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Synthesis Of ZnO NanostructuresBy Simple Chemistry

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Abstract

In this work Zinc Oxide nanostructure (NSs) were formed by wet chemistry aqueous growth using equimolar quantities of Zinc Acetate dehydrate & Hexamethylenetetramines (HMTA) (C6H12N4, 99.5%) at low temperature on commercial glass substrate at PH 6.6. The surface morphology of the grown ZnO nanostructures (NSs) was characterized using Scanning Electron Microscope (SEM). Images of ZnO nanorods, nanotubes and tetrapods, multipods and nanoflowers were achieved, the average dimensions of nanostructures were ranging between 100 to 300 nm. EDX analysis was used to confirm ZnO presence and UV visible absorption spectrum of ZnO was determined and maximum absorption wavelength was located at 370 nm. The calculated band gab was found to be 3.37 eV. XRD was used to confirm the crystallinity of ZnO (NSs).

Key words; Nanostructures, nanorods, tetrapods, nanoflowers and wet chemistry

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1. INTRODUCTION.

Nanoscience is the study of properties and applications of material at nanoscale, and nanostructures are structures usually with size between 1 to 100 nm. Nanotechnology and Nanofabrication is application of these structures into nanoscale devices[1].Physical properties of bulk material dramatically change when the material sub-divided to the nanolevel, due to the increasing of surface area and quantum confinement[2, 3].Zinc occurs naturally with mineral called zincite. The mineral always composed of amount of manganese and other elements; it has yellow to red color[4].Zinc Oxide is aIIb –VI compound semiconductor, also an important substance characteristic by large band gap of 3.4 eV and exciting binding energy of 60 m eV makes it very interesting to investigate. Zinc oxide is also having excellent chemical stability, nontoxic, and good optical, electrical and piezoelectric properties [5-8]. ZnO also has variety of nanostructures (NSs) which can be used in different of applications, such as optoelectronic devices[9], for example, solar cells, biosensors[10] as shown in the previous work, and light emitting diodes[11], UV photo detector[12], and gas, chemical sensors[13, 14]. Understanding the growth mechanism to make the desired morphology of the ZnO nanostructures (NSs)

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wanted for these applications is very important. However, a lot of procedures have been applied to the synthesis of ZnO nanostructures (NSs), such as hydrothermal chemistry[15, 16], metal organic chemical vapor deposition (MOCVD)[17], electrochemical deposition technique[18], and pulse laser deposition method[19]. The properties of ZnO NSs actually depend on its surface morphology and the shape. Also it is necessary to control their size, shape, and surface architecture to utilize its properties in various practical fields which have been challenge. However, a lot of methods have been applied to synthesize ZnO nanomaterials. In this work simple wet chemistry at low temperature were applied to synthesize ZnO (NSs) on commercial glass.

2. MATERIAL& METHODS

2.1. Experimental Methods

- **The seed solution preparation for Aluminum substrate:**

All chemicals were used from sigma Aldrich without further purification. 0.2g Zinc Acetate dehydrates was mixed in 125 ml absolute methanol (99%). Stirring were used. Until the solution be transparent, the solution was heated to 60 C°. 109 mg of KOH was dissolved in 65 ml of methanol, The KOH solution was added drop-wise to the heated Zinc Acetate solution under continuous stirring. The resulting solution was kept under

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stirring and heating 60 C° for 2 hours before it is ready for use. Then some drops of the solution was put on the glass substrate and was left to dry. Then the sample was cleaned with methanol then by deionized water.

- **The aqueous chemical growth solution for the ZnO nanowires on commercial glass substrate:**

0.274g Zinc Acetate were added in 100 ml of deionized water with concentration 0.01M.

Hexamethylenetetramine (HMTA) ($C_6H_{12}N_4$, 99.5%) was added in 100 ml of DI-water, the final ratio between the Zn concentration and the HMTA can be 1:1. The seeded substrates placed at the bottom in the growth solution and after that the solution was placed inside an oven heated at temperature 60 C° for 2 hours. Then the substrate was cleaned carefully in deionized water, dried & characterized by XRD to confirm the crystalinity, UV Visible spectroscopy for optical properties & Scanning Electron Microscope from LS10 EVO ZEISS Company for surface morphology.

3. RESULTS & DISCUSSION

The chemistry behind the formation of ZnO NSs by placing the coated substrate into solution consist of Zinc Acetate dehydrate and HMTA. The formation of $OH-$ in two steps first HMTA hydrolyze to formaldehyde and ammonia

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then the ammonia hydrolyze to $NH4^{+}$ and $OH-$, with presence of Zn^{+2} form Zn(OH)2then the formed complex decomposed to ZnO as in the following reactions[20]:

$$C6H12N4 + 6H2O \rightarrow 6CH2O + 4NH3 \quad (1)$$

$$NH3 + H2O \rightarrow OH^{-} + NH4^{+} \quad (2)$$

$$Zn^{+2} + OH^{-} \rightarrow H2O \rightarrow Zn(OH)4^{-2} \quad (3)$$

$$Zn(OH)2 \rightarrow ZnO + H2O$$

3.1 Scanning Electron Microscope (SEM) investigated the surface morphology

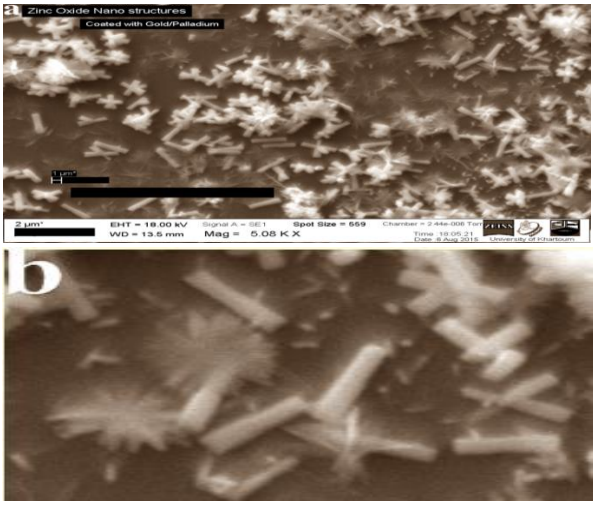

Figure 1 (a) an over view of ZnO nanostructures (NSs) at 1 µm and. (b) ZnO nanorods and nanoflowers at growth phase.

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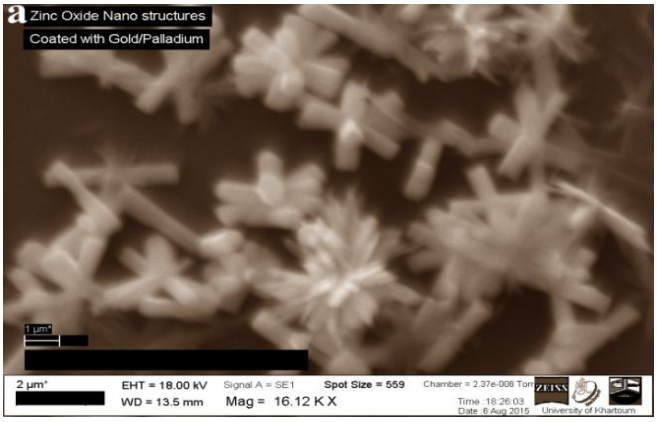
Figure 1 (a) showed the un uniform growth of various ZnO nanostructures (NSs) (nanorods, nanotubes, nanoflowers, tetrapod and multipods) with hexagonal crystal structure with short length at 1µm this due to the short time of growth 2 hour so the dimension effected with the time as shown in the previous work[15], also the un uniform distributions of ZnO nanostructures (NSs) may be due to un proper seeding, the Scanning Electron Microscope image showed variety of nanostructures in the same glass substrate spite of the reaction pH (6.6), the tetrapods, multipods, flower like structures need higher pH than the pH (6.6) each structure appeared in specific pH . as showed in the previous study[15].Figure 1 (b) showed nanorods and nanoflowers at growth phase.



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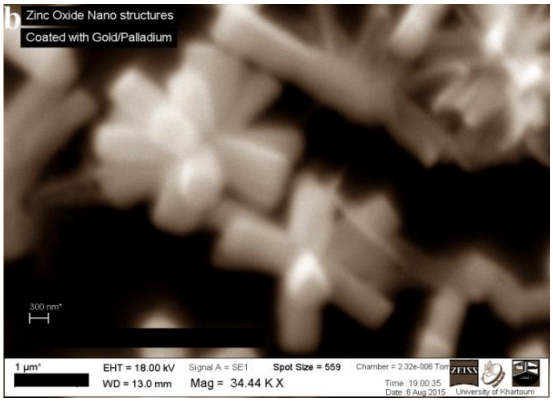

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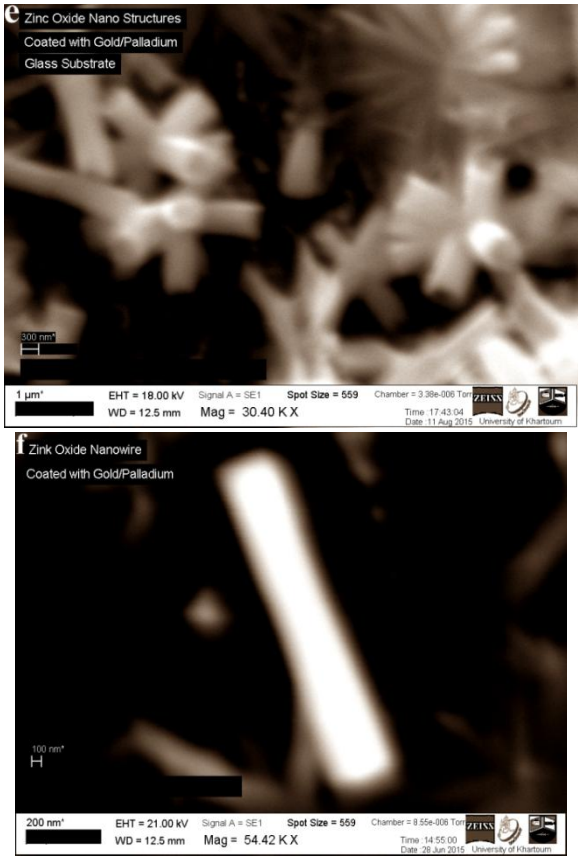

Figure 2 (a) ZnO tetrapods and flower like structures at µm, (b) ZnO multipods with size 300 nm, (c) ZnO closed multipods with spherical shape and flower like structure, (d) ZnO spherical closed multipods at 300 nm, (e) ZnO open tetrapods at 300 nm, ZnO nanorods at 100 nm scale.

Figure 2 (a) showed Scanning Electron Microscope (SEM) images of ZnO multipods with closed nanotubes and nanoflower like structure at 1µm scale, also figure 2 (b) Scanning Electron Microscope (SEM) images

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showed the multipods ZnO nanostructures at 300 nm. Images of ZnO nanostructures (NSs) obtained from (SEM) in figure 2 (c)showed spherical multipods, nanoflowers, and there was small un developed structures, this may be due to several reasons low pH, un proper seeding, short time, and low temperature. Figure 2 (d) images from scanning Electron Microscope (SEM) showed the multipod spherical shape at 300 nm size. Tetrapods structures with open tubes were achieved from Scanning Electron Microscope (SEM) image in figure 2 (e) at 300 nm, also the image showed nanoflower structure at 300 nm scale. ZnOnanorod were obtained from Scanning Electron Microscope (SEM) image at 100 nm scale I figure 2 (f), its well appeared that different ZnO nanostructures (NSs) were achieved at pH (6.6) this results differ from previous study[15] in which nanorods, tetrapods, multipods and nanoflowers at pH ranging ((6,6), (8) (9.1), (12)).The variety of structures at the same pH(6.6) may be due to the location of the glass substrate which placed at the bottom of the growth container.

3.2Energy Dispersive X-Ray (EDX) investigated the presence of (Zn) and (O)

The EDX spectrum of the ZnO grown on glass substrate was shown in figure 3, the analysis was done by the SEM (Zeiss Company) machine. EDX reveals that

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both Zinc (Zn) and Oxygen (O) are present in the Sample. Again the graph shows the presence of Mg, Si, and small amount Al, K, and Ca. This is due to the commercial glass substrate components over which the growth took place, Au and Pd were appeared in the analysis this due to sample coating process.

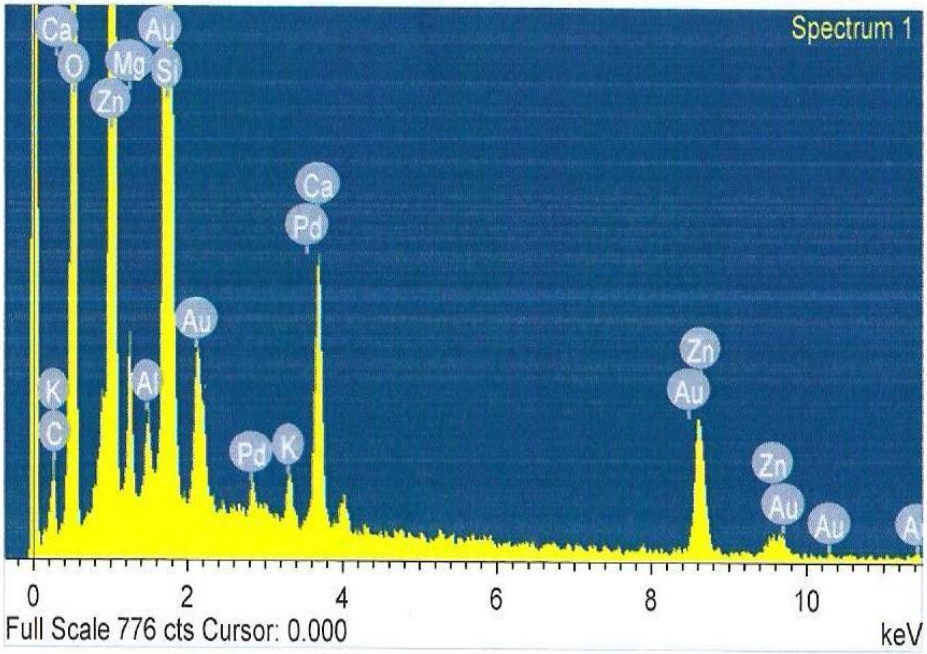

Figure**4: EDX spectrum showed the qualitative analysis for ZnO NSs grown onto the glass substrate**

3.3 X ray Diffraction (XRD) used to investigate the crystalinity of ZnO.

X ray diffraction (XRD) used to investigate the crystalinity of ZnO figure 4, The ZnO NSs that prepared had a perfect hexagonal crystal system

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with space group P63mc, and the crystallographic parameters listed in table 1.

Table 1 ZnO crystallographic parameters

No	a	b	c	Alpha (°)	Beta (°)	Gamma (°)
ZnO grown on glass substrate	3.2539	3.2539	5.2098	90.000	90.000	120.000

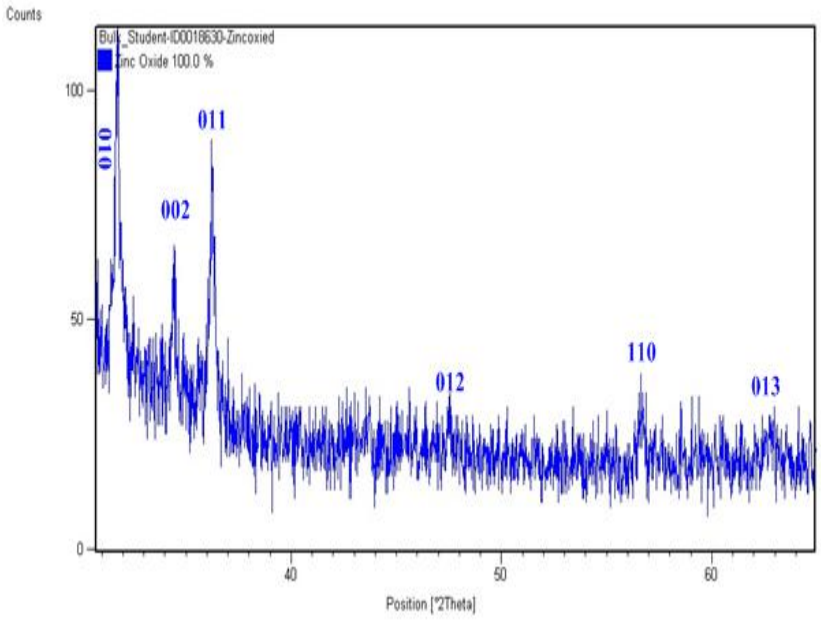

Figure 4: XRD plot for ZnO NSs

Figure, 4 showed that (010) pattern was dominant also (002) pattern was present indicated that one dimension

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nanorods, nanotubes were obtained. (011), (012), (110) and indicated the presence of two dimensional nanostructures as nanoflowers, tetrapods and multipods nanostructures these results match with Scanning Electron Microscope (SEM) images which showed the dominant of nanorods structures .

3.4The Optical Properties were investigated using Ultra-Violet and Visible spectroscopy

the absorption spectra of ZnO NSs which grown on glass substrate was recorded as function of wavelength ranging between 200-600 nm the maximum a wavelength located at 370 nm table 2 which covered almost UV range. Figure 5 shows the relation between $(\alpha h\upsilon)^2$ versus $(h\upsilon)$ plot according to equation (5) [21]the direct optical band gab resultant from the intercept of the straight line with energy axis at$(\alpha h\upsilon)^2 = 0$.

$$(\alpha h\upsilon)\cdot(h\upsilon) = \mathrm{A}\ (h\upsilon - gE)^{\mathrm{m}} \quad (5)$$

A is a constant, m is an index, which suppose the values ½, 2/3, 2, or 3 according to the transition manner of the electronic transition responsible of absorption mechanism of electron transition. The m values ½, 2/3 for directtransition is allowed or forbidden, and m values 2, 3 for allowed and forbidden indirect transition, respectively available in reference[22]. The band gap calculated using Origin lab soft ware programme and it's was found to be 3.37eV, the large band gab obtained.

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Table 2 shows ZnO maximum absorption and band gab

No	Maximum wavelength absorption (nm)	Band gab (eV)
ZnO grown on glass subatrate	370	3.37

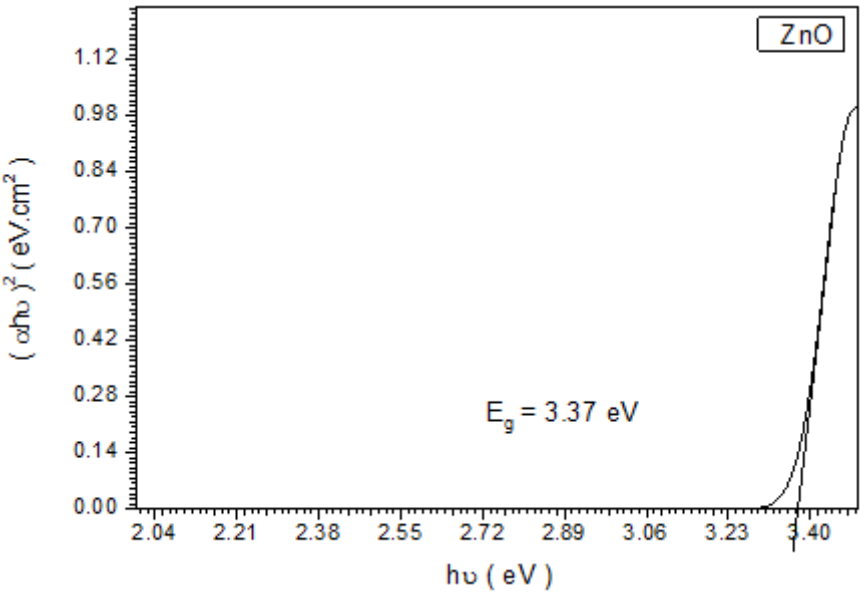

Figure 6: plot showed the relation between photon energy (hυ) and (α E)²

CONCLUSION &RECOMINDATION

The study concluded that ZnO NSs can be synthesized wet chemistry so easily at low temperature, various structures can be obtained by placing the substrate at the bottom of growth solution container. ZnO nanorods, tetrapods and multipods can be synthesized at pH 8.The maximum

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wavelength absorption covered wide range of Ultra Violet spectra so its recommended *to* use as UV photo-detector or UV protection tans, tetrapods, multipods and nanoflower nanostructures could be tested as light trap structure used for solar cell light harvesting and gas sensing.

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