

Preparation and Characterization of ZnO Nanoparticles by Simple Precipitation Method

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Abstract

The present study has devoted to prepare and investigate the physical properties of ZnO nanoparticles (ZnO NPs) by using precipitated method. Formation of the ZnO NPs was confirmed by the appearance of peak with maximum intensity around 380 nm. In addition, the properties of the developed ZnO NPs have been investigated with the aid of many analytical techniques including scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared (FTIR), and UV-Vis spectroscopy. The obtained ZnO NPs were spherical with average size of 21.8 to 32.5 nm. Moreover, the obtained results revealed that the prepared ZnO NPs used in various applications.

Keywords: ZnO NPs, simple precipitated method, SEM, XRD, FTIR, UV, band gap.

Introduction

In recent years, Semiconductor nanoparticles has gained a great attraction because of their desirable chemical and physical properties. Also it has several applications in different fields. Zinc oxide (ZnO) semiconductor, which is one of the most studied nanoparticles, has many significant properties; such as strong room temperature luminescence, high electron mobility, wide band gap, and good transparency. Tuning the surface topography of ZnO layer can be achieved by changing the fabrication conditions, including precursor content, temperature and pH[1]. The applications of zinc oxide powder are numerous due to its novel properties such as piezoelectric nanogenerator[2], nanosensors[3], UV sensors[4], gas sensors[5], solar cells [6-7], photovoltaic applications[8], biochemical imaging applications[9], photocatalysis[10], food packaging applications[11], and in water media[12]. There are different methods of ZnO nanostructure fabrication such as direct and simple precipitate[13-14], wet chemical method[15-16], thermal deposition[17], one step surfactant assisted technique[18], hydrothermal[19], sol-gel method[20], aqueous chemical route[21], pulsed laser deposition[22], electrochemical deposition[23], and self-assembly method[24]. The present study was aiming to investigate the ZnO nanoparticles prepared by a simple precipitated method at different calcinated temperature. The prepared nanoparticles were

characterized by ultra violet (UV), infrared (IR) spectroscopy, scanning electron microscope (SEM) and X-ray diffraction (XRD). The band gap was also calculated from UV spectroscopy.

Experimental

Materials

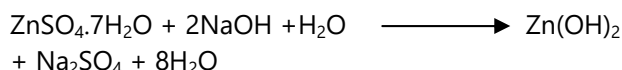
Zinc sulfate hepta-hydrate (Alfa Aesar, Germany), Sodium Hydroxide (El Nasr pharmaceutical chemical co. Egypt) and Deionized water is used for prepare ZnO nanoparticles .

Methods

Preparation Method of ZnO NPs

ZnO NPs were prepared via precipitation method; this method is relatively easy in preparation and cheap. This process was carried out by using zinc sulfate hepta-hydrate was completely dissolved in deionized water using magnet stirrer, sodium hydroxide is also dissolved in deionized water. The two aqueous solutions with molar ratio (1:2) were added to each other slowly drop by drop under continuous stirring at room temperature ($T=303$ K) for one day. Then, the white precipitate was collected, filtered and washed several times with deionized water. It was dried at air oven at 363-368 K for two days, and then grounded to a fine powder using agate mortar. The resulting fine powder was calcinated at different temperatures (273, 473, 673,

873, 1073, 1173 and 1273 K) for 2 hr, then ground for the second time.



Instrumental analysis

UV-Visible spectrophotometry

The UV-Visible spectra of the prepared ZnO NPs were measured in the spectral range of 200-800 nm using ATI Unicam double beam UV-Vis. Spectrophotometer supported by vision software V3.20. The analysis was performed at room temperature ($T=303$ K) with quartz cuvettes (1 cm optical path), and the blank was the corresponding distilled water with 0.5 ml acetic acid.

Fourier transform infrared (FTIR) spectroscopy

The FTIR spectra of the developed ZnO NPs were recorded at 303 K using Nicolet iS10 single beam spectrometer in the range of $4000\text{--}400\text{ cm}^{-1}$ at a resolution of 8 cm^{-1} . The ZnO NPs powder was compressed into a disk, and then placed into the sample holder of the spectrometer.

Morphological characterization

The morphology of the resulting nanoparticles was studied by using scanning electron microscope (SEM) (JEOL JSM 6510 Iv) operate under high vacuum, the samples used as nanoparticle powders.

X-Ray Diffraction (XRD)

The X-ray diffraction patterns of the selected ZnO NPs samples were obtained using Philips PW 1390 X-ray diffractometer. The X-ray diffraction was provided with a beam monochromator and Cu $K\alpha$ radiation at $\lambda = 1.5406\text{ \AA}$. The applied voltage was 40 kV and the current intensity was 40 mA.sec. The 2θ angle was scanned in the range of 4 to 70° , and the X-ray runs was carried out at scanning speed of $2\theta = 2^\circ/\text{min}$. The nanoparticle size was calculated by using the Debye-Scherrer equation ($D = 0.9 \lambda / \beta \cos(\Theta)$) from X-ray at different calcinated temperatures and confirmed by SEM. The crystallinity of the developed samples was also calculated with the aid of origin8 software from the area under the peak in XRD pattern.

Results and discussions

UV spectroscopy

The formation of ZnO NPs was confirmed with the aid of UV-vis spectra of the samples as shown in Figure 1. All the samples have strong absorption maximum below 400 nm [12]. The optical absorption of ZnO nanopowders calcinated at different temperatures (273, 473, 673, 873, 1073, 1173 and 1273 K) shows A strong absorption peaks at 384.6 nm, 381 nm, 384 nm, 383.5 nm, 382.5 nm, 386 nm and 384 nm respectively. It is ratio that, increasing the calcinated temperature of ZnO samples make shift to lower wavelength except sample at 1173 K. The band gap energy of the samples are measured by the extrapolation of the linear portion of the graph between the modified Kubelka-Munk function $[\alpha h\nu]^2$ versus photon energy ($h\nu$) [25], as shown in figure 2 and table 1.

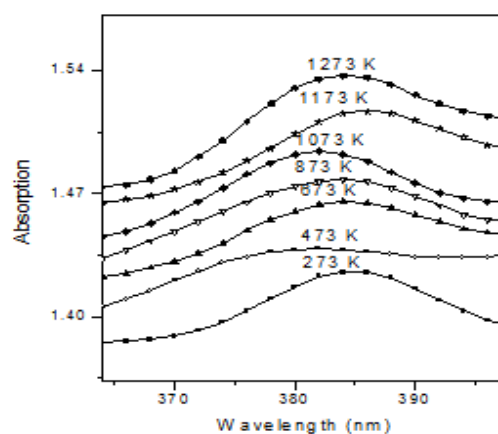


Fig.1. UV-vis spectra of ZnO calcinated at different temperatures (273, 473, 673, 873, 1073, 1173 and 1273 K).

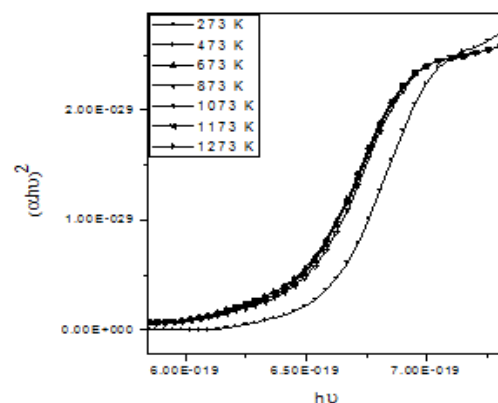


Fig.2. The relation between Kubelka-Munk function $[\alpha h\nu]^2$ versus photon energy ($h\nu$).

Table 1

ZnO samples at	273 K	473 K	673 K	873 K	1073 K	1173 K	1273 K
UV peak	384.6	381	384	383.5	382.5	386	384
Allowed direct band gap (eV)	3.861	3.969	3.872	3.826	3.894	3.891	3.899

FTIR Spectroscopy

FTIR measurements were carried out to identify the presence of ZnO and its vibration modes. Figure 3 shows the FTIR spectra of ZnO NPs with different calcinated temperatures. The spectra peak appears at about $3413\text{--}3448\text{ cm}^{-1}$ which can be assigned for the O-H stretching vibration from Zn(OH)_2 and it start to disappear with increasing calcinated temperature. Two peaks appeared at 1100 and 1632 cm^{-1} are corresponding to the stretching vibrations of the shoulders of ZnO. Besides, the narrow absorption signals appeared around $405\text{--}470\text{ cm}^{-1}$ was assigned for the Zn-O stretching vibrations[14].

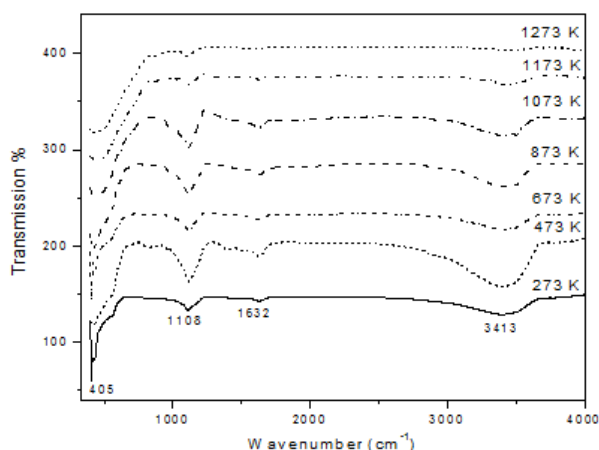


Fig. 3: FTIR spectra of ZnO NPs with different calcinated temperatures.

Scanning Electron Microscopy (SEM)

The typical scanning electron microscopy (SEM) images and the corresponding particles size distribution of the ZnO NPs developed at different calcinated temperatures are shown in Figure 4. As Figure 4 demonstrates, the developed ZnO NPs are in the nano range with spherical shapes. The ZnO NPs obtained with different calcinated temperatures (273, 673, 873 and 1073 K) showed average diameters of NPs 18, 19.5, 22.7 and 44.9 nm. It is clear that the particle size increase with calcinated temperature increases. The distribution of particles in the samples are also calculates from SEM images by measure the size of each particle separated and take the average size, then it was plotted and shown in Figure 5.

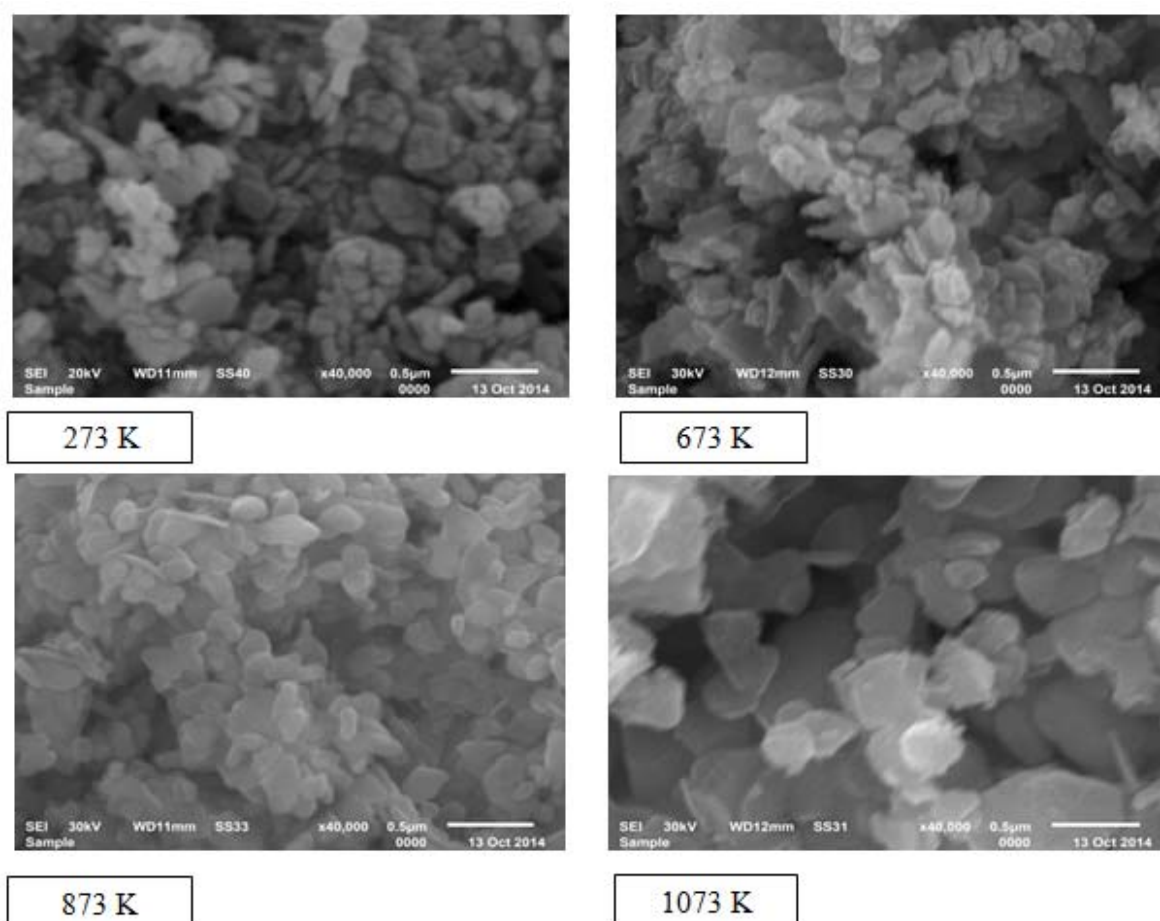


Fig. 4: The typical SEM images and the corresponding particles size distribution of ZnO NPs with different calcinated temperatures (273, 673, 873 and 1073 K) respectively.

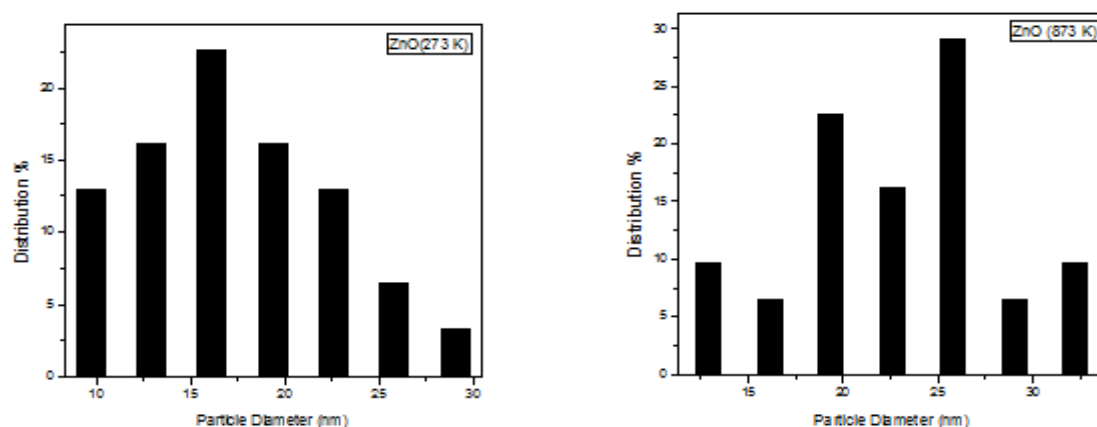


Fig.5: Relation between the particle distribution and the particle nano size at (273, 873) K.

X-Ray Diffraction Analysis

To identify the crystallinity and crystal phases of the prepared ZnO, X-ray diffraction (XRD) analysis was performed and shown in Figure 6. The X-ray diffraction pattern of ZnO NPs with different calcinated temperatures showed nine main broad

bands at 2θ values of 31.6° , 34.4° , 36.15° , 47.45° , 56.5° , 62.7° , 66.4° , 67.8° and 69° which is corresponding to (100), (002), (101), (102), (110), (103), (200), (112) and (201) crystal structure respectively[14]. The average crystallite sizes of the samples calculated by Debye-Scherrer's equation $D = 0.9\lambda / \beta \cos(\theta)$ where D is the crystallite size (nm), λ

is the wavelength of incident X-ray (nm), β is the full width at half maximum and θ is the diffraction angle[13]. The average crystallite size increase with increase in calcinated temperature in the range of (21 to 32) nm as shown in table 2 and figure 7, which agree with the results of SEM.

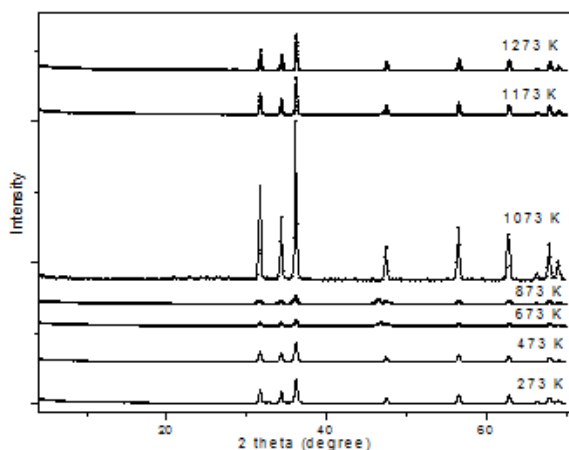


Fig.6. XRD patterns of ZnO NPs with different calcinated temperatures.

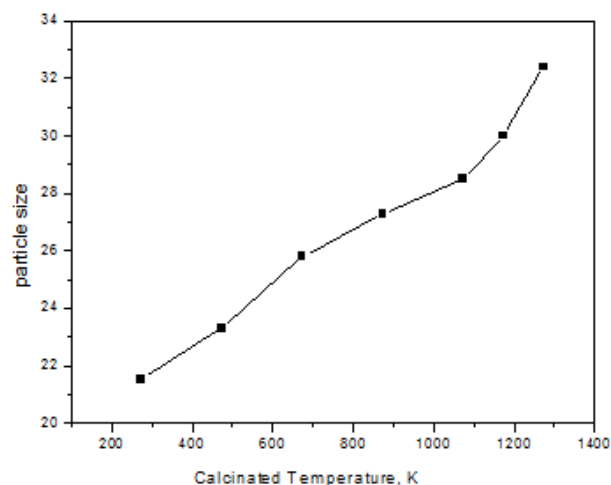


Fig.7. Plot between the average particle size from X-ray and calcination temperature.

Table 2: The average crystallite size at different calcinated temperature from x-rat and SEM.

Average crystal size of ZnO at temperature	273 K	473 K	673 K	873 K	1073 K	1173 K	1273 K
Using XRD	21.8	23.3	25.8	27.3	28.5	30	32.4
Using SEM	18		19.5	22.7	44.9		

Conclusions

In the present study, ZnO NPs were prepared by using simple precipitation method. The precursors using for starting the process were $\text{Zn}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ and NaOH with molar ratio (1:2). The obtained NPs were calcinated at different temperatures and then the structure of ZnO NPs have been studied using UV, FTIR, X-ray and SEM. The absorption peak of the prepared samples is 384 nm for as prepared sample which shifted to lower wavelength with increase calcinated temperature. Band gap energy of ZnO NPs is 3.86 eV for the as prepared sample , show increase in its value for samples calcinated at 473K and 673K (3.96 and 3.87eV) but decrease for sample at 873K (3.82 eV) and show stable value for increasing temperature than 873K with value 3.89 eV. According to scherrer fomula, the average particle size of the as prepared sample is 21.8nm and increase with increasing temperature. The obtained data from SEM show that the particle size of ZnO NPs as prepared is

18 nm and increase with increasing the calcination temperature.

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