

## Hydrothermal Synthesis of Fine Zinc Oxide Nano-Particles under Supercritical Conditions

Satoshi Ohara, Tahereh Mousavand, Mitsuo Umetsu, Seiichi Takami, and Tadafumi Adschiri\*

Institute of Multidisciplinary Research for Advanced Materials, Tohoku University,  
2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan

\*E-mail: [ajiri@tagen.tohoku.ac.jp](mailto:ajiri@tagen.tohoku.ac.jp)

Synthesis of highly crystalline ZnO nano-particles by the supercritical water hydrothermal synthesis method was examined. Zinc nitrate aqueous solution at room temperature was pressurized to 30 MPa and then mixed with potassium hydroxide solution under the same conditions to generate metal hydroxides. This mixture was then rapidly heated to 673 K by mixing with supercritical water and then fed into a tubular reactor. Residence time is about 18 s. The reaction was terminated by cooling at the exit of the reactor. Production of nanosize particles with uniform particle size distribution showed a highly crystalline ZnO phase. In addition, room temperature photoluminescence measurements were carried out to characterize the ZnO nano-particles, in relation to ultraviolet device applications.

### 1. Introduction

Recently, zinc oxide (ZnO), a wide-band-gap semiconductor, has attracted considerable research attention as a promising candidate for ultraviolet (UV) light-emitting [1] and lasing [2-6] devices, because of its large exciton-binding energy. The band gap of ZnO is 3.37 eV at room-temperature, and the exciton-binding energy of 60 meV is the largest among the II-VI compounds. Although the ZnO has the same crystal structure and optical properties as those of GaN based compounds, it is sufficiently stable compared with them. Thus it is expected that degradation of light emission properties due to the defect propagation during operation of devices may not be a serious problem for ZnO materials. This leads to expand the lifetime of devices fabricated with this material.

High crystallinity of ZnO nano-structure is one of the most important factors in achieving a high UV emission efficiency [3-7]. Therefore, it is important to synthesize the fine ZnO nano-particles with strong near-band-gap edge emission for the ZnO based UV light devices. However, the synthesis of high quality ZnO nano-particles with high UV emission efficiency has not been reported yet to our best knowledge.

We are developing a method for continuous

and rapid production of fine metal oxide particles by hydrothermal synthesis in supercritical water ( $T_c = 647$  K;  $P_c = 22.4$  MPa) [8-12], namely "supercritical hydrothermal synthesis (SHS)". This method has an advantage for the production of highly crystalline metal oxide nano-particles. The final aim of our work is to fabricate high performance UV devices by using fine ZnO nano-particles as the starting materials of the devices. In this report, synthesis of highly crystalline ZnO nano-particles by the SHS method was examined as a first step of our project.

### 2. Experimental method

#### 2.1. Supercritical hydrothermal synthesis (SHS)

Figure 1 shows a schematic illustration for the flow-type reaction cell of the SHS method used in this study. Zinc nitrate ( $Zn(NO_3)_2 \cdot 6H_2O$ ) and potassium hydroxide (KOH) were the starting materials. They were dissolved in water. The concentrations of  $Zn(NO_3)_2$  and KOH were 0.02 and 0.04 mol/L, respectively. Aqueous solution of zinc nitrate at room temperature was pressurized to 30 MPa and then mixed with potassium hydroxide solution at the same conditions to generate metal hydroxides. This mixture was fed into a reactor by a high-pressure pump at a flow rate of 2 cm<sup>3</sup>/min and mixed

with supercritical water at 723 K at a flow rate of 10 cm<sup>3</sup>/min, and thus the metal hydroxides were rapidly heated to the reaction temperature. Zn(NO<sub>3</sub>)<sub>2</sub> solution without KOH was also fed into the reactor in order to compare the morphology of ZnO production. The temperature and pressure of the supercritical water in the reactor were maintained at 673 K and 30 MPa, respectively. The volume of the reactor was 10 cm<sup>3</sup> and the reaction time was about 18 s. The tube reactor was made of SUS 316 stainless steel. At the exit of the reactor, the fluid was rapidly quenched by using an external water jacket. Then produced particles were collected by using an upstream in-line filter. In duration of the experiment pressure was controlled by using a back pressure regulator that was positioned after cooling unit.

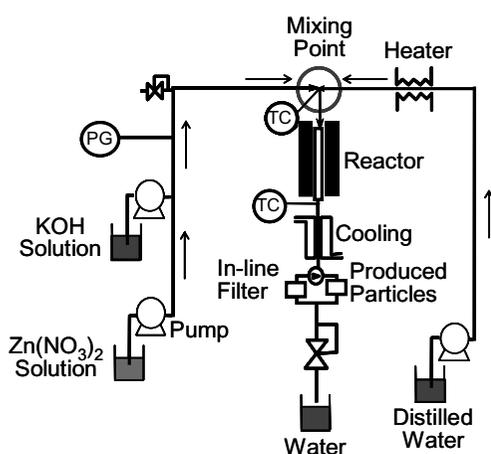


Fig. 1. Schematic of the supercritical water flow apparatus. PG, pressure gauge and TC, thermocouple.

**2.2 Characterization** The morphology of ZnO particles was observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). X-ray diffraction (XRD) with Cu-K $\alpha$  radiation was used for checking the formation and identification of present compounds in the obtained particles. Photoluminescence (PL) spectra of ZnO particles were measured with a Xe lamp (150 mW) as an excitation source. The excitation wavelength was 325 nm. The emission spectrum at room temperature was observed in the wavelength range of 350-600 nm by using a

monochromator and a photomultiplier.

### 3. Results and Discussion

Figure 2 shows the SEM photographs of ZnO particles prepared by SHS from the solution of (a) Zn(NO<sub>3</sub>)<sub>2</sub> and KOH and (b) Zn(NO<sub>3</sub>)<sub>2</sub>. In the case of synthesis from the mixture of Zn(NO<sub>3</sub>)<sub>2</sub> and KOH, the nanosize particles with uniform particle size distribution were obtained and their morphology was grain-like. A TEM image of the nanosize particles is given in Fig. 3. It was observed clearly that the particles size was about 50-100 nm. On the other hand, in the case of synthesis from Zn(NO<sub>3</sub>)<sub>2</sub> solution without KOH, its morphology became whiskers. Well-developed crystal particles with hexagonal end face were observed, as shown in Fig. 2 (b).

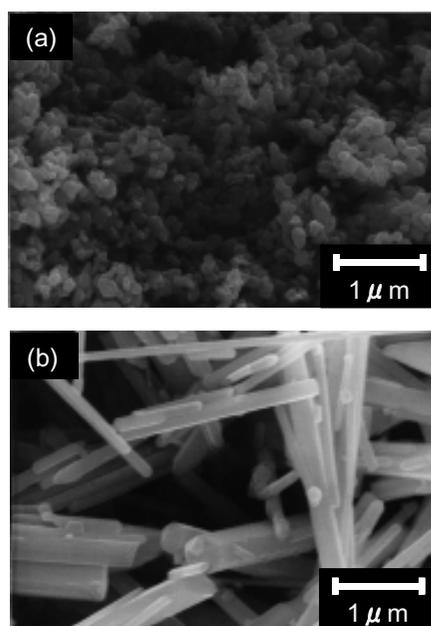


Fig. 2. SEM pictures of ZnO particles prepared from the solution of (a) Zn(NO<sub>3</sub>)<sub>2</sub> and KOH and (b) Zn(NO<sub>3</sub>)<sub>2</sub>.

Recently, it was reported that ZnO whiskers can be prepared by hydrothermal method [13,14]. However, the reaction time is in the order of hours. On the other hand, SHS requires an extremely short reaction time (18 s), which is more attractive production technique for ZnO

whiskers.

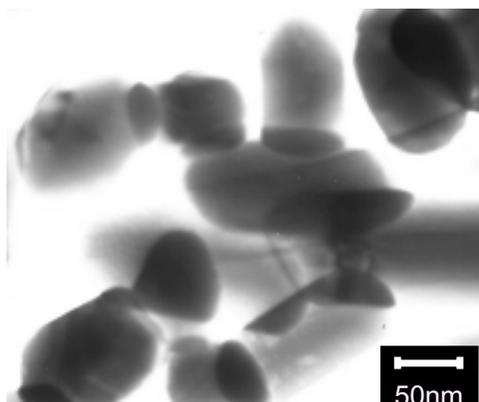


Fig. 3. TEM picture of ZnO nano-particles prepared from the mixture of  $\text{Zn}(\text{NO}_3)_2$  and KOH.

Figure 4 shows the XRD patterns of ZnO particles from the solution of (a)  $\text{Zn}(\text{NO}_3)_2$  and KOH and (b)  $\text{Zn}(\text{NO}_3)_2$ . It was confirmed that both patterns had a hexagonal wurtzite crystal structure of ZnO without another phase. Nine peaks appear at  $2\theta = 31.7^\circ, 34.4^\circ, 36.3^\circ, 47.5^\circ, 56.6^\circ, 62.3^\circ, 66.5^\circ, 67.9^\circ,$  and  $69.1^\circ$ , which correspond to (100), (002), (101), (102), (110), (103), (200), (112), and (201), respectively. It seems that both ZnO particles possess a high crystallinity, since all peaks are very sharp. The splitting of (103), (112), and (201) peaks is caused by the  $K\alpha_1$  and  $K\alpha_2$  component of Cu- $K\alpha$ . It is found that the ratio of the intensity of (100) peak to that of (002) peak of ZnO whiskers (b), as shown in Fig. 2, is considerably increased compared with that of grain-like particles (a). It is considered that the variation of the (100)/(002) intensity ratio is caused by the shear stress on the particles when it is compacted in the XRD holder to induce the whiskers to arrange their long axis vertical to the direction of the compacting force.

Figure 5 shows the PL spectrum of ZnO nano-particles prepared from the mixture of  $\text{Zn}(\text{NO}_3)_2$  and KOH. Strong near-band-gap edge emission at 380 nm has been observed at room temperature and this high UV emission seems to be caused by the high crystallinity of fine ZnO particles. Then, ZnO whiskers prepared from  $\text{Zn}(\text{NO}_3)_2$  solution without KOH also shows similar PL spectrum of ZnO nano-particles and

their UV emission intensity is an approximately one order of magnitude higher than that of the nano-particles [15]. Now, we are trying to find the best SHS conditions in order to develop the ZnO nano-particles with further improvement in UV emission efficiency.

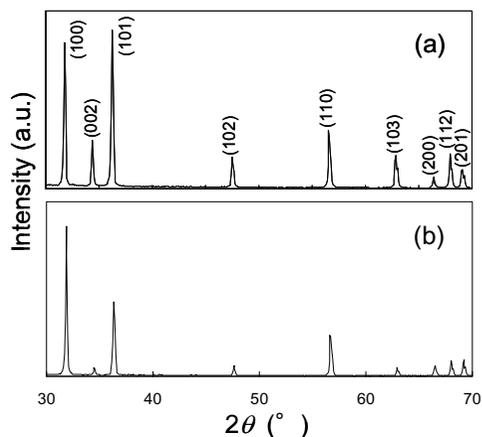


Fig. 4. XRD patterns for ZnO particles prepared from the solution of (a)  $\text{Zn}(\text{NO}_3)_2$  and KOH and (b)  $\text{Zn}(\text{NO}_3)_2$ .

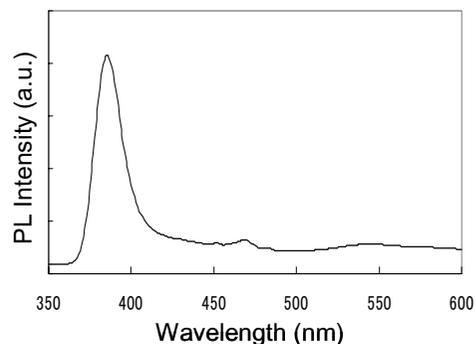


Fig. 5. Room temperature photoluminescence spectrum of ZnO nano-particles prepared from the mixture of  $\text{Zn}(\text{NO}_3)_2$  and KOH.

#### 4. Conclusions

We have described the synthesis of highly crystalline ZnO nano-particles from the mixture of zinc nitrate and potassium hydroxide aqueous solutions by SHS method. Room temperature PL spectrum of the ZnO nano-particles obtained showed the strong near-band-gap edge emission.

Optimization of the SHS conditions may provide the ZnO nano-particles with a very high UV emission efficiency. We believe the ZnO nano-particles prepared by SHS could be used as the starting materials of the UV light-emitting and lasing devices.

#### Acknowledgements

This work was partly supported by the Ministry of Education, Science, Sports and Culture, a Grant-in-Aid for the COE project, Giant Molecules and Complex Systems, 2003.

#### References

- [1] H. Ohta, K. Kawamura, M. Orita, M. Hirano, N. Sarukura and H. Hideo, *Appl. Phys. Lett.*, **77**, 475 (2000).
- [2] D. C. Reynolds, D. C. Look and B. Jogai, *Solid State Commun.*, **99**, 869 (1996).
- [3] Z. K. Tang, P. Yu, G. K. L. Wong, M. Kawasaki, A. Ohtomo, H. Koinuma and Y. Segawa, *Solid State Commun.*, **103**, 459 (1996).
- [4] H. Cao, J. Y. Xu, E. W. Seelig and R. P. H. Chang, *Appl. Phys. Lett.*, **76**, 2997 (2000).
- [5] H. Cao, J. Y. Xu, D. Z. Zhang, S.-H. Chang, S. T. Ho, E. W. Seelig, X. Liu and R. P. H. Chang, *Phys. Rev. Lett.*, **84**, 5584 (2000).
- [6] M. H. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo and P. Yang, *Science*, **292**, 1897 (2001).
- [7] D. Nezaki, T. Okamoto and M. Takata, *Key Engineering Materials*, **228-229**, 241 (2002).
- [8] T. Adschiri, M. Kanazawa and K. Arai, *J. Am. Ceram. Soc.*, **75**, 1019 (1992).
- [9] T. Adschiri, M. Kanazawa and K. Arai, *J. Am. Ceram. Soc.*, **75**, 2615, (1992).
- [10] Y. Hakuta, T. Adschiri, T. Suzuki, T. Chida, K. Seino and K. Arai, *J. Am. Ceram. Soc.*, **81**, 2461 (1998).
- [11] K. Kanamura, A. Goto, R. Y. Ho, T. Umegaki, K. Toyoshima, K. Okada, Y. Hakuta, T. Adschiri and K. Arai, *Electrochem. Solid-State Lett.*, **3**, 256 (2000).
- [12] T. Adschiri, Y. Hakuta, K. Sue and K. Arai, *J. Nanoparticle Res.*, **3**, 227 (2001).
- [13] W.-J. Li, E.-W. Shi, M.-Y. Tian, W.-Z. Zhong and Z.-W. Yin, *J. Mater. Res.*, **14**, 1532 (1999).
- [14] C.-H. Lu and C.-H. Yeh, *Ceramics International*, **26**, 351 (2000).
- [15] S. Ohara, T. Mousavand, M. Umetsu, S. Takami, T. Adschiri, Y. Kuroki and M. Takata, *Solid State Ionics*, **172**, 261 (2004).