Nano rods and flowerlike synthesis by hydrothermal growth method without catalysts

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Abstract

This study we don't use any catalyst or buffer layer before the reaction by hydrothermal method was used to prepare ZnO nano rods and flowerlike. The process has taken place inside Teflon lined stainless steel autoclave with volume 50 ml (homemade). ZnO nano rods and flowerlike were successfully synthesized using ZnO nanoparticles (20 nanometer) and NaOH (concentrations 3M) was the starting materials for the chemical reaction under stirring. The suspension was transferred into a Teflon lined sealed stainless steel autoclave and kept at 90 ^{0}C for 24 h,48 h and 72 h. The influence of the synthesis process on the morphology, the crystallinity and structural properties are studied by X-ray diffraction and field emission scanning electron microscope (FE-SEM), the experimental pattern of the films show that diffraction peaks can be assigned to the Wurtzite hexagonal-shaped ZnO as shown in the FE-SEM pictures, also the morphology of the films studied by atomic force microscope shows that the prepared thick films have high roughness specially for the powder prepared 46 h .

Keywords: ZnO, nano rods, Flowerlike, dislocation density

تحضير قضيبات اوكسيد الخارصين النانوية والزهرية بطريقة الهدرجة الحرارية بدون عوامل مساعدة

الخلاصة

بدون عوامل مساعدة تم تحضير قضيبات اوكسيد الخارصين النانوية والزهرية بطريقة الهدرجة الحرارية حيث تم تصنيع الجهاز الخاص للعملية محليا ومن خلال وضع بوتقة من التفلون بحجم 50 ملي لتر محاطة باسطوانة من الفولاذ المقاوم للصدا واستخدمت اضافة غرام واحد من حبيبات اوكسيد الخارصين النانوي الى ثلاثة مولارتي من هيدروكسيد الصوديوم ووضع بداخل البوتقة بعد مزجه .المحلول الابيض المتكون وضع بدرجة تسعون مئوية لثلاثة فترات 24 ساعة و48 ساعة و72 ساعة ثم درست تاثير التصنيع على طبيعة السطح والتراكيب البلورية المتكونة من خلال فحوصات الاشعة السينية والمايكررسكوب الماسح الالكتروني وميكرسكوب القوة الذرية حيث بينت النتائج ان النمو الحاصل كان باتجاه شكل سداسي (hexagonal) مع ارتفاع بالخشونة السطحية بالاخص بالنسبة للنموذج المتبقي للفترة 48 ساعة.

الكلمات المفتاحية:اوكسيد الخارصين ،القضيبات النانوية ،الزهريات،كثافة الانخلاعات

INTRODUCTION

Zinc oxide(ZnO) has extensive commercial use during the past 100 years .The low size (Nano, micro)materials have interesting attention due to their size dependent properties and wide range of applications in different fields such as industry, health and environment[1-5] with special important applications in optoelectronics, nano/microelectronics, sensors, transducers, and biomedicine . In the group of II-VI compound semiconductors, ZnO has received great attention due to its remarkable combination of physical and optical properties. Its wide band gap (3.37 eV) at room temperature, high excitation binding energy (60 meV) [6,7], Nanowires and carbon nanotubes and other nano structures made from different row materials (organic/inorganic).Many preparation methods are now available and give research domain for analyzing and understanding the one-dimensional nanostructures and their future applications[8,9].

Extensive efforts are currently devoted to the controlled synthesis and characterization of ZnO nanostructures. Several different methods for the fabrication of ZnO nano rods and arrays have been reported, including hydrothermal synthesis [10, 11]Vapour–liquid–solid (VLS), vapour–solid (VS) [12] processes, metal–organic chemical vapor deposition (MOCVD) [13], chemical vapor deposition [14], solution-liquid-solid growth in organic solvents [15], and template-based methods [16–17-19].Recently, one-dimensional (1D) zinc oxide materials and differently shaped ZnO nanocrystals have attracted considerable attention due to their unique properties that strongly depend on their size and morphologies and their possible use as building blocks in near-future nanodevices [12]. 2D- and 3D-shaped ZnO nanocrystals will play a significant role as the novel functional units of electronic, electromechanical and optoelectronic devices [20-22], and nanosensors [11, 12 and 23].Novel synthesis routes of ZnO nano rods for solar cells and chemical sensing applications are currently being developed. The latest research efforts are directed towards obtaining alternative, lightweight, flexible nanodevices [13, 24]

Experimental

The first step was fabricated the hydrothermal devices (temperature controller, Teflon lined stainless steel autoclave with volume 50 ml (homemade). For synthesis the nano rod and flowerlike All row materials were analytical grade (>99% shaula Spain).

The Teflon was first cleaned in a diluted HCl (20%) solution for 10 min and then rinsed in de-ionized (DI) water. Subsequently, the substrates were ultrasonically cleaned in an ethanol/acetone (1:1) mixture, then DI water, and dried in air. One gram of ZnO nanoparticles (20 nm Tecnan Spain) was added to 3 M of NaOH the aqua solution and stirred for twenty minutes, a white suspension appeared , and then the mixture stirred for 1 h without heat then the suspension was transferred into a Teflon lined stainless steel autoclave with a volume of 50 ml, the autoclave was sealed and kept at 90 ^{0}C for 24 h, 48 h and 72 h. After that the autoclave cooled down to room temperature. The obtained powder washed several times in ethanol and distilled water and dried at 80 ^{0}C for 30 min then the thick film heated at 500 ^{0}C for 1 h to remove residual organic materials. The as-prepared and rapid thermal processed ZnO Nano rods and flowerlike were characterized by X-ray diffraction (XRD) using a Rigaku (miniflex II Rigaku, 'D/B max' Japan) X-ray diffract meter equipped with a monochromatized Cu Kα radiation source (λ = 1.5406A°). The operating conditions were 30mA and 40 kV at a scanning rate of 0.02◦/s in the 2θ range from 20◦ to 90◦. Atomic Force Microscope (AFM AA3100) to study the morphology of the film surface and Field Emission Scanning Electron Microscope (FEI-SEM Model Inspect-S50) to study the structural properties of the films.

Results and discussion

Figure 1 shows the XRD patterns recorded in the range of 20–90◦ with a scanning step of 0.02◦ of ZnO nano rods prepared with 3M (NaOH) at 90 ^{0}C for 24 h ,48 h and 72 h . The data are in agreement with the Joint Committee on Powder Diffraction Standards (JCPDS) card for ZnO (JCPDS 036–1451)[25] the patterns show the strongest detected (h k l) peaks are at 2θ values of 31.74◦, 34.45◦, 36.23◦, 47.45◦, 56.57◦, and 62.87◦, corresponding to the following lattice planes: (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), respectively(see Table 1). From the diffraction pattern it's obvious that the growth is dominated in these directions and these diffraction peaks can be assigned to the wurtzite hexagonal-shaped ZnO. The lattice constants a and c were determined as a = 3.228 A°, c = 5.272 A° by using the following equation [26] by the relation:

$$\left(\frac{1}{d(hkl)}\right)^2 = \frac{3}{4}\left(\frac{h^2+k^2+hk}{a^2}\right) + \frac{l^2}{c^2} \qquad \text{... (1)}$$

The grain size [27] is calculated using Scherer's equation:

$$D = (0.9\ \lambda) / [\beta\cos\theta\ ] \qquad \text{…(2)}$$

Where D: the grain size, λ = 1.5406A°, β : the Full Width Half Maximum (FWHM) , θ :the diffraction angle. Because of the heat treatment process, the thick film undergoes dislocations in its structure. The dislocation density is calculated by the equation [28].

$$\delta = 1/D^2 \qquad \text{… (3)}$$

Where δ is the dislocation density

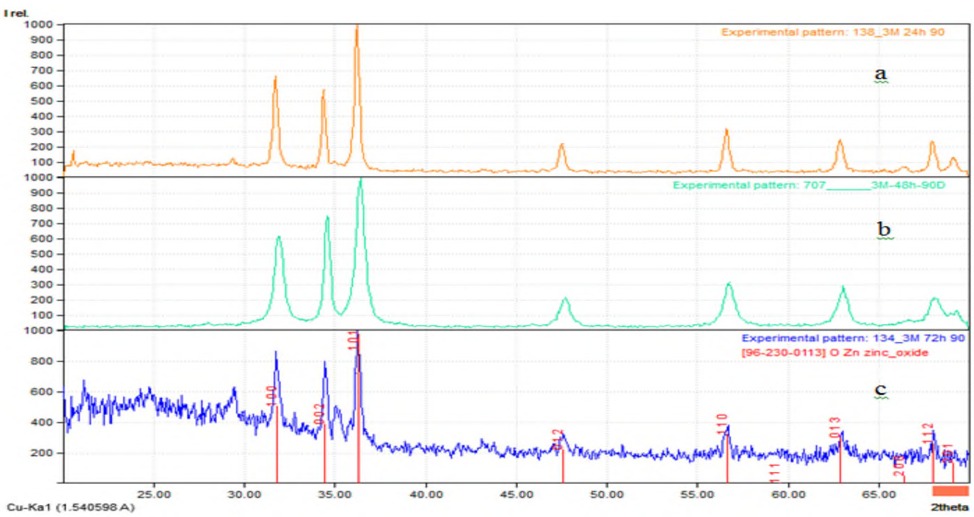


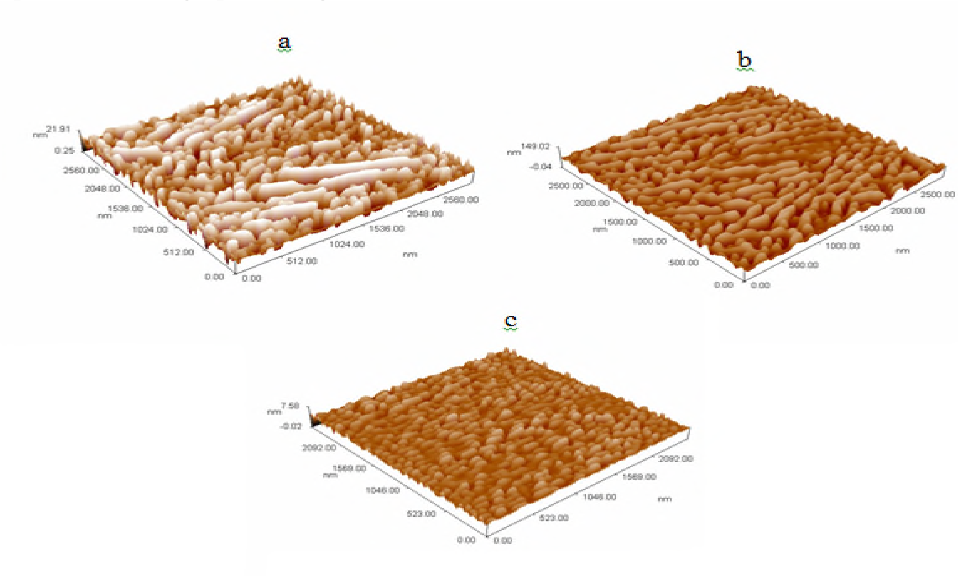
Figure (1)XRD pattern of ZnO nano rods: (a) arrays as-prepared at 90 °C for 24 (b) as-prepared at 90 °C for 48 h; (c) as-prepared at 90 °C for 72 h

Table (1) the estimated structural parameters (a = 3.228 A°, c = 5.272 A°)

Lattice plane	2θ (Deg)	FWHM (radian)	d(h k l) (A°)	Grain size (nm)	Dislocation density δ x10^{15}(line^2/m^2)
100	31.740	0.284	2.817	27.39	1.33
002	34.450	0.283	2.601	27.65	1.30
101	36.231	0.310	2.477	25.39	1.55
102	47.540	0.238	1.911	34.35	0.847
110	56.570	0.264	1.626	32.18	0.966
103	62.872	0.261	1.477	33.60	0.885

The estimated structure parameters was found closed to typical results also the dislocation density was estimated and depend on the reaction conditions such as the reaction time and temperature.

The Atomic Force microscope gives us good information about the morphology of the surface of the film. Fig.2 show the AFM pictures morphology of the surface of the ZnO thick film in three dimensions of the samples prepared at 90 °c for 24 h, 48 h, and 72 h. The roughness of the surface (SA), and root mean square (RMS) and root mean square slope for the prepared films were listed on the table 2. The cumulating distribution report of scan probe microscope (SPM) for the grains diameters of the sample indicate high percentage less than 100 nm

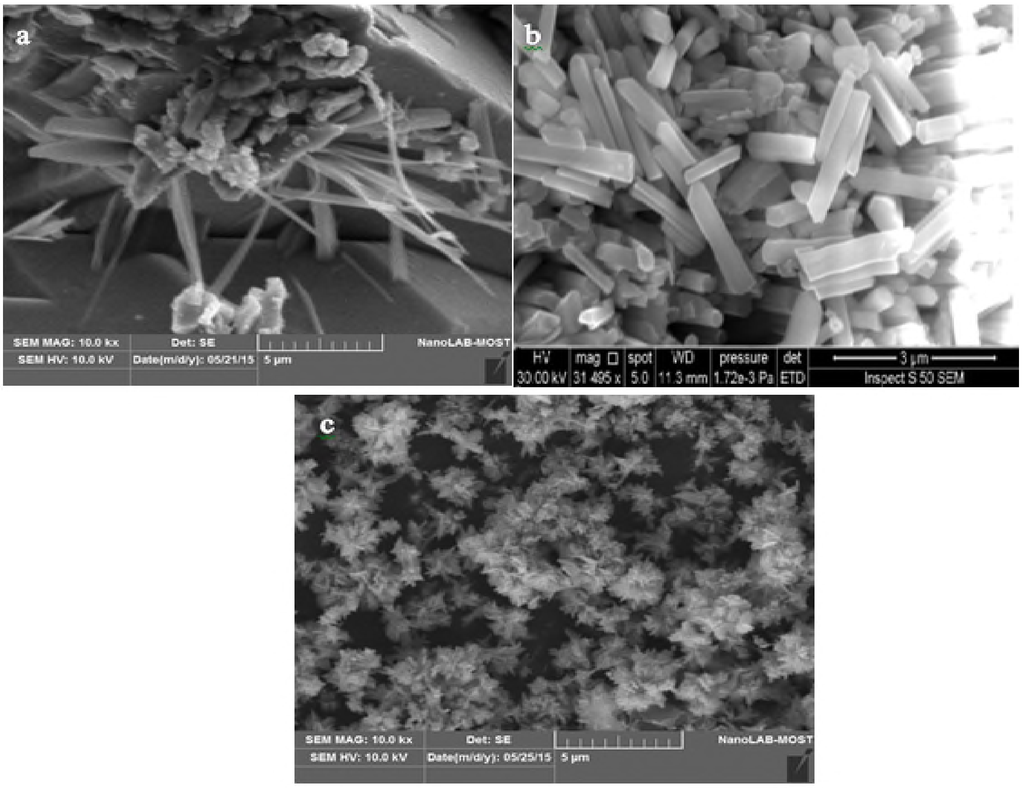


Figure(2) AFM images of the ZnO nano rods hydrothermally grown from (1g) of ZnO nanoparticles and (3M) NaOH aqueous at 90 °c for (a) 24 h, (b)48 h and (c) 72 h

Table (2) Surface roughness analyses from AFM images report.

Nano rods Prepared Of one g ZnO nanoparticles with (3M) NaOH	Surface roughness (SA) (nm)	Root Mean Square (RMS) (Sq) (nm)	Root Mean Square Slope(Sdq) (nm^{-1})	AFM image
24 h	4.84	4.6	0.35	a
48 h	21.6	18.6	1.16	b
72 h	0.68	0.548	0.065	c

SEM images of nano rods and flower like for the samples prepared at 90 ^{0}c for 24 h, 48 h, and 72 h are showed in Fig.3. The insets in Fig. 3(b) display single ZnO rods with hexagonal .The insets in Fig. 3(a) and (c) display single ZnO rods basis and corresponds to two-dimensional flowerlike. The nano rods and flowerlike depend on the time reactions and deposition condition such as the temperature [27]



Figure(3) The SEM images of the ZnO nano rods hydrothermally grown from one g of ZnO nanoparticles and (3M) NaOH aqueous at 90 ^{o}c for (a) 24 h, (b)48 h and (c) 72 h

The estimated structure parameters was found closed to typical results also dislocation density was estimated and depend on the reaction condition such as reaction time and the temperature.

Conclusions

ZnO nano rods and nano flowers assembled from nano rods were successfully synthesized with hexagonal structure by hydrothermal method. The structure of ZnO is found to be wuartze compared with (ASTM) card and agree with the results of the (AFM) and (SEM). The obtained ZnO nano rods and nano flowers gives high ratio of volume to surface with relatively high roughness especially sample as kept at 90 ^{o}c for 48 h refer to effective and enhance sensor performance in sensing applications

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