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The Role of NaOH Content, Grinding Time, and Drying Temperature in Controlling the Shape and Size of Nano ZnO Synthesized by a Green Chemistry Approach

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ZINC oxide (ZnO) has been widely exploited in different technological applications in virtue of its unique physical and chemical qualities. This study was designed to prepare ZnO nanorods for diagnostic applications using a simple, low cost, and solvent-deficient method with clarifying the effect of different experimental parameters on the shape and the size of the ZnO product. Under different experimental conditions, the synthesis was performed via a solid-state reaction of zinc sulfate and sodium hydroxide using the grinding method. The purity of nano ZnO products was investigated by X-ray diffractometer (XRD) while the size and the shape were demonstrated by high- resolution transmission electron microscopy (HRTEM). The XRD results confirmed the production of pure ZnO nanocrystals. The HRTEM micrographs illustrated the preparation of a mixture of nanospheroids and nanorods particles, nanorods with minor nanospheroids particles, and long nanorods particles when the applied mole ratio of ($ZnSO_4.7H_2O$: NaOH) was (1:2), (1:4), and (1:8) respectively. Our findings confirmed the vital role of NaOH in controlling the shape and the particle size of nano ZnO. Since ZnO nanorods can be easily prepared under mild environmentally friendly conditions, it is proposed that the described experimental conditions can be adapted for large scale production.

Keywords: Zinc oxide, Nanocrystals, NaOH, Grinding time, Drying temperature.

Introduction

Quite recently, nano ZnO has been considered as a key technological species [1] in virtue of their exclusive physical and chemical properties [2-5], such as unique optical properties [6], high electromechanical coupling that gives rise to efficient piezoelectric and pyroelectric properties [7], and diverse functionalities [8]. These merits foster the use of nano ZnO in optoelectronics [9], piezoelectric nanogenerators [10-12], photocatalysis [13-15], and photonics such as UV-photodetectors [16], light-emitting diodes [17], and UV laser [18]. In the medical sectors, ZnO nanostructures have been widely applied as luminescent oxides [19], fluorescent fluorophores for cell labeling and imaging [20, 21] (including cancer cell probes [22, 23]), chemical sensors [24-28], in antimicrobial materials [29-34], and different nanomaterials for drug delivery [35] and gene therapy [36].

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Tuning the shape and the size of ZnO nanostructures is a prerequisite to the success of the targeted application [37-39]. ZnO has a unique capacity to grow in one-dimentional (1D), two-dimentional, and three-dimentional structures. 1D nanostructures include nanorods [40, 41], nanotubes [41, 42], nanowires [43, 44], nanoneedles [45], nanoribbons [46], and nanobelts [47]. ZnO 1D-nanostructures have attracted the attention of most researchers in virtue of their advantageous features mainly fewer defects related structure [48] and many attractive anisotropy-related characters that not easy to be achieved by size-tuning of their spherical counterparts. For instance, different ZnO nanocrystals (e.g. quantum dots, nanorods, and nanowires) have been applied in cancer detection and cell imaging [43, 49]. Additionally, Zhao et al. [50] illustrated the higher intensity of fluorescent signals in the case of nanorods in comparison with nanospheres, thus making them better candidates for biomolecule detection [51, 52]. There are various methods to produce ZnO nanorods such as; catalyst-free chemical vapor deposition (CVD) method [53], CVD method [54], hydrothermal synthesis [55], thermal evaporation technique [56], and mechanochemical (grinding) method [57]. However, most of the aforementioned methods are generally complicated and expensive [57, 58]. The grinding method is typically simple, cheap, suitable for large-scale production and environmentally friendly method.

For the best of our knowledge, there are few reports describing the preparation of nano ZnO using such a method. Additionally, most of these reports revealed the applying of high temperatures [59-61] and /or chemical additives either capping agents [62] or surfactants [58, 63, 64] that may induce some obstacles such as consuming high energy and existence of chemical impurities. Moreover, there are no sufficient studies exploring the role of the grinding experiment's parameters in controlling the shape and the size of nano ZnO. Therefore, the purpose of the present study is to synthesis ZnO nanorods using the grinding method and to investigate the effect of different experiment's conditions on the shape and the size of nano ZnO.

Materials and Methods

All of the reagents applied in this study were of analytical grades and were used without further purification. Zinc sulfate heptahydrate ($ZnSO_4.7H_2O$) and sodium hydroxide pellets (NaOH) were purchased from Molekula Company (UK). Absolute ethanol was purchased from Merck KGaA Company (Germany).

Mechanochemical synthesis

ZnO nanocrystals were synthesized according to Gautam et al. [65] with some modifications in the mole ratio of reactants, grinding times, and drying temperatures. Experiment (I); in three agate mortars, $ZnSO_4.7H_2O$ (5.75 g, 0.02 mol) was put in such one with continuous grinding for 15 min. At room temperature, a subsequent mixing with NaOH pellets (1.59 g, 0.04 mol), (3.199 g, 0.08 mol) and (6.399g, 0.16 mol) took place respectively. Each mixture was then ground for 50 min. The outcome was washed and centrifuged at 6000 rpm (K centrifuge, TAIWAN) several times with deionized water (D.W.) then with absolute ethanol to get rid of the whole supernatant containing all contaminants. Finally, the end products were air-dried at room temperature then in a hot air oven (Venticell, Germany) at 120^{o}C for four hours. To investigate the effects of grinding durations and drying temperatures on the synthesis of ZnO nanorods, experiment (II) was carried out as follows. In several agate mortars, ZnSO4.7H2O (5.75 g, 0.02 mol) was put in such one with continuous grinding for 15 min then each preparation was ground with NaOH pellets (3.199 g, 0.08 mol) for 50 min or 100 min at room temperature. The washing and air drying procedures were carried out as described before at room temperature. Subsequent drying at (180^{o}C) or (120^{o}C) in hot air oven was performed. Different conditions of synthesis and samples' key are shown in table 1.

Characterization:

The purity of the ZnO powders was estimated using XRD (Panalytical Empyrean, Netherland) using copper CuKα radiation (λ=0.15406 nm) in the range of 50-800 with a step size 0.04. The shape and the particles' size were examined using HRTEM (JEM-200100- JEOL, Japan).

Results and Discussion

XRD patterns of samples (a), (z), (i), (g), (f), and (h) are shown in Fig. 1 and 2. All of the diffraction peaks were indexed using standard XRD data of ZnO (PDF cards no. 04-007-9805), (PDF cards no. 01-080-3004), (PDF cards no. 04-008-2750), (PDF cards no. 04-005-5076), (PDF cards no. 04-020-9583), (PDF cards no. 01-080-7099) respectively. The XRD patterns of all noted samples are compatible with the

TABLE 1. Different conditions of synthesis.

Sample Key	$ZnSO_4.7H_2O$: NaOH (mole ratio)	Grinding period (min)		Drying temperature (°C)	
		50	100	120	180
(a)	1:2	√	-	√	-
(z)	1:4	√	-	√	-
(g)	1:4	√	-	-	√
(h)	1:4	-	√	-	√
(f)	1:4	-	√	√	-
(i)	1:8	√	-	√	-

hexagonal wurtzite crystal structure of the standard XRD pattern of ZnO and no peaks for impurities indicating the production of pure ZnO nanocrystals. In Fig. 1, the intensity of XRD peaks increases by the increase of NaOH content revealing the increment of crystallinity while no significant changes can be observed in case of the noted samples (g), (f), and (h) as shown in Fig. 2 where NaOH content was the same.

This paper discusses the effects of precursors' different mole ratios, different grinding times, and drying temperatures on the particle size and shape of nano ZnO. Fig. 3-a shows the production of a mix of dominant nanospheroid particles with minor nanorods upon the use of ($ZnSO_4.7H_2O$: NaOH) at a mole ratio (1:2). By changing the mole ratio of ($ZnSO_4.7H_2O$: NaOH) to 1:4, the nanorods became the predominant nanostructure with the presence of minor nanospheroid particles (Fig. 3-z) that completely changed into pure long rod-shaped particles upon the use of ($ZnSO_4.7H_2O$: NaOH) at a mole ratio1:8 (Fig. 3-i). These findings are in agreement with the results obtained by Hou et al. [57]. To interpret these results, it should first refer to the expected chemical equation explaining the reaction route of the ground precursors:

$$Zn\,SO_4.7H_2O + 2NaOH \rightarrow Zn\,(OH)_2 + Na_2SO_4 + 7H_2O$$

The previous equation showed the preparation of zinc hydroxide [66] while Zeferino et al. [67] recorded the direct production of tetrahydroxozincate $[Zn(OH)_4]^{2-}$ in highly basic condition (abundant NaOH). In solid-state reaction, the phase transition or what is called phase transformation (crystal growth) was illustrated by Mnyukh [68]. He stated that "contact mechanism proceeds by the edgewise molecule-by-molecule formation of layers and layer-by-layer additions to the natural crystal face". Many studies demonstrated the effect of the basic content on the growth mechanism and the properties of ZnO nanoproduct [69, 70]. It has been established that adjusting the molar ratio of hydroxyl ions and zinc ions controls the preparation of ZnO with one-dimensional nanosized diameters [71]. Kawano and Imai [72] demonstrated the steep adsorption of $[Zn(OH)_4]^{2-}$ on the (001) plane under high basic condition enhancing the growth along C axis giving rod shape. Complete conversion to zinc oxide occurs during the drying step using a hot air oven (equations 1&2). It is expected that partial conversion occurs during grinding step as a result of heat released by the grinding process itself [66, 67] and by NaOH as an exothermic substance. Concerning the size, the current results revealed the increase in the growth rate of rod-shaped particles by increasing NaOH that reached their maximum length when the mole ratio of

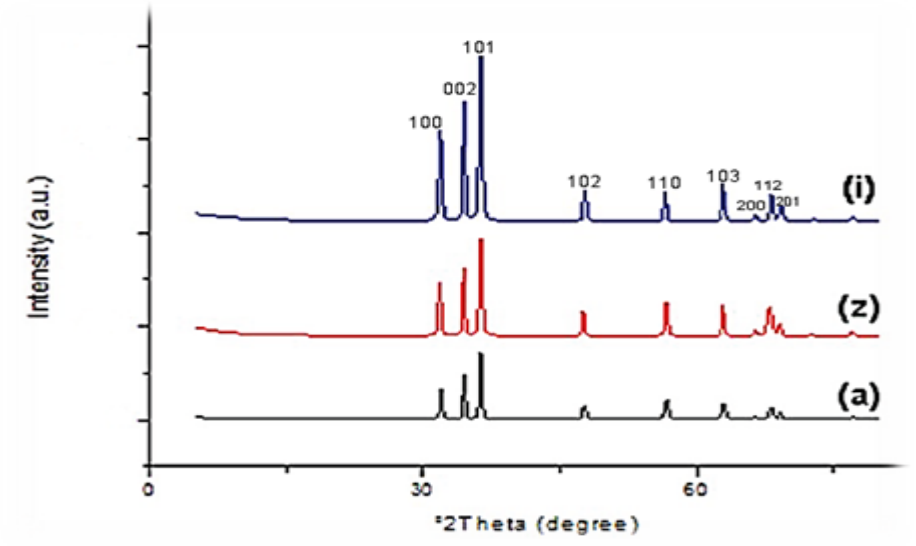

Fig. 1. XRD of samples (a), (z), and (i).

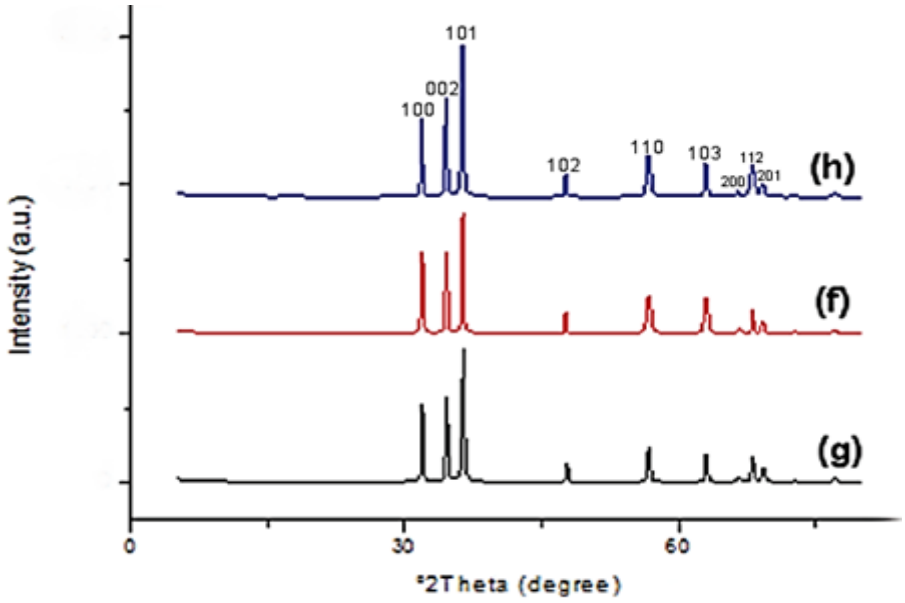

Fig. 2. XRD of samples (g), (f), and (h)

($ZnSO_4.7H_2O$: NaOH) was 1:8. Zeferino et al. [67] explained that the increase in NaOH in the reaction mix causes a decrease in surface tension that in turn fostering the growth rate of ZnO.

$$Zn(OH)_2 \xrightarrow{\Delta} ZnO + H_2O \quad (1)$$

$$(Zn(OH)_4)^{2-} \rightarrow ZnO + H_2O + 2OH^- \quad (2)$$

The effect of the grinding times and drying temperatures on the shape and the particle size of nano ZnO are shown in Fig.3z, 3g, 3f, and 3h. The results revealed no significant effect on the shape or particle size of nano ZnO. Regarding the grinding time's effect; the present results are in contrast to results obtained by Dhara and Giri [73] and Salah et al. [74] that revealed the decrease in the particle size by increasing the milling reaction time. Elucidation of this contrast can be based on one of the two following assumptions; the first assumption is that long-time grinding produces smaller particles with higher surface areas, the high surfaced particles tend to agglomerate producing larger ones [75] due to Van der Waals

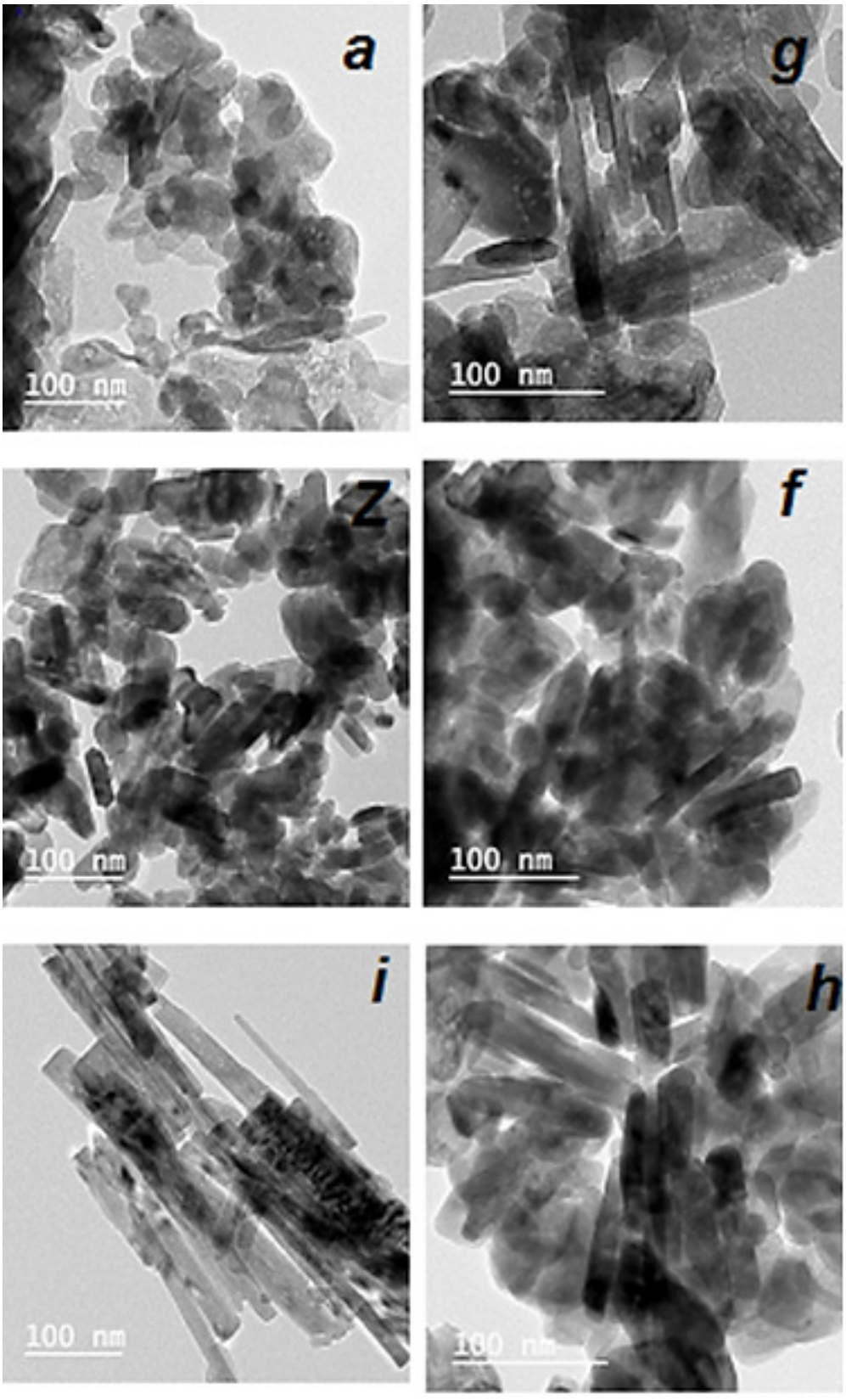

Fig. (3): HRTEM of samples (a), (z), (i), (g), (f), and (h)

or other attractive forces. On the other hand, according to results obtained by Nursyahadah et al. [76], we assume that grinding for 100 min may exceed the critical grinding time at which the crystallite size starts to increase in size due to cold welding.

As for the effect of drying temperatures; our results are incompatible with results obtained by Ao et al. [77], Sharma et al. [78], and GEMTA et al. [79] in which their results revealed the increase in the particle size by increasing the heat treatment. This contrast can be explained according to what was cited by Shaziman et al. [80] as follows. The high temperature may direct the movement of both atoms and molecules to be more violent which in turn deteriorates the crystal lattice's perfection resulting in rod particles' growth retardation. Furthermore, this contrast can be also attributed to the effect of different experimental conditions of such study. In an interesting comparative study performed by de Medeiros Machado et al. [81], it was shown that the effect of high temperature on the size of nano-ZnO varied according to the applied zinc precursor. More detailed research on the efficiency of the present ZnO nanorods product as fluorescent fluorophore to be applied in diagnostic field is currently in progress.

Conclusion

The present investigation shows the vital role of NaOH in controlling the morphology and the particle size of ZnO nanoproducts in comparison with different grinding times and /or drying temperatures. Additionally, either long grinding time or high drying temperature has no apparent effect on the shape or the size of nano ZnO particles. ZnO nanorods for a future application can be synthesized using a simple method under mild conditions with no need for organic solvents that overall complying the industrial production.

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دور هيدروكسيد الصوديوم، مدة الطحن، ودرجة حرارة التجفيف فى التحكم بشكل وحجم أكسيد الزنك النانوى المخلق باستخدام الكيمياء الآمنة

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لقد تم استخدام أكسيد الزنك حديثا على نطاق تكنولوجى واسع لما يتميز به من خصائص فيزيائية وكيميائية فريدة. وتهدف الدراسة الحالية إلى تحضير جزيئات عصوية من أكسيد الزنك النانوى بغرض تطبيقه فى مجال التشخيص الطبى وذلك باستخدام إحدى طرق التخليق البسيطة, منخفضة التكلفة, والتى لا تحتاج إلى إستعمال مذيبات. كما تهدف الدراسة إلى توضيح تأثير العوامل التجريبية المختلفة على حجم, وشكل جزيئات أكسيد الزنك. ولقد تمت عملية التخليق تحت ظروف معملية مختلفة من تفاعل كبريتات الزنك وهيدروكسيد الصوديوم باستخدام طريقة الطحن. ولقد تم فحص الجزيئات المتكونة من حيث درجة نقائها, حجمها وشكلها باستخدام كلا من اختبار «حيود الأشعة السينية» ومجهر النفاذ الإلكترونى عالى الدقة على التوالى. ولقد أكدت نتائج اختبار «حيود الأشعة السينية» إنتاج كريستالات أكسيد الزنك النانوية النقية. كما أوضح الفحص المجهرى تكون جزيئات نانوية شبه كروية وأخرى عصوية, جزيئات نانوية عصوية مع تواجد ضئيل لأخرى كروية الشكل , جزيئات عصوية طويلة وذلك عند استخدام (كبريتات الزنك: هيدروكسيد الصوديوم) بنسبة مولية (٢:١), (٤:١),(٨:١) على التوالى. تؤكد النتائج على الدور الهام لهيدروكسيد الصوديوم فى التحكم بالحجم وشكل جزيئات أكسيد الزنك النانوية. ومن ثم فإنه يمكن تحضير جزيئات أكسيد الزنك النانوية العصوية فى ظل ظروف تجريبية بسيطة وصديقة للبيئة تتناسب مع متطلبات الإنتاج على نطاق واسع.