STUDYING THE EFFECT OF POLYVINYLPYRROLIDONE (PVP) ON CHARACTERIZATION OF ZNO NANOPARTICLES SYNTHESIZED BY SOL – GEL METHOD.

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ABSTRACT

In this paper, studying synthesis zinc oxide nanoparticles (ZnO NPs) via sol - gel method and effect of adding polymer in preparation its solution. Zinc nitrate hexahydrate, Polyvinylpyrrolidone PVP, distilled water and sodium hydroxide (NaOH) were used as precursor materials. Crystallization behavior of the ZnO was studied by X-ray diffraction (XRD). Nanoparticles phases can change from amorphous to wurtzite structure at the calcination temperature (500 °C) and crystallite size by Scherrer's formula about (21.131) nm for samples prepared with distilled water and (20.035)nm for samples prepared with dissolved PVP. Morphological and structural properties were investigated by scanning electron microscopy (SEM). FT-IR spectra was indicated characteristic absorption bands of ZnO. UV-Vis absorption spectrum was shown a typical spectrum for ZnO nanoparticles. Finally, the results were shown the samples with dissolved PVP has smaller particles size, less agglomeration and narrow distribution but less purity phase when compared with samples prepared with distilled water.

KEY WORDS: Nanoparticles, ZnO, sol- gel, PVP, FE-SEM, XRD, UV, FTIR

دراسة تأثير بولي فينل بيروليدون(PVP) على خواص جسيمات لأوكسيد الزنك (ZnO) النانوية المحضر بطريقة السول – جل.

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الخلاصة

في هذا البحث تم تحضير جسيمات نانوية من أوكسيد الزنك (ZnO) بطريقة الهلام ودراسة تأثير إضافة بوليمر في محلول التحضير. نترات الزنك المائية، وبوليمر متعدد فينل بيروليدون(PVP)، ماء مقطر، هيدروكسيد الصوديوم(NaOH) استخدمت كمواد أولية لتحضير المسحوق. السلوك البلوري لأوكسيد الزنك تم دراسته باستخدام تشتت الاشعة السينية، حيث وجد ان اطوار الجسيمات النانوية تتحول من التركيب العشوائي الى التركيب البلوري عند درجة حرارة الكلسنة 500 درجة مئوية اما حجم البلورة فتم حسابها بواسطة معادلة شيرر Scherrer's formula وكان حوالي (٣١.٧١١) نانومتر للنماذج التي حضرت بالماء فقط اما النماذج التي حضرت بإضافة PVP المذاب في الماء كانت

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(٢٤.٥٣٥) نانومتر. الخواص الشكل والبناء الداخلي للجسيمات النانوية تم بيانها بواسطة المجهر الالكتروني الماسح FE-SEM. طيف FTIR اثبت وجود وخصائص حزمة أوكسيد الزنك. الطيف الممتص للأشعة فوق البنفسجية كان متقارب مع الطيف المثالي لأوكسيد الزنك. أخيرا النتائج بينت ان النماذج المحضرة بإضافة البوليمر PVP كانت ذات حجم حبيبي اقل وتكتل حبيبي اقل وتوزيع حبيبي قليل ولكن نقاوة الاطوار البلورية تكون قليل مقارنة مع النماذج المحضرة بالماء المقطر فقط.
الكلمات الافتتاحية: الجسيمات النانوية، أوكسيد الزنك، الهلام، بوليمر متعدد فينل بيروليدون، بوليمر، تشتت الاشعة السينية، المجهر الالكتروني الماسح، الاشعة فوق البنفسجية.

INTRODUCTION

Crystalline of Zinc oxide has a "wurtzite structure", which from the "space group $P6^3mc$". In the ZnO, hexagonal structure each ion of Zn^{2+} is tetrahedral connected to four O^{2-} ions in lattice and vice-versa. Zinc oxide exhibits both covalent and ionic compound because of the tetrahedral coordination of ZnO indicates the presence covalent bonds, and the strong Zn-O ionic character. The hexagonal unit cell of ZnO has lattice parameters: a = 3.2495Å and c = 5.2069Å [Chennupati J., et al, 2007].

In materials science, zinc oxide is the one of the most important n- type semiconductor materials [Agnieszka K., & Teofil J., 2014],[Mohammad V., 2010].

Zinc oxide has important attention because of the unique characterizations of morphology and dimension dependent optoelectronic. ZnO has featured properties: thermodynamic and electrodynamics properties, high chemical activity, and remarkable optical, mechanical, electromagnetic, which exhibit a wide spectrum of application: gaseous sensors, photo catalysts, fluorescent materials, and additives in many industrial products. Zinc oxide is an environmentally friendly material, so is suitable for bio application, as cancer detection and bio imaging. Various physical and chemical processes develop to get ZnO particles in micro or nano scale with different shapes. [Munusamy Th., et al, 2013].

Now days, different routs have used for preparation of ZnO nanoparticles, such as sol – gel, hydrothermal / solvothermal, micro emulsion, colloidal, rietveld method, precipitation, and physical vapor deposition methods [Agnieszka K., et al, 2014][Tatyana G. et al, 2014][Tagreed M. Al- Saadi, et al, 2014][Harish K., Renu R., 2013]. Nano powders have prepared by sol- gel process had good homogenous, high purity, and high quality. The nanoparticles morphology have depended on the type of the solvent. [T.V. Kolekar, et al, 2011].

There are many research studies of preparation of ZnO by using sol - gel method including:

T.V. Kolekar, et al [2011] have prepared nanoparticles of ZnO at room temperature. Starting materials used were zinc acetate and triton X- 100. After stirred the solution for 1hour slightly precipitation noted by added NaOH to complete precipitation, than the powder calcined at 673°K. The average particle size of nanoparticles ZnO about (10nm).

Robina A., et al [2013] have prepared nanoparticles of ZnO with particle size less than 50nm. These nanoparticles can be used in hetero junction organic solar cells. A precursor material used zinc acetate. The results was shown that ZnO has wurtzite structure with spherical particles has size less than (100 nm) and uniform size distribution.

Sanjeev, et al [2014] have prepared the Quantum of ZnO (QDS) by using the starting materials were zinc acetate dehydrate, methanol and sodium hydroxide. After calcination the synthesized samples at 500°C for 1 hour, the product had good crystallinity with the average crystalline size of the QDS ~ 14 nm.

S. Surablu, et al [2015] have studied synthesis the ZnO nano powders from an ethanol solution, zinc sulfate heptohydrate and diethylene glycol surfactant. Results show that these nanoparticles are hexagonal wuntzite in phase ZnO with a mean grain size of about 28nm. It is clear with

increasing temperature the morphology of the particles change to the spherical shape and nano powder were less agglomerate.

Riyadh M. Alwan, et al [2015] have synthesized zinc oxide nanoparticles by using zinc acetate. The results have revealed the ZnO prepared had wurtzite structure with highly crystallinity, and spherical in shape with smooth surface.

S. R. Brintha and M. Ajitha, [2015] have prepared ZnO by various methods addition to sol- gel, the aqueous solution, and hydrothermal methods. The resulted ZnO particles have found in the nanometer scale about 13nm, 14nm, and 18 nm respectively.

In the present study, a sol -gel method are used to prepare ZnO nano particles, using starting materials like Zinc nitrate hexahydrate, sodium hydroxide, and distill water, and Polyvinylpyrrolidone (PVP). Studying the morphology and nanostructure of the powder are largely affected by PVP.

PREPARATION POWDER

Raw Materials

The raw materials used in this study are presented in table (1).

Dissolving and Mixing:

In this study, ZnO nanoparticles is synthesized by sol - gel, the starting material is Zn $(NO_3)_2.6H_2O$ dissolved once in distilled water and second in distilled water with and adding PVP at 50 °C for 2hrs by using hot plate magnetic stirrer type (Stuart SB 162-3, England). To get the required PH can be added drop by drop of the sodium hydroxide (NaOH) to solution. It is stirred ultrasonically for 1hr at room temperature due to PH desired. The solution are aging for 4hr to complete the process, and then the white ZnO crystalline is settled down and precipitates. That white precipitate is filtered by using filtration paper measuring 42 then washed with excess ethanol and distilled water to remove the starting materials.

Drying and Calcination process:

The drying process is carried out for ZnO powder at 150 ºC for 5h by using porcelain basin in oven dryer type (memmert Gmbh+Co.KG, universal oven (UIS), Germany). The dried ZnO nanoparticles are calcinated at 500 ºC 1h in air by using furnace up to 1600°C for pyrolysis, type (Protherm, Turky). The heating rate was kept at 5 ºC/min.

Characterizations:

The structure of ZnO the nanoparticles are studied by the X-ray diffraction (XRD) instrument, type (Shimadzo, XRD6000, diffractometer, Japan). X-rays are generated using Copper (Cu-Kα) radiation at 30 kV, 40 mA and wavelength (λ = 1.5406 Å), radiation to generate diffraction patterns from crystalline samples of powder at ambient temperature in a 2θ range of 20° to 80°. Fourier Transmission Infrared Spectroscopy (FTIR), type model (Iraffinity- 1Shimadzu), was used to investigate the bonds. Scanning electron microscopy (FE-SEM) are studied to investigate the microstructure of the crystals and nanoparticle size, type (MIRA3 TESCAN- RMRC) (TM - 1000 Hitachi tabletop Japan). "The UV absorption measurement" was occurred in range of (200-800) nm by "UV-Visible spectrophotometer", model UV- 1800 shimadzu.

- RUSTLES AND DISCUSSION:

XRD Analysis:

Generally, XRD can be used to study the morphology and crystallinity of particles. Fig. (1) shows XRD patterns of zinc oxide powder samples after being calcined at 500 ºC for 1 hour,

comparing with standard JCDPS card. The d values and intensities of observed diffraction peaks matches well with JCPDS card (00-036-1451). The peaks are indexed as "31.78º (100), 34.43º (002), 36.29º (101), 47.54º (102), 56.59º (110), 62.85º (103), 66.36º (200), 67.95º (112), 69.07º (201) and 76.966º (202)" respectively for ZnO prepared in distilled water. The peaks are indexed as "31.91º (100), 34.56º (002), 36.39º (101), 47.67º (102), 56.71º (110), 62.97º (103), 66.47º (200), 68.05º (112), 69.20º (201) and 77.09º (202)" respectively for ZnO prepared in distilled water with added PVP. XRD diffraction pattern was exhibited no impurities due to absent any foreign peak. This proves that synthesized nanoparticles of ZnO was highly purity but there were forgone peaks shown in chart for ZnO prepared in distilled water with added PVP may be found reaction between ZnO and PVP that agree with a FTIR measurement.

The crystallite size of nanoparticles for structural limitation and evaluation of crystallite size by using Scherrer's formula at the peak (101):

$$D_{XRD} = 0.89\ \lambda / \beta \cos\theta \quad (1)$$

Where λ is" wavelength of X-ray radiation used in Å", θ is" the diffraction angle", β is "the full width at half maximum (FWHM) in radians in the 2θ scale", D_{XRD} is "the crystallite size in nm". [Cullity, 1967].

The lattice constants (a, c) of the synthesized nanoparticles, according to the hexagonal crystal wurtzite structure was determined from the main peak of wurtzite structure (١٠١) by using cellacalc program which depending on the interplanar distance, h, k and l (the miller indices). The decreasing in average crystalline size and lattice constant may be due to add PVP to dissolved solution. The structural parameters calculated from the diffraction pattern shown in Table 2.

Field Emission Scanning Electron Microscopy (FE-SEM) analysis:

The surface morphology of synthesized nanoparticles was studied by FE- SEM, from this technique can be determine the grain size of ZnO nanoparticles. Fig. (2) was explained the FE-SEM images for samples calcined at 500 °C. From Fig. (2-a) FE- SEM image is shown the grain size about (26.62-39.20) nm for ZnO prepared in distilled water, while Fig. (2-b)FE- SEM image is shown the ZnO nanoparticles formed were less agglomerated and grain size about (21.49-32.90) nm for ZnO prepared in distilled water with adding PVP. The FE- SEM images were shown the homogeneity of microstructural of ZnO nanoparticles.

Fourier transform infrared spectroscopy (FTIR):-

FTIR measurement was carried out in order to confirm the bond structure of ZnO nanoparticles. FTIR spectrum of ZnO nanoparticles, which prepared with water and with added PVP. Figure (3.3) was shown considerable absorption peaks at 3489.23 cm^{-1}, 1575.84 cm^{-1}, and 45502 cm^{-1} that band are specified to stretching vibrations of Zn–O in two samples with water and with added PVP, which was described in [R.Y.Hong et al, 2009]. The wide absorption band at 3057.17 cm^{-1} was due to stretching vibrations of O–H bond to adsorbed water at the particles surface. An absorption peak at 1375.25 cm^{-1} is specified to the C=O stretching vibration. Peaks at 1489.05 cm^{-1} and 852.54 $cm^{-1}$are assigned to the C–H in PVP solution as accepted with [Tatyana G., et al 2014].

The peaks of samples which prepared with added PVP are stretched and deformed because of that chemical reaction was happened between nanoparticles of ZnO and polymer, by coordination of the ZnO nanoparticles with the PVP by hydrogen and oxygen atoms, as evidenced in [Ilegbusi O.J. and L.I. Trakhtenberg, 2013] [Tatyana G., et al 2014]. These results are shown shifting in band due to calcination temperature, that samples are needed higher

calcination temperature than 500 °C in order to remove secondary compounds and reduced the shifting of peaks.

UV-visible Absorption:

Fig (4) was shown the absorbance and wavelength from in the range (200 to 800) nm the UV-Vis spectra of ZnO nanoparticles. The absorbance at wavelength, which because of the small particles size effect on quantum confinement. A clearly shift at blue light wavelength was absorbed. A sharp peak of UV emission was centered about 365 nm, this was indicated a blue shift in the spectrum. The peak of exciting absorption was observed because of ZnO nanoparticles found below the wavelength of band gap of bulk zinc oxide (388nm) and was represented mono dispersion of nanoparticles, which was referred for almost uniform nanoparticles size. A slight shift in the absorption peaks was observed while upon change in size or shape particles, as evidenced in [Guo L, et al, 2001] [Riyadh M. Alwan et al, 2015]. The band of UV emission was cleared by the transition of near band-edge of the board band gap zinc oxide nanoparticles, which referred to the defects like vacancies of oxygen ions and interstitials of Zn ions [Xu LF, et al, 2005]. From these figures, the ZnO nanoparticles that prepared with added PVP to dissolved solution less in shifting due no aggregation and agglomeration and small particle size as found in XRD analyses and SEM image.

CONCLUSIONS

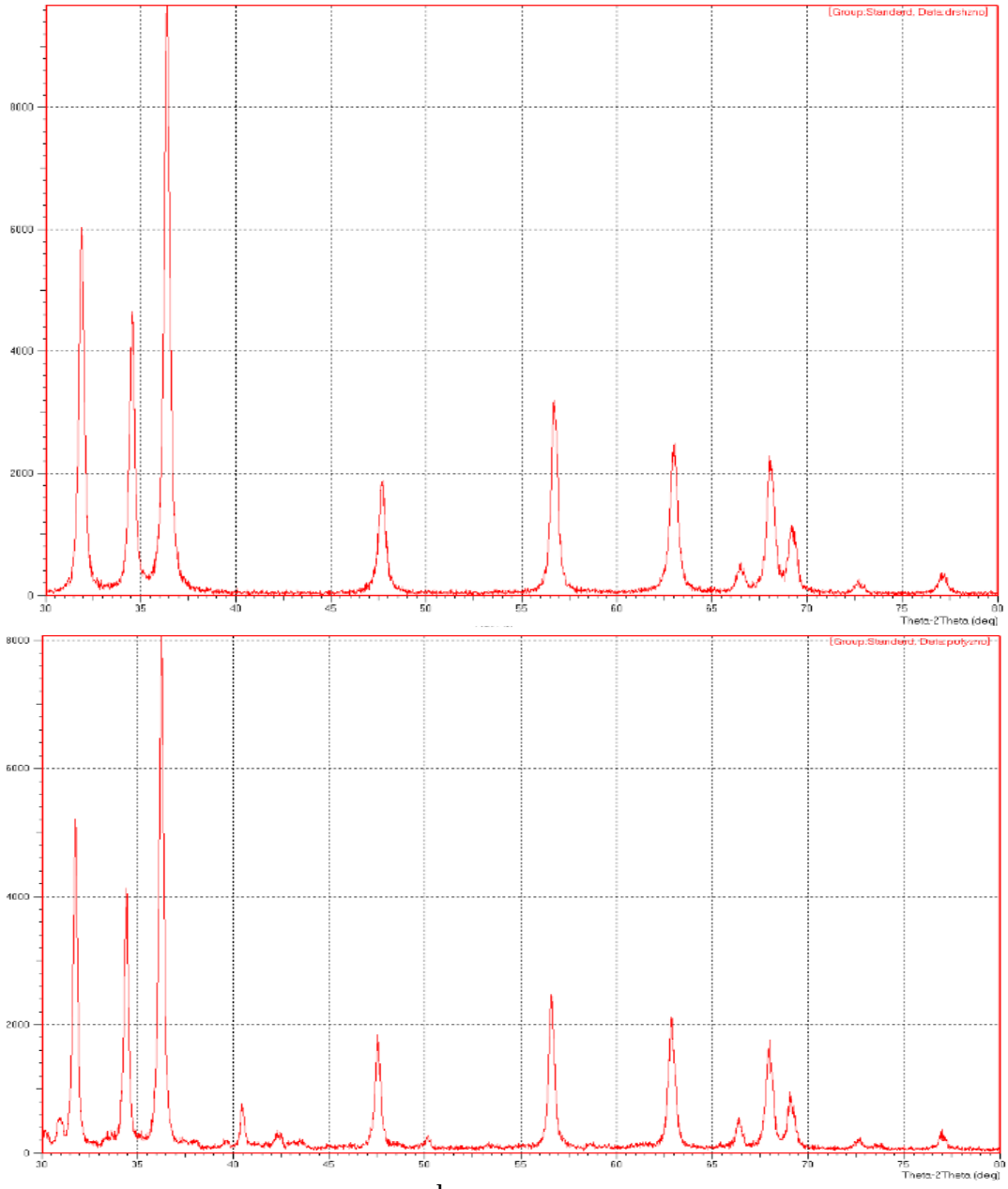
The zinc oxide ZnO nanoparticles have been prepared via the sol-gel process at low calcinations temperatures (500°C) with a cubic wurtzite structure. This work focused on the effects for added PVP dissolved in water in the preparation of ZnO nanoparticles via sol-gel process and their effect on the variation of properties. The prepared ZnO nanoparticles were characterized using XRD, FE-SEM, FTIR and UV-Vis measurements. The average particle size was found 21.49 nm for samples with added PVP dissolved in water, low agglomeration and narrow distribution but less purity phase when compared with samples prepared with distilled water, which had 26.62 nm.

Table (1) the raw materials used.

Raw materials	Formulation	Molecular weight (g/mol)	Purity %	Physical state
Zinc nitrate hexahydrate	**$Zn(NO_3)_2.6H_2O$**	**297.4815**	**99**	**Solid**
Sodium Hydroxide	**NaOH**			**Solid**
Distilled Water	**H_2O**	**1**		**Liquid**
Polyvinylpyrrolidone	**$(C_6H_9NO)_n$**	**30000**	**99.9**	**Solid**

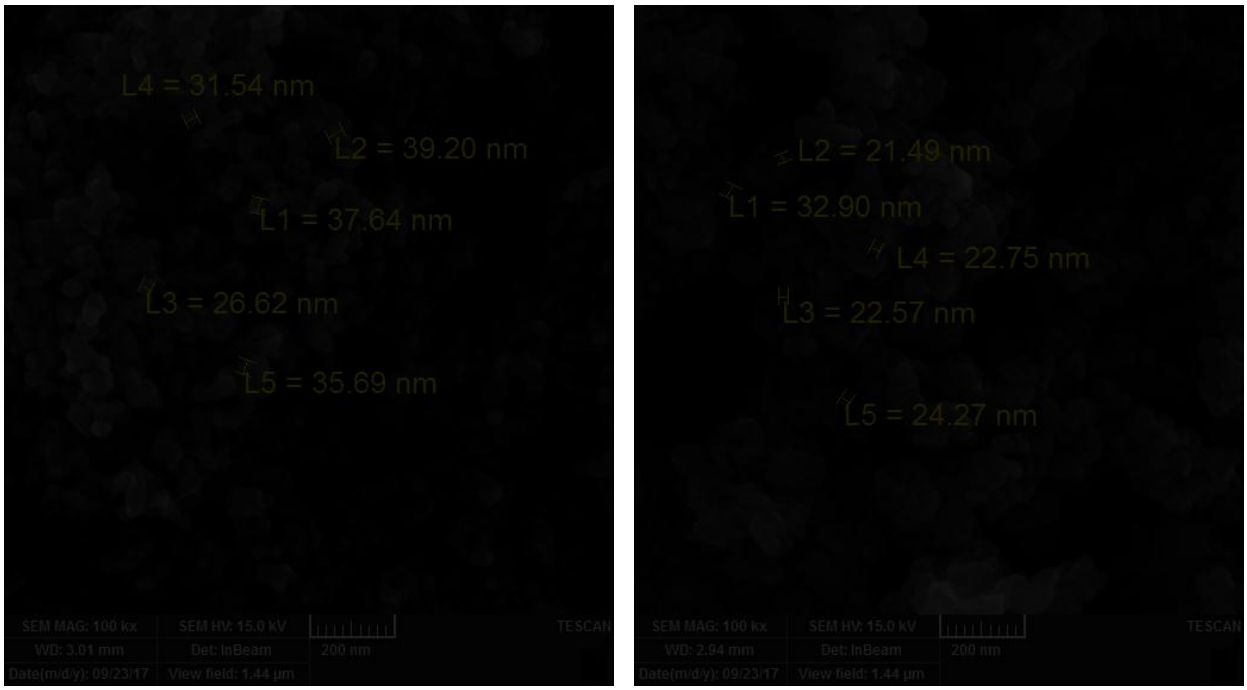
Table (2) Structural parameters of ZnO calcinated at 500°C.

ZnO	D_{XRD} (nm)	a (Å)	c (Å)
With water	**21.131**	**3.24892**	**5.20062**
With added PVP	**20.035**	**3.23653**	**5.18627**



b

Figure (1): XRD patterns of zinc oxide calcinated at 500 °C samples: a- with water to dissolved solution, b- With added PVP to dissolved solution



a b

Fig. (2): SEM of zinc oxide calcinated at 500 °C samples:
a- with water dissolved solution, b- With added PVP to dissolved solution.

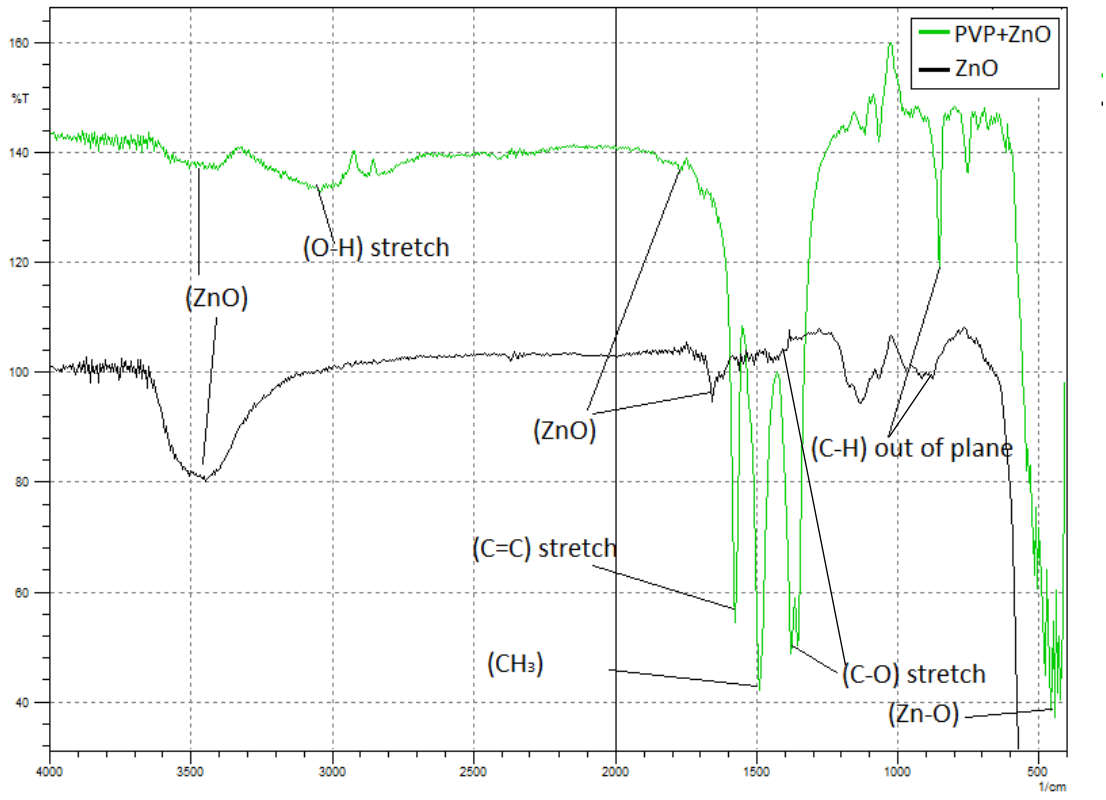
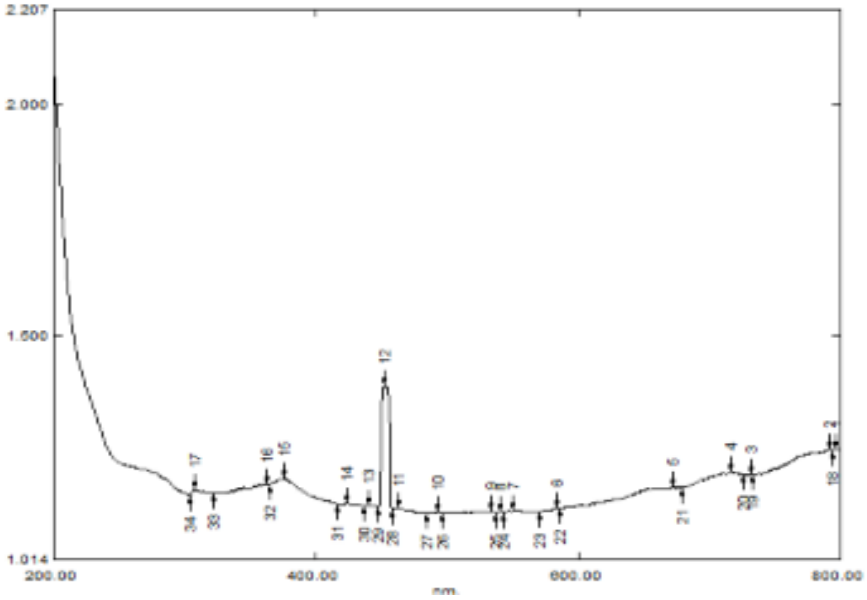
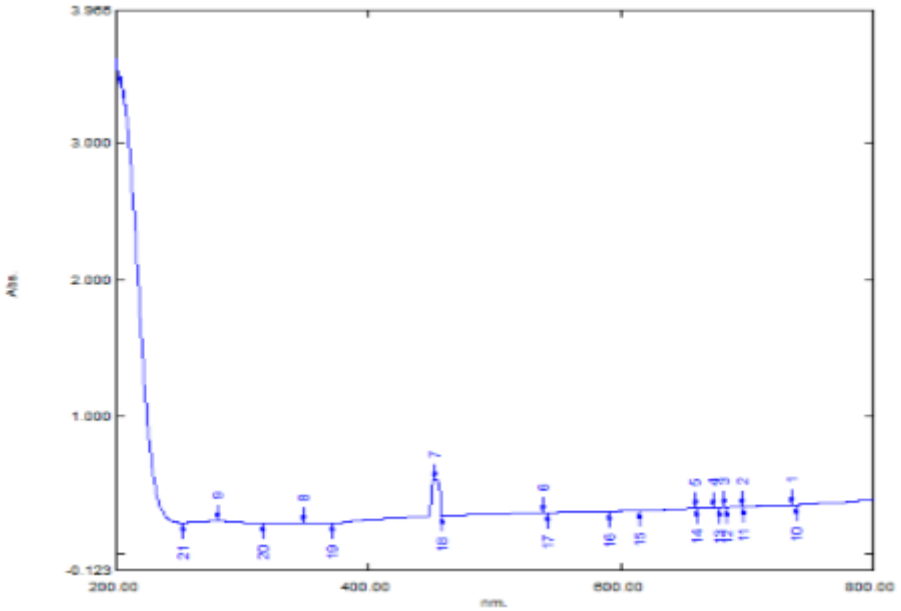


Figure (3) The FTIR spectra of ZnO samples with water and

with added PVP to dissolved solution



a



b

Figure (4): Absorption of ZnO nanoparticles as a function of wavelength a- with water to dissolved solution, b- With added PVP to dissolved solution

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