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EFFECTS OF THE DURATION OF ULTRASONIC IRRADIATION AND THE ATMOSPHERIC ENVIRONMENT ON THE CHARACTERISTICS OF ZnO NANOSTRUCTURES VIA A SONOCHEMICAL METHOD

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ABSTRACT

Nanostructured zinc oxide (ZnO) was synthesized via a sonochemical method. The effect of the duration of ultrasonic irradiation in a continuous mode on the generated particles was investigated. Additionally, the effect of flowing either air or nitrogen during the sonication process was investigated. Zinc nitrate and ammonia water-based solutions were selected as chemicals without the addition of other surfactants. The generated particles indicated that a wurtzite structure of ZnO in a hexagonal phase was formed with a crystalline size that increased as the ultrasound irradiation time increased. The morphology of the generated ZnO particles could be changed from flowerlike to needlelike structures via continuous ultrasound irradiation over one to two hours, resulting in increases in the particle lengths and decreases in the particle diameters from 200 to 80 nm. Photoluminescence intensity was also increased with increases in the ultrasonic irradiation times. Photoluminescence spectra were also influenced by the atmospheric environment. Two bands centered at 390 and 500 nm were generated under a nitrogen environment. On the other hand, a single wide band with a peak at around 430 nm was found for particles generated under an air environment. It can be applied for light emitting diodes (LED) or laser fabrication with a controlled emitting band.

Keywords: Chemical synthesis; Luminescence; Nanostructures; Oxides; Sonochemistry

1. INTRODUCTION

ZnO is a wide-band-gap semiconductor that exhibits a strong and stable broad-band emission. This makes ZnO a promising candidate for the production of ZnO-based light emitting diodes (LEDs), which could replace expensive phosphor materials such as GaN-based LEDs (Look, 2001; Pearton & Ren, 2014). Nanostructured zinc oxide with a lithium inclusion can also be used as a fluorescent powder for fingerprint detection (Choi et al., 2008). Furthermore, ZnO is attracting attention for its applications in varistors, transparent high power electronics, surface acoustic wave devices, piezoelectric transducers, gas sensing, and as a window material for displays and solar cells (Pearton et al., 2003).

Many methods have been used to generate ZnO nanostructure particles. Flame spray pyrolysis, using an organic precursor, results in a ZnO nanorod structure (Height et al., 2006). Spherical ZnO doped aluminum nanoparticles have also been successfully prepared using a spray pyrolysis method under normal and low-pressure conditions (Hidayat et al., 2008). Pulse combustion spray pyrolysis can also produce nano-sized ZnO particles

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(Widiyastuti et al., 2007). The gel-template combustion method can be used to produce ZnO nanoparticles that emit photoluminescence spectra at near-UV and green emission regions (Zhou et al., 2006). The thermal evaporation of Zn metal also results in two peaks of photoluminescence emission spectra in the ultraviolet and green regions (Hassan et al., 2013). Two peaks in photoluminescence emission spectra are also found in ZnO nanowires by using aerosol deposition followed by a hydrothermal process (Lee et al., 2014). The sonochemical method that uses ultrasound irradiation has shown promise because it is a green and feasible technique that is fast and simple. The effect of ultrasound irradiation time on the morphology of generated particles has been studied for times ranging from 15 to 60 minutes, using zinc acetate, NaOH, and ammonia solution as the starting material, which resulted in changing their structure from a nanosheet to that of a nanoflower (Zak et al., 2013). Using the same precursor, the effect of ultrasound radiation time on the luminescence properties has been investigated for the ability to tune the emission spectra by using different ultrasonic times (Kumar et al. 2014). The use of zinc nitrate and zinc acetate as precursors on growth and optical properties was also studied via sonochemical methods producing nitrogen-doped ZnO nanorods (Panda et al., 2013). Ultrasound modes, continuous and pulsed, have been compared for their effect on the characteristics of generated ZnO particles (Sahu et al., 2010). With the sonochemical method, high-power ultrasound with a high frequency was introduced into the precursor solution resulting in a complex reaction mechanism that was initiated by acoustic cavitation that produced local heating of up to 5,000 K and high pressures of approximately 1,000 atmospheres. A collapse occurred in less than a microsecond with a very high cooling rate of more than 10^{10} K per second (Manickam, 2011). Therefore, no external heating was necessary to promote the reaction.

In the present work, a simple sonochemical method was introduced to prepare a zinc oxide nanostructure using zinc nitrate as a zinc source and ammonia as a nitrogen source under either an air or a nitrogen atmospheric environment. Nitrogen is believed to be involved in ZnO luminescence by replacing oxygen in the ZnO lattice and resulting in intrinsic defects (Fan et al., 2013). Nitrogen gas bubbling in a solvothermal method was also reported to cause the modification of luminescence by the appearance of a narrow red emission (Karimipour et al., 2016). To the best of our knowledge, the effect of atmospheric environment using a sonochemical method has not been reported in previous investigations. The crystallinity, morphology, chemical bonding, and photoluminescence spectra were examined to investigate the effect of sonication time and atmospheric environment on the characteristics of the generated particles.

2. EXPERIMENTAL SETUP

Zinc nitrate tetrahydrate ($Zn(NO_3)_2.4H_2O$) 98.5%, (Merck, Kenilworth, NJ, USA) was dissolved in distillated water to prepare 100 mL of 0.2 M zinc nitrate solution. Next, 20 mL of 25% ammonia solution (Merck, Kenilworth, NJ, USA) was added to the zinc solution to obtain a turbid solution. Then, 10 drops of 25% ammonia solution were added to clarify the solution and adjust the pH to 10. This solution was continuously irradiated via an ultrasonic horn (VCX500, 500 watt, 20 kHz; Sonics & Materials, Inc., Newton, CN, USA) controlled at 40% of maximum amplitude at a temperature of 70°C under an air atmosphere for 1.0, 1.5, and 2.0 h. When synthesizing under a flow of nitrogen, the rate was 2 L/min flowing into the system, as shown in Figure 1. The generated suspension was washed by centrifugation at 10,000 rpm for 15 minutes, filtered, and dried at 130°C for 12 h to produce a dry white powder. The powder was characterized by its morphology, crystallinity, chemical bonding, and photoluminescence spectra via scanning electron microscopy (SEM) (Zeiss, Oberkoche, Germany), X-ray diffraction (XRD) (Phillips Electronics Company, Amsterdam, Netherlands), Fourier transform infrared (FTIR) (PerkinElmer, Waltham, MA, USA), and photoluminescence spectrometer (PerkinElmer, Waltham, MA, USA), respectively.

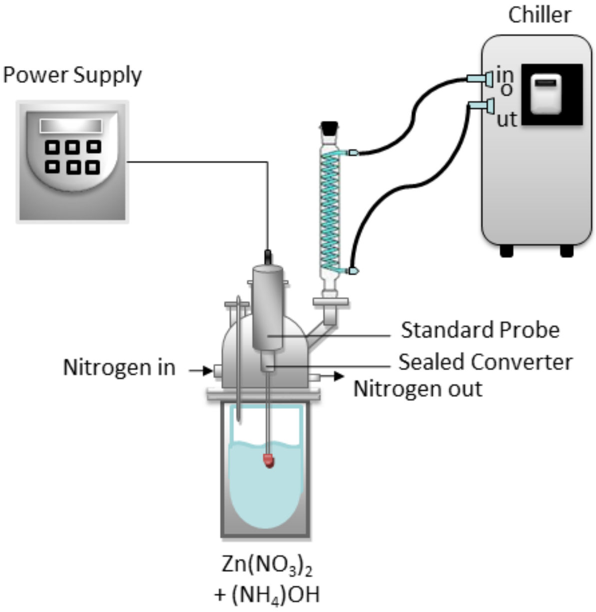

Figure 1 Schematic apparatus

3. RESULTS AND DISCUSSION

3.1. Structural Characterization

Figure 2 shows the XRD (X-ray diffraction) diffractograms of particles prepared by sonication under air and nitrogen flows with ultrasonic irradiation times of 1.0, 1.5, and 2 h. All samples were in agreement with the wurtzite structure ZnO diffraction of hexagonal phases (Joint Committee on Powder Diffraction Standards (JCPDS) No. 36-1451). Neither impurities nor other crystalline phases were observed in the samples. The selected times and the ultrasonic operation conditions were sufficient to produce crystalline ZnO particles.

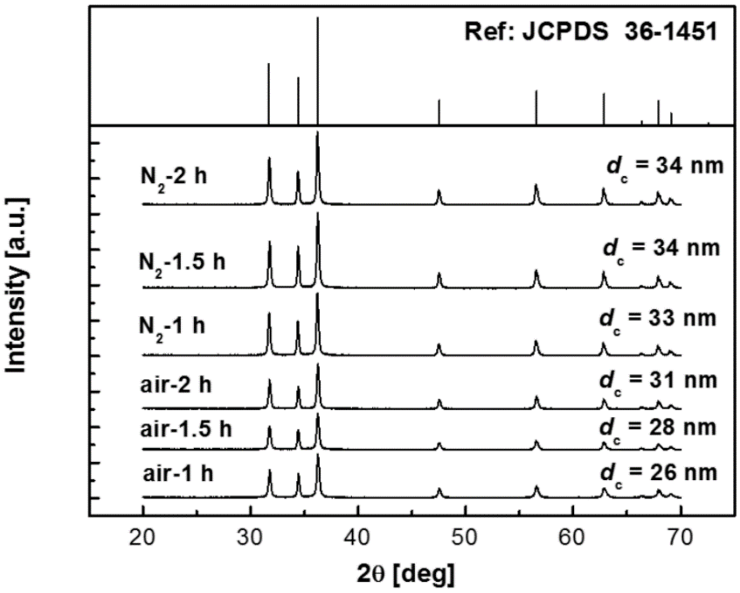

Figure 2 XRD diffractograms of samples synthesized at various ultrasonic irradiation times under flows of either nitrogen or air

The selected atmospheric environment, air or nitrogen, during sonochemical synthesis did not show a significant change in the diffractograms of the wurtzite structure ZnO diffraction.

In order to estimate the crystalline size, d_c, a Scherrer equation was used, based on the highest peak in the XRD pattern that was characterized by a (1 0 1) lattice plane at $2\theta = 36.253°$. The crystalline size increased from 26 to 31 nm as the time of ultrasonic irradiation was increased from 1 to 2 h under a flow of air. Relatively unchanged crystalline sizes of approximately 33–34 nm were generated for particles synthesized under a nitrogen flow irradiated at 1.0, 1.5, and 2.0 h.

3.2. Morphological Characterization

Figure 3a-c show the morphology of the generated particles synthesized for 1.0, 1.5, and 2.0 h under a flow of air. There were morphological evolutions from flowerlike to needlelike structures with increases in length and decreases in diameter. The regulated flowerlike structure began to break when ultrasonic irradiation was increased to 1.5 h. At 2.0 h of ultrasonic irradiation time, a needlelike structure was generated. Similar morphologies were also obtained for particles synthesized under a nitrogen flow with 1.0, 1.5, and 2.0 hh of sonication irradiation times, as shown in Figure 3d-f. This indicates that the particle morphologies were influenced only by the sonication times. The atmospheric environment during synthesis did not influence the morphologies of the particles. Increasing sonication times meant increasing the energy transfer from the sonication generator to the precursor, which changed the morphological structure, as reported in the previous investigation (Zak et al., 2013). They varied the sonication times from five to 60 minutes which changed the morphology from unstructured particles and then from nanorod to a flowerlike structure.

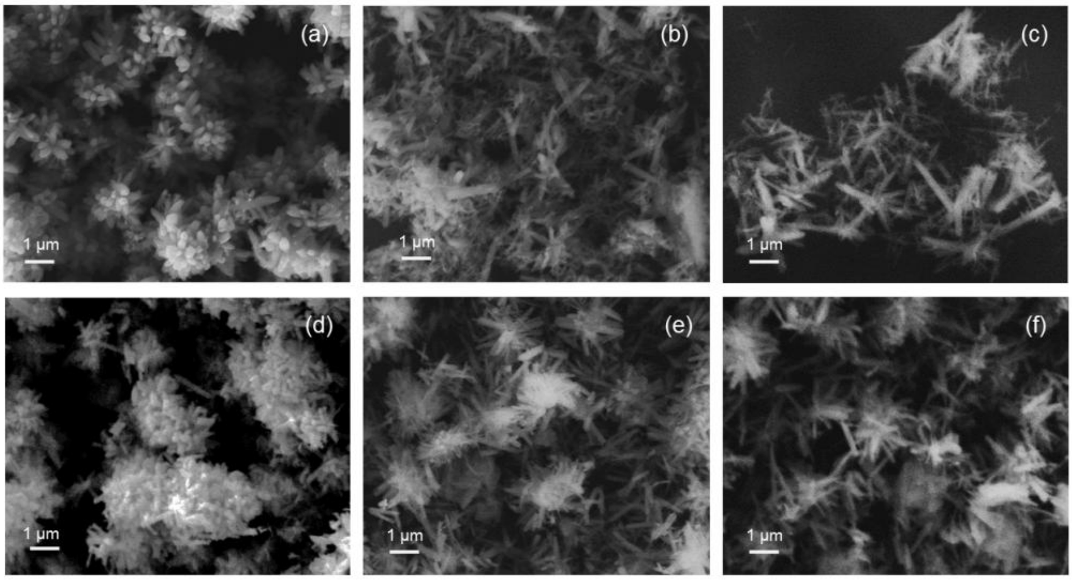

Figure 3 SEM images of the generated particles for ultrasound irradiated times: (a) 1.0 h; (b) 1.5 h; (c) 2.0 h under a flow of air; (d) 1.0 h; (e) 1.5 h; and (f) 2.0 h under a flow of nitrogen

3.3. Chemical Bonding Characterization

The FTIR spectrograms of samples in the transmittance mode were analyzed over wave numbers ranging from 4,000–500 cm^{-1}, as shown in Figure 4. All samples indicated a similar position of the reduction peak, as characterized by a specific chemical bonding. No prominent differences in FTIR spectrograms were caused by sonication times and atmospheric environment. At almost 3,500 cm^{-1}, there were broad reduction peaks of infrared absorption that were attributed to the hydroxyl group of water caused by the O-H stretching vibrations of the absorbed water. At approximately 1,380–1,350 cm^{-1}, clear reduction peaks were observed for all samples characterized by the presence of a N-O symmetric stretch (Coates, 2000). The nitrogen bonding found in the samples came from ammonia added during the synthesis. Zn-O stretching was observed at 700–500 cm^{-1} by magnifying the intensity at these wavenumbers.

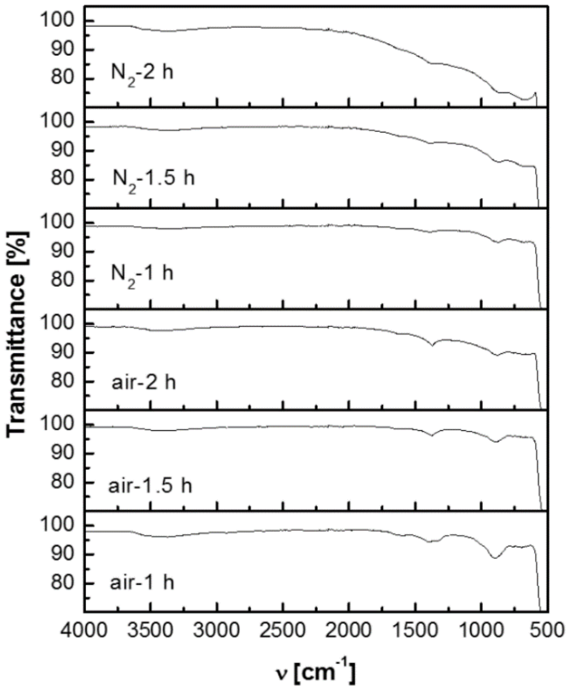

Figure 4 FTIR spectrograms of samples synthesized at various ultrasonic irradiation times under a nitrogen/air flow

3.4. Photoluminescence Characterization

Figure 5 shows the photoluminescence emission spectra of particles synthesized at 1.5 h of sonication irradiation under a flow of air that were excited at wavelengths from 225 to 275 nm. Using Gauss curve fitting, at excitation wavelengths of 225, 235, 245, 255, 265, and 275 nm, the photoluminescence emission peaks shifted to 433, 431, 426, 419, 409, and 401 nm, respectively. Among the selected excitation wavelengths, the highest intensity of photoluminescence emission spectra was obtained at a wavelength excitation of 245 nm. This excitation wavelength was selected to examine the photoluminescence emission spectra of particles synthesized under other conditions.

The photoluminescence emission spectra excited at a wavelength of 245 nm were examined under ambient temperature and are shown in Figure 6a for particles synthesized at various ultrasonic irradiation times under a flow of air. Their intensity increased with increases in ultrasonic irradiation times. The highest band gap was also wide and covered ultraviolet to green at wavelengths of 300–550 nm. An ultraviolet emission was caused by the characteristics of the near-band-edge emissions of the free exciton recombination process. However, blue and green emissions were caused by an association with oxygen vacancies and other defects. In addition, increases in irradiation time during the sonication process caused a shifting of the peaks of photoluminescence emission spectra to a higher wavelength. The peaks of the photoluminescence emission spectra for 1.0, 1.5, and 2.0 h of irradiation sonication times were positioned at wavelengths of 420, 426, and 435 nm, respectively.

Two sharp peaks of photoluminescence emission spectra were observed at wavelengths of 390 and 500 nm, as characterized by ultraviolet and green band emissions for particles synthesized under a nitrogen flow, as shown in Figure 6b. In the photoluminescence emission spectra, two peaks of ultraviolet and green bands were also obtained by a previous investigator (Thangadurai et al., 2011), which corresponded to excitonic recombination and intrinsic point defects, respectively. Nitrogen flow during the process enhanced the defect-related emissions and resulted in a higher photoluminescence of green emissions at a wavelength of 500 nm. Another previous investigator produced ZnO via a chemical vapor deposition method and reported that oxide defects were increased by decreasing the oxygen partial pressure in the atmosphere (Xu et al., 2011). Green emissions were also examined in the ZnO doped zinc film and powder by flowing 95% nitrogen and 5% hydrogen during vapor deposition, which was attributed to an oxygen vacancy-related defect (Zhang et al., 2009). In our synthesis, the partial pressure of oxygen was reduced by flowing nitrogen during the sonochemical process. When under a nitrogen flow, sonication irradiation time greatly affected the intensity of the photoluminescence emissions and scarcely tuned the peaks of the photoluminescence emissions spectra.

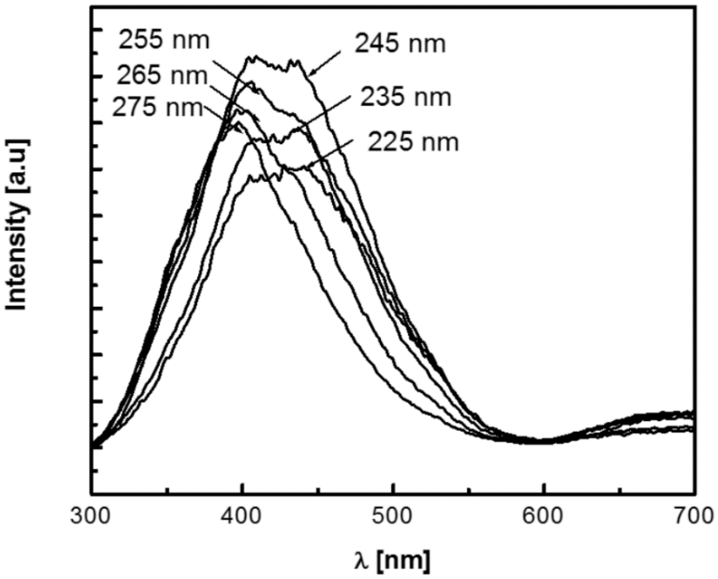

Figure 5 Photoluminescence emission spectra of particles synthesized at 1.5 h of sonication irradiation under a flow of air during an examination of various excitation wavelengths

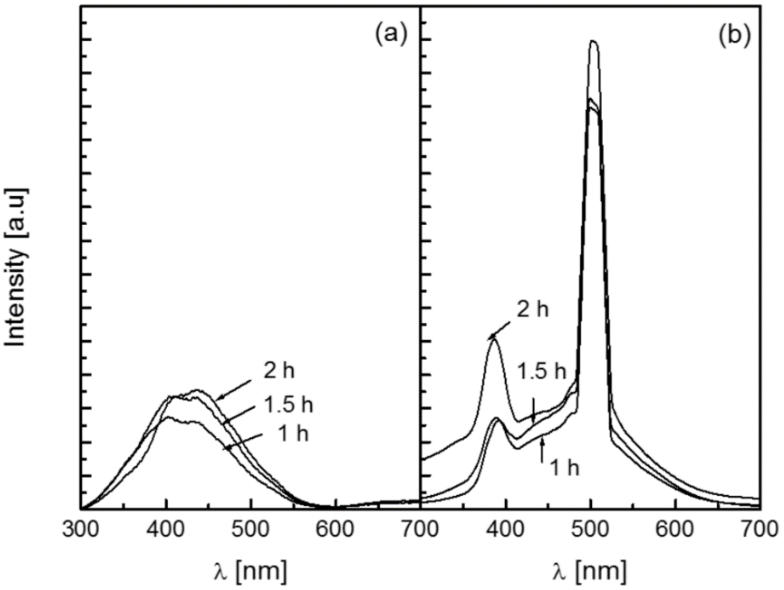

Figure 6 Photoluminescence emission spectra of particles synthesized at various ultrasonic irradiation times and under flows of (a) air and (b) nitrogen

4. CONCLUSION

Controlling the morphology of the ZnO nanostructures of a wurtzite hexagonal phase from flowerlike to needlelike was successfully accomplished by controlling the ultrasound irradiation times from 1.0 to 2.0 h via a sonochemical method under a flow of either air or nitrogen during the process. The crystalline size and photoluminescence intensity increased with ultrasonic irradiation time. When excited at a wavelength of 245 nm, particles with wide bands and peaks centered at wavelengths of 420, 426, and 435 nm, which corresponded to violet emissions, were synthesized under an air environment using sonication times of 1.0, 1.5, and 2.0 h, respectively. However, two peaks centered at 390 and 500 nm were generated under a nitrogen environment, indicating ultraviolet and green luminescence emissions, respectively.

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