

Photoluminescence and Structural Properties of ZnO Nanorods Growth by Assisted-Hydrothermal Method

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ABSTRACT

Semiconducting zinc oxide (ZnO) nanorods were obtained in bulk quantity by an hexamethylenetetramine (HMTA)-assisted hydrothermal method at low temperature (90°C) with methenamine ((CH₃)₆N₄) as surfactant and catalyst and zinc nitrate Zn(NO₃)₂·6H₂O as Zn source. The structure and phase of ZnO nanorods were studied using X-ray diffraction (XRD) and high resolution transmission electron microscopy techniques (HRTEM). The morphology of the nanostructures was studied by scanning electron microscope (SEM) method. The photoluminescence (PL) properties were investigated founding two emission bands under UV excitation.

Keywords: ZnO; Nanorods; Assisted-Hydrothermal Method; Photoluminescence

1. Introduction

Zinc oxide is one of the oldest metallic oxides semiconductors studied because its important optical and electronics properties such as: a wide band gap (3.37 eV) and high exciton binding energy (60 meV), moreover, these properties can be utilized in several ZnO complex nanostructures to the fabrication of blue emitting lasers [1], transparent semiconductors [2,3], piezoelectric devices [4], short-wavelength light emitting devices [5], blue emitting LEDs [6], chemical sensors [7], solar cells [8], magnetic structures [9], etc. ZnO in varied complex forms has been synthesized by several methods such as chemical vapor deposition on pure Si substrate [10], low-temperature wet-chemical methods [11], thermal evaporation [12], hydrothermal synthesis [13,14], rf magnetron sputtering [15,16], molecular beam epitaxy [17,18], pulsed-laser deposition [19,20]. Actually, many complex nanostructures of the Zinc oxide semiconductor (ZnO) has been synthesized by different methods such as nanocombs [21,22], nanorings [23], nanohelices/nanosprings [24,25], nanobelts [26], nanocages [27], flower-like [28], and nanorod-like systems [29-32], this last class of nanostructures are the best system for understand the transport mechanism in one-dimensional (1D) materials,

so as for developing news nanodevices wit best properties and performance. There exist various methods to obtain nanorods such as: vapour-liquid-solid (VLS) process [29,33,34], anodic alumina template [35], metal-organic vapor-phase epitaxial growth (MOVPE) [36,37], thermal evaporation method [31,38-41], spray pyrolysis technique [42], thermal decomposition reaction in solvent [43], micro-emulsion growth [44], and soft chemical method [45,46], this last method with low-cost, let a effective control of the variables that announce in the 1D ZnO nanoscale materials synthesis, it is necessary to the preparation of small diameter nanorods (diameter < 100 nm) used in the obtaining of nanodevices with goods properties opto-electronics. In this work, by means of an soft chemical assisted-hydrothermal method, ZnO nanorods were synthesized at low temperature (90°C) using as source materials Zinc Nitrate Zn(NO₃)₂·6H₂O as Zn source and methenamine ((C₆H₁₂)N₄) as surfactant and catalyst.

2. Experimental Details

2.1. Materials

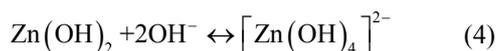
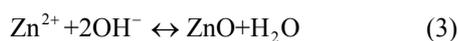
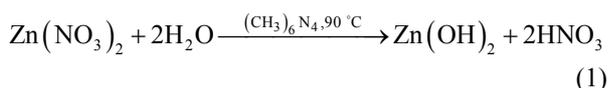
The chemical reagents used in this research were analytic reagent grade (Sigma-Aldrich) and used as received without further purification.

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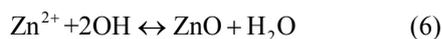
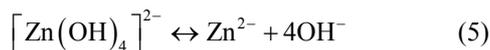
2.2. Preparation of Nanorods Nanostructures

Reaction Mechanism

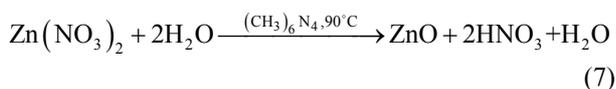
The solution precursor was prepared using zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) as Zn and O sources and hexamethylenetetramine $[(\text{CH}_3)_6\text{N}_4]$ as surfactant and catalyst under the hydrothermal reaction mechanism proposed by Zhung and coworkers [47], which found that the $[\text{Zn}(\text{OH})_4]^{2-}$ radical play a important role in the ZnO nanorods assisted-hydrothermal synthesis, merely, the $[\text{Zn}(\text{OH})_4]^{2-}$ radical produce ZnO nanorods under the chemical reactions follow:



Finally, the growth unites of $[\text{Zn}(\text{OH})_4]^{2-}$ radicals produced in reaction (4) under the dissolution-nucleation cycle produce ZnO nanorods by means of Equations (5) an (6) follow:



A resumed equation can be obtained to effect of stoichiometric calculus as follow:



The chemical Equation (7) was used to obtain 1 g of ZnO powder, merely, the solution reaction was prepared by dissolving 2 g of Zinc nitrate and 1.5 g of methenamine in deionized water under vigorous stirring

at 50°C for 1 h to form a 0.01 M equimolar solution, then the reaction solution was heated at 90°C for 2 hours. After 20 min it was observed a white ZnO powder precipitated on the flask bottom. Finally, the ZnO white powder were thoroughly washed with deionized water and allowed to dry in air at room temperature.

3. Characterization

The ZnO nanorods thus obtained were further characterized structurally by X-ray diffraction (XRD) technique using a SIEMENS D 5000 diffractometer using the $\text{CuK}\alpha$ (1.5406 Å) radiation, with a scanning speed of 1° per min at 35 KV and 30 mA. The single-crystal structure of the ZnO nanorods was observed using a JEOL FAG 2010 Fast TEM electron microscopy with a 2.1 Å resolution (point to Point), the morphology was studied using a JEM5600-LV scanning electron microscopy (SEM), the room temperature photoluminescence (PL) spectra were performed using a He:Cd laser with a wavelength of 328 nm.

4. Results and Discussion

Figure 1 shows the XRD pattern of the ZnO nanorods prepared by the HMTA assisted hydrothermal method, the diffraction pattern correspond to the ZnO with wurtzite structure (hexagonal phase space group $\text{P6}_3\text{mc}$). All of the diffraction peaks of the samples were indexed to the hexagonal phase of ZnO having lattice parameters $a = 3.249$ and $c = 5.206$ Å card No (JCPD file No. 36-1451) in good agreement with the data from the Join Committee of Powder Diffraction Standards (JPDs). No other diffraction peaks from $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Zn}(\text{OH})_2$ or other impurities have been found in the samples.

Figure 2 shows the morphology of the ZnO nanorods obtained by means of scanning electron micrographs SEM, **Figures 2(a)** and **(b)** are a top view of the ZnO nanorods, which show that the product is formed by crystals with rod-like a uniform diameter of about 400

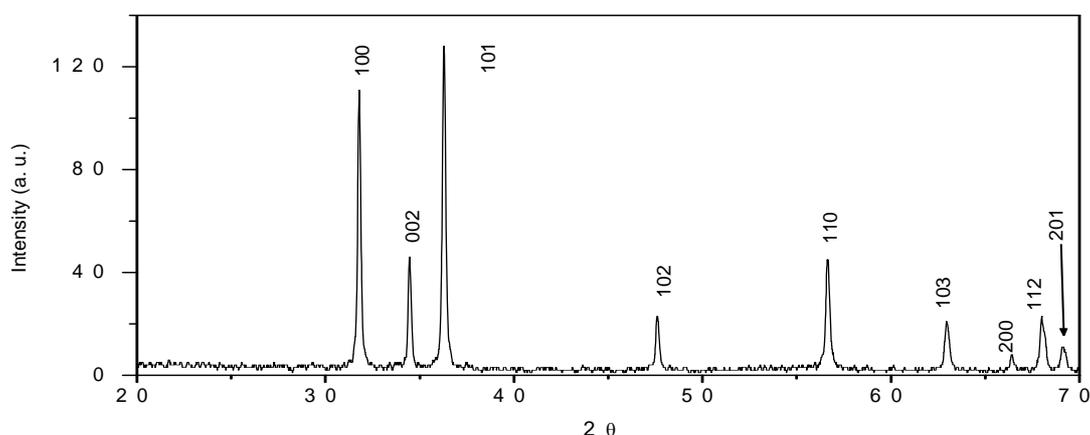


Figure 1. Diffraction pattern of the nanorods ZnO nanostructures.

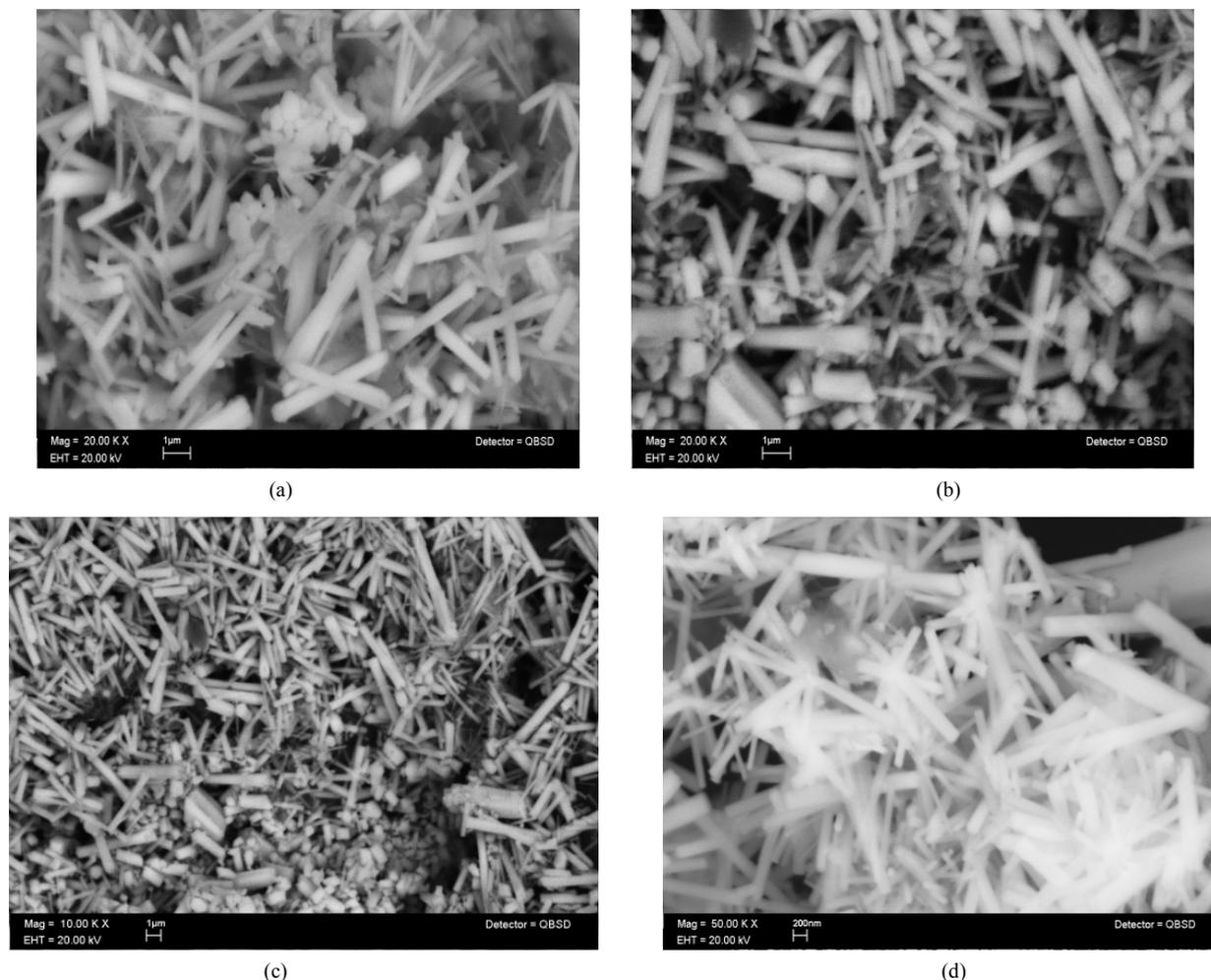


Figure 2. (a) and (b) low and (c) and (d) high-magnification SEM images of ZnO nanorods.

nm and lengths of 4 μm . From the amplified SEM image shown in **Figures 2(c) and (d)** can see the hexagonal cross section of the nanorods structures, highly dispersed and without any aggregation between them. This results are in good agreement with the results obtained by Zhang and Narges [48,49].

Figures 3(a) and (b) show the selected area electron diffraction (SAED) pattern and HRTEM image of a nanorod respectively. As can be see, this results show a good crystalline quality of the obtained material, which is consistent with the before XRD result obtained in **Figure 1**. The (SAED) pattern showed in **Figure 3(a)** reveal that the nanorods have a single crystal hexagonal structure without dislocations. The HRTEM image reveals that the nanorods preferably growth along the [002] direction (c axis), however, the image also reveals that the interplanar spacing (d) in the crystalline nanorods is 0.26 nm, which represent the distance between [002] planes of the hexagonal ZnO phase.

Figure 4 shows the room temperature photoluminescence (PL) measurement of the ZnO nanorods, the

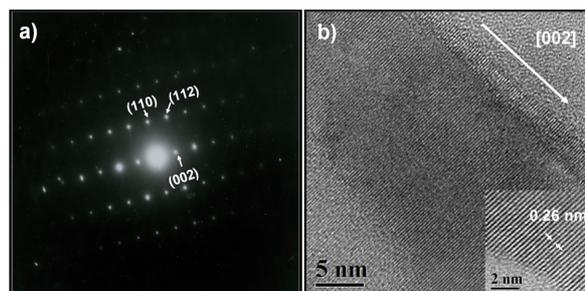


Figure 3. (a) Electron diffraction pattern from a single nanorod. (b) HRTEM image of a nanorod. The nanorod grows along [002] direction.

ZnO emission spectrum was obtained using the laser line with a wavelength of 358 nm from an He:Cd laser as the excitation source, the emission spectrum presents the two typical emission bands centered the first about 380 nm and the second with a maximum centered between 500 and 530 nm; the first band is a exciton emission band in the UV region and is caused by the radiative annihilation of excitons, the second is an intense band in the green

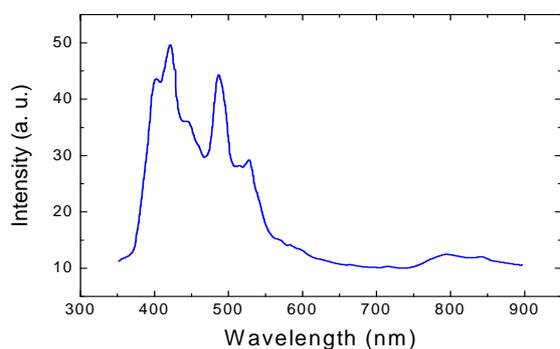


Figure 4. Spectrum of photoluminescence of the ZnO nanorods under 358 nm excitation.

region of the visible spectrum produced by the radiative recombination of an electron from a level in the conduction band and an deeply trapped hole in the bulk (V_o) of an ZnO particle [50,51]. However, **Figure 4** shows that the intensity of the band visible is less than the intensity of exciton band, this is caused by an effect of particle size as proposed by Van Dijken, which establish that as the size of the ZnO particles increases the intensity of visible emission decreases and the intensity of exciton emission increase [52]. In this case, from **Figure 2** the ZnO nanorods size (4 μm in length and 400 nm of diameter) is bigger than Dijken particles resulting thus in an decreasing of the intensity of green visible respect to that of exciton emission.

5. Conclusions

In this work ZnO nanorods were synthesized by the methenamine assisted-hydrothermal method at 90°C using Zinc nitrate as precursor and hexamethylenetetramine as surfactant and catalyst.

The analysis SEM revealed that the ZnO nanorods have a diameter of 400 nm and length about 4 μm .

The studies of SAED pattern and HRTEM image made on the nanorods obtained revealed that this material presents an wurtzite structure and all diffraction peaks were indexed to the hexagonal ZnO phase, having lattice parameters $a = 3.249$ and $c = 5.206$ Å. Also, from the same studies it is concluded that the nanorods growth along the [002] direction, and the interplanar distance is 0.26 nm.

The photoluminescence spectrum taken to the ZnO nanoros shows two bands: the first is an exciton emission band in the UV region centered at 380 nm. The second is an intense band in the green region with a maximum in between 500 and 530 nm.

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