Solution phase Synthesis of ZnO nanoparticles with assistant of microwave radiation and study its optical and structural characterizations.

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Abstract:

ZnO nanoparticles were successfully synthesized from solution phase of zinc acetate and ethanol in microwave oven. The time of preparation was decreased from several hours to several minutes due to using microwave oven.XRD of prepared ZnO Nanoparticles was study and show it has hexagonal ZnO phase with particles size in the range of 16 nm. Optical properties of ZnO nanoparticles was study using UV-vis spectrophotometer ,the absorption spectra shows the blue shift of energy band gap and by using effective mass model we estimate the particle size of ZnO powder which equal 7nm.

Key words: ZnO , nanoparticles ,solution phase ,microwave heating.

1.1 Introduction:

Research on nanocrystalline materials has increased enormously during the past years. The intense investigations are stimulated by several great application areas for this new class of materials[1]. Over the past decade, synthesis and fabrication of one-dimensional (1D) nanostructured materials have received increasing attention, due to many novel chemical and physical properties discovered or anticipated for this class of materials[2,3]. The important of this materials come from the interesting size-dependent that display new optical and electronic properties .The synthesis and characterization of zinc oxide and doped zinc oxide via different techniques have attracted considerable attention due to their application prospects in the development of materials area[4]. ZnO is an important II–VI wurtzite structure semiconductor compound due to its direct energy gap(3.32 eV) and large excitation binding energy at room temperature (60meV). One-dimensional (1D) nanostructures have quickly been considered a key technology for the next generation of high performance nanodevices in the areas of electronics, photonics, optoelectronics, mechanics, biosensors-detectors, and so on. ZnO nanostructures, have been demonstrated as a good candidate for solid state laser diodes and light emitting diodes (LEDs) in the near UV range. ZnO also exhibit great promise in the application such as field effect transistors (FETs), transducers, heterojunction solar cells, electrophotography, surface acoustic wave devices, conductive transparent conductors, UV light-emitters and chemical sensors[5-8]. Among this Nanoparticles of ZnO are currently intensively studied for use as photocatalysts and flat panel displays[9]. In addition, ZnO is an environmentally friendly material, which is desirable especially for bioapplications, such as bioimaging and cancer detection[10]. Various methods have been used to synthesis ZnO nanomaterials such as pulsed laser deposition (PLD),sol–gel process[11,12], homogeneous precipitation[13],chemical vapor deposition,[14]thermal decomposition,

hydrothermal synthesis, chemical bath deposition[15], successive ion layer adsorption and reaction (SILAR)[4], and reaction of zinc salt with base(wet chemical techniques)[16,17]. In this paper, we use the wet-chemical synthesis(Solution phase) of ZnO.

The solution phase synthesis of metal oxide nanoparticles typically involves the reaction of a metal salt with hydroxide ions. The particle size is dependent on
the kinetics of nucleation and growth from a supersaturated solution as well as processes such as coarsening, oriented attachment, and aggregation. Processes such as coarsening and oriented attachment occur at longer times and can have a large influence on particle size. This approach is used to prepare ZnO particles. The ZnO system is of particular interest since it is a semiconductor that is stable over a relatively wide pH range. The synthesis of ZnO particles from zinc salts can proceed in various alcohols with the addition of NaOH. The nucleation and growth are usually complete within the first several minutes, resulting in average particle diameters on the order of 3 nm.After completion of nucleation and growth in $Zn(CH_3COO)_2$, $ZnClO_4$, or $ZnBr_2$, the subsequent increase in particle size is dominated by coarsening, with a rate constant dependent on the anion. In addition, the nucleation and growth as well as the coarsening rates were shown to depend on the alcohol chain length. The synthesis of ZnO nanoparticles was also carried out in different alcohols (methanol, ethanol, or propanol) with NaOH, LiOH, or tetramethylammonium hydroxide as the oxygen source. The properties of the particles produced strongly depend on the reagents [18].

2. The Experimental:

All chemical materials; Sodium hydroxide (NaOH), absolute ethanol (C_2H_5OH), and zinc acetate dehydrate [$Zn(CH_3COO)_2$ - 2H2O] was of spectroscopic grade and was used without any further purification.

Chemical reactions was performed in a microwave oven (frequency 2.45 GHz, maximum power 700 W), Colloidal solution of ZnO was prepared by synthesis 0.004 moles of Zinc acetate were dissolved in 40 ml of ethanol and heated at $50C^0$ along with stirred for about 10 min and kept at microwave oven for 30 min. thus making precursor solution A. 0.004 moles of Sodium hydroxide(NaOH) were dissolved in 40 ml of ethanol and heated to $50C^0$ along with stirred for about 10 min and kept at microwave oven for 30 min., making precursor solution B. In order to make ZnO colloids, 20 ml of precursor solution A was complexed with 20 ml of pure ethanol and the solution was heated in microwave oven at $80C^0$ for 30 min.. After cooling at room temperature 20 ml of NaOH solution was mixed with the precursor solution A (for hydrolysis) in order to transform Zinc hydroxide to ZnO. The solution was kept in microwave oven at $60\sim65C^0$ for 30 mint. It was observed that solutions started precipitating after several mints. After cooling to room temperature for 2 hours the colloidal solution was centrifuged for 10 minutes at 5 k rpm. Centrifugation was performed to remove the large sized agglomerates so that only nanoparticles of almost uniform size were suspended in the solution.

X-ray diffraction (XRD) was carried out on a PanAnalytical (X'pert pro MPD 40kV 20 mA), with Cu Ka radiation (1.540 Å). Optical measurements were realized using an UV–VIS spectrophotometer model Thermo spectronic, in the wavelength range 300–1100 nm (for absorption spectra).

3- Results and discussion:

3.1 Microwave-assisted aqueous synthesis:

In conventional synthesis of ZnO nanoparticles, 3 hours of processing is required because of heat flow due to conduction. But microwave radiation causes rotation of molecules at their natural frequency and hence lead to reduction in synthesis time and uniform heating

within the sample. The essential requirement for microwave synthesis of the metal oxide is that the precursor has to have a high dielectric constant. Therefore, if the mixture of two different materials having different dielectric constant it is exposed to microwave radiation, material with higher value of dielectric constant absorbs more energy and gets heated rapidly compared to the other. The homogeneous mixing of precursor into solvent may be advantageous provided the precursor has more dielectric constant than the solvent. In this paper also we prepared ZnO nanoparticels without using microwave heating ,but it take long time and the nanoparticles was has impurity ,also the amount produce was less than it produce by using microwave heating.

3.2 Structural characterization:

The crystal structure of the resulting ZnO was investigated by XRD measurements. The XRD pattern displayed in Fig. 1 shows that all the diffraction peaks can be indexed as the pure hexagonal phase ZnO with the lattice parameters a = 3.248 Å and c = 5.208 Å , which are very close to the reported data (JCPDS File No.: 36-1451). No reflection peaks from other impurities such as $ZnO(OH)_2$ were detected.

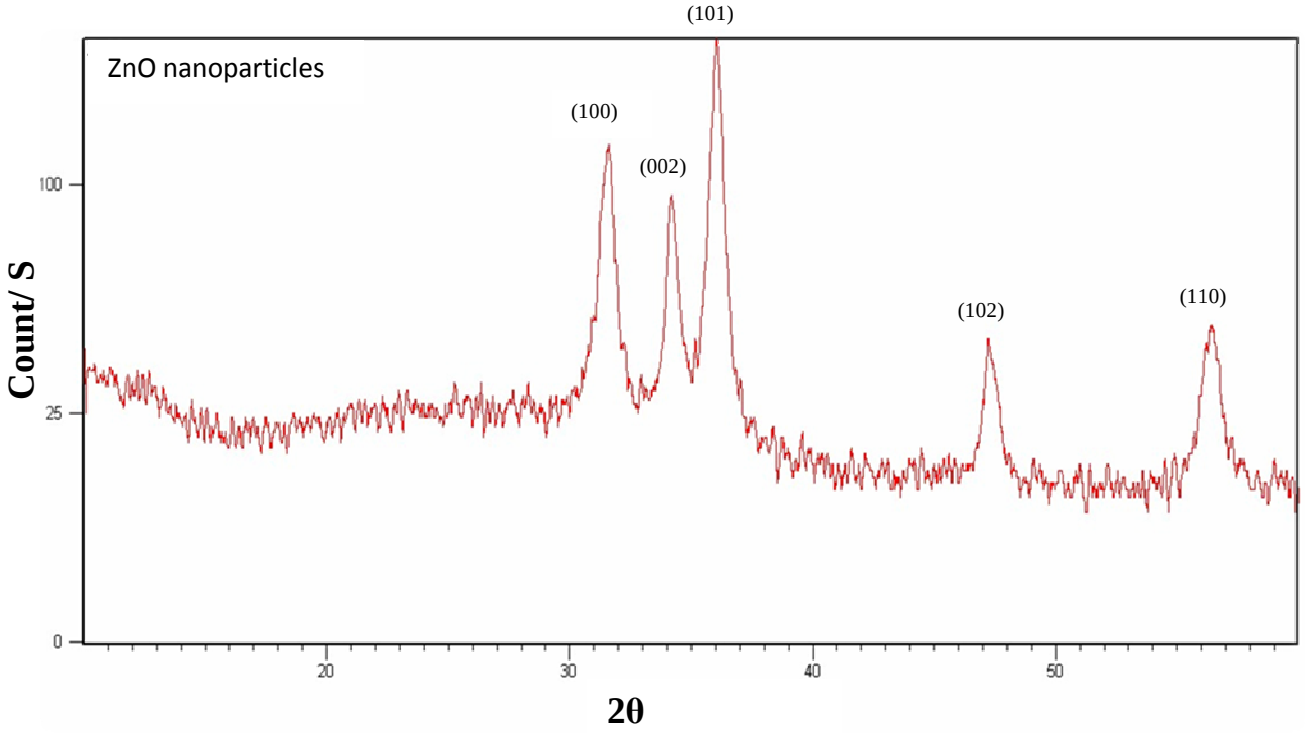

Fig 1. XRD pattern of ZnO nanoparticles as prepared.

Due to ZnO nanoparticles have hexagonal structure and the preferred orientation along c-axes in addition to fact that the preferential orientation is due to the minimization of surface energy and internal stress so the grin size or crystal size was calculated from the peak (002) of ZnO[19] using the Scherrer formula[20]:

$$D=0.9\,\lambda / \beta_{2\theta} \cos(\theta) \ldots\ldots\ldots (1)$$

λ the wavelength of X-ray used and $\beta_{2\theta}$ the full width at half maximum of (002) peak of XRD pattern, Bragg angle 2θ equal to 34.27°. The grain sizes were found to be equal to 16 nm.

3.3 Optical properties:

Optical absorption measurement is an initial step to observe the single colloid and nanoparticles behavior. Figure 2 gives the room temperature absorption spectra of the ZnO nanoparticles taken after preparation directly. From the spectrograph the absorption edge onset ($\lambda_{1/2}$) of the sample is found to occur in the 370 nm for nanocrystalline colloids and that found to be blue shifted with respect to their bulk value 385nm which could be attributed to the quantum confinement[21]. The pronounced dependence of the absorption band gap on the size of semiconductor nanocrystals is used to determine the particle size. An order of magnitude estimate of the grain size is possible from the absorption spectra. The size-dependent bandgap energy of a semiconductor nanocrystal can be obtained using an effective mass model [22]:

$$^{*}E_g = {}^{bulk}E_g + \frac{(\hbar\pi)^2}{2r^2}\left(\frac{1}{m_e^{*}} + \frac{1}{m_h^{*}}\right) - \frac{1.8e^2}{4\pi\varepsilon\varepsilon_o r} - \frac{0.124e^4}{\hbar\,(4\pi\varepsilon\varepsilon_o)^2}\left(\frac{1}{m_e^{*}} + \frac{1}{m_h^{*}}\right)^{-1} \quad \ldots\ldots(3)$$

$^{*}E_g$=band gap energy of the nanoparticle, which will be determined from UV-Vis absorbance spectrum figure (2), that determined by:

$$^{*}E_g = \frac{hc}{\lambda_{1/2}} \quad \ldots\ldots\ldots..(4)$$

Where $\lambda_{1/2}$ = wavelength absorbed by the sample and can be determined from the absorption spectra (Figure 2) ,c is the speed of light.

$^{bulak}E_g$= band gap energy of the bulk ZnO and equal to 3.32 eV.

h=plank's constant, r particle radius (m) ,m_e^{*} effective mass of a conduction band gap electron in ZnO and equal to $0.24m_e$,and m_e is the electron mass ,m_h^{*} is effective mass of a valence band hole in ZnO and equal to $0.45m_e$[23], e :electron charge ,r is the radius of particles.

ε_o=8.854 x 10^{-12} C^2. $N^{-1}m^{-2}$ (permittivity of free space)

ε=3.7 (relative permittivity of ZnO)

By solving above equation (3) to r we can calculate the particle size :

Particle size =2r …….(5)

The particles size of prepared ZnO nanoparticles was equal to 7 nm and it was approximately conform to particles size determined by using XRD (16 nm).

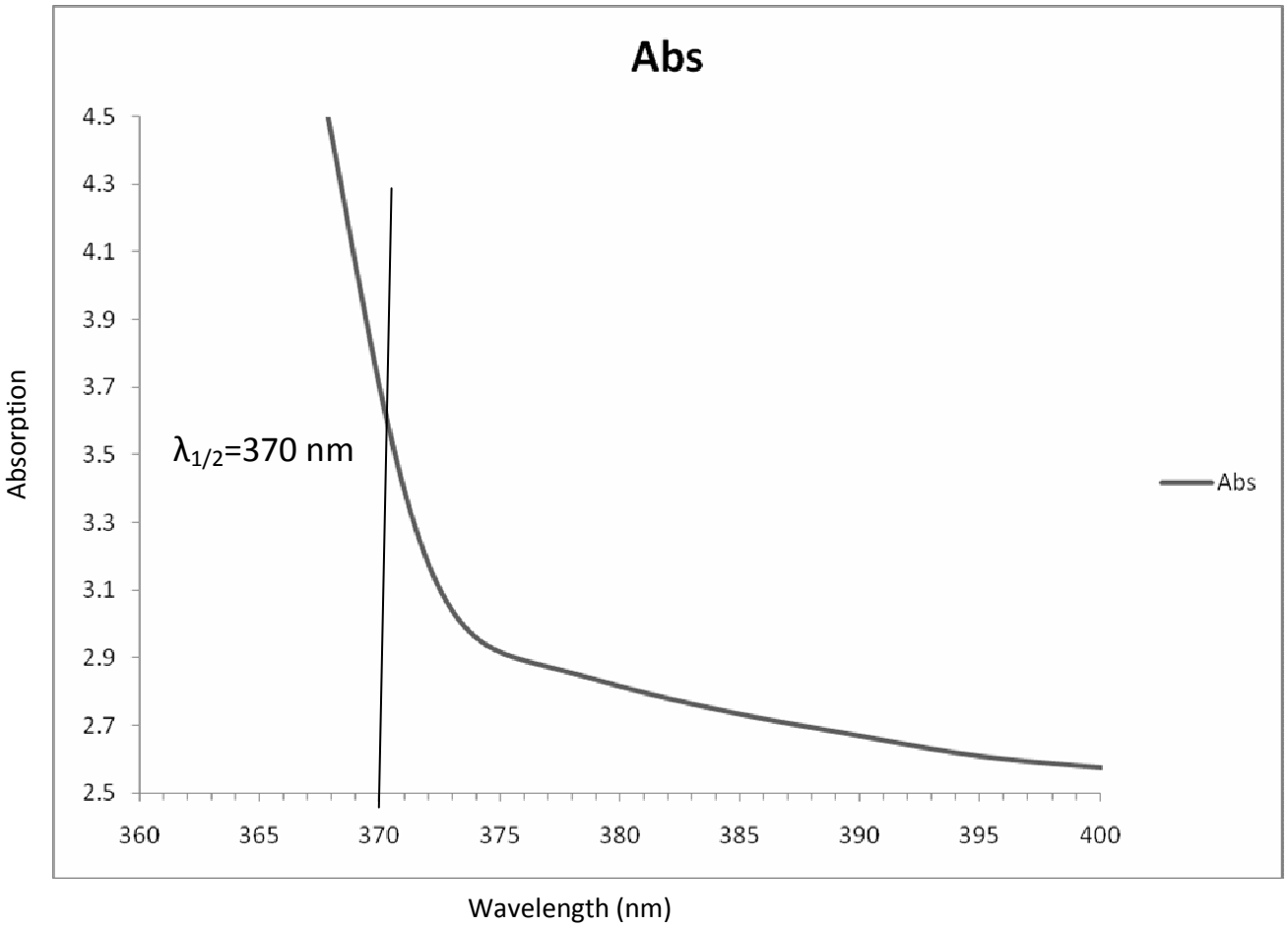

Figure 2. Absorption vs. wavelength of nanoparticles ZnO.

4. Conclusion:

ZnO nanoparticles have been successfully synthesized from methanol and zinc acetate dehydrate with NaOH in microwave oven at short time . XRD analyses proved the crystalline structure of the nanoparticles, optical absorption spectra shows the blue shift phenomena, that indicates the nanoparticles nature of ZnO by using effective mass model.

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الملخص:

الدقائق النانوية من اوكسيد الزنك حضرت بنجاح من الطور السائل لخلات الزنك والايثانول وبمساعدة فرن الموجات المياكروية .تقلص وقت التحضير من عدة ساعات الى عدة دقائق بسبب استعمال الموجات المايكروية.درست حيود الاشعة السينية للمركب المحضر واشارت الى ان المركب المحضر يملك الطور السداسي لاوكسيد الزنك وبحجم حبيبي بالمدى 16 نانو متر .كذلك درست الخواص البصرية للدقائق النانوية باستخدام المطياف البصري في المدى البصري والفوق بنفسجي للطيف, طيف الامتصاص للمركب المحضر يظهر الازاحة نحو الطيف الازرق لفجوة الطاقة وباستعمال موديل الكتلة الفعالة تم حساب حجم الحبيبات وكانت مساوية الى 7 نانو متر.