

# Ultrafine zinc oxide powders prepared by precipitation/mechanical milling

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The synthesis of ultrafine zinc oxide powders using the combination of precipitation and mechanical milling followed by subsequent heat treatment was investigated. Zinc hydroxide/oxidehydrate precursor was prepared by precipitation process using zinc chloride as the starting material. Sodium chloride was added to avoid agglomeration during the mechanical milling process. Zinc oxide particles were formed in the NaCl matrix after heat treatment and obtained after removal of NaCl. The size and structure of zinc oxide powders were studied using X-ray diffraction, transmission electron microscopy, and BET surface area measurements and thermal analysis. This has shown that the particle size of zinc oxide powder is strongly dependent on the weight ratio of sodium chloride and precursor. ZnO particles with an average primary particle size of 15 nm could be obtained when the NaCl/precursor weight ratio was 4 : 1 or above.

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## 1. Introduction

Zinc oxide and zinc oxide-based powders have been widely studied recently because of their unique optical and electrical/electronic properties and thus they can be used in many demanding technological applications [1], such as low voltage varistors [2, 3]. In order to obtain high quality zinc oxide powders with fine particle size, narrow size distribution and special morphology, various preparation techniques have been used to synthesize ultrafine zinc oxide powder [4–8], including precipitation, sol-gel, microemulsion, etc.

Recently, a new method of precipitation (or co-precipitation) combined with mechanical milling has been successfully used to synthesize various oxide powders, such as iron oxide [9] and nickel ferrite [10]. The new preparation method seems to be an economical route for the production of large quantities of ultrafine powders. As well known, precursors after chemical precipitation or co-precipitation consist of micron/submicron agglomerates of nanoscaled hydroxide or oxidehydrate particles. The bonding between these hydroxide/oxidehydrate nanoparticles is weak, as it is based on physical van de Waals forces, so that it is possible to break the bonding by repeated collisions between balls and powder during mechanical milling process with a dispersion material, such as NaCl. When the nanoparticles are dispersed in the NaCl matrix, ultrafine oxide particles can be obtained after dehydration/crystallisation and the subsequent removal of NaCl. In this work, we studied the properties of ultrafine zinc oxide powders prepared by this method, based on mechanical dispersion of precipitate particles by mechanical milling.

## 2. Experimental procedure

Zinc oxide powder was prepared through three steps: (1) precipitation process, (2) mechanical milling of the precipitation precursor, and (3) heat treatment. In the precipitation process, zinc hydroxide/oxidehydrate precursor was precipitated from zinc chloride in ammonia solution, and then the precipitate was dried in a freeze-dryer.

In the mechanical milling process, 10 g of a mixture of the zinc hydroxide/oxidehydrate precursor powder and sodium chloride powder was milled at 300 rpm for 12 hours in a Fritsch-5 Planetary Mill. 15-mm diameter steel balls were used. The weight ratio of balls and powders was around 18 : 1. In order to study how the weight ratio of zinc hydroxide/oxidehydrate precursor and sodium chloride influences the particle size of zinc oxide powder, the NaCl/precursor weight ratio was varied, such as 0 : 1 (i.e. pure precursor), 0.64 : 1, 1 : 1, 2 : 1, 4 : 1, 8 : 1 and 12 : 1.

The as-milled powders were annealed in air in alumina crucibles for one hour at a temperature between 140 and 600°C. Furthermore, the products were washed several times with deionized water in order to remove sodium chloride, resulting in ultrafine zinc oxide powders.

The structure and microstructure of zinc oxide powders were investigated using X-ray diffraction (Philips PW 3071 diffractometer with  $\text{CuK}_\alpha$  radiation) and transmission electron microscopy (JEM 100 CX II TEM). Differential Scanning Calorimetry (DSC) and thermogravimetric analysis (TGA) were carried out using a Du Pont thermal analysis system (TGA 2950 thermogravimetric Analyzer and DSC 2910 Different

Scanning Calorimeter) with a heating rate of 20°C/min. BET surface area was measured using a NOVA 2000 Surface Area Analyzer.

### 3. Results and discussion

X-ray diffraction spectra of the precursor in the as-precipitated state and after a heat-treatment at different temperatures are shown in Fig. 1. The diffraction peaks in the pattern of the as-precipitated precursor correspond to the hydroxide/oxidehydrate phases. After annealing at 140°C for one hour, the ZnO phase appears coexisting with hydroxide/oxidehydrate phases. The amount of ZnO increases significantly after annealing at 250°C. After the heat treatment at 600°C, all the peaks can be identified with the ZnO phase.

Fig. 2 shows the TGA measurements on the precursor in the as-precipitated state and after mechanical milling, respectively. It can be seen that the as-precipitated precursor lost its weight in two steps, 15–20 wt% at around 100°C and 15–20 wt% at 400–500°C. A tentative composition of the precursor is likely  $\text{Zn}(\text{OH})_2 \cdot \text{H}_2\text{O}$  estimated from the TGA curve. The water is lost in the two steps, one at around 100°C and another one at 400–500°C.

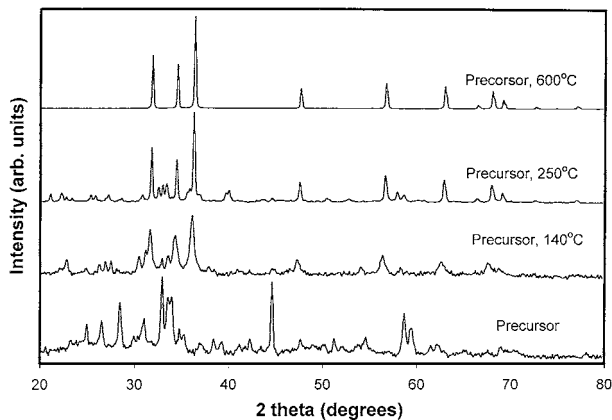


Figure 1 X-ray diffraction patterns of the precursor in the as-precipitated state (a) and after annealing at 140°C (b), 250°C (c) and 600°C (d) respectively.

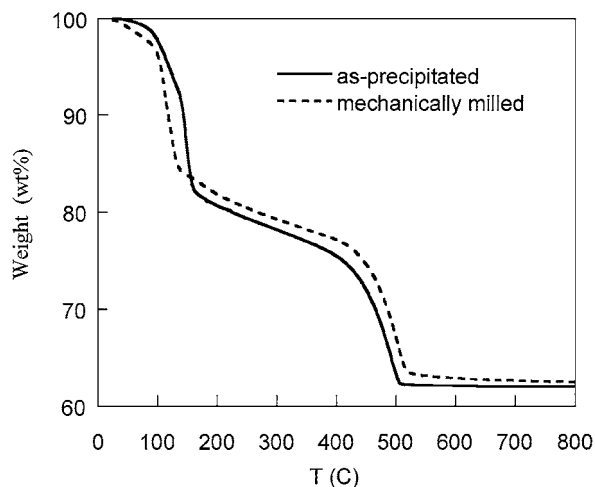


Figure 2 TGA curves of the as-precipitated precursor (a) and the mechanically milled powder (b).

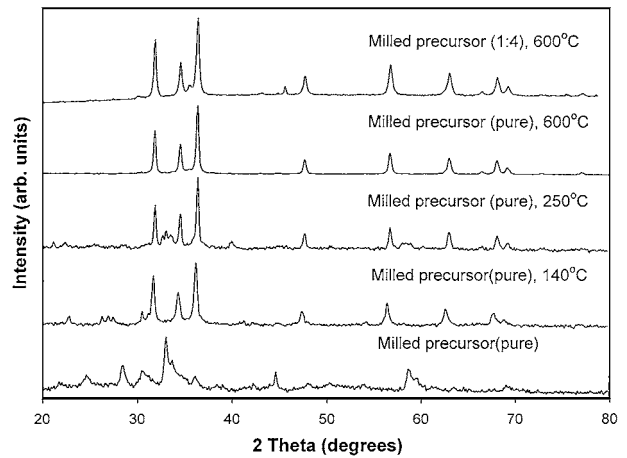


Figure 3 X-ray diffraction patterns of as-milled powder without adding NaCl (a) and after heat treatment at different temperatures (140°C (b), 250°C (c) and 600°C (d)).

Fig. 3 shows X-ray diffraction spectra of the as-milled powder (0 : 1, i.e. no NaCl was added) and the samples after heat treatment at different temperatures. The as-milled powder contained the crystalline hydrate phases. However, the peaks for the hydrate phases were broadened, indicating disordered structure or partially amorphous. The formation of single phase ZnO required a heat treatment at 600°C. The TGA curve of the mechanically milled powder is nearly identical to the TGA curve of the as-precipitated powder. This result shows that the dehydration reaction can not take place during the mechanical milling using a Fritch-5 Planetary mill. All the mechanically milled powders in this work were in the original hydrate form, independent on how much NaCl was added. A heat treatment of 600°C was required for the formation of zinc oxide.

Fig. 4 shows TEM micrographs of ZnO particles after annealing at 600°C. After the heat treatment at 600°C, ZnO particles were found in the range of 50–300 nm with a mean particle size of 167 nm, which was estimated after counting all the particles in an image.

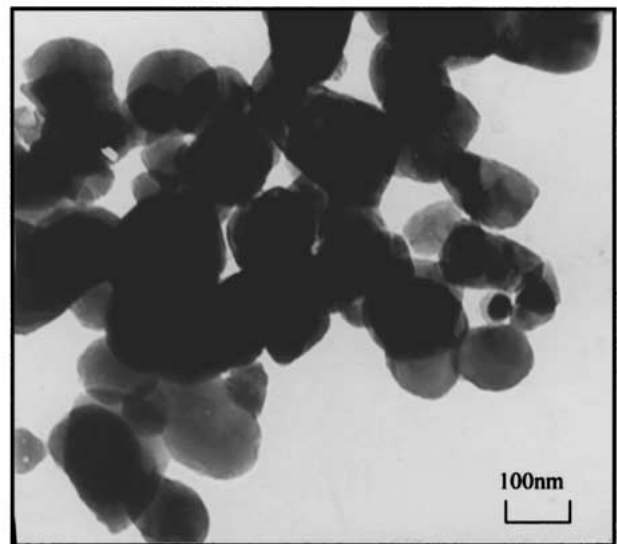
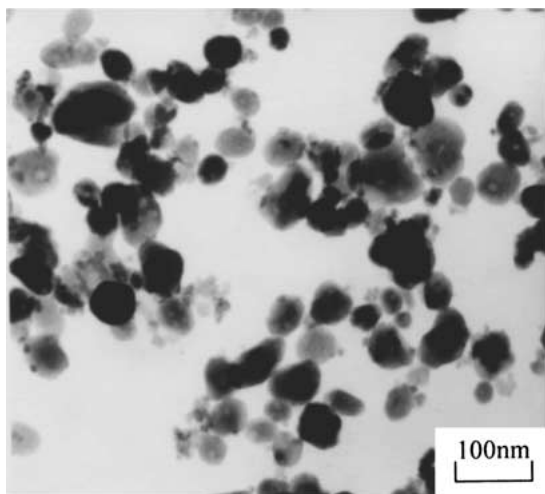
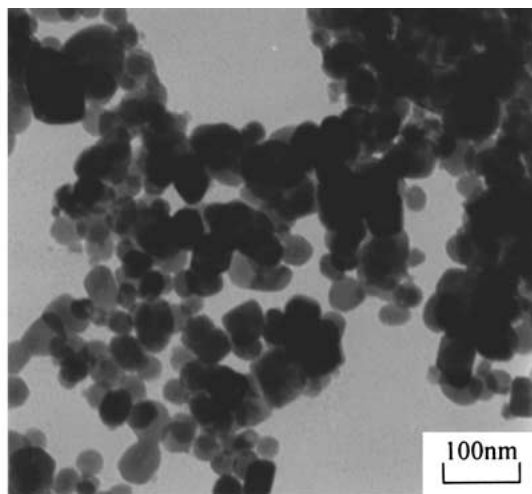


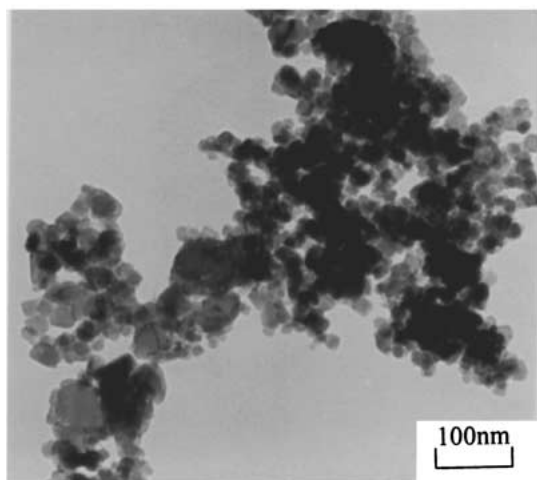
Figure 4 TEM micrographs of ZnO particles formed after annealing at 600°C.



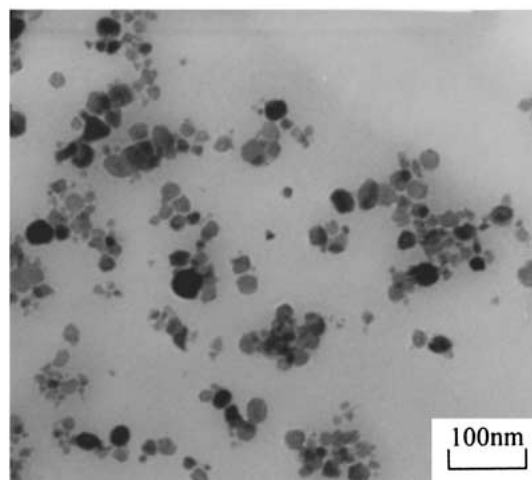
(a) 0:1



(b) 0.63:1



(c) 2:1



(d) 4:1.

Figure 5 TEM micrographs of the annealed powders after mechanical milling with different weight ratio of precursor and NaCl: (a) pure precursor (no NaCl was added) (b) 1.57 : 1 (c) 2 : 1 and (d) 4 : 1.

Fig. 5 shows the TEM micrographs of annealed samples after mechanical milling with different weight ratio of sodium chloride and precursor. After milling pure precursor, the particles have a non-uniform structure with particle sizes ranging from 20 to 150 nm (Fig. 5a). The average particle size was estimated to be around 43 nm. This result has shown that mechanical milling can lead to a reduction of the average particle size from 167 nm without milling to 43 nm after mechanical milling. There was no significant change in the particle size when the ratio of NaCl and precursor was 0.64 : 1 (Fig. 5b). The particle size was significantly reduced after milling with a larger amount of NaCl. When the ratio was 2 : 1, many small particles (10–20 nm) coexisted with larger particles (around 50 nm), as shown in Fig. 4c. After milling with a ratio of 4 : 1, a fairly uniform structure was observed. Most of the particles were found in the range of 10–20 nm. A fur-

ther increase of NaCl/precursor ratio (up to 8 : 1 and 12 : 1) did not lead to a further reduction of the particle size. TEM micrographs of the samples after milling with a higher NaCl/precursor ratio (8 : 1 and 12 : 1 respectively) were nearly the same as the Fig. 5d for the sample after milling with a ratio of 4 : 1.

The average particle size is listed in Table I in the dependence of the NaCl/precursor ratio, based on our TEM measurements. It can be seen that the average particle size becomes smaller when the weight ratio of sodium chloride and precursor increases, from 43 nm if no NaCl was added to 14 nm if the weight ratio was 4 : 1. No further significant reduction of particle size was observed, if the weight ratio was beyond 4 : 1.

The surface areas of powders are listed in Table I, based on our BET experiments. It also shows this trend, that the surface area of zinc oxide increase when the weight ratio of sodium chloride and precursor

TABLE I BET surface Areas and average particle size of the ZnO powder without mechanical milling and of ZnO samples after mechanical milling with different NaCl/precursor weight ratios

Sample	Weight ratio of precursor and NaCl	Surface area(m <sup>2</sup> /g) By BET	Particle size(nm) By BET	Particle size(nm) By TEM
1	As-precipitated	1.3	824.2	167.6
2	No adding of NaCl	5.8	184.7	42.8
3	1.57 : 1	7.0	153.1	37.8
4	1 : 1	14.0	76.5	20.9
5	1 : 2	15.6	68.7	14.9
6	1 : 4	19.8	54.1	14.1
7	1 : 8	22.2	48.3	14.0
8	1 : 12	22.3	48.0	14.0

All the samples were annealed at 600°C for the formation of ZnO from hydroxide/oxidehydrate.

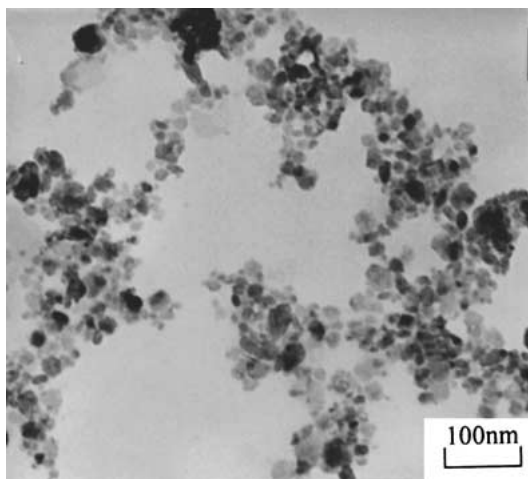


Figure 6 TEM micrographs of the precursor after milling with a precursor/NaCl ratio of 1 : 4.

increases, and it reaches a plateau when the weight ratio is more than 4 : 1. The particle size by BET is obviously larger than that by TEM. This is attributed to agglomeration during the processing of removing sodium chloride from the milled sample and subsequent drying.

In order to study the mechanism of the formation of small ZnO particles, a precursor after mechanical milling with a weight ratio of 4 : 1 was washed to remove NaCl and was investigated under TEM, as shown in Fig. 6. It can be seen that small precursor particles of 10–20 nm were formed after the mechanical milling with NaCl. The microstructure in Fig. 6 is very similar as the microstructure after heat treatment at 600°C in Fig. 5d. These results have shown that these precursor particles were dispersed in the NaCl matrix. No formation of larger ZnO particles took place during the dehydration process (annealing at 600°C), probably due to separation of precursor particles in the presence of NaCl. It should be noted that the precipitated precursor consisted of large agglomerates, which have sizes comparable to those in Fig. 4 (ZnO particles formed after annealing at 600°C).

In a separate experiment, a Spex 800 Mixer/Mill was used for the mechanical milling with a weight ratio of 4 : 1. The dehydration process took place directly in the milling process. ZnO particles with an average particle size of 10–20 nm were obtained after washing to remove NaCl without heat treatment. The microstructure under TEM was very similar as the microstructure shown in Fig. 5d. The collision energy is expected to be higher when 15-mm steel balls were used in the vibrated Spex 8000 mixer/mill in comparison with the collision energy if a Fritch 5 Planetary mill is used. The dehydration reaction may occur during mechanical milling if the collision energy is sufficiently high.

#### 4. Conclusion

In this paper, we present a new method to prepare ultrafine zinc oxide powders using the combination of precipitation and mechanical milling followed by subsequent heat treatment. Mechanical milling may lead to reduction of particle size from ~170 nm without milling to approximately 40 nm. A further reduction can be achieved by adding a dispersion medium prior to the mechanical milling. This work has shown that a sufficient amount of NaCl can result in 10–20 nm precursor particles embedded in the NaCl matrix. The average particle size decreases with increasing NaCl/precursor weight ratio, and reaches the plateau at the ratio of 4 : 1, which corresponds to a NaCl/precursor volume ration of approximately 6 : 1. When the precursor particles are separated by the presence of NaCl, the dehydration through annealing did not lead to formation of larger particles. Ultrafine ZnO particles with a mean particle size of 14 nm can be obtained after removed NaCl through a simple washing process.

In addition, this work has shown that an increase of collision energy can lead to the dehydration reaction occurring during the milling process so that ultrafine ZnO particles can be obtained directly after removal of NaCl without heat treatment.

#### References

1. T. K. GUPTA, *J. Amer. Ceram. Soc.* **73** (1990) 1917.
2. R. PUYANE, I. GUY and R. METZ, *J. Sol-Gel Sci. Techn.* **13** (1998) 575.
3. M. MATSUOKA, *Japan. J. of Appl. Phys.* **10** (1971) 736.
4. M. E. V. COSTA and J. L. BAPTISTA, *J. Eur. Ceram. Soc.* **11** (1993) 275.
5. R. PUYANE, F. TOAL and S. HAMPSHIRE, *J. Sol-Gel Sci. Techn.* **6** (1996) 219.
6. C.H. LU and C. H. YEH, *Mater. Lett.* **33** (1997) 129.
7. D. JEZEQUE, J. GUENOT, N. JOUINI and F. FIEVET, *J. Mater. Res.* **10** (1995) 77.
8. Q. P. ZHONG and E. MATIJEVIC, *J. Mat. Chem.* **6** (1996) 443.
9. X. LIU, J. DING and J. WANG, *J. Mat. Res.* **14** (1999) 3355.
10. Y. SHI, J. DING, X. LIU and J. WANG, *J. Magn. Magn. Mater.* **205** (1999) 249.

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