Spectroscopic studies of nanometric Zinc Oxide

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Abstract

Zinc Oxide nanoparticles have been prepared by chemical precipitation method using Zinc nitrate. The effect of different parameters on particle size (growth temperature, concentration of (NaOH) and time of stirring) were studied. The prepared (ZnO) nanopowder was characterized by X-ray diffraction (XRD), Transmission Electron Microscope (TEM) and Fourier-transform Infrared Spectrometer (FT-IR). (XRD) patterns proved that (ZnO) nanoparticles had a hexagonal crystal structure and the particle size varied from (11.1-18.3) nm. (TEM) picture reveals the morphology and particle size of Zinc Oxide nanoparticles. The presence of defects and impurity contents in (ZnO) nanoparticles were characterized by Fourier-transform infrared (FTIR) spectrometer.

Keywords: ZnO nanoparticle, XRD, FTIR, TEM

1. Introduction

The wurtzite zinc oxide (ZnO) is a distinctive native n-type semiconductor (Kahouli et al., 2015). It is considered as one of the most promising and novel material because of its unique catalytic, electrical, electronic, optical and antimicrobial properties as well as its low cost and extensive applications in diverse areas (Solati et al., 2016). It has a wide band gap of (3.37 e.v) and high excitation binding energy of (60 mev) at room temperature (Gyu-Chul et al., 2005; Qiuxiang et al., 2007). The high excitation binding energy of (ZnO) would allow for excitonic transitions even at room temperature, which could mean high radiated recombination efficiency for spontaneous emission as well as a lower threshold voltage for laser emission(Koet al., 2003; Zaouk et al., 2006).

Zinc oxide (ZnO) has an important role due to its unique morphology and their distinguished performance (Zhang et al., 2007) in electronics (Xu et al., 2004), optics (He et al., 2006), and photonics (Ma et al., 2006). ZnO displays a wide spectrum of applications, including gaseous sensors,fluorescent materials, photo catalysts, and additives in many industrial products, catalysts in ceramics, cosmetics and in the paint and rubber industries (Skapin et al., 2007).

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In recent times, nanoparticles have been attracting great attention for their potential applications in many fields; therefore, nanotechnology becomes a rapidly developing branch of material science, which is the science of tiny and its properties caused by smallness. Nanotechnology is defined as to decrease the size of a material by size less than (100) nanometers (Keller et al., 2010). ZnO nanomaterial has been investigated for its important properties. Many methods have been described for the production of ZnO nanostructures such as laser ablation (Scarisoreanu et al., 2005), electrochemical deposition (Berber et al., 2005), sol–gel methods (Ristiæ et al., 2005), chemical vapor deposition (Wu et al., 2002), molecular beam epitaxial (Chen et al., 1998), common thermal evaporation method(Takahashi et al., 2000) and solid–vapor phase thermal sublimation technique. Many shapes shave been synthesized under specific growth conditions such as nanocombs, nanorings, nanohelixes, nanosprings, nanobelts, nanowires and nanocages of ZnO (Wang, 2004).

In the present work, synthesis of ZnO nanoparticles is reported using chemical method. The effect of different parameters (temperature, concentration of NaOH and time of stirring) on the particle size of the synthesis ZnO nanoparticles was studied. The characterization of ZnO nanoparticles was examined using X-ray diffraction and transmission electron microscopy (TEM), (FT-IR) spectroscopy.

2. Experiment

2.1. Material and Sample Preparation

The chemical precipitation method was used to fabricate (ZnO) nanoparticles by using zinc nitrate [Zn $(NO_3)_2.6H_2O$] and sodium hydroxide (NaOH). All salts were purchased from Al Gomhouria Company, Cairo, Egypt.

ZnO nanoparticles were prepared in a similar manner as described elsewhere (Nejati et al., 2011). A 0.2 M solution of zinc nitrate and a 4.0 M alkali solution of sodium hydroxide were prepared by dissolving zinc nitrate $Zn(NO_3)_2 \cdot 6H_2O$ and NaOH, respectively, in deionized water. To prepare ZnO nanoparticles, 25 mL of the alkali solution (4.0 M NaOH) was dropped at an approximate rate of 5 mL/min into a mother solution prepared by mixing 25 mL of 0.2 M $Zn(NO_3)_2$ solution and 50 mL of deionized water with stirring. The final pH of the mixture was fixed at 13 because highly basic conditions are conducive to the direct preparation of ZnO crystals (Equations 1-3) (Kawano et al., 2008)

$$Zn(NO_3)_2 \rightarrow Zn^{+2} + 2NO_3^{-} \quad (1)$$

$$Zn^{+2} + 2OH^{-} \rightarrow Zn(OH)_2 \quad (2)$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O \quad (3)$$

On maintaining the mixture at 60˚C, precipitation occurred 2 h after mixing the solutions. The products obtained by centrifugation were washed with deionized water and then dried at 60ºC.

2.2. Techniques used

The developed samples were studied by The Philips X'Pert 1 X-ray diffractometer (XRD) with Cu-K_α radiation. The morphology of the samples was observed by transmission electron microscope JEM-2100 EXII. ZnO nanoparticles were characterized by Nicolet 6700 Thermo Scientific IR Spectrometer with Mid IR (400-4000) cm^{-1}, the samples were grinded with Kbr and formed a desk for FT-IR spectrometer.

3. Result and discussion

3.1. Factors affecting the synthesis of ZnO nanoparticles

For the development of an accurate synthesis ZnO nanoparticle, the influence of some factors such as temperature, concentration of NaOH and stirring time has to be studied.

3.1.1. Effect of Temperature

The temperature varied between 30 to 90 ^oC while keeping the rest of the experimental parameters fixed at appropriate values (concentration of NaOH at 4 mol and time stirring 2h). Fig. 1 illustrates the XRD pattern of (ZnO) nanoparticles under the growth temperature. The diffraction peaks (2θ) located at 32.140 ˚, 34.825 ˚, 36.649 ˚, 48.023 ˚, 57.118 ˚, 63.429 ˚, 68.556 ˚ and 69.660 ˚ have been keenly indexed as hexagonal wurtzite phase of ZnO. The sharp diffraction peaks apparent in the figures indicate good crystallinity of the ZnO nanoparticles. The synthesized nanopowder was free of impurities as it does not contain any characteristics XRD peaks other than ZnO peaks. The average particle size of the prepared sample was calculated through measuring the full width at half maximum (FWHM) using Scherrer formula (Khoshhesab et al., 2011). The grain size was found to range from (11.1 to 18.3) nm depending on the growth temperatures. The particle size derived from the FWHM of the more intense peak corresponding to (101) planes located at 36.649°.

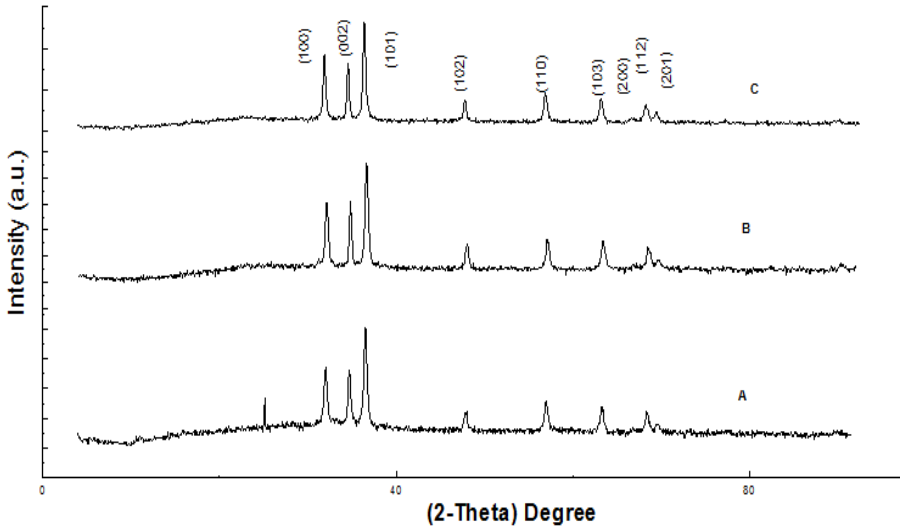

Fig. 1 XRD pattern of (ZnO) nanoparticles with changing the temperature
(A) 30˚C, (B) 60˚C (C) 90˚C
(NaOH concentration 4 mol, stirring time 2h).

Fig. 2 represents the relation between the grain size and (FWHM) of the highest diffraction peaks of ZnO nanoparticles with different temperatures. It is clear from this fig. that as the temp increases FWHM decreases and the grain size increases. This may be due to the change in different crystallographic planes (Aneesh et al., 2007).

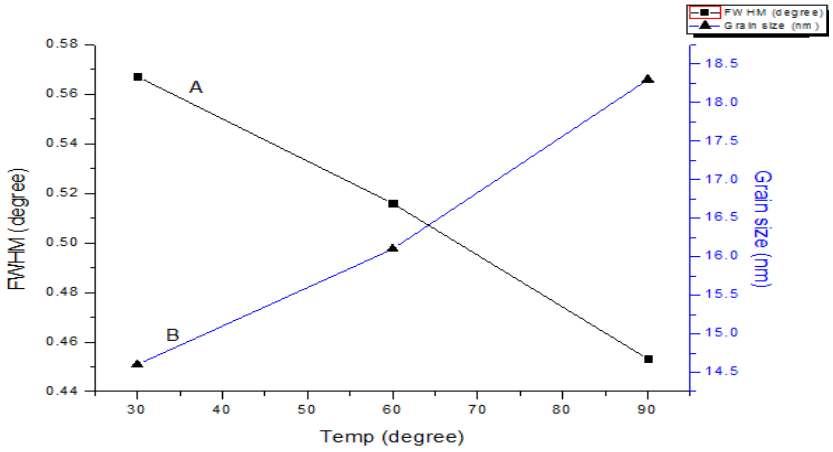

Fig. 2 The relation between (A) full width at half maximum and (B) the grain size of ZnO nanoparticles at different temperatures.

To confirm the formation of nanoparticle size for the prepared sample, the sample was studied by TEM. Fig. 3 shows (TEM) image of the (ZnO) nanoparticles synthesized at temperature 30°c, concentration of NaOH 4 mol and stirring time 2 h. It can be noticed that, the products are composed of the particles with nearly spherical shape. It has an average size about 17.5nm which confirms the particle size calculated from sherrer's equation. TEM micrographs show that some nanoparticles consist of a black core with gray shells. If the black cores are taken as the non-oxide Zn atoms and the gray shells indicate ZnO, one can see that small nanoparticles are quite ZnO (E. Solati et al., 2016).

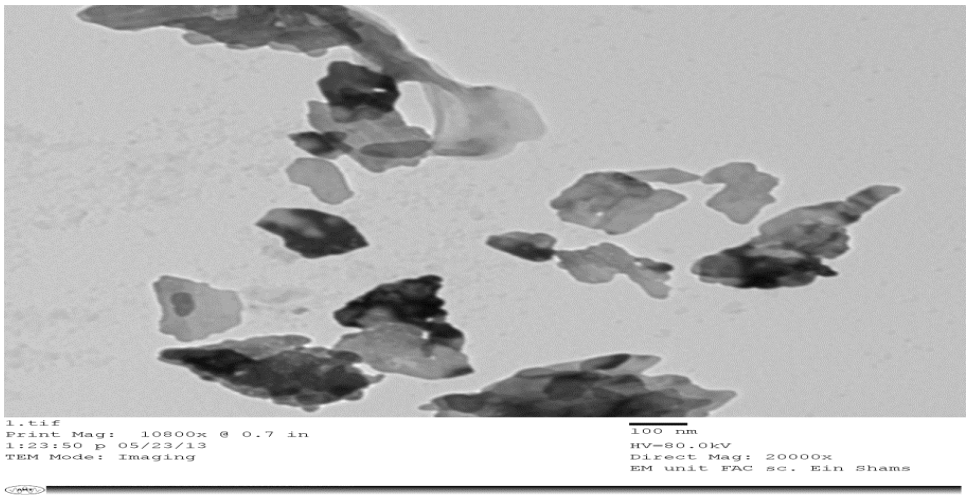

Fig. 3 Transmission Electron Microscope (TEM) of (ZnO) nanoparticle.

The FT-IR spectra of samples of ZnO nanoparticles are generally influenced by the particle size and morphology (Ismail 1991). Fig. 4 shows the FT-IR spectra of synthesis ZnO nanoparticles under the variation of temperature. The peak at 564 cm^{-1} is related to the stretching vibrations of Zn-O bonds. The peak at 3391 cm^{-1} indicates the presence of OH residue, probably due to atmosphere moisture (Becheri et al., 2008) at 30˚C. This peak is shifted to 3429 cm^{-1}at 60^{o} C and disappeared at 90°C. It should be noticed that the peak at (1504) Cm^{-1} may be attributed to the presence of bending of OH group of chemisorbed/physisorbed water molecules on ZnO surface which gradually disappear with increasing temperature (Radhika, et al., 2017). The best temp. which gives the best grain size of the synthesized ZnO nanoparticles was found to be at 30°C.

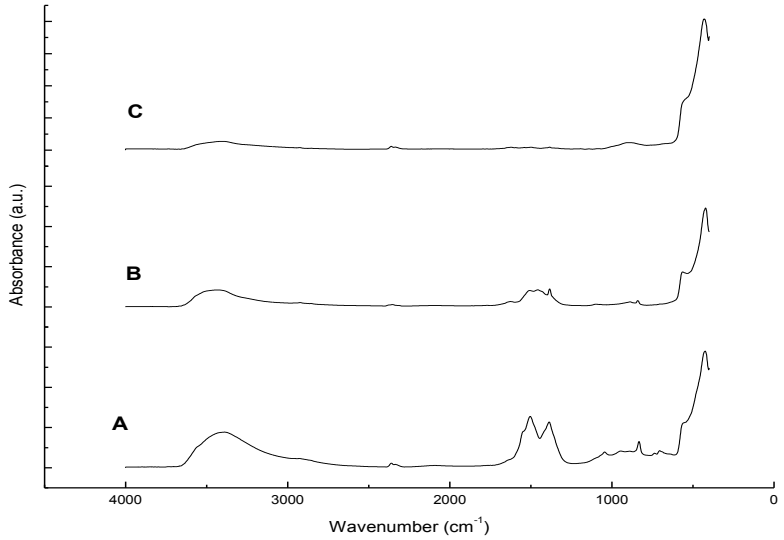

Fig. 4 FT-IR spectra of the synthesized (ZnO) nanoparticle at various growth temp. (A, B, C) (30, 60, 90) °C respectively,
NaOH concentration 4 mol, time stirring 2h.

3.1.2. Effect of NaOH Concentration

The particle size of Zinc Oxide nanoparticles is also affected by changing of the concentration of (NaOH).The concentration of NaOH varied from 2-5 mol while keeping the temperature at 30°c and time of stirring at 2h. Fig. 5 illustrates the XRD pattern of synthesized (ZnO) nanoparticles. From this pattern, it can be seen that the (FWHM) of the (101) diffraction peak decreases by increasing the concentration of (NaOH) and the grain size of synthesized (ZnO) nanoparticles increases (Aneesh et al., 2007) from 11.093 nm to 12.87 nm. This relation is depicted in Fig. 6.

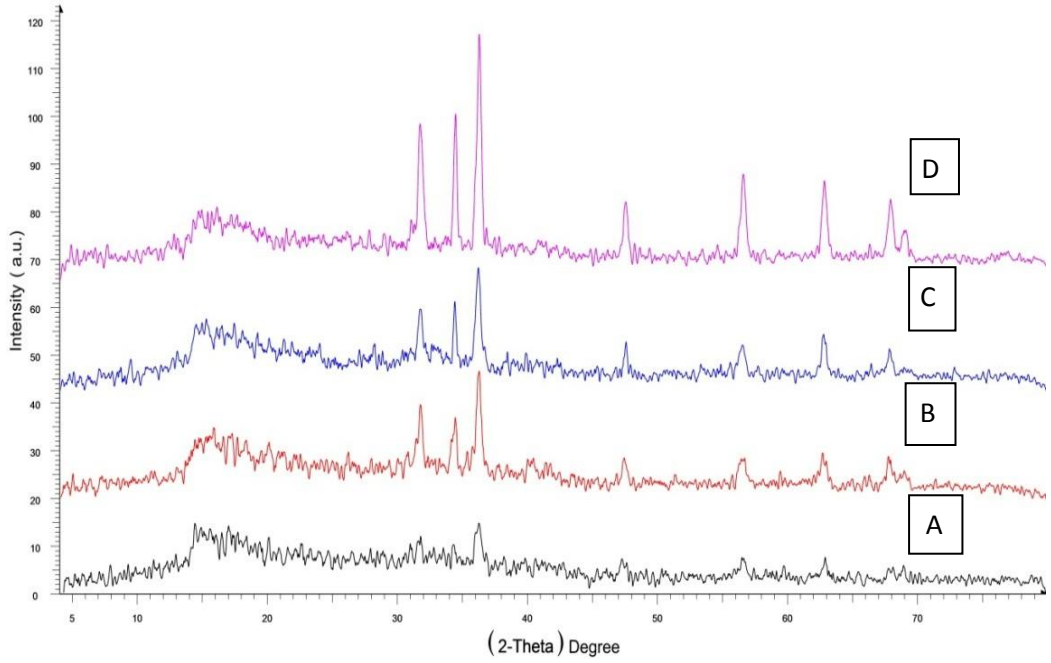

Fig. 5 XRD pattern of (ZnO) nanoparticles at temperature 30˚c, for 2 hours and at (NaOH) concentrations (A) 2, (B) 3, (C) 4 and (D) 5mol.

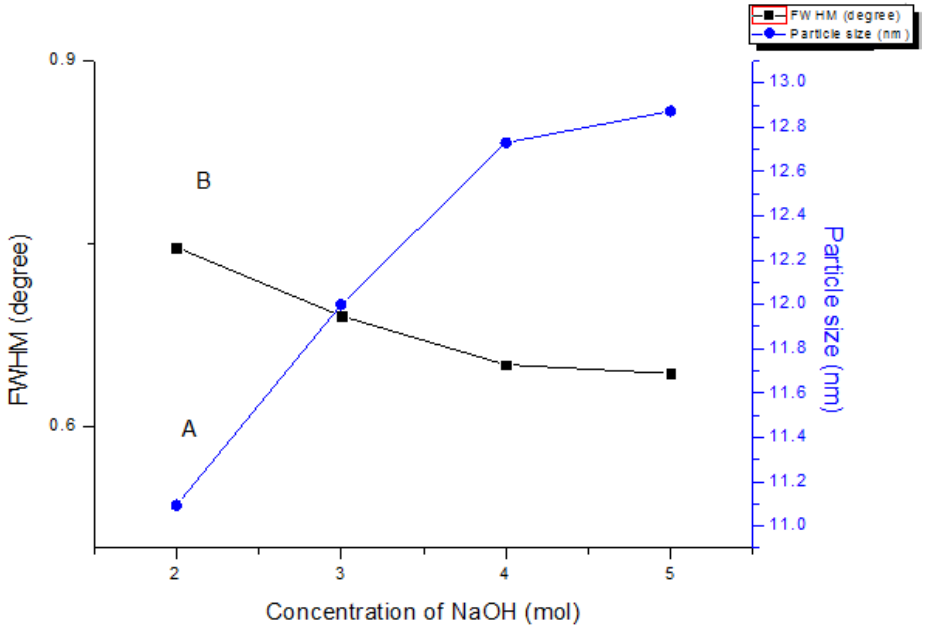

Fig. 6 The relation between (A) the changing in particle size and (B) FWHM of Synthesized (ZnO) nanoparticles with increasing the (NaOH) concentration.

Fig. 7 illustrates the (FT-IR) spectra of synthesized (ZnO) nanoparticles at temperature 30˚C, stirring time 2 hours and a variation of (NaOH) concentration from (2-5) mol. The peak that appeared at wavenumber 571cm^{-1} is related to the stretching vibrations of Zn-O. This

peak is shifted to wavenumber 671 cm^{-1} with increasing the concentration of NaOH from 3 to 4mol and appeared at the same position for the concentrations 3 and 5mol. The peak that appeared at wavenumber 3420 cm^{-1}indicates the presence of OH residue, probably due to atmosphere moisture. The best concentration of NaOH was found to be 4mol.

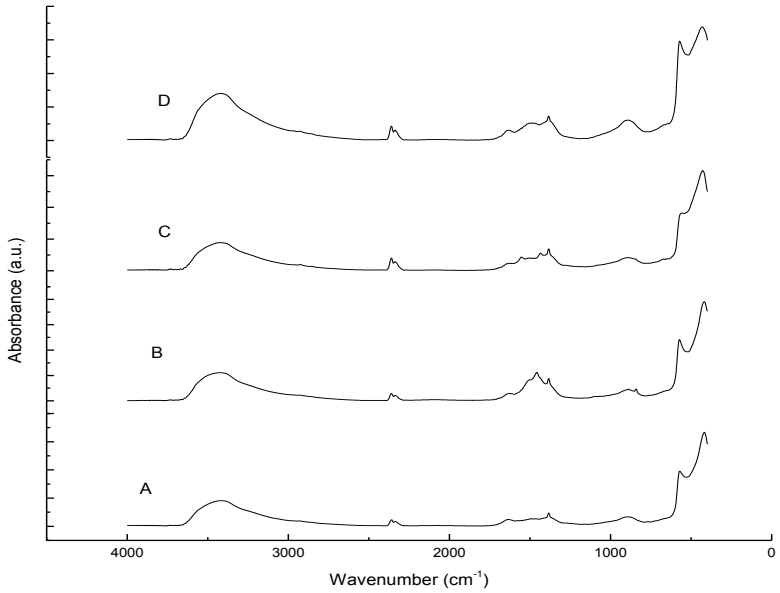

Fig. 7 FT-IR spectra of synthesized (ZnO) nanoparticle at various concentration of (NaOH) (A)2, (B) 3, (C) 4 and (D) 5 at temp 30°C for time stirring 2h.

3.1.3. Effect of stirring time

In another trial, the effect of stirring time for the prepared sample was examined. ZnO nanoparticles were synthesized by keeping the temperature at 30°C, the concentration of NaOH as 4mol and the stirring time 2h and 4h.Fig. 8 represented the (XRD) pattern of the synthesized (ZnO) nanoparticle at the two values of stirring time. It was observed that the (FWHM) of (101) diffraction peak decreases by increasing the time of stirring. So, the calculated particle size of the synthesized (ZnO) nanoparticles increased from (14.6nm) to (16.9nm).

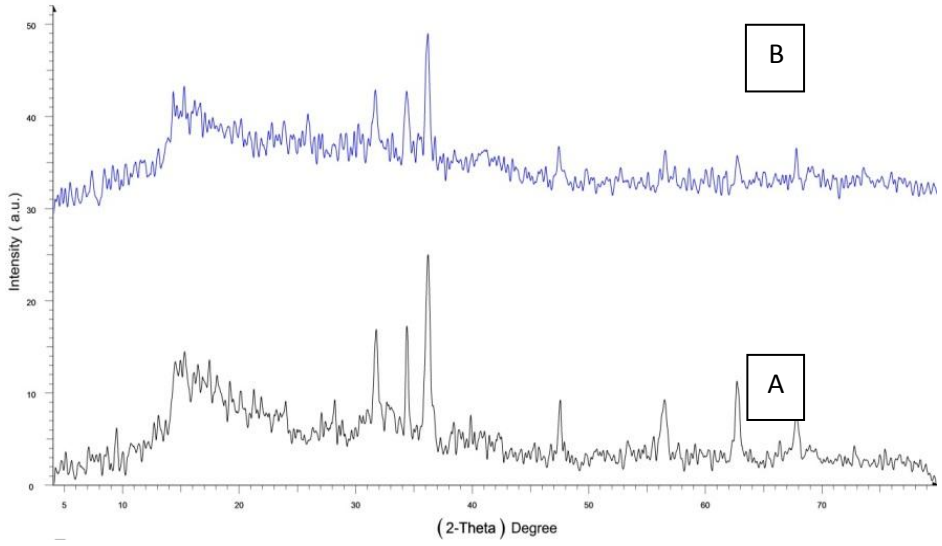

Fig. 8 XRD spectra of synthesized (ZnO) nanoparticles for stirring time (A) 2h and (B) 4 h (concentration of (NaOH) 4 M and temp 30°C).

Fig. 9 shows the variation of (FT-IR) spectra of (ZnO) nanoparticles at temperature 30˚c, concentration 4 of (NaOH) and for stirring time 2 and 4 hours.The peak appeared at wavenumber 671cm^{-1} shifted to 569 cm^{-1} when the time of stirring is increased from 2 to 4 hours. The best time of stirring of the synthesized ZnO nanoparticles was found to be 2h.

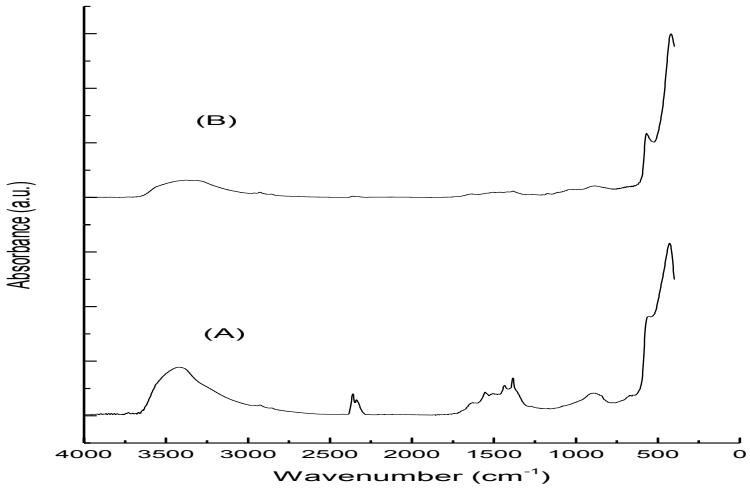

Fig. 9 FT-IR absorption spectra of synthesized (ZnO) nanoparticles at temperature 30˚C, concentration 4 of (NaOH) and for (A) 2 hours and (B) 4 hours.

4. Conclusion

Zinc Oxide nanoparticles have been prepared by Chemical precipitation method from Zinc nitrate and Sodium hydroxide. It was characterized by XRD, FT-IR spectrometer and TEM. The best synthesized ZnO nanoparticle is found to be at temp 30°C, concentration of NaOH 4 mol and stirring time 2h. The XRD and TEM studies confirmed the nanostructures

for the prepared ZnO nanoparticles. The calculated average size of the prepared ZnO is found to be 14.7 nm for peak absorbance wavelength. FT-IR absorption spectrum shows a series of absorption peaks from 500 to 4000 cm^{-1}.

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دراسات طيفية لأكسيد الزنك النانومتري

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المخلص:

تم تحضير جزيئات أكسيد الزنك النانونيه بواسطة طريقة الترسيب الكيميائي من نترات الزنك وهيدروكسيد الصوديوم. تم دراسة افضل الظروف المؤثره علي حجم الجزيئات للعينات المحضرة كدرجة الحرارة وتركيز الصوديوم هيدروكسيد وزمن التقليب .واختبرت العينات المحضرة بواسطة حيود الأشعة السينيةXRD ، مطياف الاشعة تحت الحمراء بتحوير فوريرFT-IR، المجهر الالكتروني TEM. ووجد ان افضل الظروف للتحضير هي درجة الحرارة 30 درجة وتركيز هيدروكسيد الصوديوم 4 مول وزمن التقليب ساعتان . أما حجم الجزيئات المحضرة لاكسيد الزنكالنانومترية فكان متوسط القيم المحسوبة من معادلة Scherrer formula بأستخدام الاشعة السينية14,7 نانومتر .