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Effect on Annealing Temperature on Zno Nanoparticles

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Abstract: ZnO nanoparticles were prepared via simple chemical precipitation method at different annealing temperature. The X-ray diffraction results showed that hexagonal structure of ZnO nanoparticles with grain size in the range of 25 – 50 nm has been obtained. SEM & TEM images show the formation of ZnO nanoparticles with particle size ranging from 25-50 nm (± 0.1nm). The FTIR and Raman spectra exhibited peaks corresponding to the ZnO. Optical absorption studies reveal that the absorption edge has red shifts and increased in the absorption values with increasing annealing temperature. In this report, we were able to develop a method for synthesis of nanoparticles based on the annealing temperature.
Key Word: ZnO nanoparticle, XRD, TEM, FTIR, annealing and optical property Corresponding.

Introduction

Zinc oxide is non-toxic, semiconductor with wide band gap (3.37eV) and natural n-type electrical conductivity [1]. ZnO have superior durability, greater selectivity and heat resistance than organic and inorganic materials [2]. Due to noble properties of ZnO it could be used in various materials and products, including medicine, cosmetics, concrete and solar cells [3]. ZnO is toxic to microorganism but non toxic to human beings and also have good biocompatibility to human cells [4, 5]. ZnO nanoparticles have been prepared by various methods such as thermal decomposition [6], solvothermal reaction [7], chemical vapor deposition [8], hydrothermal method [9] and chemical precipitation method [10]. This article gives a comprehensive overview of the progress that has been made within the context of one-dimensional (1D) ZnO nanostructures.

In the present investigation, the ZnO nanoparticles were synthesized by using chemical precipitation method and then the effect of annealing temperature on the syntheses ZnO nanoparticles was examined.

Experimental

ZnO nanoparticles have been prepared using the required precursors by chemical precipitation method. An aqueous solution of 0.2 M Zinc acetate dihydrate $\{Zn(CH_3(COO))_2.\ 2H_2O\}$ dissolved in water and stirred for about 30 min at room temperature. Sodium hydroxide (NaOH) (0.3 M) was added drop wise to the above mentioned solution. The colour of the solution changed into milk white coloured, indicating the formation of ZnO nano particles in the solution. The solution was stirred for 4 hours at room temperature. After the reactions completed, the supernatants were removed and the deposited precipitate was centrifuged and washed with water and ethanol several times. The samples were then suspended in ethanol and allowed to age for 2 hours without stirring. After centrifugation, the samples then dried in oven at 60°C for 2 h. Then, the as prepared ZnO nanoparticle is placed in the middle of a muffle furnace in silica crucible. The samples have been annealed at 400°C for one hour. The prepared ZnO nanoparticles at 400 °C are annealed at different temperature of 500 ºC and 600 ºC in muffle furnace.

X-ray diffraction studies have been carried out using PANalytical x-ray diffractometer and surface morphology of the samples with compositional analysis has been studied using Field emission scanning electron microscope (CARLZEISS SIGMA version). Fourier Transform Infrared spectrum has been recorded using SHIMKDZU IRAffinity – 1 instrument. Optical absorption spectrum has been recorded using JASCO-UV–Vis-NIR Spectrophotometer (JASCO V570).

Result and Discussion

Figure 1 (a-c) shows the X-ray diffraction patterns of the ZnO nanoparticles at different annealed temperature i.e., (400, 500 & 600) °C. In all the pattern, the diffraction peaks at 2θ (degrees) of 31.63°, 34.61°, 36.32°, 47.66°, 56.94°, 62.97°, 66.57°, 68.12°, 69.48°, 72.11° and 72.26° are respectively indexed as the (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) and (202) planes of ZnO. All the diffraction peaks in the 2θ range measured corresponds to the hexagonal structure of ZnO with lattice constants a = 3.253Å and c = 5.214Å and are in good agreement with those on the standard data card (JCPDS card No. 36-1451). The sharpness of the diffraction peaks suggests that the product is well crystallized. The crystallite size of ZnO is calculated using Scherrer's equation

$$D = \frac{K\lambda}{\beta Cos\theta}$$

where, D is the grain size, K is a constant taken to be 0.94, λ is the wavelength of the x-ray radiation, β is the full width at half maximum and θ is the angle of diffraction. The crystallite size has been calculated and is found to be in the range 25-50 nm for the different annealing temperature i.e., (400, 500 & 600) °C of ZnO nanoparticles. These observations indicate that the particle size of ZnO nanoparticles increase with increasing annealing temperature and the crystallite size improvement is responsible for the sharpness in the diffraction intensity peaks from Figure 1 (a) to (c).

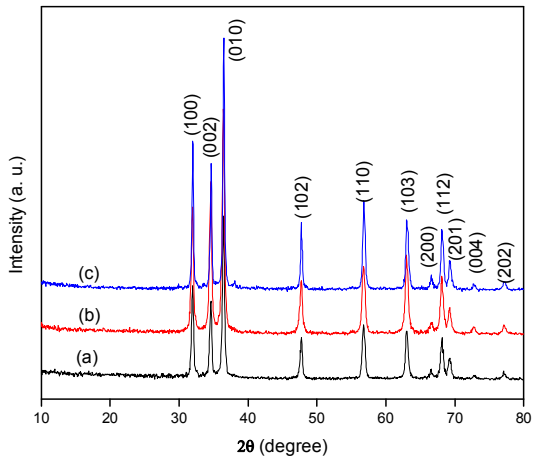

Figure 1. X-ray Diffraction pattern of ZnO Nanoparticles (a) 400°C (b) 500°C and (c) 600°C annealed samples

Figure 2 displays an SEM image of the prepared ZnO nanoparticles at different anneling temperature. SEM image of ZnO nanoparticles at 400 °C is shown in figure 2a shows the particles are small in size. As the annealing temperature increases to 500 °C & 600 °C, the particles resulting in increase of size (Figure 2(b & c)). It can be clearly seen that the size of the ZnO nanoparticles increase rapidly with increase in annealing temperature. The SEM investigations of all samples reveal that the crystallites are of nanometer size.

Figure 3(a-c) shows the transmission electron microscope (TEM) image of ZnO nanoparticles (a) 400°C (b) 500°C and (c) 600°C annealed samples. Using the particle number and particle diameter of the particle in the TEM image the particle size has been calculated. The particle size of ZnO Nanoparticles (a) 400°C (b) 500°C and (c) 600°C annealed samples is found to lie in the range of 25-50 nm (± 0.1nm).

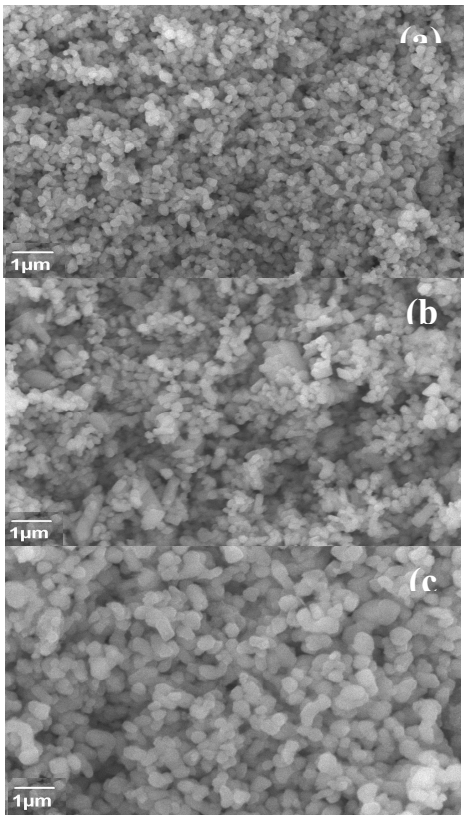

Figure 2. SEM images of ZnO Nanoparticles (a) 400°C (b) 500°C and (c) 600°C annealed samples

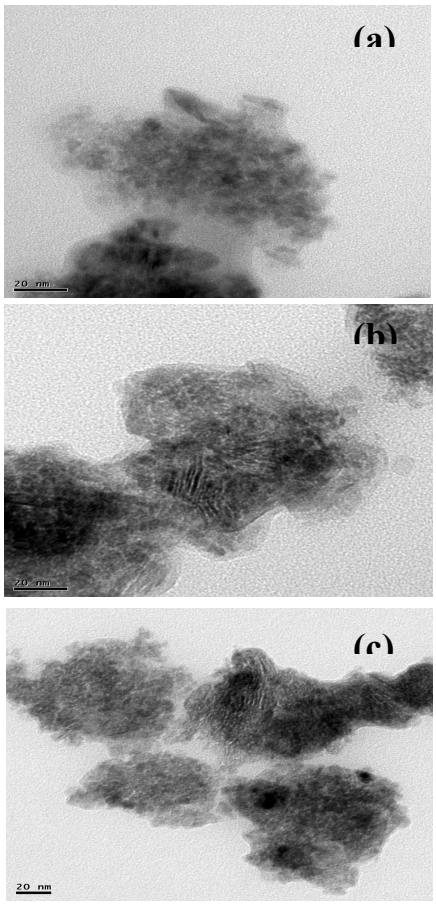

Figure 3. TEM images of ZnO Nanoparticles (a) 400°C (b) 500°C and (c) 600°C annealed samples

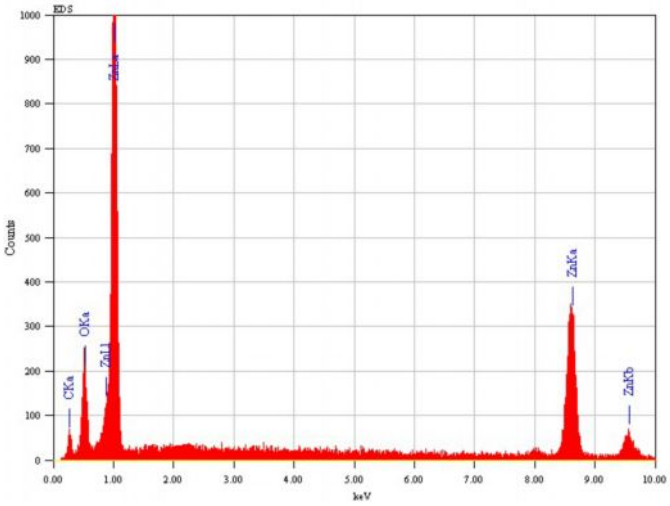

Figure 4 EDAX of ZnO Nanoparticles 400°C annealed sample

Energy dispersive X-ray analysis (EDAX) of ZnO nanoparticles are shown in Figure 4. The chemical constituents present in the ZnO sample are of Zn-49.35% and O-50.65%. In the EDAX, Zn and O are the element detected, indicating that the sample is highly pure.

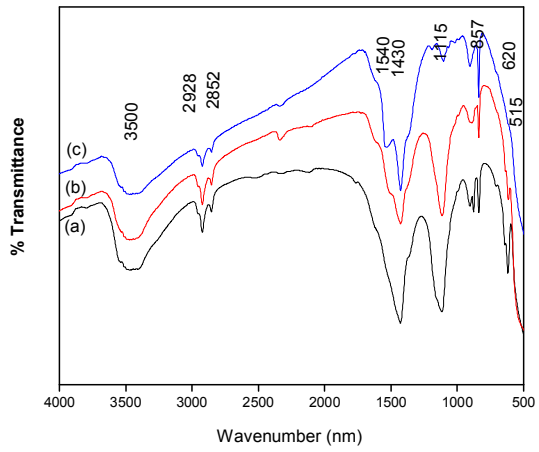

Figure 5 FTIR of ZnO Nanoparticles (a) 400°C (b) 500°C and (c) 600°C annealed samples

The figure 5 shows the FTIR spectrum of the ZnO nanoparticles synthesized by chemical precipitation method, which was acquired in the range of 500-4000 cm-1.The modes within 500 - 600 cm^{-1} are correlated to metal oxide bond (ZnO). From this FTIR we can also observe that increasing the mole concentration the sharpens of the characteristic peaks for metal oxide, suggesting that, the crystalline nature of ZnO increases with increase of particle size on increasing the mole concentration . The peaks in the range of 3500cm^{-1} corresponds to the O – H bending vibration. The modes of 2928 & 2852 cm^{-1} corresponds to the CH bonds. The adsorbed bands at 1430 and 1115cm^{-1} are corresponds to C=O bending vibrations. The absorption at 857 cm-1 is due to the formation of tetrahedral coordination of Zn. The modes at 620 and 515 cm^{-1} indicates the stretching vibrations of ZnO nanoparticles respectively diminishes gradually for raising the annealing temperature.

Optical absorption spectrum was well known that the absorption edge is related to the size of the nanoparticles. Figure 6 shows the absorption edge of the ZnO nanoparticles shows a red shift when compared to the value of bulk ZnO. This red shift was due to the increase in particle size. Absorption spectra of ZnO nanoparticles show that the absorption edge is slightly shifted towards the longer wavelength (red shift). The shift of the absorption edge to the longer wavelength indicates that the particle size increases with increasing ZnO nanoparticles annealing temperature. The optical band gap energy is calculated using the following equation.

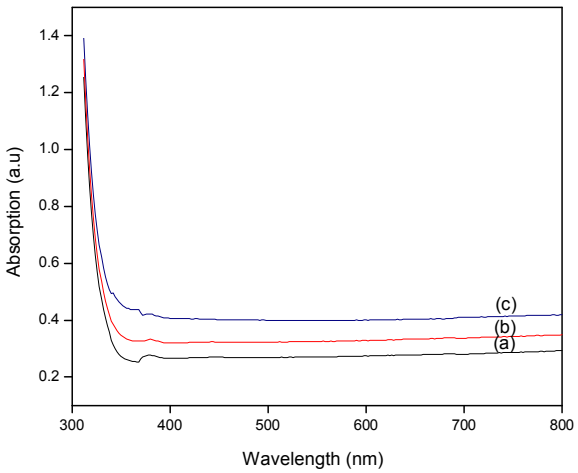

Figure 6 UV - spectrum of ZnO Nanoparticles (a) 400°C (b) 500°C and (c) 600°C annealed samples

$\alpha h\nu = A(E_g - h\nu)^n$

where α is the absorption co-efficient, t is the frequency of the incident radiation, A is a constant, Eg is the band gap of the material, h is the Plank's constant and n is equal to ½ for direct allowed transition. The band gap energy has been calculated and was found to be 3.35 to 3.41 eV for ZnO nanoparticles grown at different annealing temperatures of (400, 500 & 600) °C respectively. The band gap decreases with increasing annealing temperature. This change in band gap can be understood as due to the electronic structure dependence on the size of nanocrystals. The size is also nearly consistent with the size obtained from XRD observations (Table 1).

Table 1 Relates nanoparticles size with annealing temperature

Annealing Temperature	Nano Size from XRD (nm)	Band gap energy (eV)
400	23	3.41
500	25	3.39
600	28	3.35

Conclusions

In the present work, the nanosized ZnO particles were successfully generated by using chemical precipitation method at different mole concentration. The samples were characterized by XRD, SEM/EDX, TEM, FT-IR, and UV–Vis spectral methods. X-ray data indicates that the compound exhibits hexagonal (Wurtzite) structure with space group. The crystallite sizes were in the range of 25-50 nm (± 0.1nm) based on Debye–Scherrer equation. The red shift was noticed in UV–Vis absorption spectra, the band gaps were found to be 3.35–3.41 eV. Scanning electron micrographs suggest that all the samples were randomly oriented granular morphology.

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