J Mater Sci (2008) 43:2393–2396
DOI 10.1007/s10853-007-1823-3

NOVEL ROUTES OF ADVANCED MATERIALS PROCESSING AND APPLICATIONS

Continuous production of fine zinc oxide nanorods by hydrothermal synthesis in supercritical water

**Satoshi Ohara · Tahereh Mousavand ·
Takafumi Sasaki · Mitsuo Umetsu ·
Takashi Naka · Tadafumi Adschiri**

Received: 15 November 2006 / Accepted: 4 May 2007 / Published online: 22 December 2007

Abstract Continuous production of highly crystalline ZnO nanorods by supercritical hydrothermal synthesis was reported in this article. Zinc nitrate aqueous solution was pressurized to 30 MPa at room temperature and rapidly heated to 673 K by mixing with supercritical water and then fed into a tubular reactor. Residence time is about 10 s. Production of ZnO nanorod particles with uniform particle size distribution showed a strong ultraviolet light emission at room temperature. This article also reported in-situ surface modification of ZnO nanorods with organic reagents by the supercritical hydrothermal synthesis.

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.

High crystallinity of ZnO nanostructure is one of the most important factors in achieving a high UV emission efficiency. Therefore, many special techniques such as molecular beam epitaxy (MBE) [3], vapor phase transport process [6] and electric current heating method [7] have been used in the preparation of high quality ZnO nanocrystals with strong near-band-gap edge emission. For the ZnO based UV light devices, it is important to synthesize the fine ZnO nanoparticles with high UV emission efficiency. However, above methods are not suitable for particles production.

We have developed 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) [8–13], namely “supercritical hydrothermal synthesis (SHS)”. This method has an advantage for the production of highly crystalline metal oxide nanoparticles. The final aim of our work is to fabricate high performance UV devices by using fine ZnO nanoparticles as the starting materials of the devices. In this article, we reported the production of highly crystalline ZnO nanorods particles by the SHS method.

On the other hand, a critical issue for nanoparticle technology is particle handling. In hydrothermal synthesis, the recovery of the nano particles from the water is essential. Additionally, for spraying or coating applications, a stable dispersion without coagulation of nanoparticles in organic solvents or resins is required.

Surface modification is an effective way to control the dispersion of nanoparticles. The conventional means to control surface characteristics is with the use of surfactants, although they may not always be effective for already agglomerated particles. Another method of controlling particle interactions is via chemical reactions to modify surfaces. If the nanoparticles can be recovered in an

---

S. Ohara · T. Mousavand · T. Sasaki · M. Umetsu · T. Naka ·
T. 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

organic solvent, silanization is one way to introduce various functional groups on the particle surface via the silicate layers.

Recently, we have attempted to use an in-situ surface modification process during the SHS [14–17]. At low temperatures, phase separation takes place for water-organic systems, such that effective surface modification cannot occur. However, a homogeneous phase can be expected at higher temperatures. In this article, we also reported in-situ surface modification of ZnO nanoparticles with organic reagents by the SHS.

Experimental

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 ($Zn(NO_3)_2 \cdot 6H_2O$) was the starting material and it was dissolved in water. The aqueous solution was fed into a reactor by a high-pressure pump at a flow rate of 2 cm^3/min and mixed with supercritical water at 450 °C at a flow rate of 10 cm^3/min, and thus the solution was rapidly heated to the reaction temperature. The temperature and pressure of the supercritical water in the reactor were maintained at 400 °C and 30 MPa, respectively. The volume of the reactor was 5 cm^3. The reaction time was about 10 s, which was evaluated by total flow rate (12 cm^3/min), reactor volume (10 cm^3) and density of pure water at the reaction temperature and pressure (0.36 g/cm^3). The reactor was made of SUS 316 stainless steel tube. At the exit of the reactor, the fluid was rapidly quenched by addition of a potassium hydroxide (KOH) solution (flow rate of 10 cm^3/min) and 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. For the in-situ surface treatment experiments, several organic reagents (hexanol, hexanal, and hexylamine) were used to modify the surface of ZnO particles under supercritical conditions.

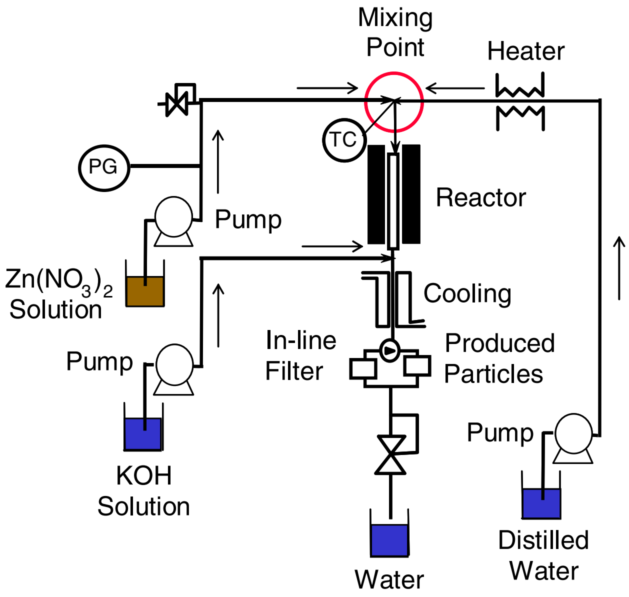

Fig. 1 Schematic of the supercritical water flow apparatus. PG = pressure gauge and TC = thermocouple

Characterization

The morphology of ZnO particles was observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). X-ray diffraction (XRD) with Cu-Kα 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 monochrometer and a photomultiplier. For the in-situ surface treatment experiments, the particles obtained were dispersed in water or chloroform to determine the affinity to either water or chloroform.

Results and discussion

Figure 2 shows the XRD pattern of ZnO particles by SHS from the solution with the concentration of 0.05 mol/L. It was confirmed that the pattern had a hexagonal wurtzite crystal structure of ZnO without another phase. Based on

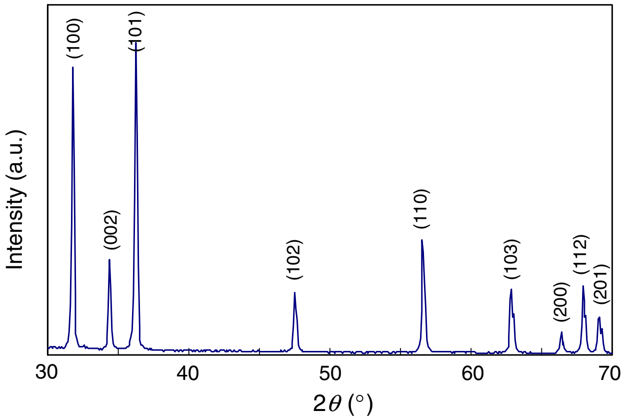

Fig. 2 XRD pattern for ZnO nanoparticles

our previous studies [12], the reaction taking place in the reactor is considered to be as follows:

$$Zn(NO_3)_2 + 2H_2O = Zn(OH)_2 + 2HNO_3 \quad (1)$$

$$Zn(OH)_2 = ZnO + H_2O \quad (2)$$

The first step (1) is the hydrolysis of a metal salt to produce metal hydrous oxide, and the second step (2) is dehydration of the hydrous oxide to produce metal oxide. Nine peaks appear at $2\theta = 31.7°$, 34.4°, 36.3°, 47.5°, 56.6°, 62.3°, 66.5°, 67.9°, and 69.1°, which correspond to (100), (002), (101), (102), (110), (103), (200), (112) and (201), respectively. It seems that the ZnO particles possess a high crystallinity, since all peaks are very sharp. The splitting of (103), (112) and (201) peaks is caused by the Kα1 and Kα2 component of Cu-Kα.

Figure 3 shows the SEM photograph of ZnO particles prepared from the solution of $Zn(NO_3)_2$. The nanosize particles with uniform particle size distribution were obtained and their morphology was rod-like. A TEM image of the nanorods particles is given in Fig. 4. The calculated mean diameter and length of theses rods are 150 nm and 600 nm, respectively.

Recently, it was reported that ZnO nanorods can be prepared by hydrothermal method [18, 19]. However, the reaction time is in the order of hours. On the other hand, SHS requires an extremely short reaction time (10 s), which is more attractive production technique for ZnO nanorods.

Figure 5 shows the PL spectrum of ZnO nanorods prepared by SHS. 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 nanorods. Now, we are finding the best SHS conditions in order to develop the ZnO nanorods with further improvement in UV emission efficiency.

In most cases, the surfaces of the metal oxide nanoparticles formed in hydrothermal conditions were terminated by hydroxyl or ether groups. Therefore, the metal oxide nanoparticles were hydrophilic and well dispersed into water and other solvents whose dielectric constant is high. The one possible way to modify the surface of the metal oxide nanoparticles is to use reagents that react with the hydroxyl group. We examined various kinds of reagents (hexanol, hexanal, and hexylamine) and succeeded in modifying the surfaces of the ZnO nanorods particles. Figure 6 shows a typical result of surface modification. On the left side, where no surface modification was performed, the ZnO nanorods were dispersed in water phase alone. In contrast, the surface modified nanorods were dispersed in the chloroform alone. Here, we modified the original surface of ZnO nanorods particles with hexylamine that puts alkyl groups on the outer surface.

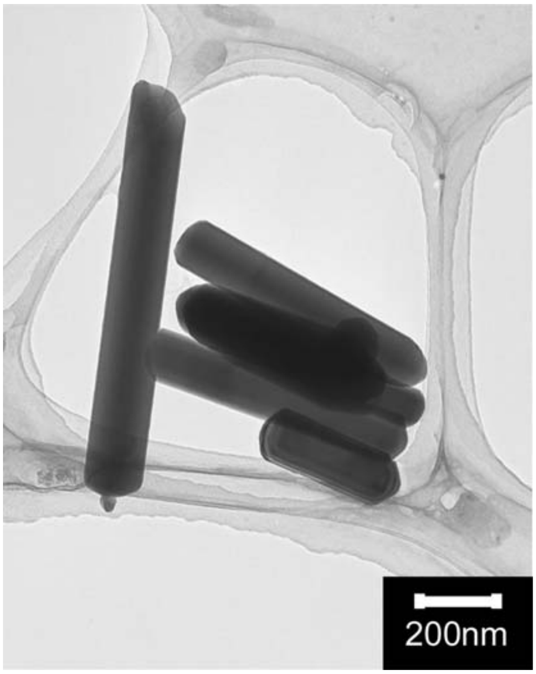

Fig. 4 TEM picture of ZnO nanorods

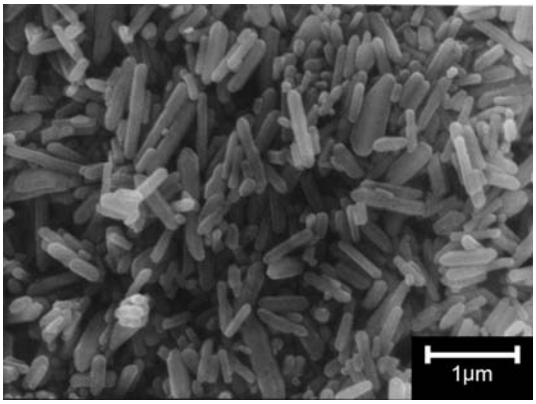

Fig. 3 SEM picture of ZnO nanorods

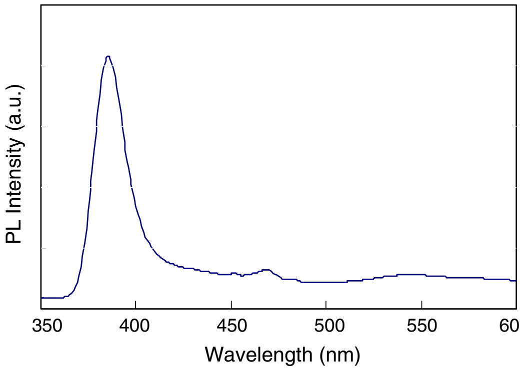

Fig. 5 Room temperature photoluminescence spectrum of ZnO nanorods

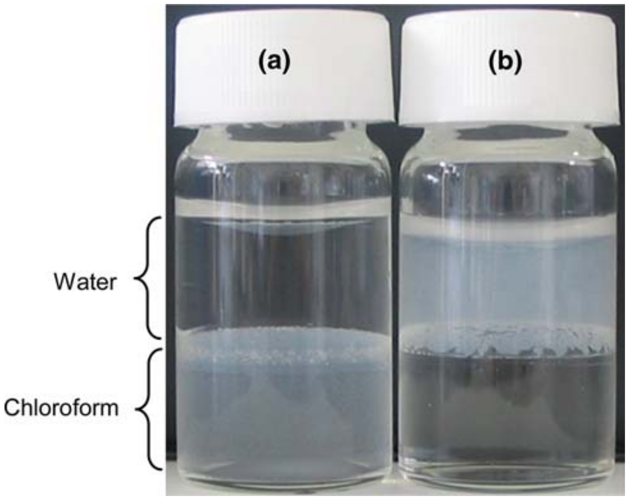

Fig. 6 Dispersion properties of (**a**) surface modified ZnO nanorods in a water/chloroform binary system and (**b**) non-modified nanorods

Therefore, the surfaces of the ZnO nanorods became hydrophobic. This result indicates that in situ surface modification is convenient and rational method to control the properties of metal oxide nanoparticles.

Conclusion

We have described the production of highly crystalline ZnO nanorods particles from the zinc nitrate aqueous solutions by SHS method. Room temperature PL spectrum of the ZnO nanorods obtained showed the strong near-band-gap edge emission. In addition, we have described the in-situ surface modification of ZnO nanorods with organic reagents by the SHS. We believe the ZnO nanoparticles prepared by SHS could be used as the starting materials of the UV light-emitting and lasing devices.

Acknowledgement This work was supported by a Scientific Research Grant from the Ministry of Education, Science, Sports, and Culture of Japan. This research was also partly supported by the Hosokawa Powder Technology Foundation and the Murata Science Foundation.

References

1. Ohta H, Kawamura K, Orita M, Hirano M, Sarukura N, Hosono H (2000) Appl Phys Lett 77:475
2. Reynolds DC, Look DC, Jogai B (1996) Solid State Commun 99:869
3. Tang ZK, Yu P, Wong GKL, Kawasaki M, Ohtomo A, Koinuma H, Segawa Y (1996) Solid State Commun 103:459
4. Cao H, Xu JY, Seelig EW, Chang RPH (2000) Appl Phys Lett 76:2997
5. Cao H, Xu JY, Zhang DZ, Chang S-H, Ho ST, Seelig EW, Liu X, Chang RPH (2000) Phys Rev Lett 84:5584
6. Huang MH, Mao S, Feick H, Yan H, Wu Y, Kind H, Weber E, Russo R, Yang P (2001) Science 292:1897
7. Nezaki D, Okamoto T, Takata M (2002) Key Eng Mater 228–229:241
8. Adschiri T, Kanazawa M, Arai K (1992) J Am Ceram Soc 75:1019
9. Adshiri T, Kanazawa M, Arai K (1992) J Am Ceram Soc 75:2615
10. Hakuta Y, Adschiri T, Suzuki T, Chida T, Seino K, Arai K (1998) J Am Ceram Soc 81:2461
11. Kanamura K, Goto A, Ho RY, Umegaki T, Toyoshima K, Okada K, Hakuta Y, Adschiri T, Arai K (2000) Electrochem Solid-State Lett 3:256
12. Adschiri T, Hakuta Y, Sue K, Arai K (2001) J Nanoparticle Res 3:227
13. Ohara S, Mousavand T, Umetsu M, Takami S, Adschiri T (2004) Solid State Ionics 172:261
14. Mousavand T, Takami S, Umetsu M, Ohara S, Adschiri T (2006) J Mat Sci 41:1445
15. Zhang J, Ohara S, Umetsu M, Naka T, Hatakeyama Y, Adschiri T (2007) Adv Mater 19:203
16. Mousavand T, Ohara S, Umetsu M, Zhang J, Naka T, Adschiri T (2007) J Nanoparticles Res 9:1067
17. Mousavand T, Ohara S, Umetsu M, Zhang J, Takami S, Naka T, Adschiri T (2007) J Supercritic Fluids 40:397
18. Guo L, Ji YL, Xu H (2002) J Am Chem Soc 124:14864
19. Liu B, Zeng HC (2003) J Am Chem Soc 125:4430