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Synthesis of ZnO Nanoparticles by Mechanochemical Processing

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Abstract: *Some characterization and microstructural features of mechanochemicaly milled ZnO powders are presented in this study. It is shown that the application of mechanochemicalZnO nanoparticles is a simple technique for preparation of nanocrystalline powders. Synthesised powders are analysed by X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and Photon Cross Correlation Spectroscopy (PCCS).*

Keywords: *nanoparticle, agglomeration, mechanochemical processing, X-ray diffraction.*

1. INTRODUCTION

Powders with particles of uniform shape and narrow size distribution lying in the nanometer range have been shown to possess interesting properties. Nanoscale oxide particles are gaining increasing technical importance for classic areas of application such as gas sensors, catalysts, pigments, UV-absorbers, passive electronic components, optic and ceramic materials [1-3]. Mechanochemical processing is a novel method for the production of nanosized materials, where separated nanoparticles can be prepared. The method has been widely applied to synthesize a large variety of nanoparticles, including ZnS, CdS, ZnO, $LiMn_2O_4$, SiO_2 and CeO_2 [4-9]. Milling of precursor powders leads to the formation of a nanoscale composite structure of the starting materials that react during milling or subsequent heat treatment to form a mixture of separated nanocrystals of the desired phase within a soluble salt matrix. The separation of the nanoparticles will occur due to existence of NaCl that prevents the subsequent agglomeration ZnO nanoparticles during calcination. Removal of the salt matrix is usually carried out through simple washing. For example, ultrafine ZnO powder was synthesized by the milling and subsequent heat treatment of a $ZnCl_2$, NaCl and Na_2CO_3 powder mixture. Removal of the NaCl with a simple washing process resulted in separated ZnO particles [10, 11].

2. EXPERIMENTAL PROCEDURE

The starting materials were (space group: $P2_1/n$) monoclinicsystem $ZnCl_2$ granules (analytical reagent 98.0%), monoclinicsystem(space group: C2/m) Na_2CO_3 powder (analytical reagent, 99.0%) and cubic system(Fm3m)NaCl (analytical reagent, 99.5%). All the starting materials were dried in air at 150^0C. The NaCl was used as an inert diluent and added to the starting powders. The mixture of starting powders was milled in a ball mill with zirconia balls of 10mm in diameter and 50ml with speed 1200rot/min by High Speed Ball Mill (Desktop High Energy Vibratory Ball Mill, USA). The precursor was calcined at 400^0C in air in a porcelain crucible for 0.5h to prepare the ZnO nanoparticles. Since the mechanochemically formed $ZnCO_3$ nanoparticles were isolated in the NaCl matrix, sintering of the ZnO powder did not occur during heat treatment. Removal of the salt by-product was carried out by washing the powder with de-ionised water. The washed powder was dried in a spray drier. Powder characterization was carried out using PCCS (Nanophox, Sympatec), XRD (Cu-Kα radiation), SEM (Hitachi, TM3000), AFM (SMM-2000, <PROTON-MIET>).

3. RESULTS AND DISCUSSION

A stoichiometric mixture of the starting materials was milled corresponding to the following reaction equation:

$$ZnCl_2+Na_2CO_3+ 8NaCl \rightarrow ZnCO_3+ 10NaCl$$

NaCl was added to the reactants so that the volume ratio of the $ZnCO_3$: NaCl in the product phase was 1:10.

3.1 XRD measurement

XRD measurements have carried out at ambient conditions on a (Enraf Nonius Delft) powder diffractometer. A step size was 0.02^0, integration time was 5s per step and scan range $2\vartheta=14^0$-60^0. Phase analysis have done by <<X'Pert HighScore Plus>>program. X-ray spectra were refined using the program FULLPROF. X-ray data were collected on full automatic diffractometer (Enraf Nonius DelftDiffractis 583) with $CuKa_1$ radiation at 40kV and 30mA. The XRD patterns of the milled $ZnCl_2$, Na_2CO_3 and NaCl powders: (a) the starting mixture; (b)milled for 1h ; (c) after calcination at 400^0C for 0.5 h and (d) after washing with water three times are shown in Fig. 1.

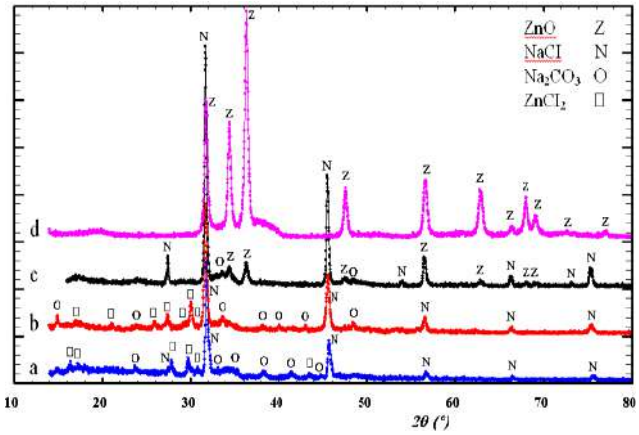

Figure 1: *The XRD patterns of the milled $ZnCl_2$, Na_2CO_3 and NaCl powders: (a) the starting mixture; (b) milled for 1h ; (c) after calcination at 400^{0}C for 0.5h and (d) after washing with water 3 times.*

Only the peaks associated with NaCl, ZnCO3 and Na_2CO_3 were observed in the patterns of the starting materials (Fig. 1a). After 1 hour milling of the mixture, only typical NaCl peaks were detected (Fig. 1b). A new peak associated with ZnO was observed in the pattern of the sample after thermal treatment of the as-milled powder. As shown in Fig. 1c, the pattern of the powder heated at 400^{0}C consisted of peaks corresponding to ZnO and NaCl after washing, only those peaks of ZnO remained, indicating the complete removal of the NaCl by-product phase (Fig. 1d).

The calculated phase quantity for these x-ray patterns are shown in Table 1.

Table 1. The phase quantity for NaCl, $ZnCl_2$andNa_2CO_3 x-ray patterns.

X-ray patterns	Chemical formula	Quant. wt.%
Fig 1. (a)	NaCl	46.2
	$ZnCl_2$	32.8
	Na_2CO_3	20.9
Fig 1. (b)	NaCl	52.2
	$ZnCl_2$	19.9
	Na_2CO_3	27.7
Fig 1. (c)	NaCl	74.3
	$ZnCl_2$	20.7
	Na_2CO_3	4.8
Fig 1. (d)	ZnO	100.0

As can be seen, the quantity of NaCl increased from 46.2% to 74.3% after milling for 1h and calcination at 400^{0}C, but the quantity of $ZnCl_2$ decreased from 32.8% to 19.9% after milling for 1 hour. On the other hand, the quantity of Na_2CO_3 increased from 20.9% to 27.7% after milling for 1 hour, while decreased to 4.8% after calcinations at 400^{0}C. It means that, Na_2CO_3 phase was not removed. The phase of 20.7% ZnO observed after calcination at 400^{0}C for 0.5h. Then, ZnO powder participated after washing 3 times.

Debye Scherrer equation is used for calculating the mean crystallite size

$$D_c = \frac{K \cdot \lambda_{K\alpha 1}}{B_{(\Delta(2\theta))} \cdot Cos\theta_{max}}. \qquad (1)$$

Here, the mean crystallite size estimated from the XRD peak (Fig. 2d) width at 2θ=36.29^0 using the equation (1) was defined to be 23.0 nm.

3.2Photon Cross Correlation Spectroscopy (PCCS)Analysis

Samples of ZnOcalcinated at 400^{0}C and washed 3 times were inserted into double distilled water and suspension was prepared. After that, it was inserted into transparent uvette (Eppendorf Uvette®, Sympatec Item No.NZ0020) with dimensions 12.5x12.5x3.6 mm, volume of 50-2000µl. Then uvette is placed in thermostat bath with filled clean water filtered by 022µm filter. It has to be orthogonal to the incoming laser beam with 632.8 nm wavelength. The water level should be ¾ of the bath height. The data was calculated by WINDOX 5. Particle size and cumulative distribution of ZnO are depicted in Fig. 2.

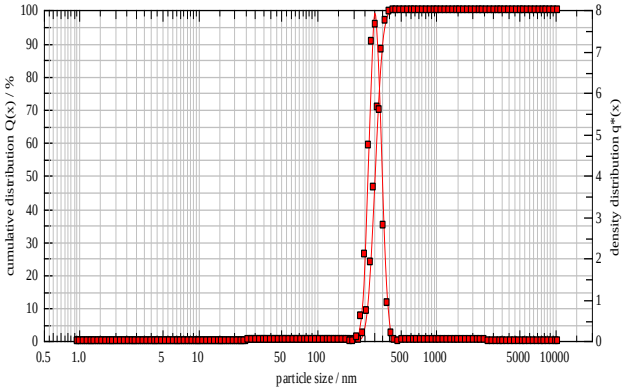

Figure 2: *Cumulative and Density distribution of ZnO suspension particles heat treated at 400^{0}C and washed with water 3 times.*

The following parameters of commercial and prepared ZnO were measured. As a result of this measurement, commercialZnO have the mean diameter of 1.4 µm, particle size distribution of 100nm÷2.4µm, particle specific surface area (Sv) of 4.18m^2/cm^3. While, for prepared ZnO, the mean diameter is 300.21nm, particle size distribution equals to 55nm÷880nm, particle specific surface area (Sv) is 20.15m^2/cm^3. On the other hand, there were not determined particles less than 55nm.The sample contained 0.02% (volume persent) nanoparticles in the range of 55÷100nm.

3.3 SEM and AFM measurement

Figures 3 and 4 show a typical SEM and AFM micrographs of the heat treated and subsequently washed ZnO powders.

The big crystals (Fig. 3a) were observed in 100 µm scale with 8000x magnification, but "fluff wool" like particles (Fig. 3b) have appeared in 100 µm scale with 8000x magnification after mechanochemical processing.

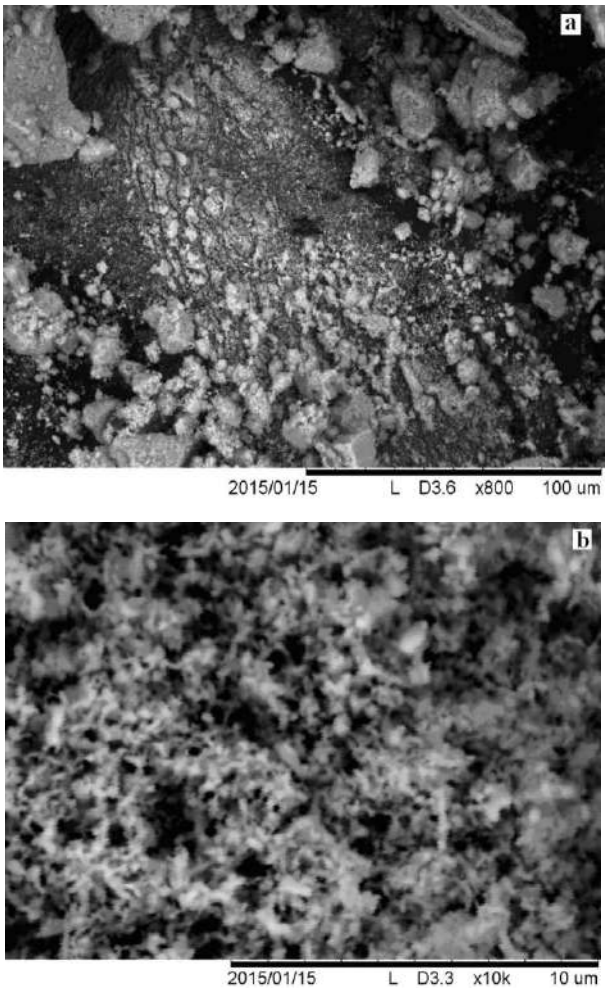

Figure 3*: SEM micrograph of ZnO powder heat treated at 400^{0}C and washed with water 3 times: (a) 100μm scale with 8000x magnification; (b) 100μm scale with 8000x magnification.*

Also, surface topology of ZnO powder calcinated at 400°C and washed 3 times was studied CMM-2000 AFM microscopy. This microscope is worked in atomic force and tunnelling regime. Samples were chosen as a 10/2 mm. MSCT Cantilever <Veeco> was applied. In the experimental procedure, probe scanning step was 7.3nm, scanning speed was 86.77 μm/s in scale of 3.75μm x 3.75μm. The diameter of individual particles appeared in scale of 3.75 μm x 3.75μm was calculated of 24 nm. This result is in agreement with mean crystallite size (23nm) estimated from the XRD peak (Fig.4).

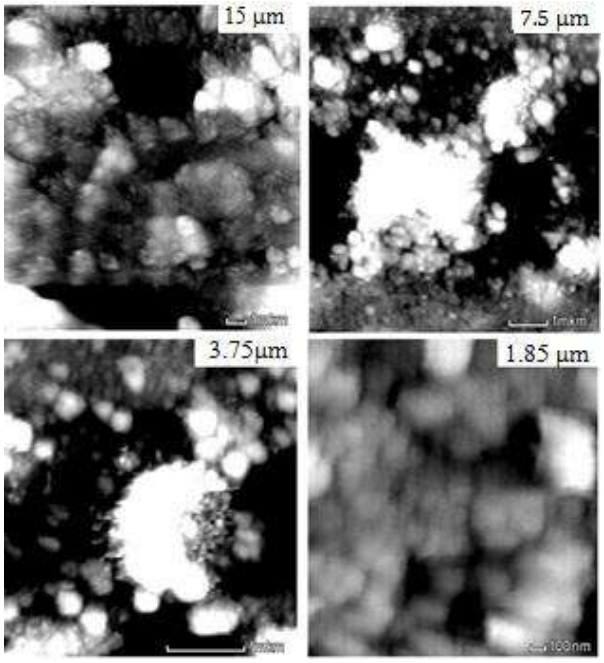

Figure 4*: AFM micrograph of ZnO powder heat treated at 400°C and washedwith water 3 times: scanned at scale 15x15μm, 7.50x7.50μm, 3.75x3.75μm, 1.85x1.85μm in X, Y coordinates.*

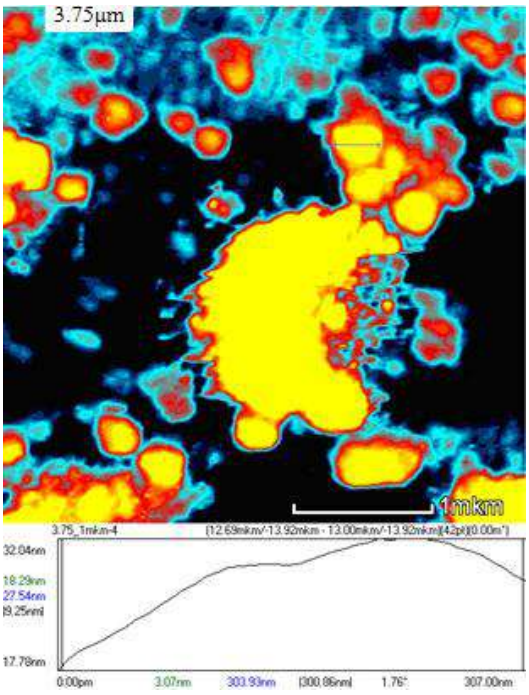

Figure 5*: AFM micrograph of ZnO powder heat treated at 400°C and washed with water 3 times: scanned at scale 3.75x3.75μm in X, Y coordinates*

Besides individual particles, some agglomerated big particles (Fig. 5) were appeared. The diameter of these particles (horizontal blue line) was calculated ~300.86nm. It can be noticed that, the particle size measured by AFM microscopy is in good agreement with measurement of PCCS. In addition, results of this

work are corresponding to the data of papers [11] and [12].

4. CONCLUSIONS

Zinc oxide (ZnO) nanoparticles can be successfully prepared by heat treatment of the milled powder obtained synthesized by mechanochemical reaction of $ZnCl_2$ and Na_2CO_3 with NaCl as a diluent. Heat treatment of the as- milled powders at 400^0C led to the thermal decomposition of $ZnCO_3$, leaving ZnO nanoparticles embedded in the NaCl matrix. After washing with water, amounts NaCl decreased significantly and Na_2CO_3 phase removed completely. Only, nanosizedZnO, calcinated in hexagonal structure with an average particle size of ~23nm was obtained. On the other hand, the mean diameter (~300.21nm) of particles calculated by using PCCS is corresponding to the diameter (~300.86nm) of agglomerated big particles measured by AFM microscopy.

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