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Structural and Optical Properties ZnO Nanorods Prepared by Hydrothermal Method

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ZnO nanorods were synthesized in the presence of cationic surfactant N-cetyl-N,N,N-trimethyl ammonium bromide (CTAB) at 180 °C using hydrothermal method with zink nitrate tetrahidrate and ammonia as starting materials. The synthesis sample was calcinations at three different temperatures of 300, 500, and 700 °C for 2 h, respectively. Structural and optical properties are studied by using X-ray diffractometer (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), and Ultrasonic Violet Visible (UV Vis). XRD results indicate the formation of pure phase hexagonal wurzite, crystalline size maximum in 700 °C calcination temperature. SEM results indicate the particle size decrease with increase in calcination temperature to 700 °C. The TEM micrograph shows the presence of ZnO nanorods with diameter around 77 nm. Optical properties by UV Vis analyzed show that band gap values increase with the increase in calcination temperature, high transmittance values are observed by increasing the calcination temperature, and low reflectance observed by increases the calcination temperature.

Keywords: ZnO nanorods, CTAB, Hydrothermal, Calcination, Optical properties.

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1. INTRODUCTION

Zink oxide (ZnO) is a unique material with a direct band gap (3.37 eV) and large exction binding energy of 60 meV [1, 2]. In recent years, one dimentional (1D) nanostructures in the form of nanorods, nanowires or nanotubes, appear as an exciting research area for their great potential of addressing space-confined transport phenomena as well as application in nano devices [3]. There are various methods for synthesis of ZnO nanorods, like sol gel [4] and hydrothermal [5]. Hydrothermal is one of the most common and promising methods for the synthesis of isometric zinc oxide crystals. This method enjoys advantages such as a one-step synthesis without any additional process like calcinations and milling; low level of aggregation, high purity, nonpolluting, inexpensive and narrow particle size distribution. Moreover the hydrothermal method, due to the low-temperature reaction in water under a sealed environment is consistent with the green chemistry. The only drawback is that the products prepared in aqueous solution are usually poor in terms of shape and size control. Fortunately, surfactants coupled with hydrothermal method are able to modify the surface chemistry of nanomaterials by changing their hydrophobic or hydrophilic properties. Therefore, the desired size and shape can be tailor-made [5].

In the present paper, we have prepared ZnO by additing a cationic surfactant like N-cetyl-N,N,N-trimethyl ammonium bromide (CTAB) by simple and inexpensive hydrothermal method to be able promote the formation of ZnO nanorods. Effect of calcination on structural and optical properties of ZnO nanorods were investigated.

2. DETAIL EXPERIMENTAL

ZnO nanorods were synthesis similar to our previous work with little modification [6]. In a typical procedure, $Zn(NO_3)_2{\cdot}4H_2O$ was dissolved in 100 ml of deionized water to make 0,1 M of $Zn(NO_3)_2$ solution. Ammonium hydroxide was added to this solution until gain pH 7, followed by vigorous stirring for 1 h. A white precipitate ($Zn(OH)_2$) was produced which was collected by centrifugation and washed thoroughly with deionized water. Then the precipitate was transferred into 100 ml water containing of CTAB (Aldrich) and changed in a 100 ml capacity autoclave with Teflon liner. Hydrothermal reaction was carried out at 180 °C for 24 h. After reaction completely, it was cooled to room temperature and powder collected by centrifugation. Powdered sample was thoroughly washed with deionized water and ethanol. The final product was taken and dried at 80 °C for 12 h. Finally, sample was calcination in furnace at temperature 300, 500, and 700 °C.

3. RESULT AND DISCUSSION

3.1 X-Ray Diffraction

Fig. 1 shows the XRD pattern of the product. The recorded XRD spectra clearly indicate that the hydrothermal ZnO begin to crystallize even at the low temperature calcination at 300 °C. All of the diffraction peaks can be indexed within experimental error as hexagonal ZnO phase (Wurtzite structure) with lattice constants $\alpha = 3.253$ Å and $c = 5.215$ Å by comparison with the data from ICSD cards No. 67848 with $2\theta = 36.52°$[101]. The strong and narrow diffraction peaks indicate that the material has a good crystallinity and size [7]. By increasing in calcination temperature, intensity of diffraction peaks of ZnO was increased, which indicated by strengthening of ZnO phases [8].

As the calcination temperature increases, the nanoparticle crystallite size increases, since the energy that needed to the atoms arranges itself into the same larger

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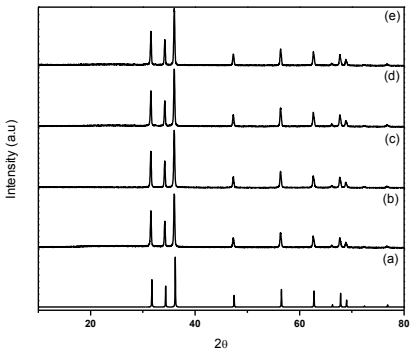

Fig. 1 – XRD patterns of ZnO calcined at different temperature (a) ICSD N0. 67848 (b) before calcination, after calcinated at (c) 300 °C (d) 500 °C (e) 700 °C

Table 1 – Average crystallite size of ZnO obtained from XRD

Calcination temperature (°C)	Crystallite size, D (nm)
Before calcination	35,387
300	36,632
500	36,357
700	37,480

crystalline plane is high and produce high crystal size [Table 1]. Crystallite size for ZnO nanorods was calculated using Debye-Scherer formula given in Eq. 1 [9]. Increased calcination temperature has an impact on increasing crystallite size.

$$D = \frac{k\lambda}{B\cos\theta}, \quad (1)$$

where B is full width at half maximum (FWHM), k is constant of proportionality, λ is the X-ray wavelength and θ is the Bragg's diffraction angle.

3.2 Scanning Electron Microscopy (SEM)

Fig. 2 shows the SEM micrograph of ZnO prepared with CTAB under calcination treatment. The existence of a rod-like structure is with a μm scale diameter, but its size decreases with increasing calcination temperature.

Calcination treatments show that it is evident that these rods are united by the clusters. There are also a visible number of secondary structures grown on the surface of ZnO products and these would also be a potential contributor for all the blue shift emission in the UV spectrum, a result confirmed already in our UV absorption spectrum. This result is in accordance with the results of previous research [10].

3.3 Transmission Electron Microscopy (TEM)

Fig. 3 shows that before and after calcination that the as prepared exhibits rod-like. The nanorods mostly appear as distinct rods without bending and agglomeration was minimized to a larger extent, which implies that the ZnO nanorods were grown from spontaneous nucleation with high crystal perfection. This result is in accordance with the results of previous research [11]. Diameter of nanorod in the synthesis present is 69-85 nm. Maiti et al [12] and Sun et. al. [13], have same reported the formation of ZnO nanorods diameter is 70-100 nm.

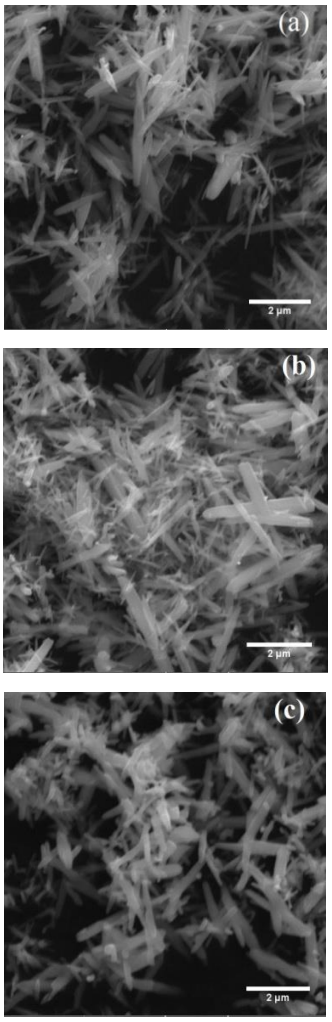

Fig. 2 – SEM image of ZnO nanorods calcinated at (a) 300 °C (b) 500 °C (c) 700 °C

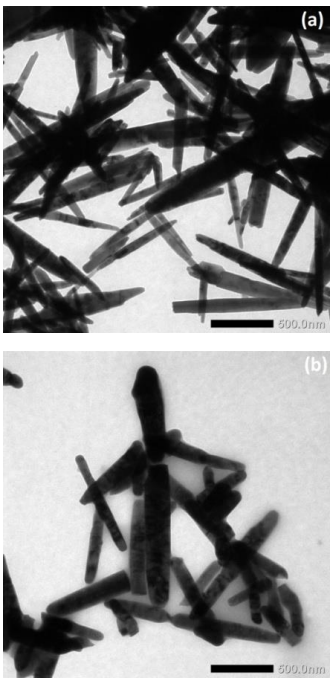

Fig. 3 – TEM image of ZnO nanorods (a) before calcination (b) calcinated at 700 °C

3.4 Surface Area Analyzer

Calcination treatment shown surface area of zink oxside crystal. It is due to the pore that was originally contained template will be opened, so the surface area will increase. The increasing of surface area is not slightly which only about 7 m^2/g (Table 2).

Table 2 – Surface area ZnO nanorods before and after calcination (BET method)

ZnO Nanorods	Surface Area (m^2/g)
Before calcination	14,794
Calcination of 700 °C	21,734

3.5 Optical Properties

The optical properyies studies are performed to evaluate the potentially useful optical qualities of the ZnO nanorods. UV Vis absorption spectrum prepare by different calcination temperature conditions is shown in Fig. 4. Absorption material ZnO nanorods is in range 330-390 nm. There is a significant blue shift in the excitonic absorption for ZnO nanorods with calcination temperature. The blue shift in the exciton absorption indicates the quantum confinement effect has depend on the change of the width or diameter [7].

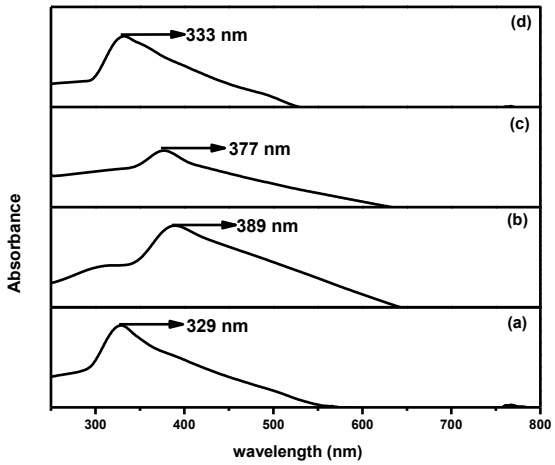

Fig. 4 – Spectrum absorbance of ZnO nanorods (a) before calcination, calcinated at (b) 300 °C (c) 500 °C (c) and (d) 700 °C

Determination of band gap energy value using Tauc Plot method by drawing linear line on ploting $(\alpha h\nu)^2$ with photon energy $(h\nu)$ $(y = 0)$. The photon energy symbolized by $h\nu$ and from the α function can be plotted in the area around the semiconductor energy gap in the graph whose vertical axis $(\alpha h\nu)^2$ and the flat axis are hv.The calculation result of band gap value, E_g was 2.5-2.6 eV (Fig. 5). Band gap ZnO in the present work is observed to be greater than that of bulk ZnO, that might be attributed to the smaller particle sizes as compared to bulk material. The band gap value ZnO bulk are 3.324 eV [10].

Fig. 6 shows transmittance of ZnO nanorods. It was observed that transmittance of ZnO nanorods increased with the increase of calcination temperature. This can be explain due to the formation of smaller crystallites [14] as observed in XRD data. Maximum transmittance was observed for sample calcined at 700 °C.

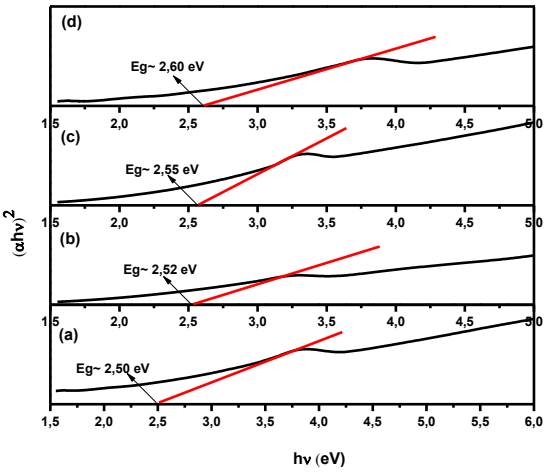

Fig. 5 – Band gap energy estimation of ZnO nanorods before calcination (a), calcinated at 300 °C (b), 500 °C (c), and 700 °C (d)

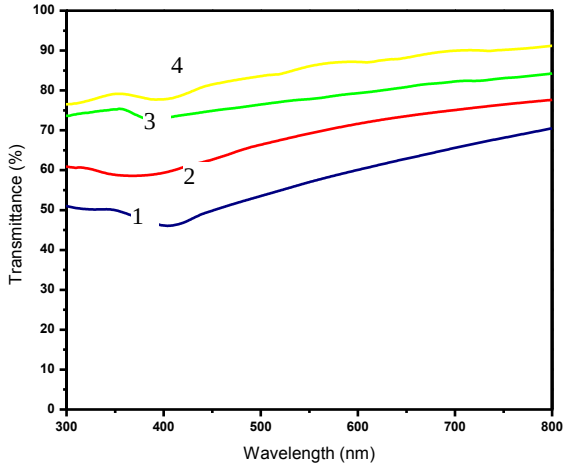

Fig. 6 – Spectrum transmittance material ZnO nanorods before calcination (1); calcinated at 300 °C (2); 500 °C (3); 700°C (4)

Fig. 7 shows reflectance of ZnO nanorods. It was observed that reflectance of ZnO nanorods decrease with the increase of calcination temperature.

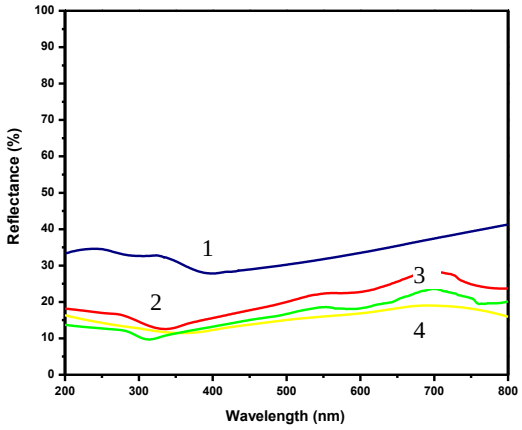

Fig. 7 – Spectrum reflectance material ZnO nanorods before calcination (1); calcinated at 300 °C (2); 500 °C (3); 700 °C (4)

4. CONCLUSIONS

ZnO nanorods were successfully synthesized by a simple hydrothermal and calcinated at different tem-

perature 300, 500, and 700 °C in order to study the effect of calcination on structural and optical properties of ZnO. XRD result showed formation of hexagonal wurzite structure of ZnO with increased crystallinity. Increased calcination temperature has an impact on increasing crystallite size. The calculation result of band gap value, Eg was 2.5-2.6 eV. High crystalline size decreases reflectance and increases transmittance.

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