea+glycine).

corresponding to the near-band-edge emission [29] which originates from free exciton emission and the other peak corresponding to ionized oxygen vacancies [30] with change for different fuels. High intensity oxygen vacancies peak at 632 nm is obtained for ZnO nanoparticle synthesis by urea with citric acid and band to band peak is eliminate. UC2 shows maximum band edge intensity and ZG3 shows maximum defect related emission.

4. Conclusions

ZnO nanomaterials were successfully synthesized by the combustion method using different fuels ratio. The XRD patterns were consistent with polycrystalline ZnO having the hexagonal wurtzite structure. The ZnO NPs size changed for different fuels with the minimum crystallite size of 26–40 nm obtained by using Glycine, citric acid with Urea at different ratio. The chemical band study shows that OH group has least intensity at higher Urea content. There is little change observed in bandgap with different fuel contents. In the ZnO powder synthesized with different fuels using glycine the band to band PL peak intensity was negligible compared to the defect related emission.

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References

[1] Wang X, Song J, Wang ZL. Nanowire and nanobelt arrays of zinc oxide from synthesis to properties and novel devices. Journal of Materials Chemistry.
2007;17:711-720. DOI: 10.1039/ B616963P

[2] Jun JH, Seong H, Cho K, Moon BM, Kim S. Ultraviolet photodetectors based on ZnO nanoparticles. Ceramics International. 2009;**35**:2797-2801. DOI: 10.1016/j.ceramint.2009.03.032

[3] Lin HM, Tzeng SJ, Hsiau PJ, Tsai WL. Electrode effects on gas sensing properties of nanocrystalline zinc oxide. Nanostructured Materials. 1998;**10**:465-477. DOI: 10.1016/ s0965-9773(98)00087-7

[4] Wang ZS, Huang CH, Huang YY, Hou YJ, Xie PH, Zhang BW, et al. A highly efficient solar cell made from a dye-modified ZnO-covered TiO₂ nanoporous electrode. Chemistry of Materials. 2001;**13**:678-682. DOI: 10.1021/cm000230c

[5] Kitano M, Shiojiri M. Benard convection ZnO/resin lacquer coating—A new approach to electrostatic dissipative coating.
Powder Technology. 1997;93:267-273.
DOI: 10.1016/S0032-5910(97)03283-X

[6] Zheng MJ, Zhang LD, Li GH, Shen WZ. Fabrication and optical properties of large-scale uniform zinc oxide nanowire arrays by onestep electrochemical deposition technique. Chemical Physics Letters. 2002;**363**:123-128. DOI: 10.1016/ S0009-2614(02)01106-5

[7] Wu R, Xie CS. Formation of tetrapod ZnO nanowhiskers and its optical properties. Materials Research Bulletin. 2004;**39**:637-645. DOI: 10.1016/j. materresbull.2003.12.009 [8] Curridal ML, Comparelli R, Cozzli PD, Mascolo G, Agostiano A. Colloidal oxide nanoparticles for the photocatalytic degradation of organic dye. Materials Science and Engineering C. 2003;**23**:285-289. DOI: 10.1016/ S0928-4931(02)00250-3

[9] Kamat VP, Huehn R, Nicolaescu R. A "sense and shoot" approach for photocatalytic degradation of organic contaminants in water. The Journal of Physical Chemistry. B. 2002;**106**:788-794. DOI: 10.1021/jp013602t

[10] Rasmussen JW, Martinez E, Louka P, Wingett DG. Zinc oxide nanoparticles for selective destruction of tumor cells and potential for drug delivery applications. Expert Opinion on Drug Delivery. 2010;7(9):1063-1077. DOI: 10.1517/17425247.2010.502560

[11] Udom I, Ram MK, Stefanakos EK, Hepp AF, Goswami DY. One dimensional-ZnO nanostructures: Synthesis, properties and environmental applications. Materials Science in Semiconductor Processing. 2013;**16**(6):2070-2083. DOI: 10.1016/j. mssp.2013.06.017

[12] Janotti A, Van de walle CG.
Fundamental of zinc oxide as a semiconductor. Reports on Progress in Physics. 2009;72:126501-126529. DOI: 10.1088/0034-4885/72/12/126501

[13] Kong YC, Yu DP, Zhang B, Fang W, Feng SQ. Semiconductor nanowiresideal bridge between macro Newton world and micro quantum world. Applied Physics Letters. 2001;**78**:407. DOI: 10.1063/1.1342050

[14] Xing YJ, Xi ZH, Xue ZQ, Zhang XD, Song JH, Wang RM, et al. Optical properties of the ZnO nanotubes synthesized via vapor phase growth. Applied Physics Letters. 2003;**83**:1689. DOI: 10.1063/1.1605808 [15] Zhang BP, Binh NT, Segawa
Y, Kashiwaba Y, Haga K.
Photoluminescence study of ZnO
nanorodsepitaxially grown on sapphire
(1120) substrates. Applied Physics
Letters. 2004;84:586-588. DOI:
10.1063/1.1738520

[16] Guo L, Yang S, Yang C, Yu P. Highly monodisperse polymer-capped ZnO nanoparticles: Preparation and optical properties. Applied Physics Letters. 2000;**76**:2901. DOI: 10.1063/1.126511

[17] Chu SY, Yan TM, Chen SL. Characteristics of sol–gel synthesis of ZnO based powders. Journal of Materials Science Letters. 2000;**19**:349-352. DOI: 10.1177/1464420714550192

[18] Liu B, Zeng HC. Hydrothermal synthesis of ZnO nanorods in the diameter regime of 50 nm. Journal of the American Chemical Society. 2003;**125**:4430-4431. DOI: 10.1021/ja0299452

[19] Aimable A, Buscaglia MT, Bowen P. Polymer-assisted precipitation of ZnO nanoparticles with narrow particle size distribution. Journal of the European Ceramic Society. 2010;**30**:91-598. DOI: 10.1179/1743280411Y

[20] Sun ZP, Liu L, Zhang L, JiaD Z. Rapid synthesis of ZnO nano-rods by onestep, room-temperature, solid-state reaction and their gassensing properties. Nanotechnology. 2006;**17**:2266-2270. DOI: 10.1088/0957-4484/17/9/032

[21] Patil KC, Aruna ST, Mimani T.Combustion synthesis: An update.Solid State & Materials Science.2002;6:507-512. DOI: 10.1016/S1359-0286(02)00123-7

[22] Noori NR, Mamooryb RS, Alizadehb P, Mehdikhani A. Synthesis of ZnO nano powder by a gel combustion method. Journal of Ceramic Processing Research. 2008;**9**(3):246-249. DOI: 10.1016/S1470-1804(99)80057-1 [23] Sousa de VC, Morelli MR, Kiminami RHG. Combustion process in the synthesis of ZnO-Bi₂O₃. Ceramics International. 2000;**26**:561-564

[24] Hwang CC, Wu TY. Synthesis and characterization of nanocrystalline ZnO powders by a novel combustion synthesis method. Materials Science and Engineering B. 2004;**111**:197-206

[25] Pathak TK, Kumar A, Swart CW, Swart HC, Kroon RE. Effect of fuel content on luminescence and antibacterial properties of zinc oxide nanocrystalline powders synthesized by the combustion method. RSC Advances. 2016;**6**:97770-97782. DOI: 10.1039/ C6RA22341A

[26] Yu J, Li C, Liu S. Effect of PSS on morphology and optical properties of ZnO. Journal of Colloid and Interface Science. 2008;**326**:433-438. DOI: 10.1016/j.jcis.2008.07.052

[27] Pathak TK, Swart HC, Kroon RE. Structural and plasmonic properties of noble metal doped ZnO nanomaterials. Physica B. 2018;**535**:114-118. DOI: 10.1016/j.physb.2017.06.074

[28] Dressel M, Gruner G.
Electrodynamics of Solids, Optical
Properties of Electron in Matter.
Cambridge: Cambridge University
Press; 2002. pp. 159-165. DOI: 10.1017/
CBO9780511606168

[29] Huang MH, Wu Y, Feick H, Tran N, Weber E, Yang P. Catalytic growth of zinc oxide nanowires by vapor transport. Advanced Materials. 2001;**13**(2):113-116. DOI: 10.1002/1521-4095(200101)13:2<113::aidadma113>3.0.co;2-h

[30] Pathak TK, Kroon RE, Swart HC. Photocatalytic and biological applications of Ag and Au doped ZnO nanomaterial synthesized by combustion. Vacuum. 2018;**157**:508-513. DOI: 10.1016/j.vacuum.2018.09.020