Preparation and Study of morphological properties of ZnO nano Powder

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ABSTRACT

In this work, ZnO nanostructures for powder ZnO were synthesized by Hydrothermal Method. Size and shape of ZnO nanostructureas can be controlled by change ammonia concentration. In the preparation of ZnO nanostructure, zinc nitrate hexahydrate [$Zn(NO_3)_2 \cdot 6H2O$] was used as a precursor. The structure and morphology of ZnO nanostructure have been characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray diffraction (XRD). The synthesized ZnO nanostructures have a hexagonal wurtzite structure. Also using Zeta potential and Particle Size Analyzers and size distribution of the ZnO powder

Keywords: Hydrothermal method, ZnO, nanostructure.

تحضير ودراسه لخصائص التركيبيه والطوبوغرافيه لباودر اوكسيد الخارصين النانوي

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الخلاصه

في هذا العمل، حضرت تراكيب نانويه لباودر اوكسيد الخارصين بطريقه الهيدرو-حراري ,شكل وحجم التراكيب النانويه لاوكسيد الخارصين يمكن السيطره عليها بواسطه تغير تركيز الامونيا . في تحضير التراكيب النانويه تستخدم نترات الخارصين هيكسايدرات كمحفزات . شخصت البنيه ومورفولوجيه التراكيب نانويه لاوكسيد الخارصين بواسطه المجهر الالكتروني الماسح ومجهر القوى الذريه وحيود الاشعه السينيه للتراكيب نانويه لاوكسيد الخارصين المحضره تمتلك تراكيب سداسيه ,وباستخدام كل من جهازجهد زيتا و جهاز تحليل الحجم الحبيبي لمعرفه تحليل الحجم الحبيبي والتوزيع الحجمي لباودر اوكسيد الخارصين المحضر .

الكلمات الرئيسيه : الطريقة الهيدرو-حراري, اوكسيد الزنك, البنية النانوية.

1. INTRODUCTION

Nano particles have been attracted increasing attention in recent years and their different types have been used in concrete mixtures in order to improve both the mechanical and physical properties of the concrete , **Sahereh, 2013**.

Zinx oxid nanostructure always in the center of attention due to their fascinating properties ,**Donya, et al., 2013**. It has a unique material because it has exhibits semiconducting and piezoelectric dual properties on optical, semiconducting, piezoelectric, and magnetic and gas sensing properties. It exhibits interesting properties including, high exciton binding energy (60 mV), high chemical stability, high catalytic efficiency, strong adsorption ability and low growth temperature makes it an excellent candidate for room temperature UV lasing application, **Rizwan, et al. 2009**, **Radu 2011**.

Due to its vast industrial applications, ZnO powder has attracting considerable attention ,it has been used in the rubber manufacture and cigarettes (used as a filter), and it has used as a coating agent various paints and as an additive in the manufacture of concrete and ,**Matei1 et al., 2014** , **Manish and Shakti 2010**. Ceramic, cement, glass, and adhesive, sealants, lubricants, pigments, fire retardants, pigments and , ZnO has used for concrete manufacturing, improves the processing time and the resistance of concrete against water ,**Vigneshkumar, 2014**.

Furthermore, ZnO has an environmentally friendly material, which has desirable especially for bio-applications such as bio-imaging and cancer detection ,**Munusamy, et al., 2013**. It has extensive applications in water purification ,**Gnanasangeetha, and Sarala, 2013**. It is also used as an additive in food products such as breakfast cereal. It has used in a host of other creams and ointments that are used to treat skin diseases ,**Manish, and Shakti, 2010**.

Fernandez, et al., 2001. demonstrated that ZnO has huge impact on setting time (ST) and retards the ST with respect to that of the cement. They also measured unconfined compressive strength (UCS) and showed that the UCS of the final product decreases at short ages in presence of ZnO.

The efficiency of ZnO as a photocatalyst increases with the increase of surface to volume ratio compared with bulk ZnO materials. The main advantage of ZnO is relative ease of preparation of phoptocatalytic nanostructures.

Number of simple as well as complex forms of ZnO nanostructures was reported in literature including, nanorods, nanobelts, nanotubes, nanorings and hierarchical structures ,**Yang ,2010**.

On the other hand some of the above reported structures show superhy drophobicity due to high surface roughness. ZnO nanorod was relatively easily show high activity due to high surface area compared to ZnO nanoparticles mostly due to their high purity and crystalline ,**Elias, et al., 2008, Yu., et al., 2007**.

In this paper, different shapes of ZnO nanopartical and nanorod were synthesized with a single precursor at relatively low temperature by employing simple solution method. ZnO nanostructure was synthesized by variation of ammonia concentration in the preparation of ZnO nanoparticles. The results indicated that addition of high amount of ammonia to aqueous solution of Zn $(NO_3)_2 \cdot 6H_2O$ could greatly affect the morphology and size of ZnO. We suggest a procedure of preparation of ZnO nanorod and nanopartical powder, to add to concrete activity to the material.

2. EXPERIMENTAL WORK

2.1 Materials

Chemical materials zinc nitrate [Zn $(NO_3)_2 \cdot 6H_2O$], ammonia solution (2%) (NH_3), 1,4- butanediol ($C_6H_{12}O$) were supplied by Fluke Company (Germany).

2.2 Preparation of ZnO Nanopowder

The preparation of zinc oxide nanostructure described as: (1.20 g) zinc nitrate hexahydrate [Zn $(NO_3)_2 \cdot 6H_2O$] was dissolved into 50 ml of distilled water. Then, 5ml of NH_3 aqueous solution (2%) for solution (A) and 10 ml of NH_3 aqueous solution (2%) for solution (b) was added drop by drop to an aqueous solution of zinc nitrate. This results rising of solution pH to 9.7 for sample (A) and 12 for (B). Resulted $Zn(OH)_2$ precipitate was separated by centrifugation at 2800 rpm for 5 min and then dispersed in 50 ml of 1,4-butanediol. The solution with the dispersed Zn $(OH)_2$ was heated at 105°C for 10 h in a closed glass bottle. Then separate the obtained particle from the solution and centrifuged at 3000 rpm for10 min and washed several time with methanol to remove the remaining ions in the final product, and finally, the precipitate was dried at 80°C for 6h.

2.3. CHARACTERIZATION TECHNIQUES

The crystalline structure of the powder has been determined by using x-ray diffraction (Philips PW 1050 X-ray diffract meter of 1.5^{o}A from Cu-Kα. Additionally, the surface morphology and optical properties were examined using: Scanning Electron Microscopy (SEM,the VEGA easy probe), also by Atomic Force Microscopy (AFM) (Digital Instruments Nanoscope II) and Scanning Probe Microscope (AA3000). Zeta potential and Particle Size Analyzers and size distribution of the ZnO powder were analyzed using (NanoBrook 90Plus Particle Size Analyzer).

3. RESULT AND DISCASSION

Fig.1 shows the SEM images of the products with different amount of ammonia concentration. The surface morphology of the sample is showed in **Fig**.**1a.**

A different shape of nano sphere ZnO have been shown the obtained size of full array of a nano spheres structure with diluted ammonia was 50 ml of NH_3 which includes some nanorods forming. As amount of ammonia concentration increase nanorods forming the crystalline as shown in **Fig 1.b**. It was found that the addition of ammoni has affected on structure and morphology ZnO.

Fig. 2 shows AFM image of ZnO powder deposition on glass substrate by sputtering methods. Also the three dimensional AFM pictures of ZnO films are shown in right side on the same figure. From this image, it can be seen that the dispersion of ZnO nanoparticles is relatively uniform with the average diameter with root mean square (RMS) surface roughness is about 140 nm and 5.3nm respectively. As concentration of NH_3 aqueous solution increases, the RMS roughness of the films and the grain size dropped to about 62 nm and 2.68 nm respectively as shown in **Table1**.

Phase composition and phase purity of the obtained products were identified by XRD as shown in **Fig.3 a,b**. Relatively strong and sharp peaks in the XRD pattern confirm that the products are ZnO .Hexagonal phase with a wurtzite structure, no diffraction peaks of Zn or other impurities were observed in the spectrum, which indicates excellent crystal quality of the products. The particle size histograms of ZnO nanoparticles (illustrated in **Fig. 4a**) ZnO nanostructures with pH=12 the particles range in size from 10 to 50 nm and the particles range in size from 60 nm to150 respectively ,with mean diameter of 60nm when concentration of NH_3 decreased at pH equal to 9.7 the particles increased with range in size from 26.8 to 93 nm and the

particles range in size from102 nm to388.2 respectively ,with mean diameter of 162.3nm as shown in **Fig.4b**.

ZnO nanopowder was determined at pH 9.7 with zeta potential values -156.93 mV and a mean particle size of 162.3.nm. As the pH increased to 12, the zeta potential dropped to -165.65 mV and consequently decreases an mean particle size of 60nm

The ZnO NPs were found to partially disaggregate due to surface charge repulsion. (**Li, et al., 2013, Ma, et al., 2013, Omar, et al., 2014**) as shown in **Fig.5**

4. CONCOLUTION

1. The synthesis of ZnO nano powder is demonstrated by hydrothermal methods
2. XRD pattern show that all the diffraction peaks in the pattern can be easily indexed as the pure hexagonal phase of ZnO with a wurtzite structure.
3. The SEM images of nanospherers and nanorods with increase pH depends on the concentration of ammonia .
4. Zeta potential and particle size analyzer surely zeta potential values -156.93mV and an average particle size of 162.3.nm for pH 9.7. As the pH was increased, to 12, the zeta potential dropped to -165.65 mV and consequently decreases an average particle size of 60nm.

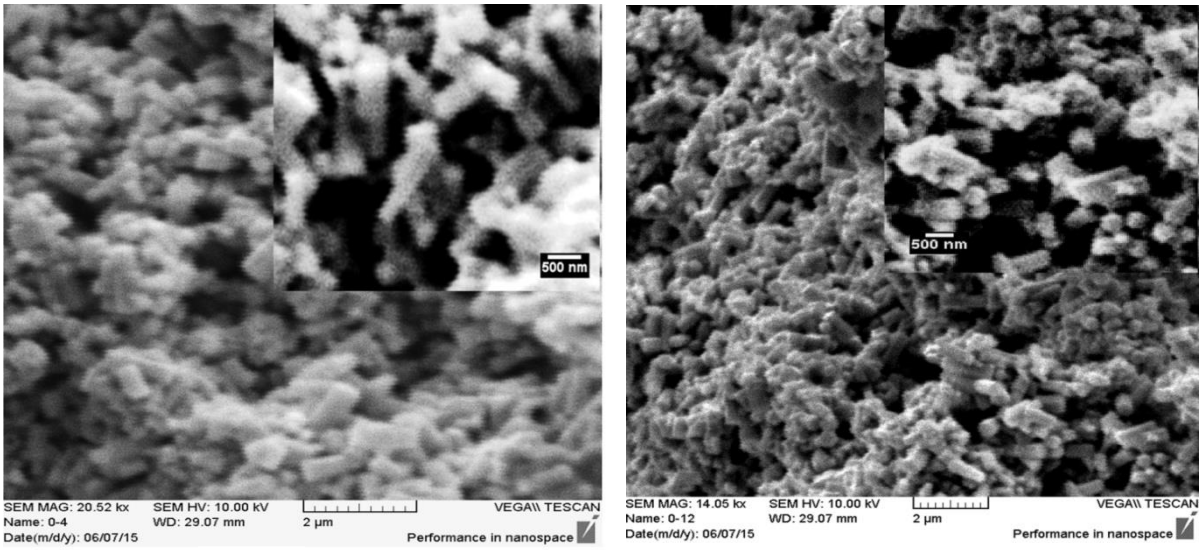
REFERENCES

- -A. Matei1, V. Tucureanu and I. Dumitrescu, 2014, *Aspects Regarding Synthesis and Applications of ZnO Nanomaterials*, Bulletin of the Transilvania University of Braşov , Series I: Engineering Sciences, . No. 2, 56.
- -Donya R., Mohd Z.B. H. and Yun H. T ., 2013, *Hydrothermal Synthesis of Zinc Oxide Nanoparticles using Rice as Soft Biotemplate*, Ramimoghadam et al. Chemistry Central Journal ,Vol. 7, PP.136.
- -F. M. Omar, H. A.l Aziz, and S. Stoll, 2014, *Aggregation and Disaggregation of ZnO Nanoparticles: Influence of pH and Adsorption of Suwannee River Holmic Acid*, Science of the Total Environment,Vol.468-469, PP.195-201.

- -Fernández O., Chacon E., and Irabien A., 2001, *Influence of lead, Zinc, Iron (III) and Chromium(III) Oxides on the Setting Time and Strength Development of Portland Cement,* Cement and Concrete Research, Vol.31,pp.1213-1219 .
- -Gnanasangeetha D. and Sarala T. D., 2013, *One Pot Synthesis of Zinc Oxide Nanoparticles via Chemical and Green Method,* Research Journal of Material Sciences, Vol. 1(7), PP.1-8.
- -Jamil E., Ramon T. Z., Guillaume-Y. W. and Claude L. C., 2008, *Conversion of ZnO Nanowires into Nanotubes with Tailored dimensions*, Chem. Mater, Vol.20, PP .6633–6637.
- -Li M., Lin D., and Zhu L., 2013, *Effects of Water Chemistry on the Dissolution of ZnO Nanoparticles and Their Toxicity to Escherichia Coli*, Environ Pollut, Vol.173, PP.97–102.
- Lili Y., 2010, *Synthesis and Characterization of ZnO Nanostructures*, Ph.D. Thesis, Department of Physical Electronic Division, Linköping University, SE-601 74 ,Norrköping, Sweden.
- -Ma PPH., Williams P., and Diamond S., 2013, *Ecotoxicity of Manufactured ZnO Nanoparticles Areview,* Environ Pollut, Vol.172, PP.76–85.
- -Manish K. and Shakti S. S.,2010, *Zinc Oxide Nanostructures Synthesized by Oxidization of Zinc*, Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of Bachelor of Technology in Metallurgical & Materials Engineering.
- -Munusamy T., Kai-L. H. and Jiunn-F.L., 2013, *Preparation and Morphology Studies of Nano Zinc Oxide Obtained Using Native and Modified Chitosans*, Materials, Vol. 6, PP. 4198-4212.
- -Q. J. Yu, W. Y. Fu, C. L. Yu, H. B. Yang, R. H. Wei, M. H. Li, S. K. Liu,Y. M.Sui, Z. L. Liu, M. X. Yuan, G. T. Zou，G. R. Wang, C. L. Shao, and Y. C. Liu, 2007, *Fabrication and Optical Properties of Large-Scale ZnO Nanotube Bundles Via a Simple Solution Rout*, J. Phys. Chem. C, Vol.111 ,PP.17521-17526.
- -Radu O., 2011, *Nanomaterial and Nanotechnology in Civil Engineering*, Buletinul Institutului Politehinic Diniasi, Publicat de Universitatea Tecnica,

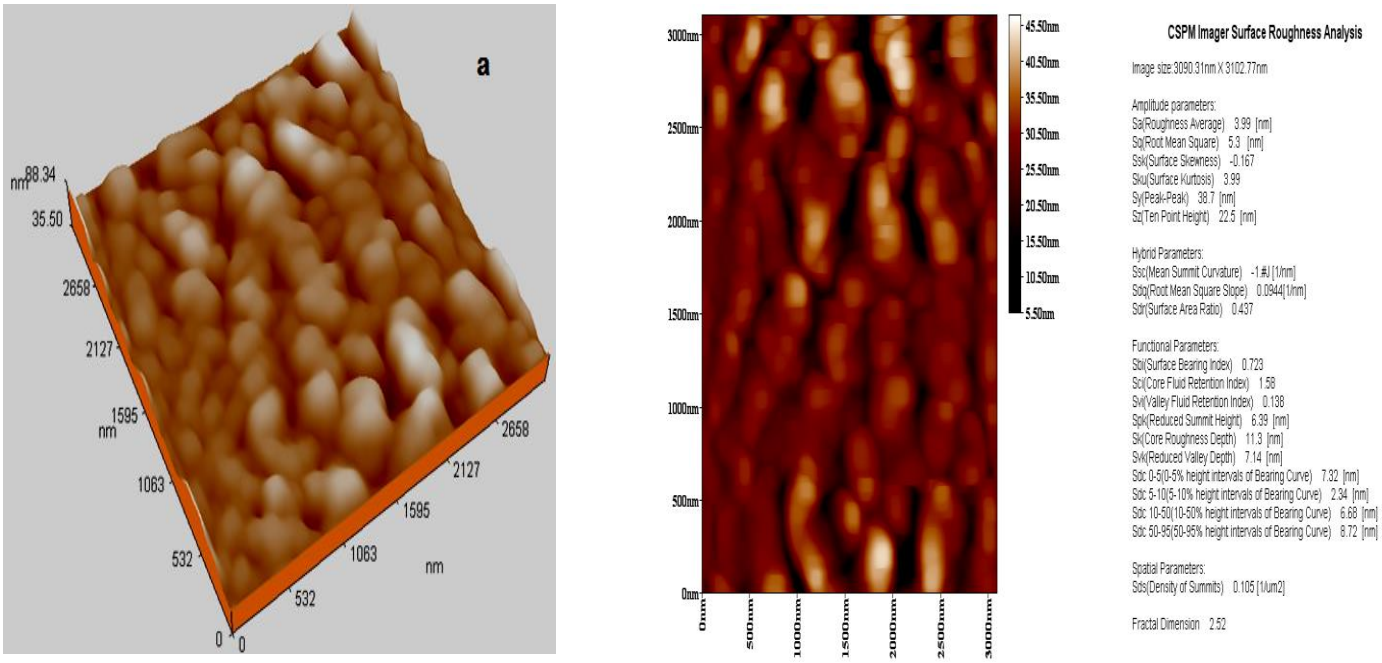
Gheorghe Asachi" din Iasi, Tonul LIV (LVIII), Fasc. 4, Sectia, Constructii ,Arhitectura.

- -Rizwan W.,Young-Soon K. and Hyung-Shik S., 2009, *Synthesis, Characterization and Effect of pH Variation on Zinc Oxide Nanostructures*, Materials Transactions, Vol. 50, PP. 2092 – 2097.
- -Sahereh M., 2013, *Nanotechnology Applications in Construction Industry*, Journal of Basic and Applied Scientific Research, Vol.3, PP. 391-396.
- -Vigneshkumar C., 2014, *Study on Nanomaterials and Application of Nanotechnology and Its Impacts in Construction*, Discovery, Vol., No. 23(75), PP.8-12

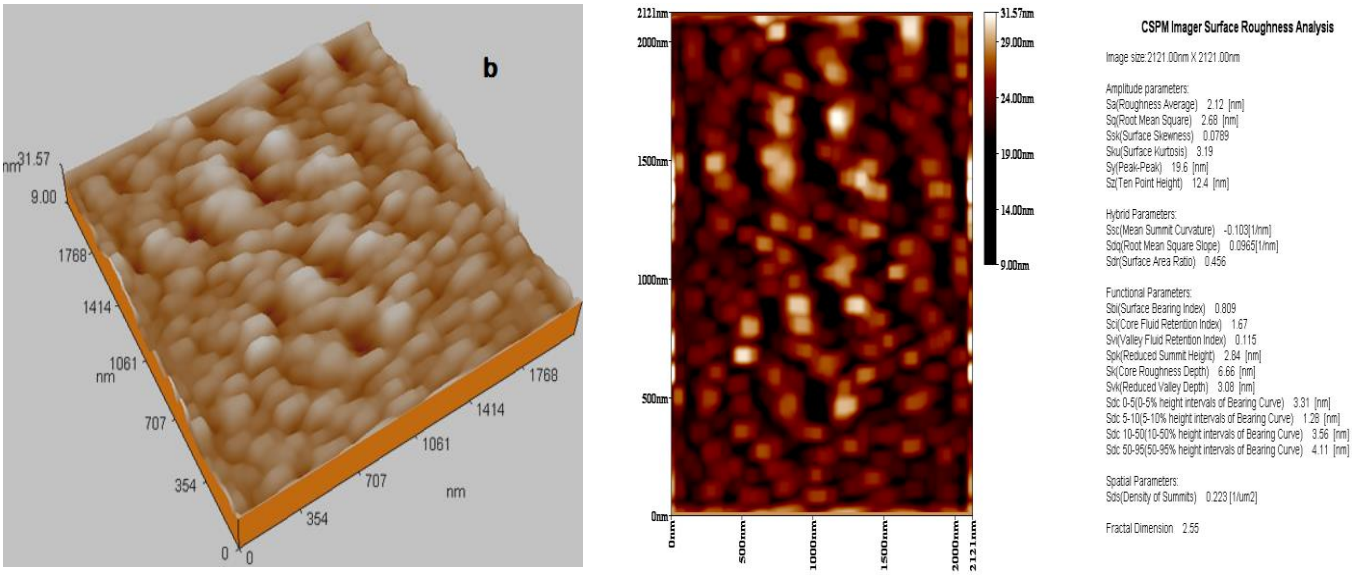


b **a**

Figure 1. SEM image of ZnO nanostructure at different concentration at pH=9.7 (a) pH=12(b).



(A)



(B)

Figure 2. AFM images of the ZnO powder at different concentration a) pH=9.7 ,b)pH= 12.

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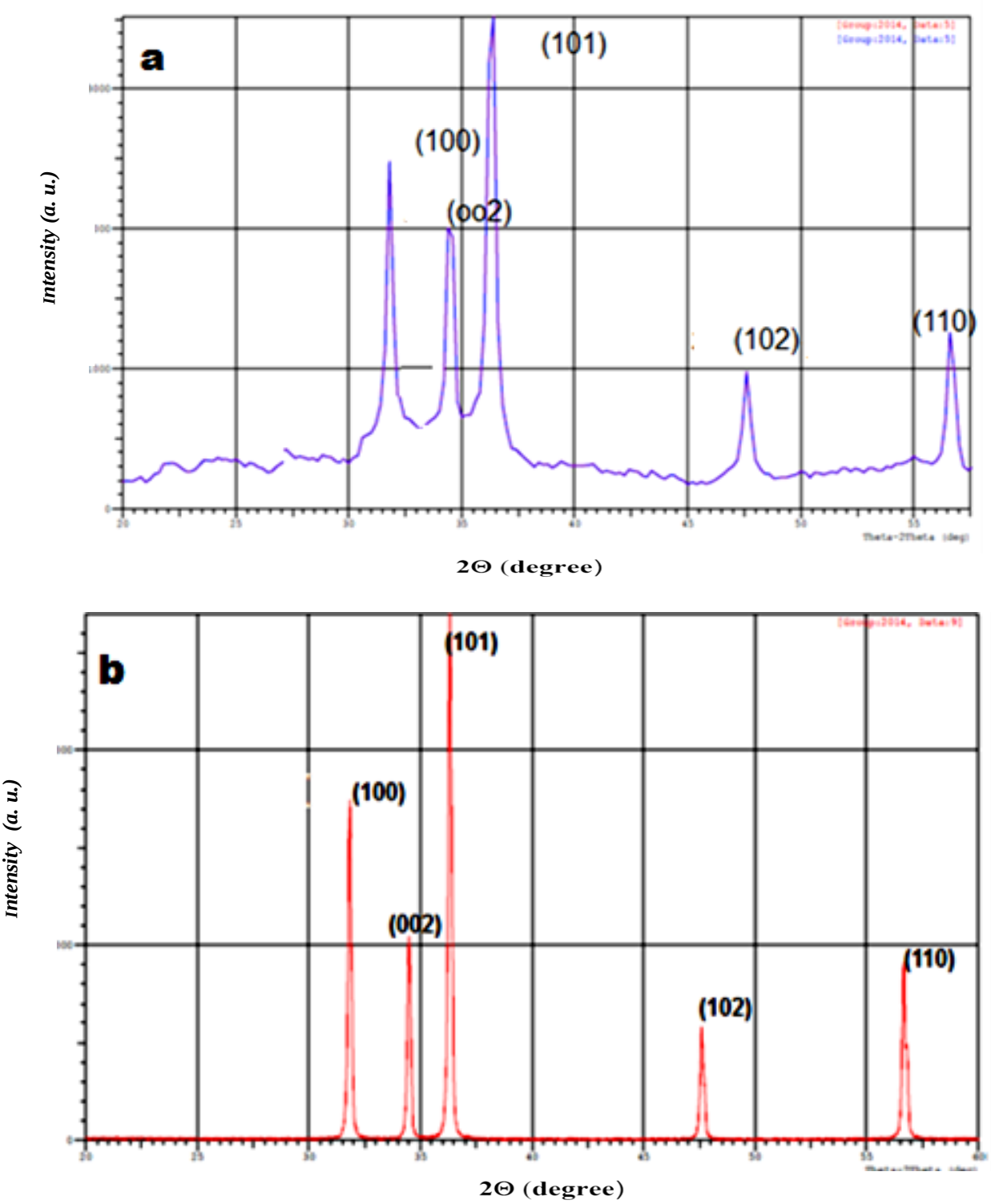
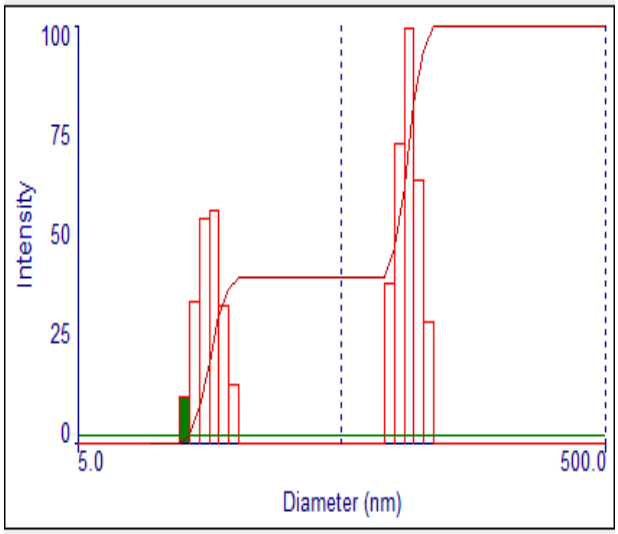


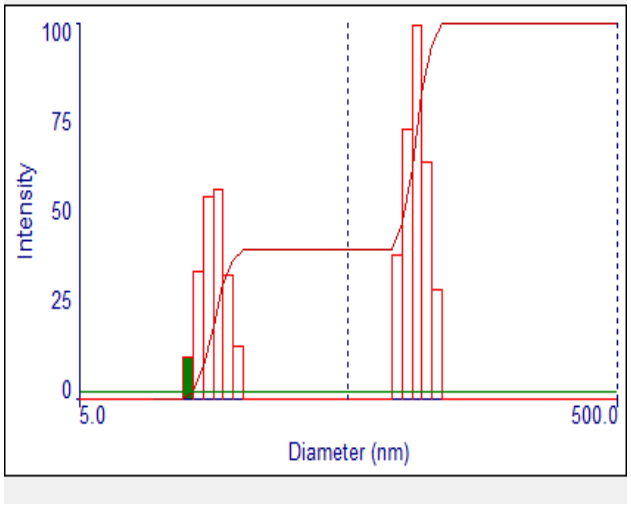
Figure 3. XRD patterns of ZnO nanostructures changed with different amount of ammonia (a) 5 ml solution of ammonia with pH=9.7, (b) 10 ml solution of ammonia with pH=12.



d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)
9.9	0	0	25.1	0	40	63.9	0	40
10.7	0	0	27.3	0	40	69.5	0	40
11.7	0	0	29.8	0	40	75.7	38	48
12.7	11	2	32.4	0	40	82.4	72	62
13.9	34	9	35.3	0	40	89.7	100	82
15.1	54	20	38.4	0	40	97.6	63	94
16.4	56	31	41.8	0	40	106.3	29	100
17.9	33	37	45.5	0	40	115.7	0	100
19.5	14	40	49.5	0	40	126.0	0	100
21.2	0	40	53.9	0	40	137.1	0	100
23.1	0	40	58.7	0	40	149.3	0	100

a)ZnO nanostructures with pH=12

size distribution using the software of (PSA),for sample(a)



d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)
26.8	0	0	67.2	0	44	168.4	0	44
29.2	0	0	73.1	0	44	183.1	0	44
31.7	0	0	79.4	0	44	199.0	6	45
34.4	0	0	86.3	0	44	216.4	39	52
37.5	22	4	93.9	0	44	235.2	78	66
40.7	53	13	102.0	0	44	255.7	100	83
44.3	82	28	110.9	0	44	278.0	66	95
48.1	61	39	120.6	0	44	302.2	28	100
52.3	29	44	131.1	0	44	328.5	0	100
56.9	0	44	142.5	0	44	357.1	0	100
61.8	0	44	154.9	0	44	388.2	0	100

b) **ZnO nanostructures with pH=9.7**

size distribution using the software of (PSA),for sample(a)

Figure 4. Show the result of PSA of ZnO nanostructures different pH concentration.

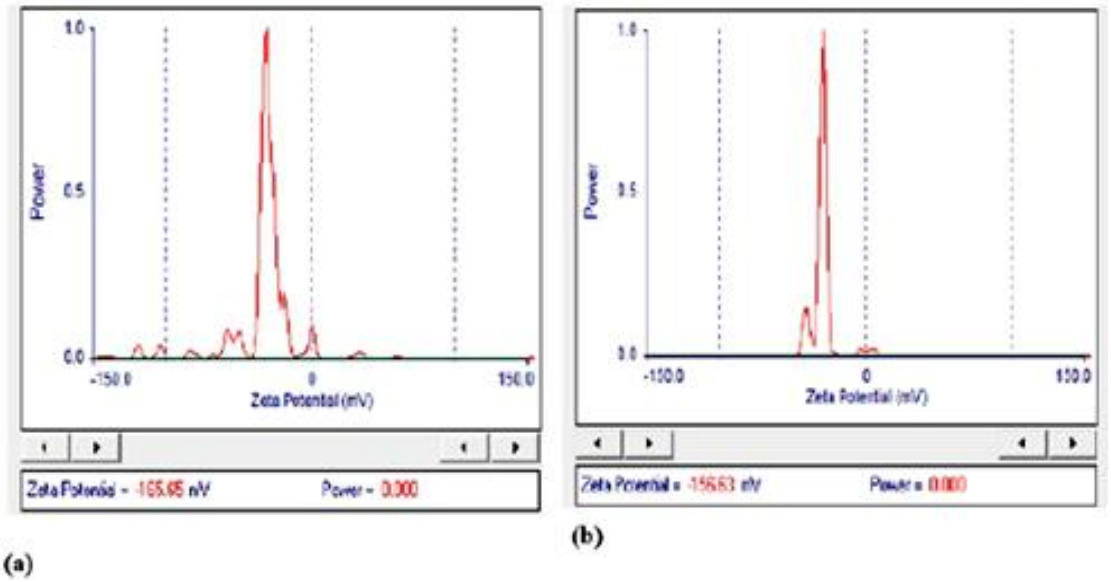


Figure 5. Show the zeta potential of ZnO nanostructures different concentration a) ZnO nanostructures with pH=12 b)ZnO nanostructures with pH=9.7

Table 1. The grain size,zeta potential and root mean square of the ZnO different concentration for solution.

Sample	Grain size in AFM(nm)	Grain size in PSA(nm)	Root Mean Square (RMS) (nm)	Zeta potential (mV)
pH=9.7	**140**	**162.3**	**5.3**	**-156.6**
pH=12	**62**	**60**	**2.68**	**-165.63**