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Synthesis of Zinc Oxide Nanostructures Growth by the role of pH variation

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Abstract. In this paper, we study on the morphology variation of zinc oxide (ZnO) nanostructures by varied the pH of precursor via hydrothermal method. The Zinc chloride and ammonium hydroxide were used as precursor, which was heated at 180°C for 24 hours. The pH of the precursor was varied from 7, 8, 9, 10 to 11 by the controlled amount of ammonium hydroxide. The samples were characterized with X-ray diffraction (XRD), Scanning electron microscope (SEM) and Ultraviolet-Visible (UV-Vis) spectroscopy. XRD pattern shows that the ZnO nanostructured exhibit the hexagonal wurtzite structure and average crystallite size is calculated. The morphology images revealed the rod and flower like structure for all samples. UV-Vis spectroscopy (UVs) shows the absorption or reflectance peaks of zinc oxide was around 350 to 450 nm. pH value was found key to the structure control of studied.

1. Introduction

Recently, shape control has raised significant study in the fabrication of semiconductor nanocrystals, metal nanocrystals, and other inorganic materials (Xu el at., 2004). Many deposition techniques have been employed to synthesize nanostructure such as nanowires, nanobelts, nanobridges, nanonails, nanoribbons, nanorods, nanotubes (Wahab et al, 2009). ZnO has been used to induced the formation of many different nanostructures such as nanowires, nanorods, nanospring, nanorings, nanobelts, nanotubes and nanoflowers (Gomez et al. 2013). There are various methods that can be used to fabricate and synthesis the ZnO nanostructure. The processes are such as hydrothermal, chemical vapor condensation, sol gel, micro emulsion, and sonochemical (Hasnidawani, et al., 2016). Nanomaterial can be classified in (0-D) is nanoparticles like quantum dots and Nano dots whereas (1-D) is like nanowires, nanorods, nanotubes for example like thin films layers and surfaces. For (2-D) the example is like coatings, thin-film-multilayers like biopolymers, carbon nanotubes, nanowires and inorganic nanotubes. The example for (3-D) is like bulk of nanostructure which like powders and other nanostructures including fractal structures, fullerenes and nanoparticles. Nanorods are one-dimensional (1D) nanostructures and have received great interest because the have versatile applications. Nanoflower are (3D) nanostructured show a sharp and strong UV emission band at 520 nm in the visible region.

ZnO nanostructure have been involved in a wide range of application such as in sensors, biomedical, optoelectronics, and solar cells (Wang, 2004). The ZnO also widely used in capacitors, electrophotography, conductive thin film, protective coating and as an ultraviolet resistant additive (Hasnidawani, et al., 2016). The wide variety of application are due to the properties of the ZnO nanomaterial itself that have a wide band gap which is 3.37 eV (Hassan, Hashim, & Al Douri, 2014). This is because a greater band gap allows for higher breakdown voltage and an ability to sustain large electric fields. Furthermore, ZnO has displayed nontoxicity, chemical stability and electrochemical activity (Gomez et al. 2013). The electrical properties of ZnO nanostructures is crucial for developing their future applications in nanoelectronics. Field effect transistors (FETs), fields emission devices, piezoelectric nanogenerators, biosensor, p-n heterjunction diodes such as light-emitting diodes and photovoltaic cell had been used ZnO nanostructures for devices applications (Hahn, 2011). An attractive material for optoelectronic applications owing to its wide band gap of 3.37 eV, large bond strength and large exciton binding energy at 60 meV.

Hydrothermal method can prepare many types of structure such as rod, flake, flower like ZnO nanostructure without using any substrate at ambient pressure and low temperature (Sambath et al., 2012). This study was aimed at preparation of ZnO particles with varied the pH value controllable morphologies by a simple hydrothermal method and identified the morphology and physical properties.

2. Methodology

The nanostructures were prepared from zinc chloride (ZnCl) and ammonium hydroxide (NH_4OH). The mixed solution was stirred for 1 hour at room temperature to achieve homogenization. The pH will be adjusted from 7, 8, 9, 10 and 11 by controlled the amount of ammonium hydroxide. Then, the solution heated using Teflon lined steel autoclave at 180^oC for 24 hours. The precipitate obtained was washed several times with ethanol and distilled water. After washed several times, precipitation filtered with vacuum pump followed with dried at 60^oC for 12 hours and examined in terms of their structural and physical properties.

The X-ray diffraction (XRD) pattern of the prepared ZnO was recorded using Bruker D2 Phaser with Cu Kα radiation at the Brag angle ranging from 10^o to 90^o. The crystallinity and crystal phases were determined by XRD. The absorbance spectra have been recorded using a UV-1280 Multipurpose UV-Visible Spectrophotometer. The optical properties of the samples were also studied by the UV-visible (UV-vis) absorption in the range from 200 to 800 nm at room temperature. Samples were observed using scanning electron microscopy (SEM) for surface morphological images using JEOL-JSMIT-100.

3. Results and Discussion

Figure 1 shows the X-ray diffraction (XRD) pattern of zinc oxide nanostructures as a function of pH variation 7, 8, 9, 10 and 11. The detected (h k l) peaks were at 2θ values of 31.7°, 34.4°, 36.2°, 47.5°, 56.6°, 62.8°, 66.3°, 67.9°, 69.0°,72.5°, 76.9°, 89.6° are correspond to the lattice plans (100), (002) (101) (102) (210) (103) (200) (212) (201) (004) (202) and (203) respectively. All the diffraction peaks can be indexed to hexagonal wurtzite structure of ZnO with lattice parameter constant of a= 3.249 Å and c=5.206 Å comparison with the standard with the agreement COD 9008877 (Ghoderao et al.,2018). The intensity of the graph is increasing with the increasing in pH value may be due to the different precursor used as Sambath et al., (2012) reported the intensity of the pH value is decreasing with the increasing in pH. The sharp peak of the XRD graph is corresponds to the 101 indicate a high crystalline of the samples. The strongest peak corresponds to the 101 plan is more prevalent for the nanostructure as reported by Lupan at al. (2007). No diffraction peaks from impurities were detected.

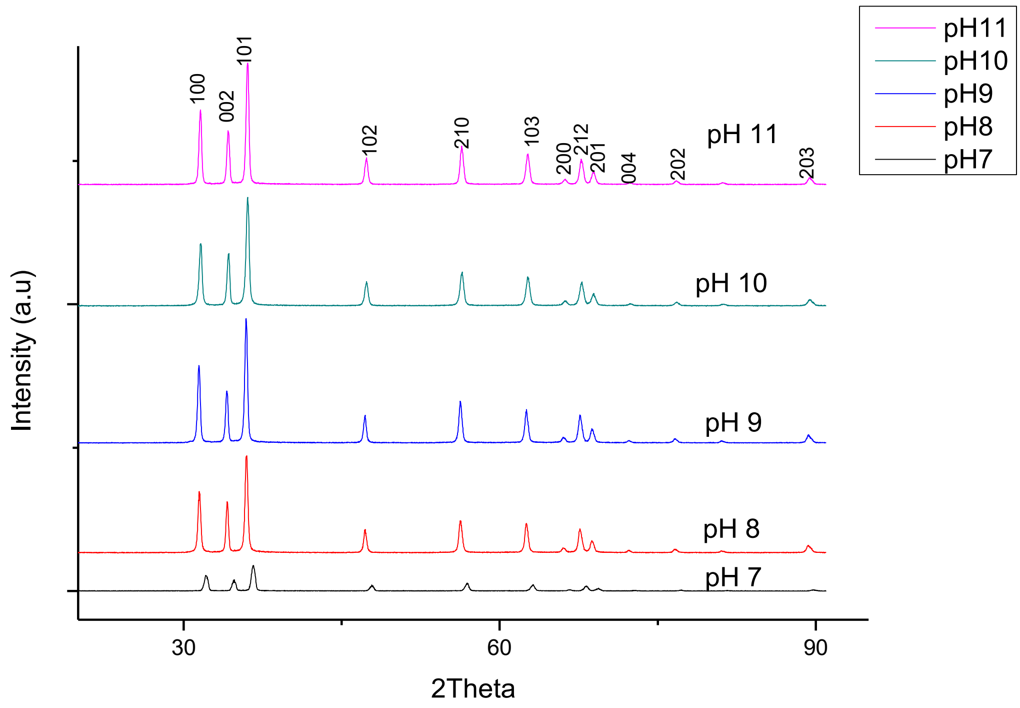

Figure 1. X-ray diffraction patterned of ZnO nanostructures prepared at different pH values

The optical properties of grown zinc oxide nanostructures synthesized at various pH 7, 8, 9, 10 and 11 conditions were examined by room temperature UV-vis spectroscopy. The UV-vis absorption spectra of all the samples synthesized at various pH conditions shown in Figure 2. The absorbance peak is around 350 to 450 nm can be referred to Suresh et al., (2015). Refer to Ghoderao et al., (2018) the intensity of the absorbance is increasing with increasing the pH value. However, the intensity of the absorbance for Ph 7 is increase and decrease when it comes to pH 8, pH 9 and Ph 10 and the peak is slightly increase for pH 11. This is may be due to the different pH used for ZnO synthesize.

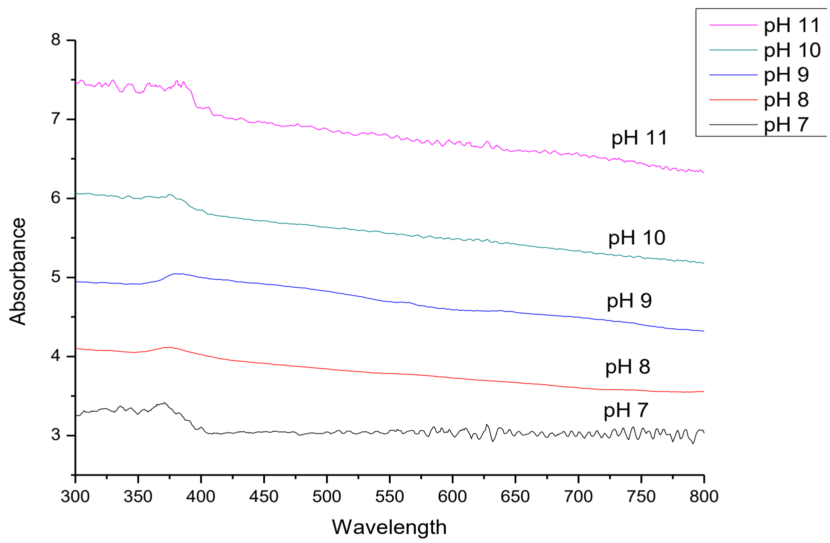

Figure 2. UV-Vis spectra of ZnO nanostructures prepared at different pH conditions

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Scanning electron microscope image of the ZnO nanostructured synthesized at the pH values of 7,8.9.10 and 11 are presented in Figure 3. Figure 3 shows the morphology variation structure was observed hexagonal rod-like structure at pH 7. Figure 3 (b-c) shows hexagonal rod-like structure decreased the size. nanostructure at pH 10, where nanorods are seen forming from rod-like structure to flower-like structure. Synthesis at pH 11, results in a complete flower like morphology composed from hexagonal nanorods. From the above observations, it is obvious that morphological characteristics of the ZnO controlled by the pH of the precursor.

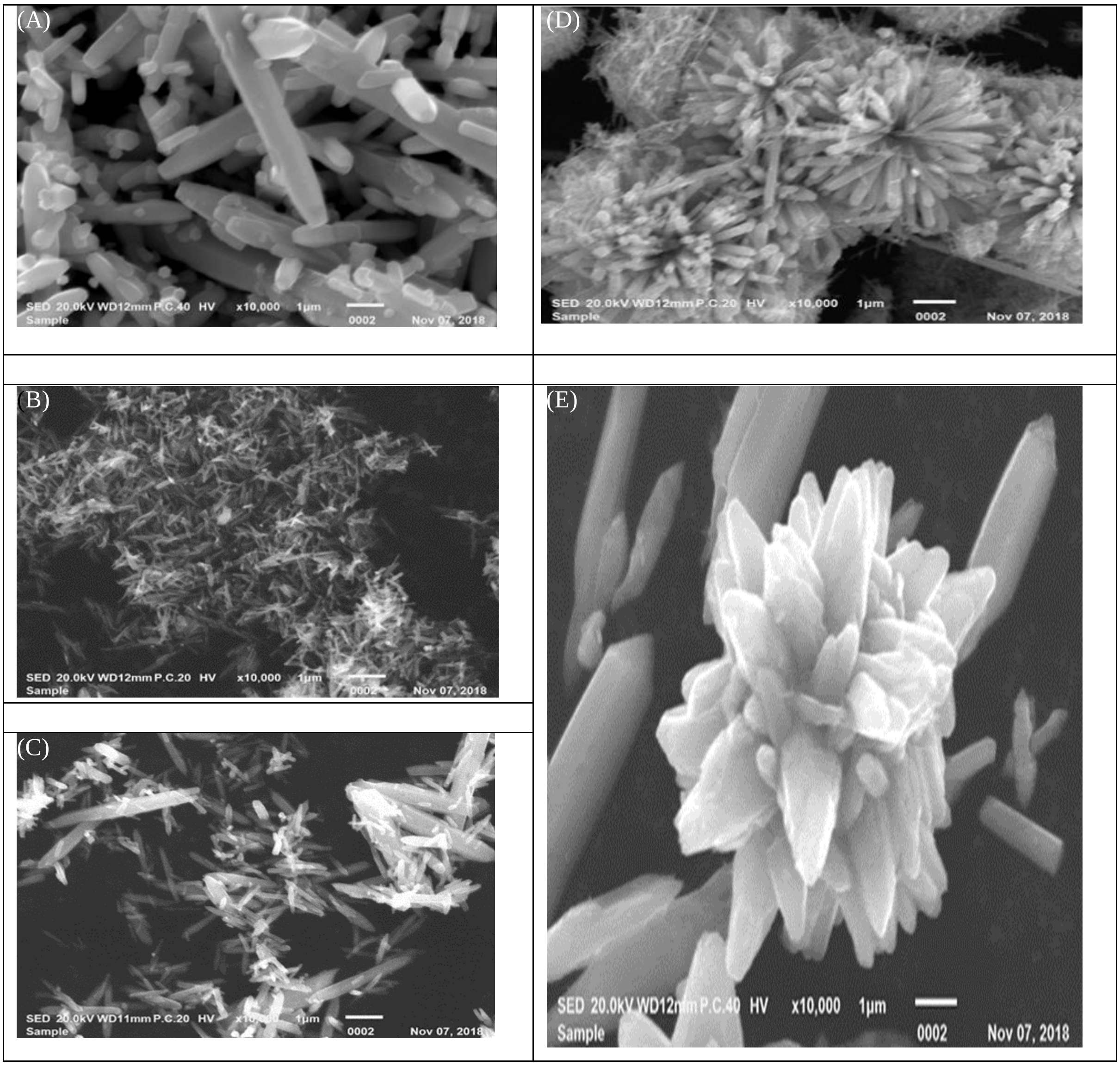

Figure 3. SEM image of ZnO nanostructures prepared at different pH values: (A) pH 7, (B) pH 8, (C) pH 9, (D) pH 10 and (E) pH 11

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4. Conclusion

In summary, the effect of pH on the morphological zinc oxide (ZnO) nanostructured has been examined. The crystallized ZnO powders with different morphology have been successfully prepared by a convenient hydrothermal method. Upon using different amount of ammonium hydroxide as solvents, the morphologies such as rod and flower like structure of the ZnO powders are obtained. It has been found that pH values were increased from 7 to 11 significantly influences the shape structures. Therefore, it is possible to control the shape of the ZnO nanostructure by adjusting the pH precursor. The UV-Vis absorbance spectra indicated that the band gap of the prepared samples depends on the morphology of the nanostructures formed.

Acknowledgments

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