Category: Nanotechnology and Emerging Areas

Hydrothermal growth and characterization of ZnO nanomaterials

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***Abstract*— ZnO nanostructures are synthesised by hydrothermal method from zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$) using water as a solvent. NaOH solution in water is used to adjust the pH of the growth solution. The ZnO nanostructures are synthesised from solution with pH varying from 7 to 12. The structural, morphology, and optical properties of the grown ZnO nanostructures are characterized by XRD, FESEM, EDS, UV-vis and photoluminescence spectroscopy. The growth of hexagonal shaped nanocrystals is observed at pH value of 7 and as the pH of the growth solution is increased the morphology of the nanomaterials changes from hexagonal rod shapes to hexagonal platelet shapes.**

Index Terms— ZnO, Nanomaterials, and hydrothermal growth

I. INTRODUCTION

Zinc oxide is a wide direct bandgap semiconducting and piezoelectric material. ZnO has bandgap energy of 3.36 eV and bulk free excitonic binding energy of ~ 60 meV at room temperature [1]. The wide bandgap along with excitonic stability at room temperature has attracted a great deal of attention on ZnO for blue and ultraviolet optoelectronic devices. In recent years, the nanostructures of ZnO are widely under investigation by researchers due to their fascinating morphologies, physical properties, and applications in efficient optoelectronic devices operating in blue and ultraviolet region [2]. ZnO nanostructures are promising candidate for ultraviolet laser devices operating at room temperature [3]. The quantum confinement in nanostructures enhances the exciton oscillator strength and quantum efficiency of optical transitions [4]. Researchers have adopted various methods such as chemical vapour deposition (CVD), physical vapour deposition, electrodeposition, thermal evaporation, aqueous synthesis, and hydrothermal techniques to prepare ZnO nanostructures [5]. In the present work, we have synthesised ZnO nanostructures by hydrothermal method. The crystal structure, surface morphology and optical properties of the synthesised ZnO nanostructures are studied.

II. EXPERIMENTAL DETAILS

In the present work ZnO nanostructures are synthesised by hydrothermal method from $Zn(CH_3COO)_2.2H_2O$ using water as a solvent. The synthesis of ZnO nanostructures are carried out in a 50 ml capacity teflon lined stainless steel autoclave. The grown nanostructures are characterized by powder XRD, UV-visible absorption spectroscopy using Shimadzu 1800 spectrophotometer, and FESEM imaging using ULTRA 55, FESEM (Karl Zeiss) equipped with energy dispersive x-ray spectroscopy (EDS). PL is measured using Perkin Elmer LS-55 fluorescence spectrometer.

In order to synthesize the ZnO nanostructures, 0.1 M solution of $Zn(CH_3COO)_2.2H_2O$ is prepared in 50 ml of water under continuous stirring. The pH of the prepared $Zn(CH_3COO)_2.2H_2O$ solution is adjusted to the required value by adding the NaOH solution prepared in water. In the present work ZnO nanostructures are synthesised using 0.1 M $Zn(CH_3COO)_2.2H_2O$ solution with pH varying from 7 to 12. The synthesis of ZnO nanostructures are carried out by transferring the prepared solution to the teflon lined stainless steel autoclave. The autoclave is then heated using an oven, and maintained at 160°C for 8 hour. After the growth the autoclave is allowed to cool naturally to room temperature and the resulting white powder product is washed with methanol, filtered, and then dried in air in an oven at 100°C.

III. RESULTS & DISCUSSIONS

The grown ZnO nanostructures are characterized by powder XRD, FESEM, EDS, UV-visible spectroscopy, and photoluminescence spectroscopy. Figure 1 shows the powder

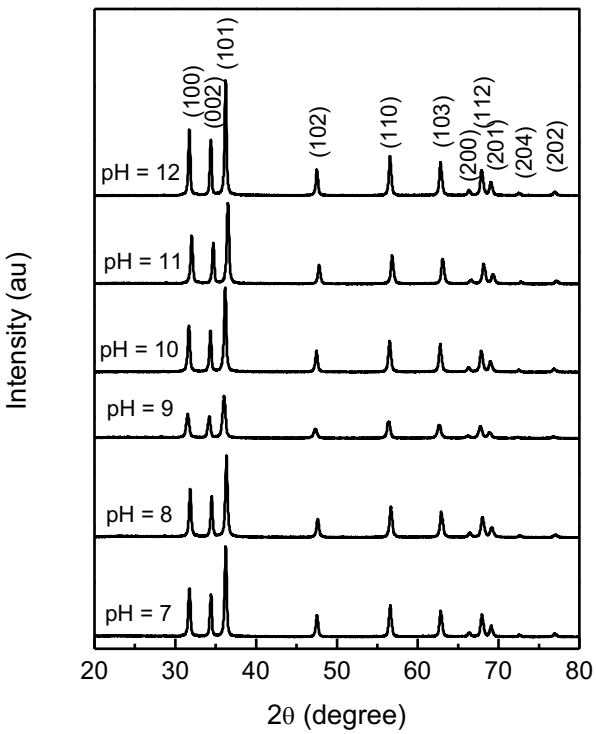

FIG. 1. Typical XRD pattern of the synthesised ZnO nanostructures.

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DOI: 10.1007/978-3-319-03002-9_154,

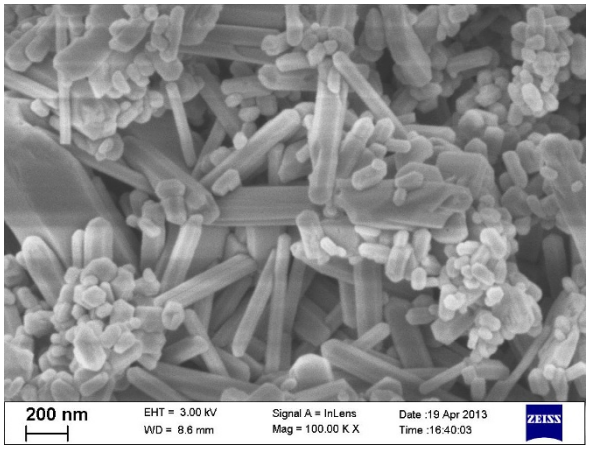

FIG.2(a). FESEM image of the ZnO nanostructures grown from 0.1M $Zn(CH_3COO)_2.2H_2O$ solutions with pH = 7.

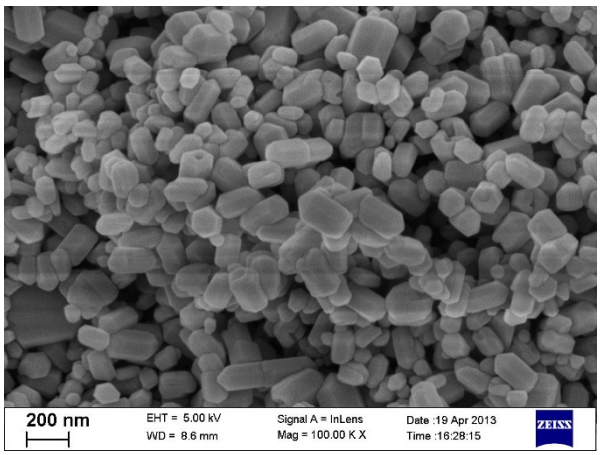

FIG.2(b). FESEM image of the ZnO nanostructures grown from 0.1M $Zn(CH_3COO)_2.2H_2O$ solutions with pH = 8.

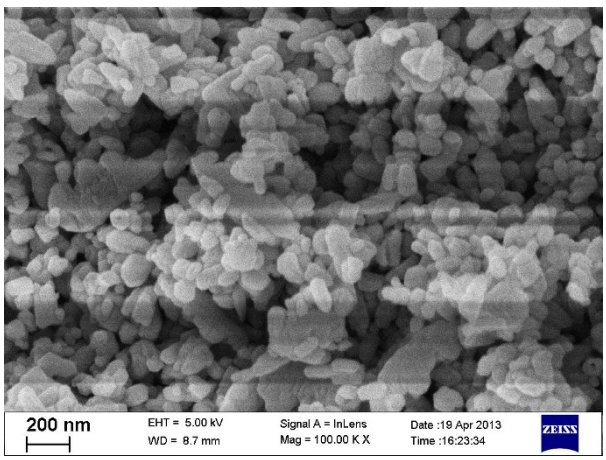

FIG.2(c). FESEM image of the ZnO nanostructures grown from 0.1M $Zn(CH_3COO)_2.2H_2O$ solutions with pH = 9.

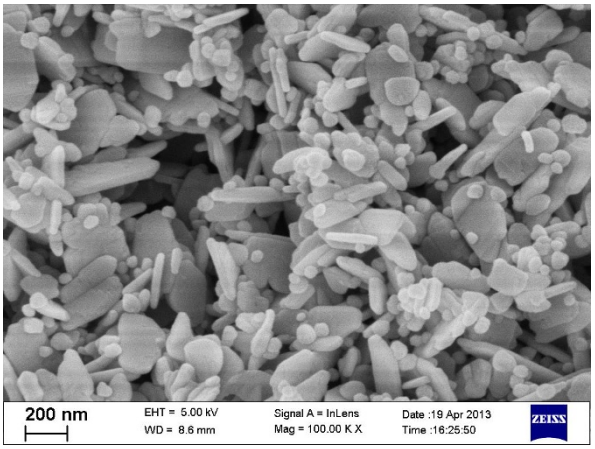

FIG.2(d). FESEM image of the ZnO nanostructures grown from 0.1M $Zn(CH_3COO)_2.2H_2O$ solutions with pH = 10.

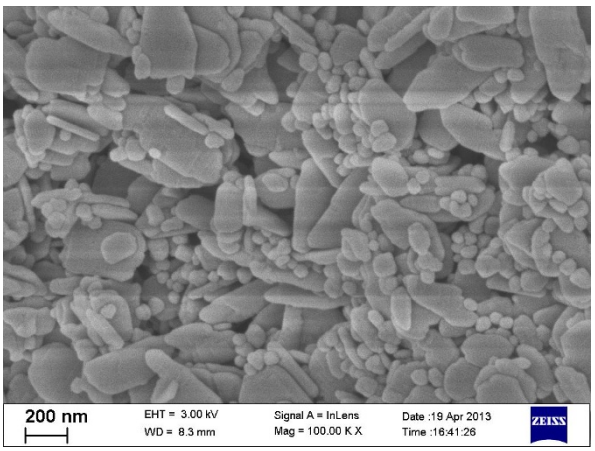

FIG.2(e). FESEM image of the ZnO nanostructures grown from 0.1M $Zn(CH_3COO)_2.2H_2O$ solutions with pH = 11.

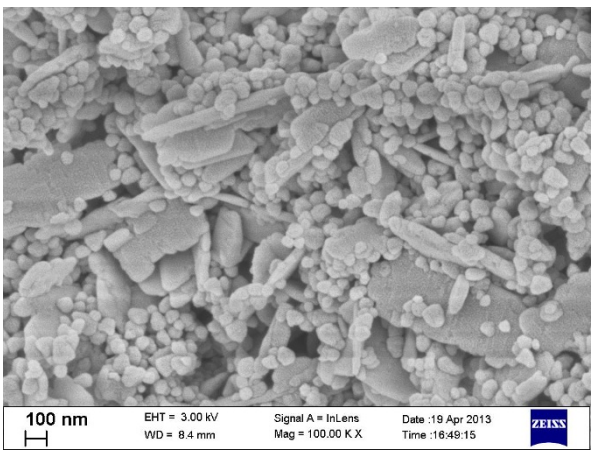

FIG.2(f). FESEM image of the ZnO nanostructures grown from 0.1M $Zn(CH_3COO)_2.2H_2O$ solutions with pH = 12.

XRD pattern of the hydrothermal synthesised ZnO nanostructures from 0.1M $Zn(CH_3COO)_2.2H_2O$ solutions with pH value varying from 7 to 12. The XRD pattern indicates hexagonal wurtzite structure (JCPDS card no. 36-1451) of the ZnO nanostructures. The narrow diffraction peaks indicate high purity and good crystalline quality of the grown nanostructures. Figure 2(a) – 2(f) shows the FESEM images of the ZnO nanostructures grown from 0.1M $Zn(CH_3COO)_2.2H_2O$ solutions with pH = 7, 8, 9, 10, 11 and 12, respectively. Hexagonal rod shaped nanostructures are formed for pH = 7 and as the pH of the growth solutions is increased, the morphology of the nanostructures gradually changes from hexagonal rod shaped structures to hexagonal platelet structures. The Zn and O atomic percentage obtained from EDS indicates that the synthesized ZnO nanostructures are nearly stoichiometric. The EDS values obtained for ZnO nanomaterial grown from solution with pH=8 is shown in Table 1. For investigation of the optical properties of the nanomaterials UV-visible and PL spectra of the samples are recorded. The UV-visible absorption spectra of the nanostructures are shown in Fig. 3. The UV-visible absorption spectra show a strong exciton absorption peak in the UV region. This excitonic peak exhibits a blue shift relative to the bulk exciton absorption due to quantum confinement effect in the nanostructures [6]. The appearance of the sharp excitonic peaks indicates the high crystalline quality of the grown nanostructures [7]. The room temperature PL spectra of the samples are shown in Fig. 4. The PL spectra consists of a strong near-band edge emission centered at around 394-400 nm which is attributed due to the recombination of excitons [8], a weak peak around 422 nm corresponding to violet emission due to an electron transition from a shallow donor level of neutral zinc interstitial (Zn_i) to the top of the valance band [9], a peak around 484 nm corresponding to blue emission associated to the intrinsic defects such as vacancies or interstitials of O and Zn and their complexes in ZnO nanostructures [10]. A small green emission was observed at 528 nm, it is associated to the oxygen and zinc vacancies in the literature [10].

TABLE 1. The weight/atomic percent of Zn and O elements obtained from EDS in the ZnO nanostructures synthesised from 0.1 M $Zn(CH_3COO)_2.2H_2O$ in water with pH = 8**.**

Element	Weight (%)	Atomic (%)
O K	21.74	53.17
Zn L	78.26	46.83
Totals	100.00	

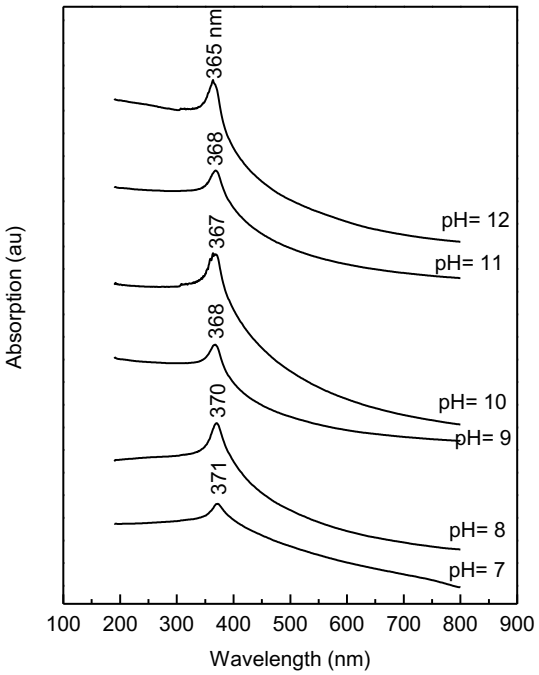

FIG.3. Typical UV-visible spectrum of the synthesized ZnO nanostructures.

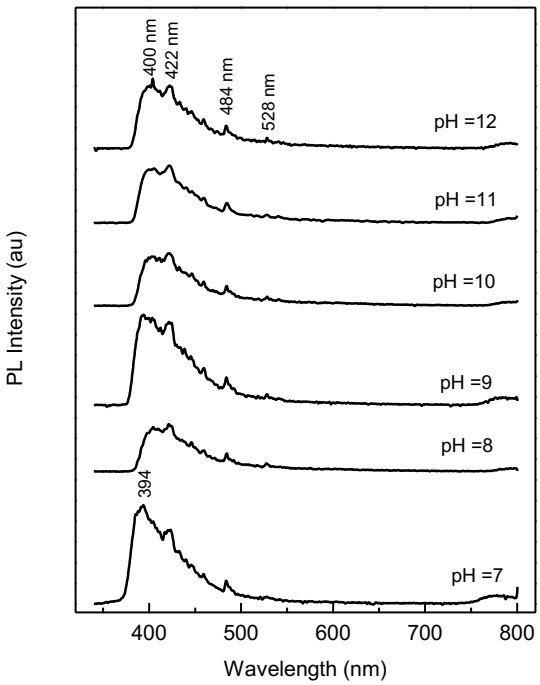

FIG.4. Typical PL spectrum of the synthesized ZnO nanostructures

IV. CONCLUSIONS

ZnO nanostructures are synthesised by hydrothermal method from $Zn(CH_3COO)_2.2H_2O$. The grown nanostructures are characterized by powder XRD, UV-visible absorption spectroscopy, FESEM imaging and EDS. The XRD patterns indicate the wurtzite structure of the grown nanostructures and the narrow XRD peaks indicate good crystalline quality of the grown nanostructures. The EDS results indicate that the synthesized ZnO nanostructures are nearly stoichiometric and free of impurities. The UV-visible absorption spectra of the nanostructures show strong exciton absorption peak with blue-shift relative to the bulk exciton absorption in all of the synthesised nanostructures. The appearance of the sharp excitonic peak in all these samples, indicate the high crystalline quality of the grown nanostructures. The growth of hexagonal shaped nanorods is observed at pH value of 7 and as the pH of the growth solution was increased above 7 the morphology of the nanostructures transforms from nanorods to platelet shaped nanostructures.

V. REFERENCES

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