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# Optical and Structural Properties of Controlled pH Variation on Zinc Oxide Nanostructured via Hydrothermal Method

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**Abstract.** Zinc oxide (ZnO) had been interested today because of their unique and versatile properties in electronic devices. ZnO nanostructured was synthesized via hydrothermal method by varied the pH value from 7, 8, 9, 10 and 11. The effect of different pH values from 7, 8, 9, 10 and 11 was changed the morphological, structural and optical properties. The samples were examined with Scanning Electron Microscope (SEM), X-Ray Diffraction (XRD) and Ultraviolet- Visible (UV-Vis) spectroscopy. SEM is to observe the morphology images of ZnO nanostructured grains. XRD revealed the detail information on the crystallographic structure and phase formation of the materials. Lastly, UV-vis spectroscopy is to measure the UV absorption for all samples. From SEM result, it had shown that the hexagonal nanorods was obtained at pH 7 and pH 11 whereas nanorods is obtain at pH 8, 9 and 10. XRD revealed that the ZnO nanostructure exhibits the hexagonal wurtzite structure and the average crystallite size of ZnO nanoparticle was calculated. UV-vis spectroscopy shows the absorption of ZnO at 300-373 nm. The resulted show the pH values effect the nanostructured growth of zinc oxide semiconductor properties in the morphology obviously and structured.

## Introduction

Zinc oxide (ZnO) nanoparticles had been highly interested among researchers because of various applications like gas sensors, chemical sensors, biosensors, superconductors, cosmetics, optoelectronic devices, etc [1]. ZnO semiconductor, having a direct wide band gap 3.37 eV and a large exciton binding energy, 60 meV. Its highly preferred due to the multitasking metal oxide and attractive properties [2]. Several physical and chemical procedures had been used to synthesize ZnO such as solution base methods, chemical precipitation, sol gel, hydrothermal, sonochemical, and photochemical reduction techniques are widely used [3]. The problems during synthesizing nanoparticles are stability and aggregation, control crystal growth, morphologies, sizes and distribution are important issues and continue to be solved [2]. Deposition technique had been employed for the synthesis of ZnO nanostructures nanowires, nanobelts, nanobridges, nanonails, nanoribbon, nanorods and nanotubes. The pH of solution appears to be critical parameter for the phase formation, particles size and morphology of the structure during synthesizing process [4]. The properties of ZnO normally depends on the synthesize method and conditions during processing. One-dimensional (1-D) nanostructures which is nanorod are focused mostly on the correlation of nanoarchitecture morphology. Its highly preferred multitasking metal oxide of attractive properties. The optical transparency to visible light of ZnO also provides it an opportunity to replace conventional transparent conductive indium tin oxide [5]. The properties of ZnO normally depends on the synthesis method and conditions during processing. In this paper, we report the synthesize of ZnO nanostructures by various pH values using hydrothermal method. Then, the optical and structural characterization of ZnO nanostructures also shown in this paper.

## Materials and Method

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 achieved homogenization. The pH were 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 180ºC 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 60ºC 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 20º to 90º. The crystallinity and crystal phases were determined by XRD. Samples were observed using scanning electron microscopy (SEM) for surface morphological images using JEOL-JSMIT-100.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.

## Result and Discussion

Fig. 1 shows the X-rays diffraction (XRD) pattern of ZnO nanostructures as a function of increasing pH values. The typical patterns for the ZnO obtained sharp diffraction peaks imply their good crystallinity. The detected (h k l) agreed with [Sambath et al., 2012] peaks were corresponding to lattice planes (100), (002), (101), (102), (210), (103), (212), (201), (202), and (203), respectively. The intensity of (100) and (101) peaks is increases with the pH values at 8, 9 and 10 respectively. Meanwhile, the intensity of (002), (102) and (103) is decreases for value pH 11. This variation of formation at different pH values may due to the morphologies of SEM images. XRD pattern of samples showed at pH value 7 the peaks do not sharp. But when increasing the pH value, the peaks for (101), (002) and (100) revealed the sharp peaks. No impurities are observed in the peaks, indicating high purity of the product.

The crystallite size, D of the structures calculated from XRD pattern was shown in Table 1.0. The D are obtained from the Debye-Scherrer's equation using Eq. 1:

$$D = (k\lambda)/(d\cos\theta) \tag{1}$$

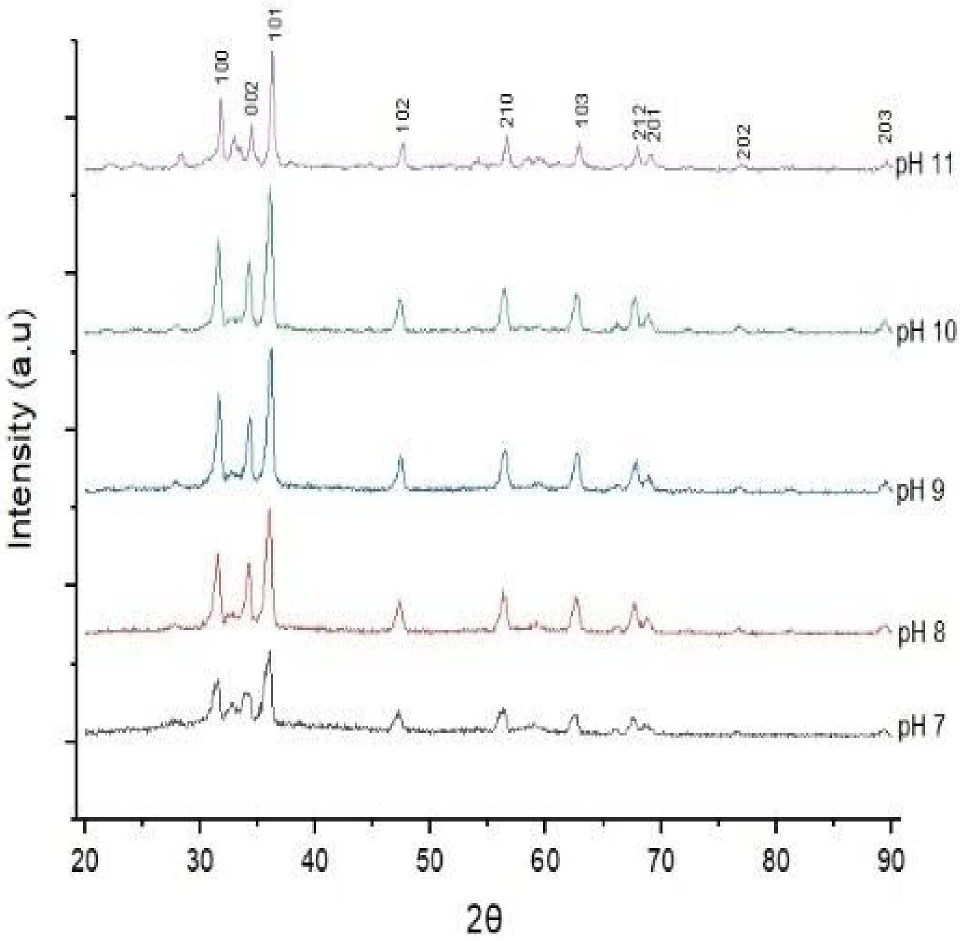


Fig 1 XRD patterns of ZnO nanostructures at different pH values

From the Fig 2, the crystallite size shown increases at pH 8, but pH 9, 10 the D decreases as the function of the pH values increasing for all samples shows. The crystallite size calculated using Eva software seen in Table 1 shown that ZnO trend. The sizes of the crystallite also affected the morphology and UV-vis spectroscopy.

Table 1 Crystallite size of ZnO nanostructures at different pH values

| No | pH value | Crystallite size, D (nm) |
|---|---|---|
| 1 | 7 | 27.33 |
| 2 | 8 | 39.19 |
| 3 | 9 | 31.62 |
| 4 | 10 | 30.18 |
| 5 | 11 | 33.85 |

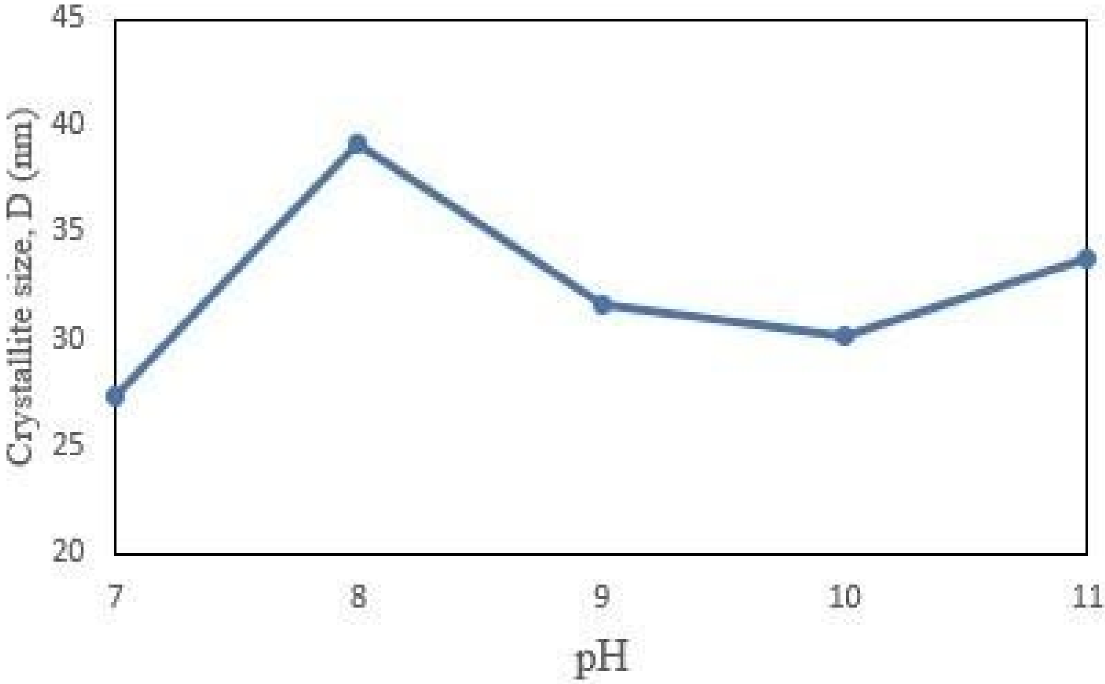


Fig. 2 Crystallite size of ZnO nanostructures at different pH values

The SEM image of ZnO nanostructured at different pH values are shown in Fig. 3. It is observed that the morphology obtained from ZnO was hexagonal nanorod like structure. Fig 3 (a) shows the image of ZnO hexagonal nanorod and agglomerate structure when synthesized at the pH 7. Fig 3 (b),(c), (d) presents the structure agglomerate and no grain boundaries. Grinding and filtration process may cause the agglomeration. Nanorod are one-dimensional (1D) nanostructures have great interest because they have versatile applications such as nanoelectronics devices, photovoltaic system, chemical and bio sensor. In addition, 1-D nanostructures had many valuable properties in which direct band-gap and large exciton binding energy so that easier to fabricate optoelectronic nanodevices.

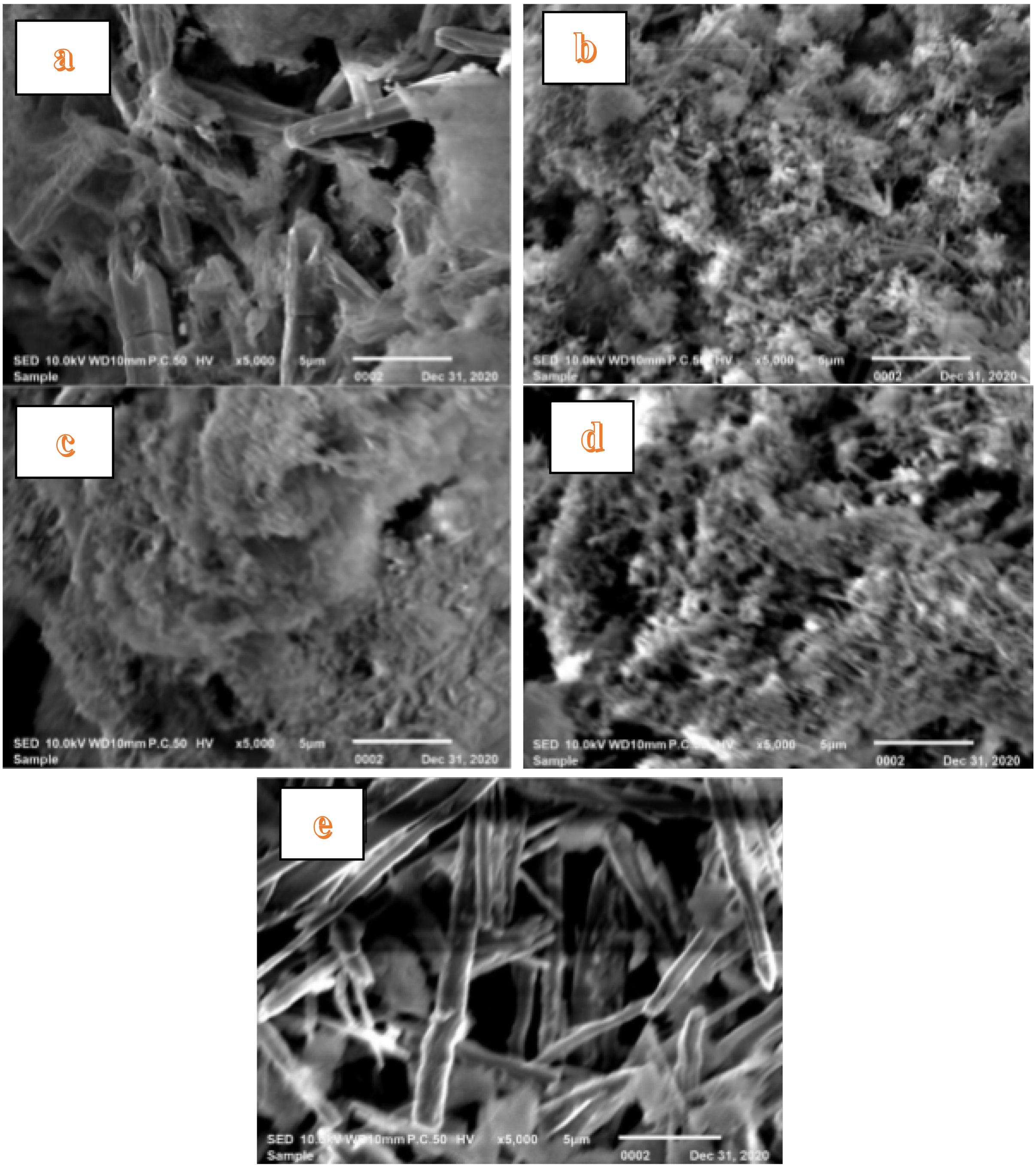


Fig. 3 Micrograph image of ZnO nanostructures at different pH values

The UV-visible absorption spectra for all samples shown in Fig. 4 present a well define absorbance peak around 300- 373 nm. This result can be agreed with Suresh et al., (2015) stated that the UV-vis for ZnO nanoparticles is at 370 nm. Almost all the visible spectrum radiation are transmitted by the ZnO nanoparticles. The absorption below 400 nm is assigned to the intrinsic band gap absorption of ZnO, due to electron transitions from the valence band to the conduction band [5]. The band gap energy can be determined by extrapolation to the Tauc Plot relation in Eq 2.

$$(\alpha h\nu)1/n = A(h\nu - Eg) \quad (2)$$

The intensity of the absorbance is started to increase from pH 7, 8, 9 and 10 around 370 nm while when it comes to pH 11 the peak is decreasing until 333 nm. This may be affected by the different pH condition that used for synthesized the nanostructured

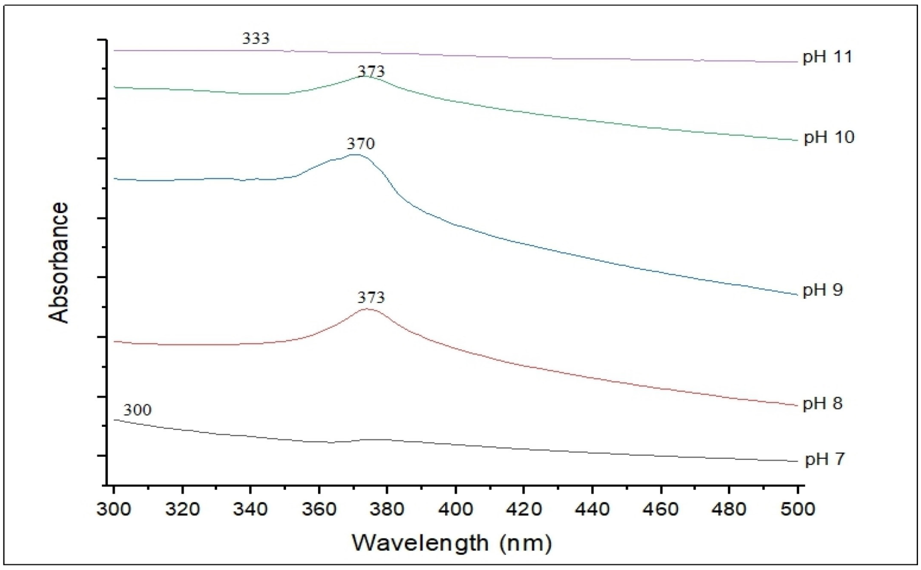


Fig. 4 UV vis spectrum of ZnO nanostructures at different pH values

## Summary

ZnO nanostructured were synthesize by hydrothermal method. The XRD examination verified the production of wurtzite shape nanostructured. SEM images confirm the formation of granular ZnO nanostructures. The absorption peak is found to be at 373 nm for pH 8 and pH 10. The growth of ZnO nanostructured is a compatible and promising in semiconductor devices. ZnO obviously are highly demand because of the achievement versatile properties.

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