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Preparation and characterization of ZnO nano-particles

تحضير ودراسة خواص حبيبات اوكسيد الزنك النانوية

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ABSTRACT

ZnO plays an important role in many semiconductors technological aspects. In the present work zinc oxide nano particles were prepared by chemical method , using (Zn $(NO_3)_2.6H_2O$) and (NaOH)with different concentrations(0.25,0.5,0.75, and,1)M(which lead to different PH) at 70ºC,and study the effect of temperature on the shape and particle size . A variety of techniques like X-ray diffraction (XRD),Scanning Electron Microscopy (SEM)and (AFM). X-ray diffraction revealed the quartzite structure of ZnO . The obtained show that no impurities were found in the XRD pattern. Also the diffraction peaks are intensive and very sharp. Thus high purity hexagonal ZnO nanocrystals could be obtained by this synthesis process, and (SEM)and (AFM)show that the result were nano particle with particle size (15-30),(20-35),and(20-40)nm for the three first concentration ,and for the last one, the SEM image demonstrates clearly the formation of Short rods ZnO nanoparticles of diameter ~25-62 nm and length ~ (200 nm -500 nm) .

الخلاصة

يعد اوكسيد الزنك من المواد المهمة في تكنولوجيا المواد اشباه الموصلة . في الدراسة الحالية تم تحضير جسيمات اوكسيد الزنك النانوية بالطريقة الكيميائية . باستخدام نترات الزنك المائية ونسب مختلفة من هيدروكسيد الصوديوم (0,25 و0,5و0,75 و1) مول وبدرجة حرارة تحضير ^{0}c 70 ودراسة تأثير درجة حرارة التحضير على شكل وحجم الحبيبات لاحد التراكيز المحضرة . العديد من التقنيات استخدمت لدراسة خواص المسحوق المنتج مثل جهاز حيود الشعة السينية والمجهر الالكتروني الماسح وغيرها .وبينت النتائج ان الحبيبات الناتجة وحسب المنحنيات المستحصلة من حيود الاشعة السينية ذات نقاوة عالية وتركيب بلوري سداسي .وبينت الدراسة ايضا ان شكل الحبيبات يعتمد على تركيز هيدروكسيد الصوديوم حيث كان شكل العينات للتراكيز الثلاثة الاولى كروي ويتراوح حجمها الحبيبي (15-30)و(20-35)و(20-40) نانو متر وللتركيز الاخير كان شكل العينات على شكل قضبان نانوية قصيرة بنصف قطر يتراوح (25-62) وطول (200-500) نانومتر.

Keywords: ZnO nanorods, chemical method, changing growth temperature

1. INTRODUCTION

Zinc Oxide (ZnO) is a wide band gap semiconductor with qurtzite structure. The physical and chemical properties of nanoscale particles are different when compared with the bulk materials[1]. The ZnO is known to be a wide band gap (3.37 eV) with a high exciton binding energy(60 meV) and exhibit the most sheeny and numerous configuration of nanostructure that one material can form. Also, ZnO as an important

semiconducting material has a wide range of applications in gas sensors, chemical absorbent, nanogenerators, electrical and optical devices, electrostatic dissipative coatings, and advanced ceramics[2]. ZnO nanoparticles has been prepared by various methods such as thermal decomposition , solvothermal reaction reactive electron beam evaporation technique , chemical vapor deposition , hydrothermal method [3]. As a method for preparing high-quality ZnO powders, the solochemical synthetic route has advantage to obtain high crystallized powders and with high purity, without necessity of any posterior treatments. The particle properties such as morphology and size can be altered via this method by adjusting of parameters such as reaction temperature. Compared with other techniques, this synthetic route presents as advantages the production of nanostructures in a short reaction time and in relatively low temperatures. Due the simplicity, versatility and low cost of this route, the solochemical method is a process extremely viable for industrial production of zinc oxide[4].

In this article we report a simple chemical method to synthesis ZnO nanoparticles and study the change grain size in different concentration of preparation .Among control of the particle size is one main concern for nanostructured material synthesis because electrical and optical properties of nanomaterials depend on both size and shape of the particles[5]. Therefore, it is desired to synthesize nanomaterial in a controllable size by a simple approach.It is a soft chemistry method which allows to prepare oxide or metal nano particles with controlled size and shape [6].

2. Experimental

Materials

The materials used in this study were Zn(NO3)2.6H2O with different concentration of NaOH ,
the properties of the materials used in this study are shown in table (1).

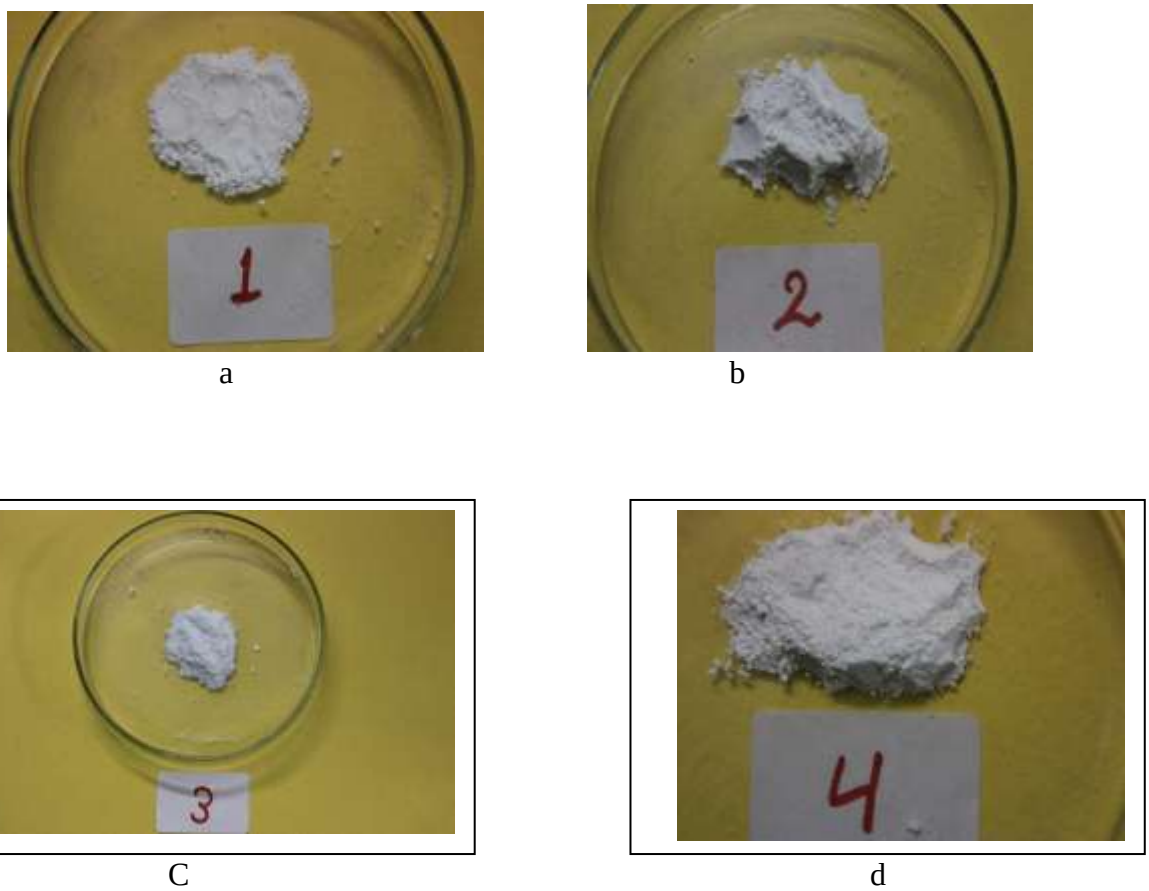
Table (1): Some chemical properties of the row materials .

Raw material	Chemical formula	Molecular Weight	Purity	Physical characteristics	Manufacturer
Znic nitrate hexahydrate	Zn(NO3)2.6H2O	297.51	98.5%	Colorless crystals	Scharlau(Spain)
Sodium Hydroxide	NaOH	40	98%	White pellets	CCG(U.K.)

2.1. Preparation of nanopartiacals

The wet chemical method were used to prepare zinc oxide (ZnO) nanoparticles [7]. using zinc nitrate and sodium hydroxide as precursors.(0.25 ,0.5 ,0.75 .and 1) M of

NaOH which prepared by dissolving (40 gm) of NaOH in 1liter (1000 ml) of deionized water. The solution was stirred at 70ºC . 0.5M of $Zn(NO_3)_2.6H_2O$ was prepared by dissolving (37.175 gm) $Zn(NO_3)_2.6H_2O$ in (250 ml) of deionized water , and then addied to the basic solution drop by drop, the solution was keeping stirring and heating for 3h . After the completion of reaction, the solution is allowed to settle for 10 mints and the supernatant solution was then discarded carefully. The remaining solution centrifuged at 10,000 × g for 10 min and the supernatant then discard. Thus produced nanoparticles wash five times using deionized water. Then dried at 70°C for overnight. During drying, complete conversion of Zn $(OH)_2$ into ZnO takes place. Obtained powder is white as shown in figure (1a) ,the other samples prepared as the same way but with different concentration for NaOH ,and the result powder shown in figure(1-b,c,d) . At last the fifth sample was prepared with (1)M NaOH ,but with preparing temperature 80 ^{0}C .



a b

C d

Fig. (1):ZnO nanorods prepared with a) 0.25M ,b) 0.5M ,c) 0.75M and d) 1 M of NaOH at 70℃

3. RESULTS AND DISCUSSION

3.1. X-ray Diffraction

A typical XRD pattern of the prepared (powders) is shown in figures (1,2,3,and 4), the sample synthesized at 70 ºC and different concentration (.25,.5,.75 ,and1)M for NaOH respectively . The pattern is indexed with hexagonal unit cell structure . The result were compared with the observed relative peak intensities to that of their standard values. There is a small difference in the relative peak intensities of the (100) to (002) as observed in our case imply that the ZnO nanorods fabricated by different methods exhibit different preferred orientations. Furthermore no impurities were found in the XRD pattern. Also the diffraction peaks are intensive and very sharp. Thus high purity hexagonal ZnO nanocrystals could be obtained by this synthesis process Agreement with results obtained by Samanta [8] .All of the diffraction pattern can be indexed to the hexagonal ZnO phase (Wurtzite Structure) by comparison with the data from JCPDS card 36-1451 . However, the XRD patterns of the nanoparticles are considerably broadened due to the very small size of these particles used Scherrer equation(1):

$$D = \frac{KT}{\beta \cos \theta} \quad \ldots (1)$$

Where
D is the crystal size
K is the shape factor
λ is the emitted wavelength of X-ray source
β is the full-width at half maximum FWHM (degree),
θ is the diffraction angle in (degree) .

The strong and narrow diffraction peaks indicated that the product has good crystallinity. Agreement with Soosen [9].

Table(2):The main peaks of XRD , grain size in (nm) and the experimental interatomic spacing (d) which is obtained from Bragg′s law.

0.25M NaOH	2θ(Deg.)	FWHM (Deg.)	hkl	Grain size (nm)	d_{hkl} Exp.(Å) (nm)
	31.8008	0.401	(100)	21	2.812
	34.4061	0.371	(002)	22	2.604
	36.3218	0.451	(101)	19	2.471
	47.5862	0.561	(102)	15	1.909
	56.7050	0.502	(110)	18	1.622
0.5M NaOH	2θ(Deg.)	FWHM (Deg.)	hkl	Grain size (nm)	d_{hkl} Exp.(Å) (nm)
	31.7241	0.373	(100)	22	2.818
	34.4061	0.265	(002)	31	2.604
	36.2452	0.374	(101)	22	2.476
	47.5096	0.375	(102)	23	1.912
	56.6284	0.454	(110)	20	1.624
0.75M NaOH	2θ(Deg.)	FWHM (Deg.)	hkl	Grain size (nm)	d_{hkl} Exp.(Å) (nm)
	31.7241	0.383	(100)	22	2.818
	34.4061	0.225	(002)	37	2.604
	36.2452	0.352	(101)	24	2.476
	47.5862	0.422	(102)	21	1.909
	56.6284	0.417	(110)	22	1.624
1 M NaOH	2θ(Deg.)	FWHM (Deg.)	hkl	Grain size (nm)	d_{hkl} Exp.(Å) (nm)
	31.7383	0.255	(100)	32	2.817
	34.4299	0.143	(002)	58	2.603
	36.2243	0.270	(101)	31	2.478
	47.5888	0.243	(102)	36	1.909
	56.6355	0.315	(110)	29	1.624

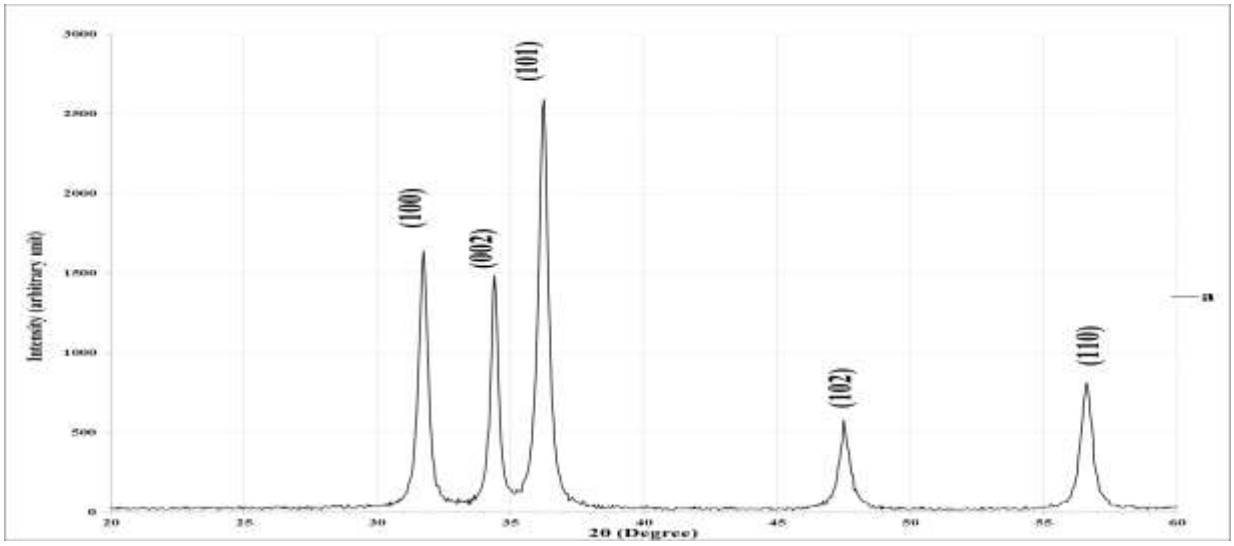


Fig.2: XRD of ZnO nanoparticals synthesized with 0.25M of NaOH at 70 ºC.

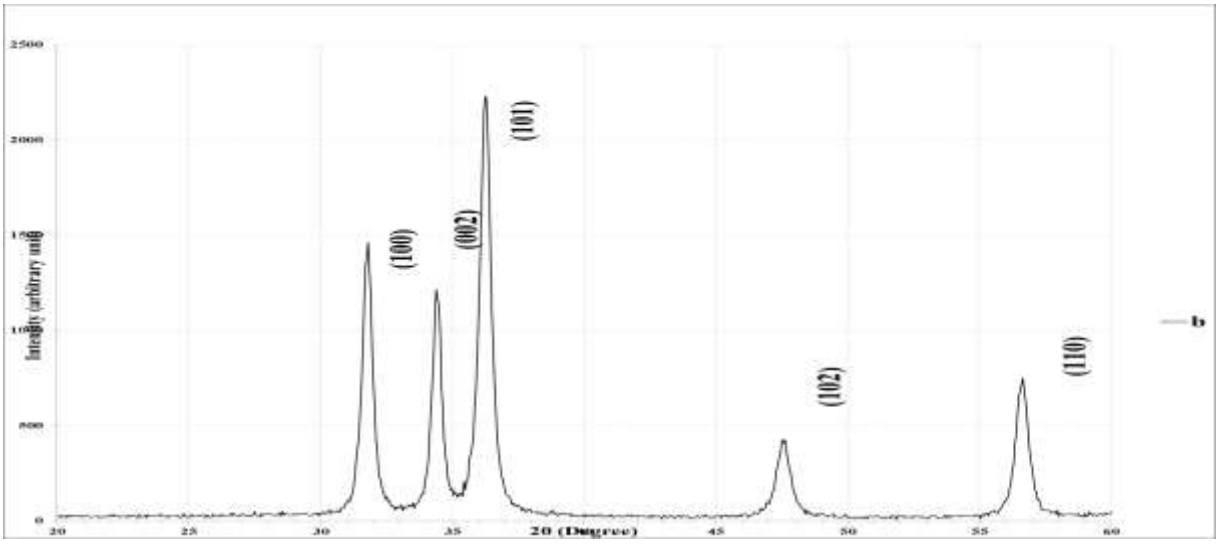
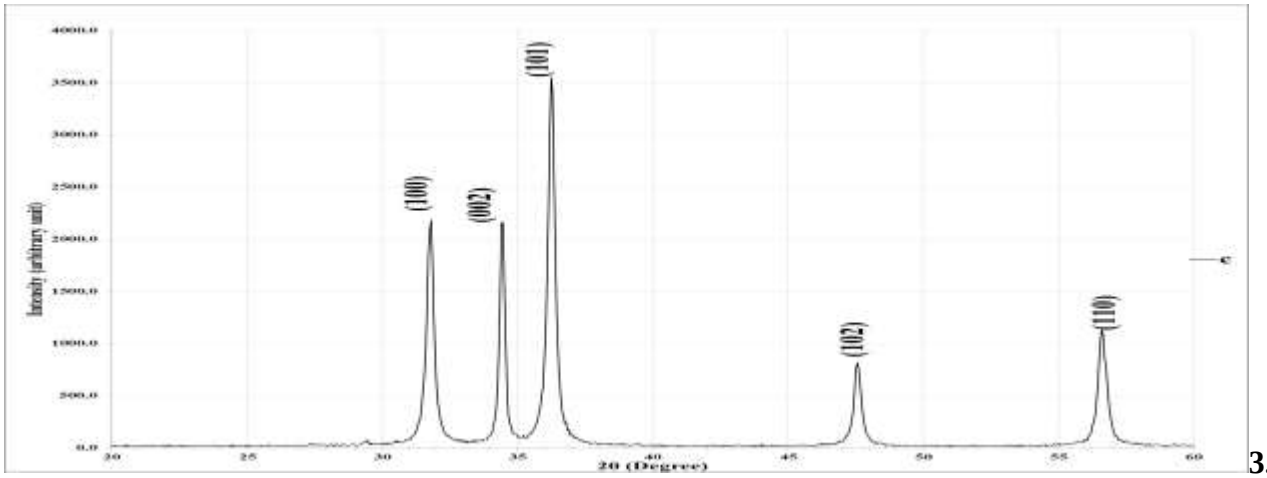


Fig .3: XRD of ZnO nanoparticles synthesized with 0.5M of NaOH at 70 ºC.



3.2

Fig .4: XRD of ZnO nanoparticles synthesized with 0.75M of NaOH at 70 ºC.

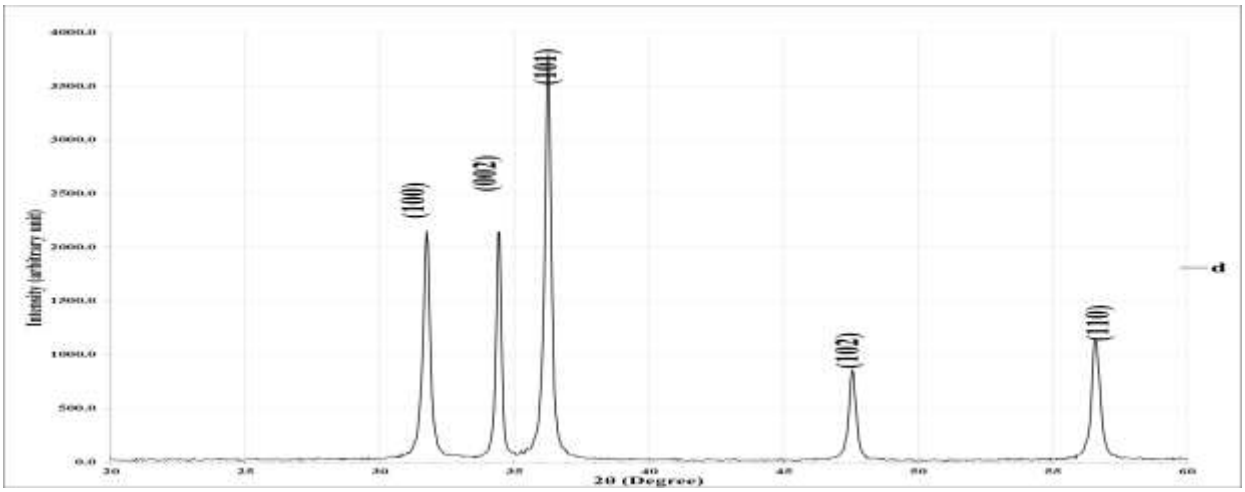
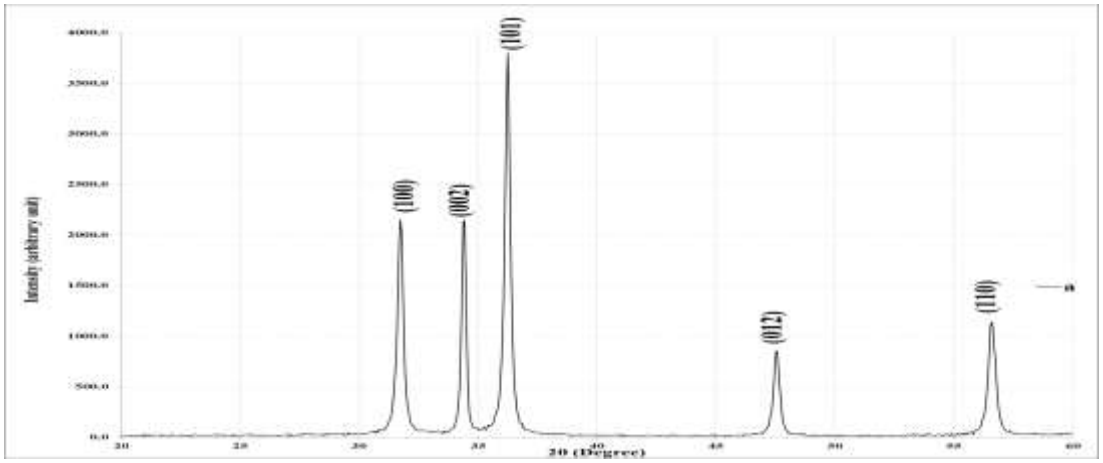


Fig .5: XRD of ZnO nanoparticles synthesized with 1 M of NaOH at 70 ºC.



.Fig 6 XRD of ZnO nanorods synthesized with 1 M of NaOH at 80 ºC .

Scanning Electron Microscopy

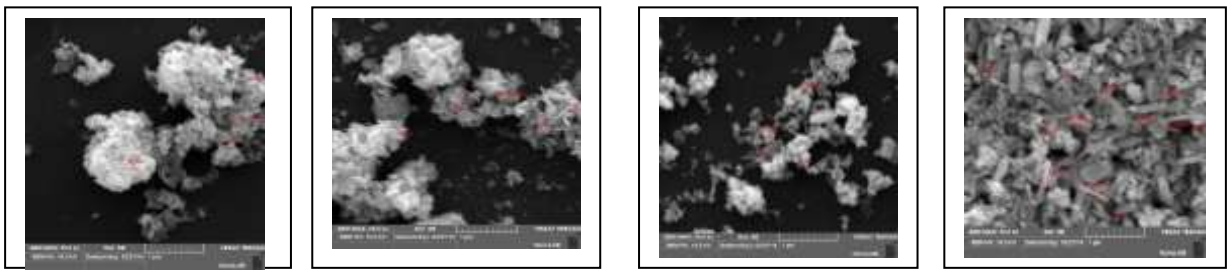
Figure (7-a) shows the SEM morphology of the synthesized nano particles for sample P1(0.25M NaOH). The image clearly shows the formation of spherical ZnO nanoparticles, with particle size about 15-30 nm .

The morphology of the prepared sample analyzed by SEM is shown in Figure (7-b) for ZnO nanoparticles sample P2 (0.5 M) of (NaOH). The image clearly shows the formation of more regularity and smaller particle size 20-35 nm .

Figure (7-c) shows The morphology of the prepared sample analyzed by SEM for sample P3(0.75M) of NaOH. The image clearly shows the formation of irregular shape of ZnO nanoparticle. Careful examination of the individual formed of nanoparticle ZnO indicates that the diameters of the particles vary from 20-40 nm. It is interesting to observe a irregular hexagonal shaped pyramid like nanoparticles grown in the chemical bath.

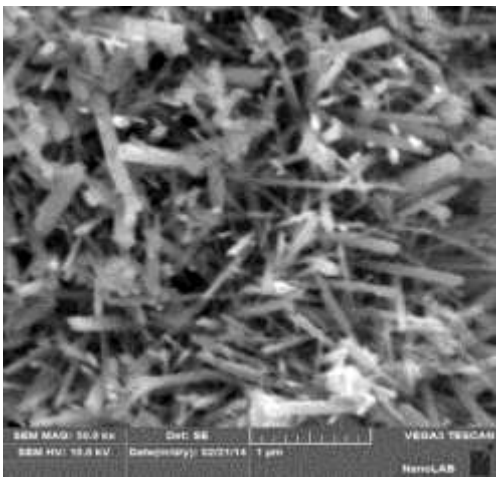
The morphology of the prepared sample analyzed by SEM for P4 (1M) NaOH is shown in Figure (7-d) . The SEM image demonstrates clearly the formation of Short rods ZnO nanoparticles of diameter ~25-62 nm and length ~ (200 nm -500 nm) .

Figure(8) shows the morphology of the prepared ZnO nanorods P5 (1M) NaOH at 80^0C preparation . It reveals the most striking feature of the obtained product is ZnO nanorods. The powder contains ZnO nanorods of diameter ~30-50 nm and length ~ (500nm-1μ) . The SEM images have taken from different region of the distributed sample and it was observed that the rods are randomly distributed in the powder sample and gathered together.



a b c d

Figure (7) : SEM image of the prepared ZnO nanoparticles samples,a- P1,b-P2,c-P3,and d-P4 at70 ^{0}C.



Fig(8) The SEM image of ZnO a) nanorods synthesized 1 M of NaOH at 80 ºC

3.3. Growth mechanism of ZnO nanoparticles

The growth mechanism has been proposed by several researchers according to the condition of the experiments [8]. In the context of our synthesis, we depict the mechanism of ZnO nanorod formation as follows: When zinc nitrate solution is added with the NaOH solution under constant stirring it produces $Zn(OH)_2$colloidal particles. During the hydrothermal decomposition, a part of this colloidal $Zn(OH)_2$dissolves into $Zn^{2+}$and OH^- and it continues further to form $Zn(OH)_4^{2-}$.

When their concentration reaches to the degree of supersaturation, ZnO nuclei form. The basic reactions are [8]:

$$Zn(NO_3)_2.6H_2O + 2NaOH = Zn(OH)_2 + 2NaNO_3 + 6H_2O$$
$$Zn(OH)_2 + 6H_2O = Zn^{2+} + 2OH^- + 2H_2O = Zn(OH)_4^{2-} + 2H^+$$
$$Zn(OH)_4^{2-} = ZnO + H_2O + 2OH^-$$

3.3.a. Influence of the Growth Temperature

The effect of temperature on the ZnO nanostracture was investigated. In our experiments, ZnO nanorods prepared with (1M) of (NaOH) . Our growth temperature was 70℃ The SEM images of this samples are shown in Figure(3a) and Figure(3b) , it can see that diameter and length of rods decreased These results may be explained by the nucleation and growth of particles in a solution. Particle morphology is influenced by the factors such as supersaturation, nucleation and growth rates, colloidal stability, recrystallization and aging process. Generally, supersaturation, which is highly dependent on solution temperature, has a predominant influence on the morphology of the precipitates. A highly supersaturated solution possesses high Gibbs free energy. The tendency of a system to lower its Gibbs free energy is the driving force in the processes of nucleation and growth of particles. The relation between Gibbs free energy change per unit volume, ΔG_v, and supersaturation is given by the following equation(2):

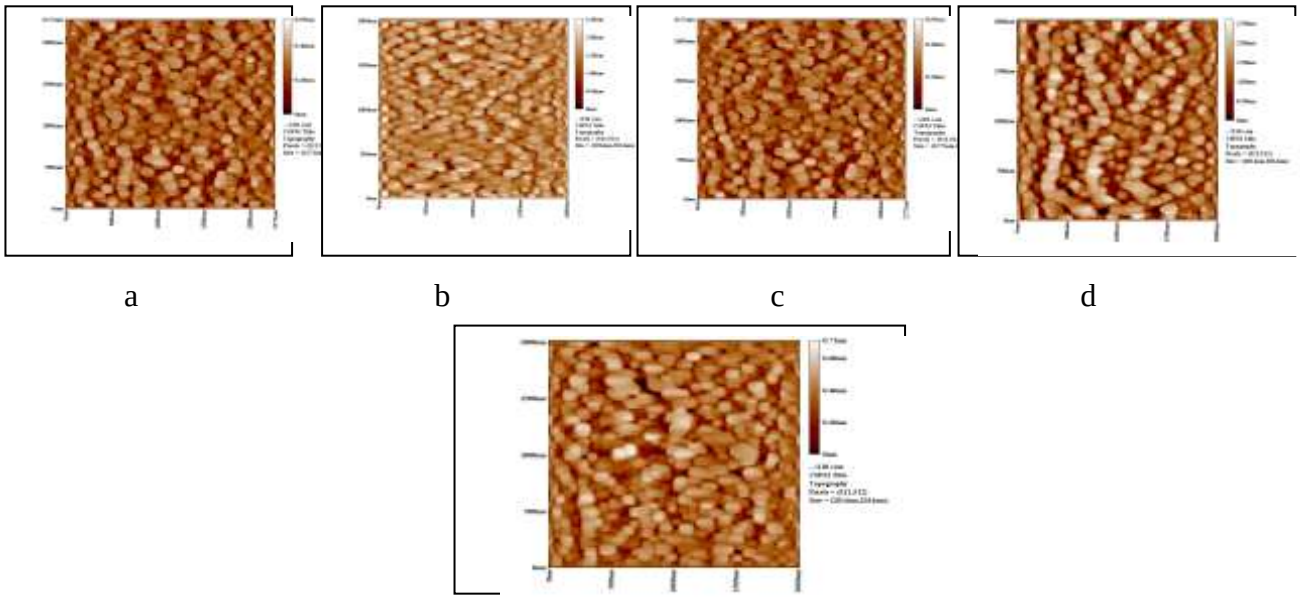
$$\Delta G_v = -\left[\frac{KT}{\Omega}\right]\ln\left(\frac{C}{C_o}\right) = -\left[\frac{KT}{\Omega}\right]\ln(1+\sigma) \qquad \ldots(2)$$

where C is the concentration of the solute , C_o is the equilibrium concentration or solubility, k is the Boltzmann constant, T is the temperature, Ω is the atomic volume and σ is the supersaturation defined by $(C - C_o)/C_o$. Without supersaturation (i.e. σ = 0) , ΔG_v is zero , and no nucleation would occur. It is clear from the relation that ΔG_v can be significantly increased by increasing the supersaturation for a system. Now the supersaturation is temperature as well as rate of reaction dependent [12] . At low temperature a higher supersaturation leads to large reduction in Gibbs free energy. This energy reduction appears as an increased surface energy favouring continued nucleation with smaller sizes.

An increased temperature leads to the increased solubility and hence reduced supersaturation of the solution and as a consequence large size particles were obtained. The high temperature favours a fast hydrolysis reaction and results in the high supersaturation, a large ΔG_v which in turn leads to the formation of a large number of small nuclei.

Atomic Force Microscope Analysis (AFM)

The grain size (grain diameter) and average roughness of ZnO nanoparticles by using chemical method have been measured using AFM as shown in Figures(9 a,b,c,and d) for ZnO nanoparticles samples P1 , P2, P3, and nanorods sample P4 and P5 respectively.Table (4) lists the grain size (grain diameter) and average roughness of ZnO nanoparticles of each sample ,with increase in the concentration of NaOH the ph increase respectively and that coues to increase the average diameter while decrease the roughness.



a b c d

e

Fig (9-a,b,c,d and e) : AFM images for sample P1,P2,P3,P4, andP5 .

Table (3) lists the grain size (grain diameter) and average roughness of ZnO nanoparticles

The sample code	Avg. Diameter (nm)	average roughness (nm)
P1(0.25M) NaOH	82.24	0.712
P2(0.5M) NaOH	82.48	0.258
P3(0.75M) NaOH	87.94	0.315
P4(1 M) NaOH	92.61	0.411
P5(1 M) NaOH(80 ^{0}C	95.78	0.845

Conclusion

The main conclusions summarized are :

1-The change in NaOH concentration leads to change in ph which leads to change in shape and size of ZnO nanoparticle size.

2-The results of SEM morphology show that the particle size increase with increasing the concentration of NaOH and the shape of produce particle become to be nano rod with diameter 25-62 nm and length (200-500) nm at 1M of NaOH ,the length of rods increase with increasing preparation temperature .

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