Effect of Milling Speed and Time on Ultrafine ZnO Powder by High Energy Ball Milling Technique

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Abstract. The particle size of commercial zinc oxide (ZnO) powder has been found in micron scale. For the improvement of ZnO properties, size reduction in nanoscale is required. In this work, the particle size of ultrafine ZnO powder was reduced by high energy ball milling technique. Commercial grade ZnO powder with average size 0.8 μm was used as starting material. Milling speed and time of high energy milling process are considered as crucial parameters affecting size reduction of ZnO particles. Crystalline structure, surface morphological and particle size of the milled samples were investigated by X-ray diffractometer (XRD), scanning electron microscopy (SEM) and particle analyzer, respectively. The results suggested that ZnO patterns after milling process with various milling speed and time were identically in hexagonal crystalline phase affirmed by XRD result. SEM images indicate that size of ZnO products distinctly decrease according to the increase of milling time and speed. ZnO particle size after milling process was found in ultrafine power in range of 200-400 nm. These results suggest that particle size of the commercial ZnO powders can be effectively minimized to few hundred nanometer range depending on force attraction and suitable rotation during milling process with specific speed and time. Moreover, the significant milling parameters will be studied to find the optimum condition for the production of ZnO particles in nanoscale.

1. Introduction

In presence, Zinc oxide (ZnO) is widely used as a functional material regarding its prominent properties including wide band gap semiconducting behavior (3.37 eV), high electron mobility, thermal and chemical stability, large exciton binding energy and non-toxicity [1]. Therefore, ZnO materials have been implemented in many demanding technological applications such as photocatalytic oxidation technology, transparent electronic device, ultrasonic transducers and gas sensors [2-5]. To enhance ZnO properties for specific applications, synthesis of ZnO particles in nano-scaled is required. Bottom-up process is a proper process to synthesize ZnO nanoparticles, for instance, chemical vapor deposition, hydrothermal process, spay pyrolysis, precipitation method [6-9]. However, commercial ZnO powder has been found in micron scale. Bottom-up techniques are unsuitable in ZnO powder precursor. On the other hand, top-down process could be alternative route to reduce material particles down to nano-scale and could be properly applied in industrial process. High energy ball milling process is a kind of appropriate technique for size reduction of materials by mechanical mechanism relating to high surface area of the product [10]. In milling process, the containers are rotated with high speed resulting to high centrifugal force for particle reduction. Hence,
precursor material is milled by large energy in the process with the collision and friction of balls with the container wall under high speed milling process.

In this work, ZnO nanopowders were prepared by high speed ball milling process operating at room temperature. Milling speed and time in milling process are considered as crucial parameters that affect to size reduction of ZnO particles. The morphologies, crystal structure and particle size analysis were investigated to find out the influence of these parameters on ZnO product.

2. Materials and method
Commercial zinc oxide (ZnO) powder with average particle size of 800 nm was used as precursor material for high energy planetary ball milling method. 5 g of ZnO powder and 150 g of zirconia balls with diameter 1 mm were loaded in zirconia containers. The ball milling process was operated at room temperature and ambient air atmosphere. The milling speed was varied from 200 to 600 rpm for 10 min while milling time was varied in range of 0 to 30 min at speed 500 rpm. ZnO ultrafine powders after milling process were investigated by various techniques. Crystalline structure and phase identification was characterized by X-ray diffractometer (XRD). Surface morphologies of before-/after-milled products were monitored by scanning electron microscopy (SEM). Meanwhile, averaged ZnO particle sizes were monitored by particle analyzer.

3. Results and Discussion

3.1. Characterization of ZnO particle size analysis before/after milling process
The average particle size of ZnO powders milled at different milling speeds and times is depicted in Figure 1. Precursor ZnO powder is found to be in 0.5-0.8 microcrystal particles. Regarding the effect of milling speed, ZnO particle size is drastically decreased with increasing milling speed as shown in Figure 1(a). Based on experimental result, the optimized speed for ZnO powder in high energy milling process is found to be at 500 rpm that results to the smallest average particle size of about 225 nm. Due to strong high impact in milling process, the fractures and collisions between balls and material are enhanced by higher speed resulting to particle size reduction in the product [11]. Meanwhile, size reduction of ZnO powder can be affected by milling time (Figure 1(b)). In our case, the smallest particle size is obviously occurred at 10 min operation time with milling speed of 500 rpm. After milling time increase beyond 10 min, ZnO particle size tends to increase owing to the agglomeration of ZnO particle by the accumulation of high energy in milling process.

![Figure 1](image-url)

**Figure 1.** Average particle size of ZnO powder with (a) different milling speeds during 10 min and (b) different milling times operated at 500 rpm.
3.2. Characterization of crystal structure of milled ZnO nanopowders

XRD patterns of ZnO powders milled at different speeds and times are shown in Figure 2. The prominent peaks located at 2θ of 31.3º, 34.4º, 36.9º, 47.7º, 56.5º, 63.0º, 68.0º, 69.0º and 72.5º correspond to (100) (002) (101) (102) (110) (103) (200) (112) (201) and (004) planes, respectively (JCPDS No. 36-1451). All diffraction peaks of milled ZnO nanopowders with various operated speeds and times exhibit same pattern without impurity or contaminated phase comparing to precursor ZnO. For the samples operated at different milling speeds as illustrated in Figure 2(a), the XRD patterns of milled ZnO powder show identical peak pattern and sharp intense peak of pure crystallite ZnO powder at low speed around 200 to 300 rpm. Moreover, peak intensity insignificantly drops by the effect of high attraction in high speed rotation around 500 rpm. Meanwhile, XRD patterns of ZnO nanopowders with various milling times are also depicted in Figure 2(b). As milling time increases, the (002) main peak is noticeably widened indicating the size reduction of the sample. The crystallite size of all samples by prominent three peaks at 2θ = 31.7º, 34.5º and 36.6º were calculated by Scherrer’s equation; D = kλ/βcosθ where D is the crystallite size, k is a constant at 0.9, λ is the wavelength of radiation, β is the peak full width at half maximum (FWHM) and θ is the diffracting angle [12] as shown in Table 1. These results suggest that size of ZnO nanopowders could be significantly reduced by high energy milling method without post-annealing process corresponding to XRD patterns.

![Figure 2. XRD patterns of ZnO powder milled at (a) different milling speeds during 10 min and (b) different milling times operated at 500 rpm.](image)

| Crucial parameter | ZnO precursor | 200 rpm | 300 rpm | 400 rpm | 500 rpm | 600 rpm | 5 min | 10 min | 20 min | 30 min |
|------------------|---------------|---------|---------|---------|---------|---------|-------|-------|--------|--------|
| Milling time     | 25            | 40      | 29      | 27      | 24      | 22      | -     | -     | -      | -      |
| Milling speed    | 25            | -       | -       | -       | -       | -       | 40    | 25    | 28     | 22     |

Table 1. Crystallite size of ZnO nanopowders with different milling speed and time by high energy ball milling process.
3.3. Characterization of milled ZnO surface morphologies

![SEM images of ZnO powder milled for 10 min with different speeds](image)

**Figure 3.** SEM images of ZnO powder milled for 10 min with different speeds; (a) as-received, (b) 200 rpm, (c) 300 rpm, (d) 500 rpm and (e) 600 rpm.

![SEM images of ZnO powders milled at 500 rpm with different times](image)

**Figure 4.** SEM images of ZnO powders milled at 500 rpm with different times; (a) as-received, (b) 10 min, (c) 20 min, (d) 30 min.
SEM morphologies of ZnO powders milled at different speeds at 0 to 600 rpm are depicted in Figure 3. As-received ZnO powder exhibits the difference in its size and its morphology is found to be quasi spherical and rod shape. After milling process, ZnO particle size and shape significantly change to fine powder depending on the milling speed. In Figure 4, as the milling time was varied, ZnO particle size was slightly changed to small particles with good dispersion, specifically at operating time of 10 min corresponding to particle size analysis in section 3.1. However, ZnO particles could be aggregated with prolong milling time due to high accumulation of thermal energy relating to the induction of large particles. Therefore, particles size, size distribution, homogenous powder is highly influenced by milling speed and time. In addition, it is suggested that particle size reduction and shape morphology could be controlled by high speed and optimized milling time in milling process.

4. Conclusions
In summary, ZnO nanopowders were prepared by high energy ball milling process. ZnO particle size was reduced from 500 nm to 250 nm after milling process at 500 rpm in 10 min due to mechanical force with ball and material mechanism. XRD patterns of ZnO nanoparticles exhibit single phase of ZnO hexagonal structure without any impurities. Meanwhile, the reduction of ZnO crystallite size after milling process was obviously occurred depending on the variation of milling speed and time. Meanwhile, SEM images indicated that surface morphology of ZnO structures were in small and fine particles corresponding to the deterioration of crystallite size at (101) plane in XRD.

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