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Microwave-assisted hydrothermal synthesis and characterization of ZnO nanorods

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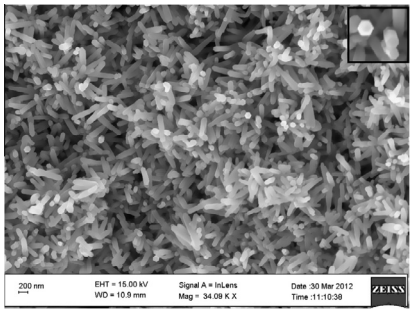
HIGHLIGHTS

- ZnO nanorods of wurtzite phase were synthesized by microwave-assisted hydrothermal route.
- The optical parameters were studied using Kubeleka–Munk approach.
- The obtained optical band gap of the studied sample is 3.17 eV.
- The electrical conductivity mechanism is controlled by thermally activated process.

GRAPHICAL ABSTRACT



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ABSTRACT

For the purpose of this study, the nanorods of zinc oxide were synthesized by rapid microwave-assisted hydrothermal route. The microstructure and surface morphology of the sensitized nanorods were characterized by X-ray diffraction (XRD), field emission scanning electron microscope (FE-SEM) and transmission electron microscope (TEM). XRD results indicate that synthesized ZnO nanorods have wurtzite phase. The calculated value of the particle size using Debye Scherrer formula and Williamson Hall plot was found to be 20–28 nm and 35.3 nm, respectively. Low uniformity distribution of rod-like morphology (60–80 nm in diameter and average length about 250 nm) are seen in TEM micrographs. The optical parameters of the prepared ZnO nanorods have been calculated using Kubeleka–Munk approach for the UV–vis diffuse reflectance spectrum. It is found that the direct transition optical band gap of the studied sample is 3.17 eV. The direct current electrical conductivity (σ) was increased from 6.7×10^{-8} to 3×10^{-7} Ω^{-1} cm^{-1} with increasing the temperature (T) in the range (300–425 K). The obtained variation of σ with T refers that the conductivity mechanism is controlled by thermally activated process.

Introduction

Zinc oxide (ZnO) is a wide band-gap II–VI semiconductor that has attracted resurgent interest as an electronic material for numerous applications. It has attracted much research interest

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for their unique optical, acoustic, luminescent, electronic and optoelectronic properties. In recent years, many methods have been used to synthesize ZnO material as one-dimensional (1D) nanostructures with different morphologies including nanowires, nanorods, nanoneedles, nanorings, quantum dots and other superstructures [1–8]. The unique properties derived from the unique morphologies would open up new opportunities for ZnO nanomaterials to be used as utilized in various functional devices [9].

ZnO nanomaterials can be synthesized by several well-established synthesis methods, such as sol–gel [10], spray pyrolysis [11], sputtering [12], hydrothermal [13], solvothermal [2] and others. In most cases, the high synthesis temperature leads to the formation of strong aggregates in the ZnO nanomaterials, which subsequently have to be excessively milled resulting in poor control of particle morphology and size distribution [14]. Among of the various synthesis methods of nanomaterials; the hydrothermal technique has several advantages over others synthetic methods, among which are: the one-step synthesis without high temperature calcinations and milling, low aggregation levels and narrow crystallite size distributions, in addition to high purity and excellent control of particle morphology and size [14]. Recently, the hydrothermal microwave-assisted synthesis has attracted wide interests as a novel heating model in material science due to its various advantages including normal atmospheric pressure reacting, short reaction time, rapid heating, low reaction temperature, homogeneous thermal transmission, and the phase purity with better yield [15–18].

In this respect, by considering both the advantage of hydrothermal and microwave-assisted methods, this work focuses on the preparation of ZnO nanorods using microwave-assisted hydrothermal synthesis route. Optical parameters such as; optical energy gap, refractive index and the both parts of complex dielectric constant were studied using Kubeleka–Munk approach for the UV–vis diffuse reflectance spectrum. Moreover, the variation of direct current conductivity with temperature for the synthesized ZnO nanorods were studied.

Experimental procedure

Materials and synthesis

Zinc acetate dehydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$, ⩾98%), sodium hydroxide (NaOH, ⩾98%) and absolute ethanol (CH_3CH_2OH, ⩾99.5%) were purchased from Aldrich. All chemicals were used without further purification.

In a typical one-pot synthesis of ZnO using microwave-assisted hydrothermal method, 5.01 mM of $Zn(CH_3COO)_2{\cdot}2H_2O$ was completely dissolved in 10 mL of distilled water, and then 120 mM NaOH was slowly added into the solution and stirred to form a transparent solution. After adding 100 mL ethanol into the solution, the mixture was loaded into a teflon container. Subsequently, the mixture was radiated (400 W, 100%) at 140 °C for 45 min in a microwave oven (CEM MARS-240/50, frequency 2.45 GHz, maximum power 1600 W), and then cooled at room temperature. The precipitate was filtered and washed with distilled water for several times. Finally, the obtained white solid product was dried in a vacuum furnace at 70 °C for overnight.

Characterizations

The crystal structure of the nanopowders was characterized by a Bruker AXS D8 X-ray diffractometer using Cu K_α radiation (λ = 1.5418 Å) at power of 1600 W (40 kV, 40 mA). The morphology and microstructures of the obtained particles were characterized by transmission electron microscope (TEM), of type JEOL-JEM-1011 operated at 300 kV. Samples for TEM were prepared by air-drying a drop of a dispersed as-product powder in ethanol onto a carbon mesh and then covered with thin film of platinum. Also, field-emission scanning electron microscope (FE-SEM, Zeiss/Supra 55) was used to investigate the morphology of the synthesized samples. Whereas, the elemental analysis of the synthesized nanopowders was checked by energy dispersive X-ray spectroscopy (EDX) unit attached to the FE-SEM. The diffuse reflectance spectrum of the investigated sample was performed using Shimadzu UV–VIS-NIR 3600 spectrophotometer with an integrating sphere attachment. The two-probe method was employed to measure the direct current (dc) conductivity of ZnO nanorods pellet sample. The pellet sample was obtained by applying 5 ton cm^{-2} pressure to form a circular disc with a thickness of about 0.557 mm and a diameter 6.5 mm. The dc conductivity was measured as a function of temperature using Keithley-6517A electrometer. The temperature was controlled using a Lakeshore 331 S temperature controller.

Results and discussion

Structural and morphological characterization of the synthesized ZnO nanostructures

XRD pattern of the prepared ZnO nanopowder sample is shown in Fig. 1. All the diffraction lines are assigned well to wurtzite phase corresponding to the standard crystallographic data in the reference pattern (JCPDS 36-1451), indicating that the synthesized powder was a single phase. In order to calculate the crystalline size (D) of the prepared powder, one can use the value of full width at half maximum (FWHM) for the obtained diffraction peaks using the following known Debye Scherrer equation [19,20]:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \tag{1}$$

where λ, β and θ are the X-ray wavelength, FWHM of the diffraction peak and the Bragg diffraction angle, respectively. The estimated particle size using Debye Scherrer equation for all recorded diffraction lines emerges that the investigated ZnO powder in nano-size between 20 and 28 nm. Whilst, the corresponding value of D for the maximum intensity peak (101) was found to be 28 ± 3 nm.

Although of the Debye Scherrer method is a well known method that uses XRD patterns to predict the crystal size based on FWHM of the diffraction peak, it has not taken in account

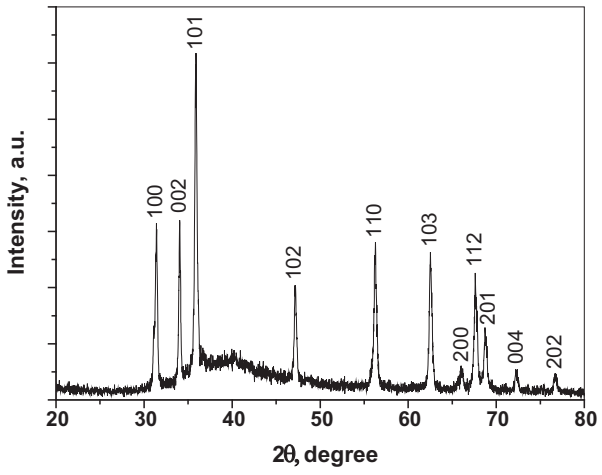

Fig. 1. XRD pattern of the ZnO sample synthesized by microwave-assisted hydrothermal technique.