Ph Dependent Structural, Morphological and Optical Properties of Pristine Zinc Oxide (ZnO) Nanocrystals

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Abstract: Versatile, cost effective and simple method of preparing ZnO nanocrystals was reported. Organometallic precursor derived ZnO nanocrystals were structurally possessed the hexagonal wurtzite structure with lattice constants a=3.249Å, c=5.206Å and the properties are strongly dependent on pH was also inferred. The morphological analysis was in accordance with the DLVO theory as supports the pH dependent aggregation of nanocrystals. The HR-TEM analysis confirmed the nanophase formation of the end product with an average particle sizes ranged from 10 to 35 nm. The peak shift in the band edge absorption towards the lower region tendency varied with varying pH of the growth environment and the increased band gap supplemented the nanophase nature of ZnO. The FT-IR analysis showed the existence of superfluous water and CO_2 molecules on the ZnO nanocrystals. The present study concluded the pH dependent growth of ZnO related materials.

Keywords : ZnO nanocrystals, Structural aspects, optical analysis, pH dependence.

1. Introduction

Over the past few decades, nanostructure materials and their devices have attracted a great deal of scientific and technological attention owing to their novel properties that are strongly influenced by quantum effects[1-3]. They exhibit tunable and novel optical, magnetic and electrical properties are opened new perspective of designing ideal instruments. Nanostructured materials are of enomorous interest, from the point of view of discovering new physical phenomena as well as their exploitation possibilities in novel devices. As the size and dimensionality of the material decrease, its electronic structure and its related properties change tremendously due to the reduction in the density of states and effective length scale in electronic motion[4-7].

In the nano era, energy levels of the materials are predominantly determined mostly by the materials surface. Owing to the fundamental properties, these materials result with the transition from the bulk band structure to individual localized energy levels; this is due to quantum confinement effects. The size-induced changes in the electronic structure significantly changed optical properties of nanomaterials[8].

ZnO material with hexagonal wurtzite crystal structure is a promising material for manufacturing photo detectors, blue and ultraviolet laser diode, transparent field effect transistors(TFET). In solution growth of ZnO nanowires, two types of crystal nucleation exhibit complete.i.e. Homogenous nucleation produces Zero dimension ZnO particles and heterogeneous nucleation produces one dimension nanowires. The rich defect

chemistry of ZnO gives rise to a wide range of properties including piezoelectricity, Ferro electricity, wide band gap semi conductivity, room temperature Ferro magnetism, huge magneto optic effect and chemical sensing. Due to its chemical thermal stability wide band gap of 3.37eV and large excitation binding energy (60 meV) and so ZnO is considered as a promising material for the fabrication of opto electronics and electronic devices[9-14].

The main objective of the present work is to prepare nanostructured zinc oxide with appreciable physical and chemical properties. To this, we are prepared the ZnO at different pH levels of the growth medium. Moreover there are limited number of literature are available that deal with the preparation of nano materials under different pH values that further motivated the authors to prepare the material in this perspective. The synthesized powder materials are to be confirmed from the result of XRD and UV- Visible Spectroscopy. The structure and its related properties are evidenced from XRD analysis. The surface morphology of the powder is visualized from SEM and HRTEM micrographs. The band edge absorption value and the functional group analysis were performed from the optical study namely UV Visible absorption and FT- IR studies.

2. Experimental Method

To prepare the Zinc Oxide nano powder, 1 gm of $Zn(CH_3COO)_2$ $2H_2O$ powder is mixed with the distilled water. The above solution is vigorously stirred for ten minutes and the proceeding is made in room temperature. After ten minutes vigorously sterilize 1.5ml of aqueous ammonia is added above solution changed to milky white. The ammonia is acting as pH varying agent and the structure determining parameter. It liberates the Zinc ion from the zinc precursor and leads the reaction to the formation of Zinc Oxide and some related compounds. The pH of the medium is kept at 9.0 and 10.0.

$$Zn (CH_3COO)_2\ 2H_2O_{(S)} + H_2O + NH_{3(L)} \rightarrow ZnO_{(S)} + NH_4(COOCH_3)_2.H_2O_{(L)} + H_2O + H_{2(G)}$$

The above content is placed in a constant temperature bath for five hours, which is ascertained as growth period. The pH of the solution is maintained at 9.0. The resultants product is dried in a hot air oven. Before keeping the product into the oven it is thoroughly cleaned using ethanol and water. The synthesized product was analyzed using standard analytical methods with respect to its structural and optical properties. Simillar protocol was followed for the pH 10.0 grown sample.

3. Results and Discussion

3.1 Structural Analysis

The XRD pattern of the ZnO nanostructures are show in the Figure-1. All the diffraction peaks are in good agreement with hkl value of hexagonal ZnO with lattice constant a=3.2546 Å, c=5.2126 Å and for other sample a=3.2525 Å, c=5.2068 Å the corresponding average size of the particles obtained by Debye-Scherrer formula are 4 -10 nm (Table-1). The sharp peaks confirm crystalline nature of ZnO nano particles. The sample exhibits the XRD pattern with strong intensity peak with the Miller indices of (101). The enhanced (101) peak is dominant over other peaks and it indicates with its cell constants of hexagonal wurtzite structure. Furthermore, the cell parameters are well agreed with the previously reported values for ZnO (JCPDS -361451). The cell constant values are found to be a=3.249Å, c=5.206Å. From the discussion the preferential orientation of the growth is directed to (101) plane for the optimized growth condition. In addition to the predominant peak eight characteristic additional peaks are also identified in the spectrum and their plane values are indexed. As the pH of the growth medium is increased to 10.0, the intensity of the peak is also increased which resembles the increased crystalline nature of the sample. The results are strongly supported by Viswanathan et al (2003).

The results reveal that the resultant nanostructures are in wurtzite hexagonal phase. There is no observation for the presence of impurity since the XRD pattern does not contain any impurity peaks in it. The average grain size has been calculated from the powder pattern using Scherrer- Warren approximation D=0.915λ/ β cosθ where 0.915 is Scherrer constant for spherical particle, λ is the X-ray wavelength (1.515 Å), β is the peak width of half-maximum, and θ is the Bragg diffraction angle in radian.The average particle size value is found to be 4 to 10 nm.
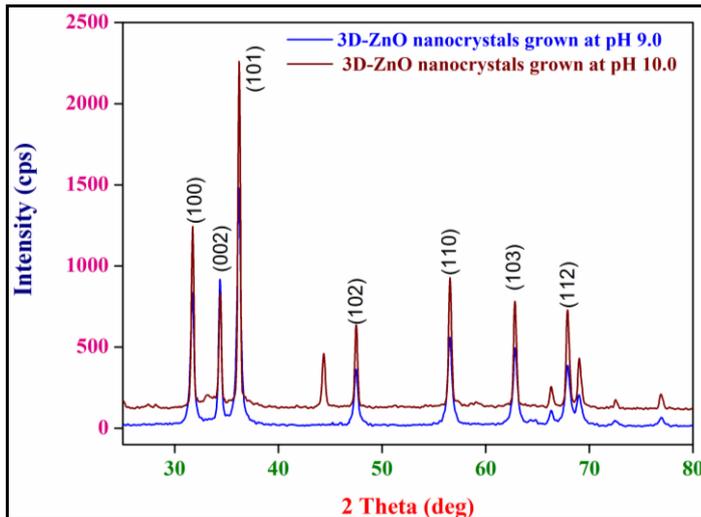
Figure – 1 X Ray Diffraction pattern of ZnO nano particles synthesized at pH 9.0 and 10.0

The crystalline properties evaluated from the XRD pattern is tabulated in Table-1. It gives that the crystalline properties of the material grown under pH 10.0.

Table – 1 Crystalline properties of pH 10.0 grown ZnO nano particles

2θ (Deg)	hkl	d value (Å)	Grain (nm)	Strain	Dislocation density (Kg/m³)
31°36'	100	2.8186	8.024	.04515	1.3028
34°42'	002	2.6063	8.076	.04486	1.2860
36°22'	101	2.4780	8.1136	.04465	1.274
47°50'	102	1.9118	4.818	.07518	3.6125
56°54'	110	1.6263	8.767	.0413	1.0907
62°'**50**	103	1.4784	10.319	.03511	0.7878
66°28'	200	1.3990	10.50	.0345	0.7608
67°42'	112	1.3800	8.266	.0438	1.2269
69°00'	201	1.3693	10.65	.0340	1.655

Optical Infra-red spectroscopic studies

The UV- Visible absorption spectrum (Figure - 2) illustrates the strong exciton absorption edge that features at ≈ 369 nm which is blue shifted by ≈ 6 nm with respected to the bulk absorption that exist around 375 nm[17, 18] with the calculated band gap of 3.36 eV. The observation of blue shift for the nano materials is obvious and is caused by the following reason: the stronger exciton effect is an important character of quantum confinement in nano structured semiconductors and is the results of the carriers are confined in a small and well defined region that makes the electron and hole only in a potential well. At the same time, it can enhance the coupling interaction with each other. Then the exciton bound to be stronger and the binding probability reaches the maximum value. Hence noticeable peak is observed in the absorption spectrum is the resemblance of reduced particle size. The synthesized sample was scanned for functional group analysis using FTIR spectroscopy (Figure-3). The FT-IR spectrum of pH 10.0 grown sample shows the peaks at 410 cm^{-1} and 513 cm^{-1}.are attributed for the presence of Zn-O bands[19]. However, the reference spectra of ZnO powders often show its peaks at around ≈ 512 cm^{-1} and ≈ 406 cm^{-1}. Therefore, it is found that the characteristic peaks are blue shifted. The broad absorption peaks at ≈ 3433 cm^{-1} and 1635 cm^{-1} are attributed the presence of hydroxyl groups and C=O vibrations and are originated from the superfluous water and CO_2 molecules. Peaks at ~2924 and ~2854 cm^{-1} are attributed to the asymmetric and symmetric stretching vibrations of $-CH_2$ group which is originated from the precursor materials[20].
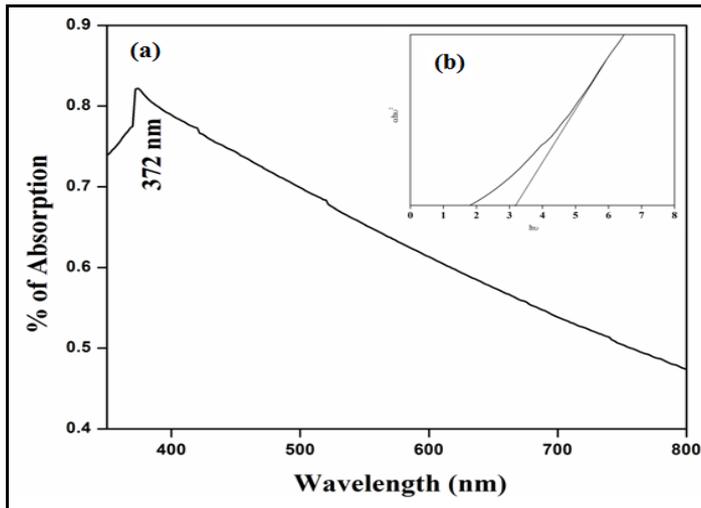
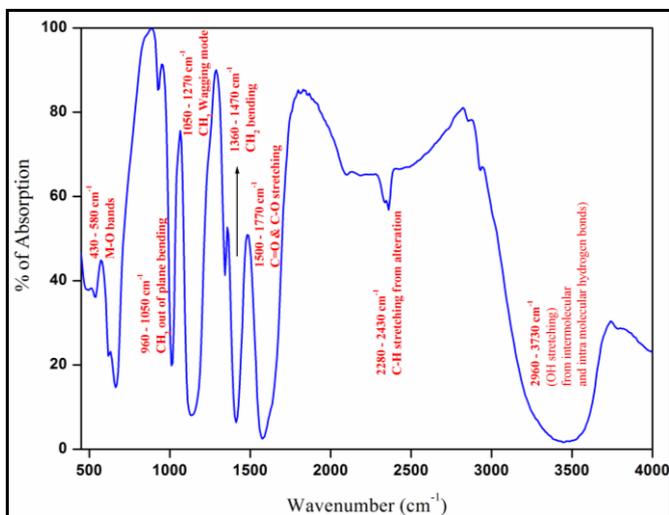**Figure – 2 UV – Visible absorption spectrum of pH 10.0 grown ZnO nano particles**

Figure – 3 FT – IR absorption spectrum of pH 10.0 grown ZnO nano particles

3.2 Morphological Analysis

The high resolution Scanning Electron Microscopic image of the synthesized ZnO nanostructures are shown in the Figure - 4(a). The above SEM pictures depict that the crystalline morphology of the grown nanostructures. The agglomerations of the particles have observed in the picture. The solid like shapes infers the ZnO particles. Since the samples are subjected to morphological analysis after the annealing process, the EDS analysis only has the Zn and O in its count. Some of the Au traces are also found in the spectrum which is caused by gold coating to the sample owing to the precautionary aspect of the sample (Graphs not presented). Further confirmation of the nanophase formation the same product subjected to Transmission Electron Microscopic (TEM) analysis and the micrographs are shown in Figure - 4(b). The images obtained from the above tool show that the grown systems possess spherical structure with particles of ≤50 nm. The TEM images of as-synthesized ZnO nanospheres, reveals the general morphology of as-obtained ZnO nanospheres. Most of the outer diameters range from 37 to 52 nm. The SAED pattern (pattern not given) obtained for the sample shows diffuse rings indicating the polycrystalline nature of as-synthesized ZnO nanospheres.

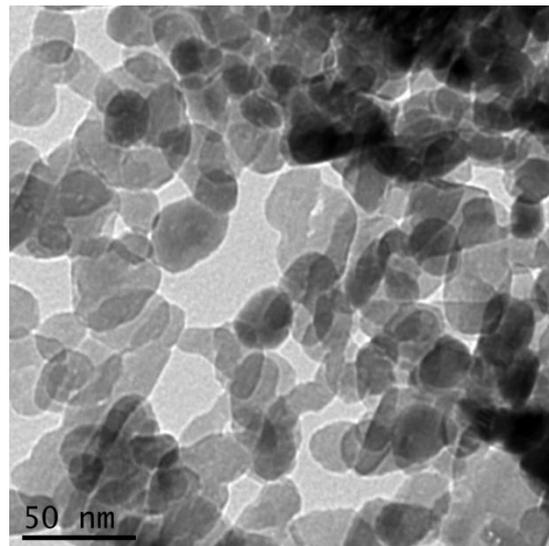**Figure – 4(a) HR SEM micro graphs of pH 10.0 grown ZnO nano particles**

Figure – 4(b) HR TEM micro graphs of pH 10.0 grown ZnO nano particles

4. Conclusion

In summary, we prepare the 3D-ZnO Nanostructures by simple wet chemical synthesize method using zinc acetate dyhydrate as the precursor material. The as prepared Nanostructures exhibit the hexagonal wurtzite structure. The orientation of the Nanostructures preferred to the (101) plane, which is evidenced in XRD pattern. The possible growth mechanism is reported. The optical and thermal analysis of the 3D-ZnO is also explained and the Nanostructures show the strong excitonic absorption at 369 nm. This method can be considered as a promising method for the preparation of novel functional nanostructures of ZnO.

Acknowledgment

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