CHARACTERIZATION OF DIFFERENT BATH MOLARITY DEPENDENT ZINC OXIDE NANOPARTICLES BY HYDROTHERMAL SYNTHESIS

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Abstract

Synthesis of Zinc Oxide nanoparticles (ZnO NPs) were made by using the prepared precursor solution of zinc nitrate hexahydrate (Zn $(NO_3)_2$.$6H_2O$) and different molarity of sodium hydroxide (NaOH) (1 M, 1.5 M) with solvent deionized water through the hydrothermal synthesis. The hydrothermal reaction was carried out at the temperature range (100°C – 150°C) for 7h. After the hydrothermal reactor was naturally cooled to room temperature, the obtained product was filtered and annealed at 200°C for 1h. The obtained Zinc Oxide (ZnO) nanoparticles were characterized by X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and UV-Vis spectroscopy**.** The hexagonal wurtzite structure of good crystallinity of ZnO NPs was revealed through the XRD patterns and the crystallite sizes were 29.72 nm and 28.60 nm. The two morphologies of spherical and rod-like structures were found in SEM micrograph. The estimated energy band gaps were 3.06 eV and 3.08 eV obtained through the Tauc' s plot method.

Keywords: Hydrothermal Synthesis, Zinc Oxide, XRD, SEM, UV-Vis

Introduction

Semiconductor nanomaterials have been received great attentions. Among these various semiconductor nanomaterials zinc oxide is a versatile material because of its physical-chemical properties such as mechanical, electrical, optical, magnetic and chemical sensing properties. Zinc oxide a chemical compound found naturally in the mineral called zincite has attracted much attention in recent times due to its low cost and because it can be obtained by simple techniques [S. S. Kumar,2013]. Chemical synthesis is one of the important techniques which can be performed by using a range of precursors and different conditions like temperature, time, concentration of reactants, and so forth. Various chemical synthetic methods have been developed to prepare such nanoparticles [S.R.Brintha,2015].

Hydrothermal technique is a promising alternative synthetic method because of the low process temperature and very easy to control the particle size. The hydrothermal process has several advantages over other growth processes such as use of simple equipment, catalyst-free growth, low cost, ease of large scale production, eco-friendly and less hazardous [S.R.Brintha,2015]. The low reaction temperature makes this method attractive for microelectronics and plastic electronics. This method has also been successfully employed to prepare nano scale ZnO and other luminescent materials [A. Ramar Chandra Reddy, 2015]. This work intended to investigate the formation and characterization of ZnO nanoparticles depending upon the different bath molarity of NaOH solution.

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Experimental Procedure

ZnO nanopowders were synthesized by hydrothermal method using the starting materials zinc nitrate hexahydrate ($Zn(NO)_3.6H_2O$) and sodium hydroxide (NaOH). Zinc nitrate hexahydrate ($Zn(NO)_3.6H_2O$) aqueous solution of 0.5 M was firstly prepared using the solvent deionized water (DIW).An aqueous solution of 0.5 M zinc nitrate hexahydrate ($Zn(NO)_3.6H_2O$) were mixed with different molarity of NaOH (1 M and 1.5 M) solution. The mixture solution of zinc nitrate hexahydrate ($Zn(NO)_3.6H_2O$) and sodium hydroxide (NaOH) were stirred at 80°Cfor 20 minutes by magnetic stirrer. The final pH of the mixed solution was highly basic with pH of 14. The mixture solution was put into a Teflon-lined stainless steel bomb for hydrothermal reaction at 100°C -150°C for 7 h. After hydrothermal reaction, the reactor was naturally cooled to room temperature. The obtained product was filtered and washed with de-ionized water till the pH of the final solution was 7.Finally, the as-prepared sample was calcined at 200°C for 1h.

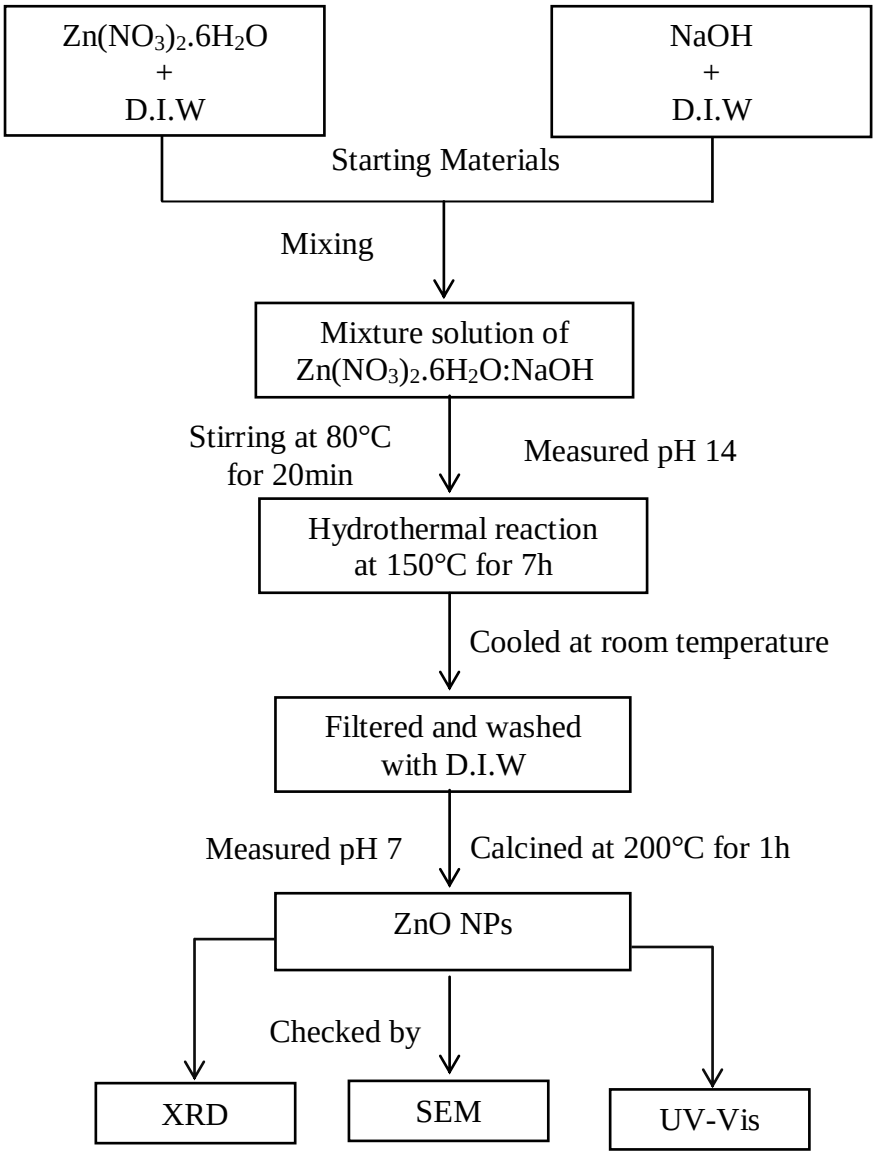

Figure 1 The block diagram for the preparation ZnO nanoparticles

Figure 2 Schematic diagram of home made Teflon-lined stainless steel vessel

Results and Discussion

XRD Analysis

Experimentally obtained diffraction patterns of the sample were compared with the standard powder diffraction files JCPDS (Joint Committee on Powder Diffraction Standard) (79-0206 > Zincite, syn-ZnO).The reflection planes (100), (002),(101), (102),(110) (103),(200),(112) and (201) of ZnO hexagonal wurtzite structure were occurred at the corresponding 2θ value. The most intense diffraction peak (101) plane was found at 2θvalue of 36.242 (deg). All the resulting diffraction peaks were coincideed with those of the standard library file (79-0206 > Zincite, syn-ZnO). The crystallite size of (101) plane was 29.72 nm. The lattice parameters of the ZnO hexagonal crystal were a=b= 3.2514 Å, and c=5.2046 Å.

Fig.2. showed the XRD patterns of ZnO particles with NaOH 1.5 M. It is cleared that the intensity of (101) plane was higher than that of ZnO with NaOH 1 M. All the resulting peaks were coincident with those of the standard library file (79-0206 > Zincite, syn-ZnO).The most intense (101) peak was formed at 2θ value of 36.291(deg). The crystallite size of ZnO hexagonal crystal structure was 28.6 nm with lattice parameters a=b= 3.2460 Å and c=5.2043Å. The crystallographic properties of the obtained ZnO NPs were compared with the standard library file and shown in Table (1) and (2).

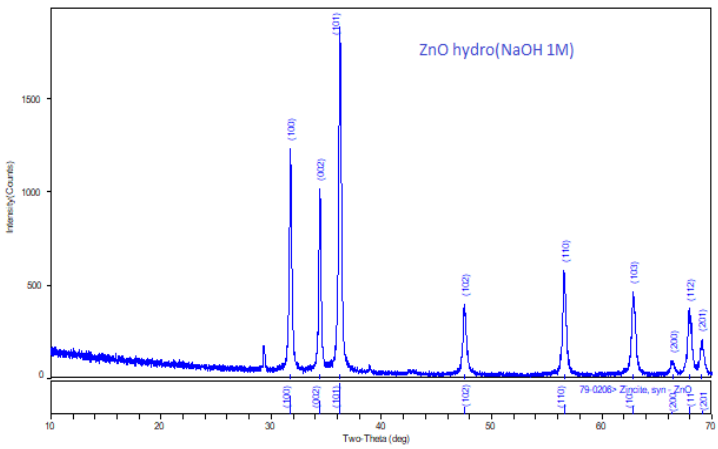

Figure 1 XRD patterns of ZnO NPs by hydrothermal synthesis with (1M NaOH)

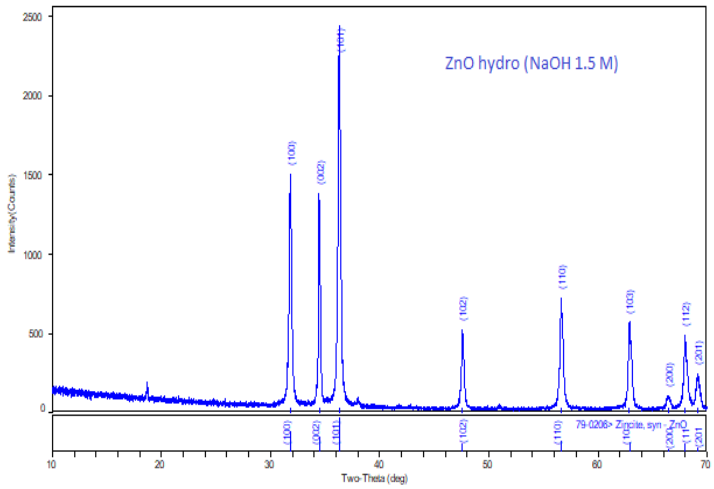

Figure 2 XRD patterns of ZnO Nps by hydrothermal synthesis with (1.5 M NaOH)

Table 1 Comparison of the standard and observed values of crystalline ZnO

Sample	The most intense peak	2θ value(degree)		FWHM(rad)	Crystallite Size (nm)
		Observed	Standard		
ZnO (1M NaOH)	101	36.242	36.251	0.281	29.72
ZnO (1.5 M NaOH)	101	36.291	36.292	0.292	28.60

Table 2 Comparison of standard and observed values of the lattice parameters and hexagonality of the ZnO Nps

Lattice parameter (Å)	Standard (Å)	Observed values	
		ZnO (1M NaOH)	ZnO (1.5 M NaOH)
a	3.2495	3.2514	3.2460
c	5.2069	5.2046	5.2043
c/a	1.6330	1.600	1.603

SEM Analysis

The micrograph of ZnO particles were examined by Scanning Electron Microscopy (SEM). SEM micrographs of hydrothermal synthesized ZnO particles were shown in figure.4&5.The granular morphology of the ZnO NPs with (1M NaOH) were both the spherical and rod like structure in figure.4. The estimated granular sizes were in the range of (0.28- 0.48 µm) range. The SEM images of the ZnO NPs with (1.5 M NaOH) revealed that the rod-liked structures of ZnO NPs granules were abundantly found and which were exhibited with different orientations. The estimated granular sizes were between the range of 0.16 µm to 0.32µm.

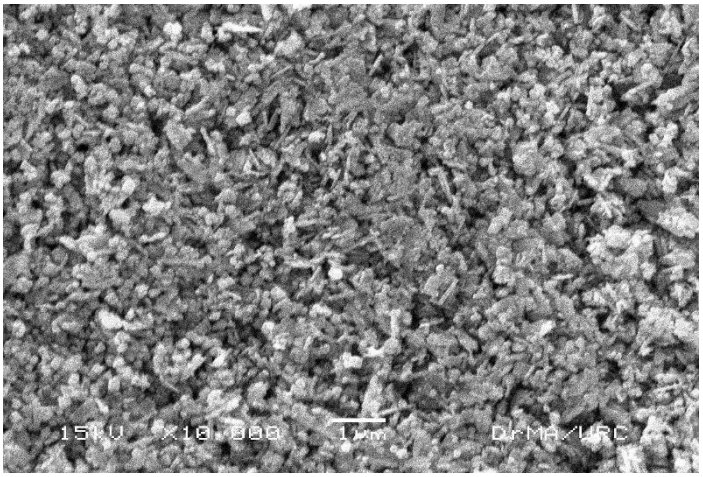

Figure 3 SEM micrograph of ZnO crystals with bath molarity of NaOH (1 M)

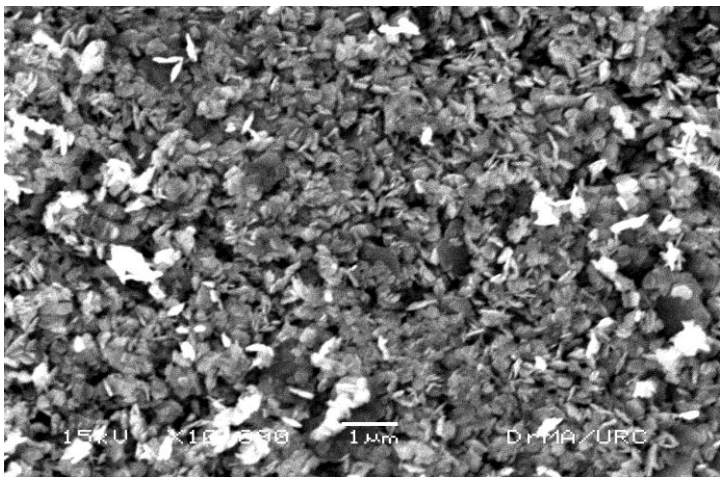

Figure 4 SEM micrograph of ZnO crystals with bath molarity of NaOH(1.5 M)

UV-Vis Analysis

The optical properties of the ZnO were determined by UV-Vis Spectrophotometer. The optical band gap was determined by using Tauc's plot method. The absorbance spectrum of the ZnO NPs with NaOH 1 M and 1.5M including Tauc's plot were shown in Fig.5(a), (b) and Fig.6 (a), (b).The absorption wavelength was 375 nm and 377nm for ZnO NPs. Tauc's plot showed the variation of $(\alpha h\nu)^2$ with the photon energy ($h\nu$) in eV. The E_g can be obtained by extrapolating the linear portion to the photon energy axis. The obtained optical band gaps values were 3.06 eV and 3.08 eV.

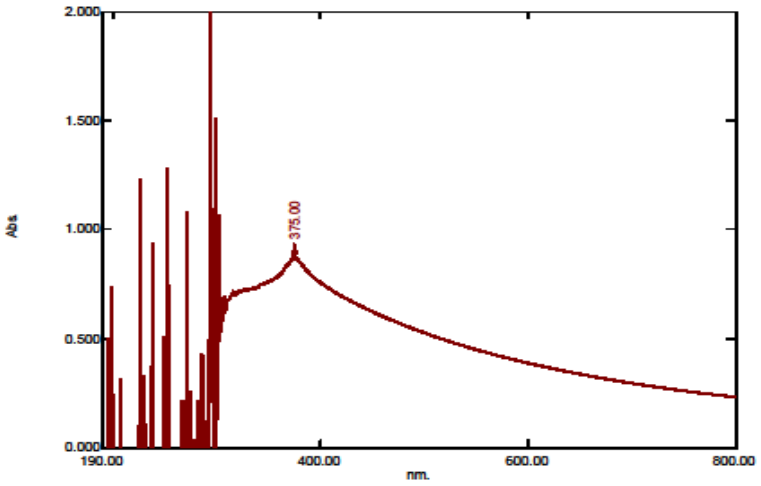

Figure 5(a) Absorption spectrum of ZnO NPs with (1 M NaOH)

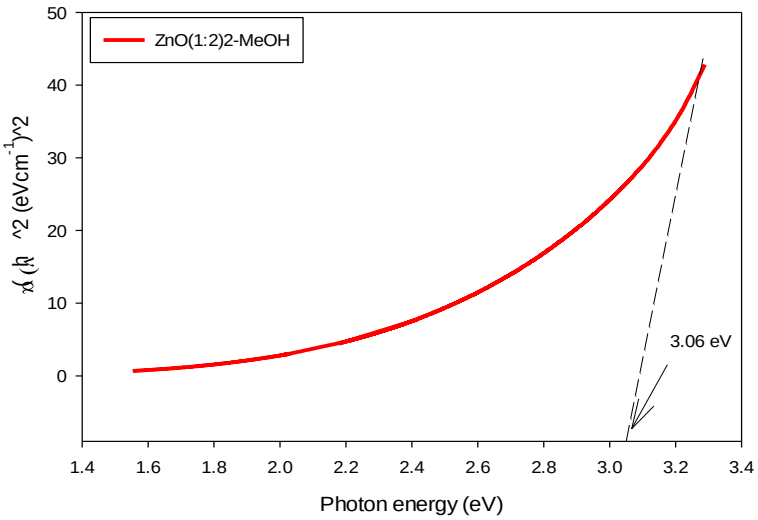

Figure 5(b) Tauc's plot of ZnO NPs with (1 M NaOH)

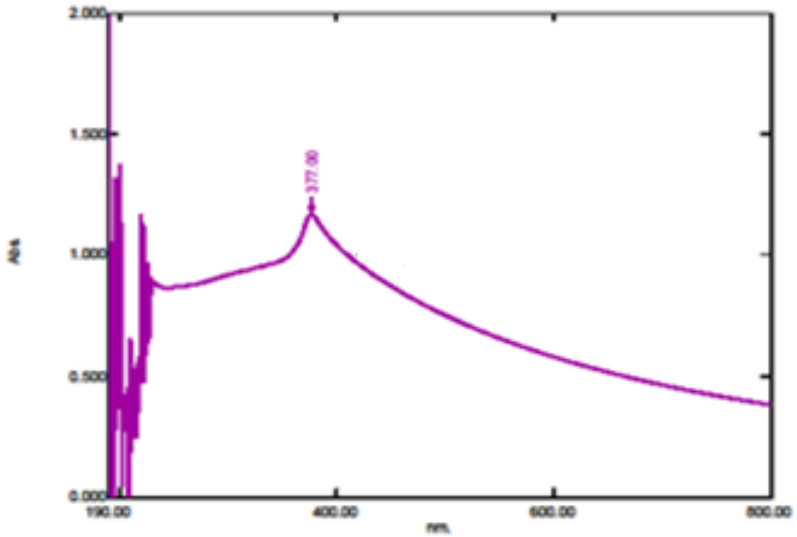

Figure 6 (a) Absorption spectrum of ZnO NPs with (1.5 M NaOH)

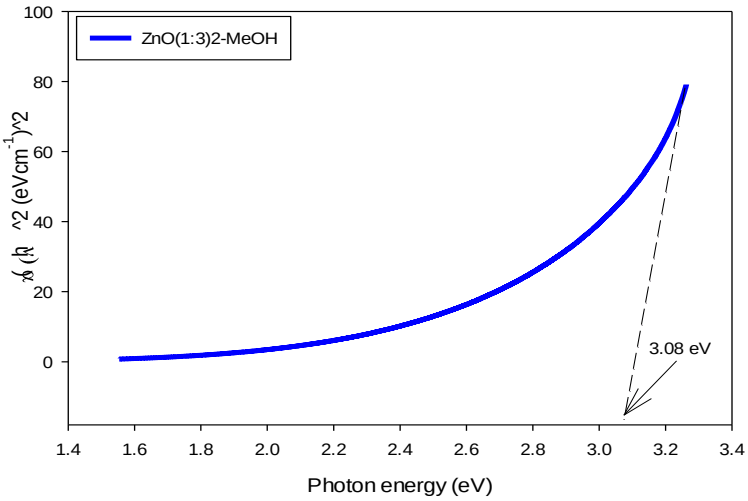

Figure 6 (b) Tauc's plot of ZnO NPs with (1.5 M NaOH)

Conclusion

Zinc oxide ZnO nano particles were successfully synthesized with the hydrothermal synthesis with different bath molarity of NaOH concentration. The XRD patterns confirmed that the crystal structure was wurtzite hexagonal ZnO and the crystallite sizes were 29.72 nm and 28.60 nm which were in the range of nanoscale. The good crystallinity of ZnO nanoparticles were apparently found through the XRD results.The two different morphologies of SEM micrographs were in accordance with the different bath molarity. The rod like structures of the ZnO NPs resulted in the strong enhancement of the electric field. The estimated granular sizes of the ZnO NPs were consistent with the crystallite size obtained from XRD results. The optical band gaps obtained from Tauc's plot were 3.06 eV and3.08 eV. These values were approximately equal to the typical value of wide band gap ZnO (3.3 eV).Moreover, the smaller the crystallite size, the greater the optical band gap. The results obtained from all the characterization techniques: XRD, SEM and UV-Vis were well consistent with each other. It was concluded that ZnO nano particles were successfully synthesized by a promising versatile hydrothermal synthesis.

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