Mechanochemical effects of ZnO powder in a wet super-fine grinding system by instrumental characterization

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Mechanochemical effects of ZnO powders in a wet grinding system were characterized by the changes of ZnO particle micrograph, crystal structure, surface group, and water solubility during the grinding process. In addition, the Williamson–Hall formula was used to show the trend of changes in ZnO crystal size and lattice deformation. The results suggested that in a wet grinding system, the primary function of mechanical power was to prompt formation of crystal defects on ZnO rather than reduction in crystal size of ZnO. The mechanical grinding activated ZnO particles, decreased the binding energy between Zn and O, improved the solubility of ZnO, and formed more associating hydroxyls. As the concentration of Zn2⁺ in solution increased to a certain level, recrystallization of ZnO might take place. Both crystal size and lattice deformation of ZnO showed fluctuation under the combined action of recrystallization and formation of crystal defects.

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1. Introduction

Mechanochemistry refers to reactions, normally of solids, induced by the input of mechanical energy, such as by grinding in ball mills (James et al., 2012). The effects of mechanochemical treatment involved in a series of physical and chemical changes of powder, such as reduction of particle size, increase of specific surface area, disorder of crystal structure, formation of lattice deformation, and change of crystal size, etc. (Feng and Aldrich, 2000). Many studies were conducted on chemical reactions and material syntheses under mechanochemical treatment conditions. Synthesis of ZnAl₂O₄ spinel could be achieved by mechanochemical reaction between ZnO and Al₂O₃ (Zdujić et al., 1992). The α-Fe₂O₃ particle surface could be activated and the reactive barrier with different materials could be decreased after being wet ground (Du et al., 2009). Mechanical activation could also change the defect structure of ZnO crystal lattice so that its optical properties might be affected (Sćepanović et al., 2006). As such, mechanochemistry is becoming a mainstream technique for effective and advantageous material synthesis with less dependence on unsustainable solvent uses (James et al., 2012).

Zinc oxide (ZnO), with a crystal structure of wurtzite, has a wide range of applications including functional devices, catalysts, pigments, optical materials, cosmetics, UV-absorbers and additives in many industrial products (Tsuzuki and McCormick, 2001). Nanocrystalline ZnO powders could be created with intensive mechanochemical treatment in the presence of ZnO and Al₂O₃ (Zdujić et al., 1992), or using ZnCl₂ and Na₂CO₃ as reagents, followed by a heat-treatment (Tsuzuki and McCormick, 2001).

Most of the abovementioned studies were conducted under dry-grinding conditions. Basic studies on the effects of ZnO mechanochemistry in a wet super-fine grinding system were rarely mentioned in recent years. In comparison to drying milling, catalysts obtained by mechanochemical treatment of Ca(OH)₂ and ZnO powders with added water exhibited the highest catalytic activity (Kesić et al., 2012). Therefore, the present study was intended to explore the effects of ZnO powder in a wet super-fine grinding system, through the analyses of variable ZnO characteristics, such as particle micrograph, solubility in water, crystal structure, surface atomic group, and binding energy of surface elements as affected by grinding time.

2. Experiment

2.1. Sample and reagents

The material used was ZnO purchased from Dalian ZnO manufactory with a purity of 99.6%. It has a relatively uniform particle size distribution with a mean particle size of 200–300 nm. To promote better ZnO dispersion, triethanolamine (TEA) with a purity of 99% was used in the experiments. It was provided by Xilong chemical factory of Shantou in Guangdong, China.
2.2. Preparation and characterization of samples

The mechanochemical treatment was performed in a GSDM-003 wet grinding mill with a mixing rotor of 50 mm in diameter and a milling barrel of 1 L, to which 300 g ZnO powder, 300 mL distilled water, and 1.5 g TEA were added. The mixture was ground at a speed of 1350 rpm with zirconia ceramic balls (mean particle size of 1.0 – 1.2 mm). Samples were taken and double-filtrated using a 0.22 μm filter after being ground for different time periods and the filtrates were analyzed for Zn dissolution using a PE Optima 7000 DV inductively coupled plasma atomic emission spectrometry (ICP-AES) with a detection limit of 1 μg/L. Changes in particle morphology were observed using a Quanta 600 FEI Scanning electron microscope at a voltage of 15 kV and a current of 0.4 nA. Changes in crystallinity after samples being ground for different time periods were determined using a P-general XD-3 X-ray diffractometer with Ni-filtered CuKα radiation at 30 kV and 20 mA. The samples were back loaded to minimize preferred orientations and scanned under a continuous mode with a speed of 4° 2θ/min from 15 to 90°. A 0.3 mm receiving slit and 1° divergent slit were used. The FTIR spectra were acquired by a Nicolet 750 micro Fourier transformation infrared spectrometer (Thermo Scientific) using KBr pressing method. The absorbance data were collected by accumulating 256 scans at a resolution 4 cm⁻¹ in the range of 4000–400 cm⁻¹. A PHI Quantera SXM X-ray photoelectron spectroscopy (ULVAC-Phi, Chanhassen, MN) was used to characterize the surface groups of ZnO particles. The beam size was 100 μm in diameter and the beam power was 25 W. The spectra were acquired with 280 eV pass energy and a step size of 1 eV. The lattice deformation and crystalline size of ZnO samples were calculated by the Williamson–Hall equation with the Jade5.0 XRD analysis software.

3. Results and discussion

3.1. Particle micrograph analysis

The mean particle size of raw ZnO was 200–300 nm and the ZnO particles formed extensive aggregation (Fig. 1a). After 3 to 6 h mechanical grinding, there was no apparent change in particle size (Fig. 1b, c), demonstrating that mechanical grinding exerted little impact on the formation of fresh surface of ZnO. In contrast, a significant decrease in d50 and d90 of MgO was observed under a similar wet superfine grinding process for 6 h due to its large initial grain size at 4.5 and 9.5 μm, respectively (Du et al., 2013). The consistent particle size over 3 and 6 h grinding as observed in Fig. 1 may suggest that the main effect of wet mechanical milling of nanometer ZnO particles was to generate crystal defects instead of reducing particle size. Previous results showed that zinc oxide milled under vacuum or in the presence of oxygen could create various types of defects, resulting in an increased amorphous fraction, as well as higher surface area (Castricum et al., 2001). And the degree of defects was affected by the conditions of mechanical treatment, such as intensity and duration of processing (Kakazey and Vlasova, 2008). On the other hand, aggregation of ZnO particles was significantly weakened with extension of grinding time. As breakage and agglomeration of particles took place mainly at lower and higher levels of specific energy input (Pourghahramani and Forssberg, 2006), the results suggested that mechanical force was most likely to promote dispersion of agglomerated particle under wet-grinding condition. Similarly, dispersion of α-Fe₂O₃ powder increased significantly after being wet-ground (Du et al., 2009).  

3.2. Solubility in water

The concentrations of Zn²⁺ in the filtrates collected at different accumulative grinding time periods increased from 0.11 mg/L for raw ZnO to 0.66 mg/L after ZnO powder was ground for 6 h (Fig. 2). The equilibrium Zn²⁺ concentration was significantly affected by the particle size and it decreased from 15 mg/L to 3.4 mg/L as the diameter of
ZnO nanoparticles increased from 4 to 130 nm (Mudunkotuwa et al., 2012). In this study, the mean particle size was 200–300 nm before and after grinding. The increase in Zn$^{2+}$ solution concentration after grinding in this study was at a much slower pace, due to a larger mean particle size, and agreeing well with the minute particle size change after 3 to 6 h grinding. In comparison, the solubility of MgO and $\alpha$-Fe$_2$O$_3$ in water increased after being mechanochemical activated (Du et al., 2009, 2013). In contrast, the solubility of KMgPO$_4$ and NH$_4$MgPO$_4$ produced from a dry mechanochemical process showed a systematic decrease as the milling speed increased from 0 to 700 rpm (Solihin et al., 2010). It was postulated that under the effects of mechanical grinding, the interaction between H$_2$O molecule and Zn$^{2+}$ on the surfaces of activated ZnO particles was enhanced, which may be attributed to an increase in crystal defect and accumulation of energy on the surface of ZnO after grinding (Kakazey et al., 2004). Meanwhile, the weakening of particle aggregation after grinding (Fig. 1b,c) may facilitate enhanced contact between ZnO particle and H$_2$O molecule, resulting in a slight increase in ZnO solubility. As the concentration of Zn$^{2+}$ increased to a certain level, possible recrystallization of ZnO could occur in the wet super-fine milling system, which may offset the enhanced dissolution. Thus, the change in concentrations of Zn$^{2+}$ reflected combined effects of formation of crystal defects and recrystallization.

3.3. Crystal structure analyses

ZnO had good cleavage on (101) and (001) crystal faces. The peak intensities of (101) and (102) crystal faces decreased persistently as grinding time increased (Fig. 3 and Table 1). Similarly, talc exhibited a preference rupture along the perfect cleavage plane of (001) (Palaniandy and Azizli, 2009). Overall, it could be generalized that crystal defects of ZnO emerged and the degree of crystallinity decreased as mechanical grinding proceeded. Thus, the intensities of characteristic peaks corresponding to each crystal face decreased. With further mechanochemical grinding, recrystallization along all crystal faces of ZnO would increase the degree of crystallinity. Moreover, owing to the size and density differences of each crystal face, the formation of crystal defects and recrystallization along different faces would be different. Consequently, the intensity of every characteristic peak showed different trends of change at different accumulative grinding time periods.

Crystal size and lattice deformation of ZnO ground at different accumulative time periods were calculated with the Williamson–Hall approach using the Jade 5.0 XRD analysis software. Williamson–Hall plots can be applied to a Gaussian profile (Santra et al., 2002). In this approach, a linear regression of peak integral width $\beta$ against $4 \times \sin \theta$ in radius would yield information on crystal size and strain (Mote et al., 2012):

$$B_{hkl} \cos \theta = \frac{0.9\lambda}{D} + 4\varepsilon \sin \theta \tag{1}$$

where $\theta$ is the Bragg diffraction angle, $\lambda$ is the wavelength of the radiation, $\varepsilon$ is the average crystal strain, and $D$ is the crystal size. For profile analysis, the nine intensive reflection peaks (100), (002), (101), (102), (110), (103), (112), (201), and (203) were selected (Fig. 4). In contrast, reduction of crystalline size of ZnO was considerable at the very beginning of milling under a high intensity condition using a high-speed planetary ball mill (Zdijuć et al., 1992). The lattice deformation observed in this study was much less than that using a high-energy ball milling process in air (Amirkhanlou et al., 2012). Thus, under wet super-fine grinding condition, the lattice deformation could be drastically reduced.

A slight increase in crystal size was notice after 3–4 h of grinding. A similar observation was found for SiO$_2$–TiO$_2$ bulk gel after being mechanochemically ground for 10 h and the increase in particle size was attributed to competition between the processes of aggregation and grinding (Ting et al., 2008). Under intensive grinding condition, if the initial powder was already represented by the particles with a

![Fig. 2. Changes in concentration of Zn$^{2+}$ after different accumulative grinding time periods.](image_url1)

![Fig. 3. XRD patterns of ZnO after ground for different accumulative time periods.](image_url2)
mean size close to the minimum, increasing grinding time could result in a slight increased in particle size (Karagedov and Lyakhov, 2003). More than half of the energy transferred to ilmenite in 4 h of planetary milling during the mechanical activation was lost as heat during the breakage of bonds while a large part of the stored energy was reflected as strain energy and structural disorder (Sasikumar et al., 2009). The results from this study may also indicate that the applied energy was stored and converted into surface energy, thus, resulting in surface activation.

### 3.4. Surface groups analyses

Similar to SEM observations and XRD analyses, the FTIR spectra of raw ZnO, and ZnO ground for 3 and 6 h showed minute differences (Fig. 5). The broad absorption band at 3442.3 cm$^{-1}$ corresponded to stretching vibration of associating hydroxyls formed by weak hydrogen bonding as well as van der Waals interaction (Hong et al., 2009). A wide absorption peak at 433.3 cm$^{-1}$ was attributed to the stretching vibration of Zn–O bond (Hong et al., 2009). The wavenumber of absorption band corresponding to associating hydroxyls after samples being ground for 3 h shifted from 3442.3 to 3426.9 cm$^{-1}$ with a slight decrease in peak intensity. At the same time, absorption band at 433.3 cm$^{-1}$ was broadened and shifted to 462.8 cm$^{-1}$. This suggested that 3 h of mechanical grinding prompted formation of crystal defects, slight reduction of crystal size, and increase of lattice deformation so that the frequency of stretching vibration increased and the corresponding peak shifted to higher wavenumbers. At the same time, more associating hydroxyls were generated on the surface of ZnO particles that could accumulate a great amount of surface energy. The hydrogen bonding between hydroxyls could be intensified and the stretching vibrational frequency decreased, which resulted in the corresponding peak moving to a lower wavenumber and the intensity of characteristic peak weakened. When ZnO was ground for 6 h, the absorption peak of Zn–O bond decreased to 443.2 cm$^{-1}$, while the broad absorption band of associating hydroxyls shifted to 3434.6 cm$^{-1}$ with a slight increase in intensity. Mechanical activation of ZnO powder causes a decrease in the intensity of Raman spectra as well as redshift of some Raman modes attributed to the formation of intrinsic defects by mechanical activation of ZnO (Štepanović et al., 2006). The redshift (∼2–8 cm$^{-1}$) and peak broadening are consequences of the intrinsic defect formation by mechanical milling, combined with confinement size effects (Vojislavljević et al., 2008). The combined action of recrystallization and formation of lattice defects in the wet super–fine system and crystal size and lattice deformation of ZnO presented fluctuating changes, leading to reduction of Zn–O bond stretching vibrational frequency and decrease in wavenumbers of absorption peak. Meanwhile, the amount of associating hydroxyls on the surface of ZnO particles could be reduced and strength of hydrogen bond between associating hydroxyls weakened. The corresponding absorption peak moved to a higher wavenumber and its intensity increased.

### 3.5. Surface elements analyses

The XPS patterns of O$_{1s}$ consisted of two peaks of which the peak O$_{1s}$ at 527.6 eV belonged to O atom located in the crystal lattice of ZnO while the peak O$_{2s}$ at 528.8 eV was O atom originated from hydroxyls of Zn–OH (Al-Gaashani et al., 2013). After 6 h of mechanical grinding, the binding energy of O$_{1s}$ decreased slightly to 527.2 eV. Meanwhile, the peak intensity also decreased. In contrast, the binding energy of O$_{2s}$ increased slightly to 529.0 eV and the relative peak intensity with respect to O$_1$ also increased (Fig. 6a). A shift of the O$_{2s}$ peak to a higher energy suggested that the oxygen vacancies in the ZnO nanorods were reduced and that OH groups were desorbed (Lee et al., 2010). The XPS map of Zn$_{2p}$ included Zn$_{2p1/2}$ located at 1041.8 eV and Zn$_{2p3/2}$ situated at 1018.8 eV (Al-Gaashani et al., 2013). After being ground for 6 h, the binding energy of the peaks decreased to 1041.2 eV and 1018.2 eV, respectively. The binding energy difference between the Zn$_{2p1/2}$ and Zn$_{2p3/2}$ remained at 23 eV before and after grinding, agree well with published values (Das et al., 2010; Al-Gaashani et al., 2013).

In addition, the atomic concentrations of Zn and O on the surface of ZnO particle were about 2/3 and 7/18, respectively, based on XPS data analyses. The reduction of the binding energy of O$_{1s}$ and Zn elements and the reduction in intensity of their corresponding peaks suggested that mechanical grinding could promote a reduction of surface lattice order. Meanwhile, the overflow of O$_{1s}$ and dissolution of Zn atom increased. The increase of the binding energy of O$_{2s}$ and the intensity of

### Table 1

Peak intensities of different crystal faces of ZnO at different accumulative grinding time periods.

<table>
<thead>
<tr>
<th>Grinding time (h)</th>
<th>Crystal face (hk1)</th>
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<th>(201)</th>
<th>(112)</th>
<th>(103)</th>
<th>(110)</th>
<th>(102)</th>
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</table>

![Fig. 5. FTIR spectra of ZnO samples ground for 0, 3, and 6 h.](image-url)
the corresponding peak showed that mechanical grinding promoted formation of more associating hydroxyls on the surface of ZnO particles.

4. Conclusion

On the basis of analysis of mechanochemistry of ZnO in the wet super-fine grinding system, the following conclusions could be drawn:

(1) The mechanical force could be mainly applied for prompting formation of ZnO crystal defects in wet grinding system, that is, the mechanical force activated the surface of ZnO powder, decreased the binding energy between Zn and O, and increased the solubility of ZnO. As a consequence, when the concentration of Zn\(^{2+}\) reached a certain level, recrystallization occurred. The crystal size and lattice deformation of ZnO presented fluctuant change under the combined action of recrystallization and formation of crystal defects in the grinding system.

(2) By mechanical grinding, partial mechanical energy was converted into surface energy stored in ZnO particles, which eventually activated ZnO particles. There were more associating hydroxyls formed on the surface of activated ZnO particles after super-fine grinding in a wet system.

References


