Synthesis of ZnO Nanoparticles by Decomposition of Zinc Peroxide

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Zinc peroxide sols were prepared by the peptization of $Zn(OH)_2$ using 1 mol/L of H_2O_2 aqueous solution at 348 K for 2 h. Firing the dried sol powder at 573 K for 2 h formed almost monodispersed ZnO nanoparticles whose average diameter was 19 nm.

Zinc oxide (ZnO) is an n-type oxide semiconductor and shows both photoconductivity and photocatalytic activity.[1,2] ZnO nanoparticles also show size-dependent electronic and optical properties, which are known as quantum-size effects.[3] In order to obtain high catalytic activity and good electronic characteristics, it is important to regulate particle size and to maintain appropriate preparation of monodispersed nanoparticles.

It has been reported that ZnO nanoparticles can be obtained by hydrolysis of zinc alkoxide, which is very sensitive to humidity and difficult to use in ZnO synthesis.[4] Therefore, it is recommended that a simple method of preparation be employed. In this study, we investigated a simple means of preparing ZnO nanoparticles. We used zinc peroxide (ZnO_2) as a precursor of ZnO nanoparticles. At temperatures above 473 K, zinc peroxide decomposes to ZnO.[5] If a method of synthesizing sols with dispersion of zinc peroxide nanoparticles can be found, it will lead the way to the production of ZnO nanoparticles and ZnO films.

The sols containing zinc peroxide particles were prepared as follows: 100 mL of $Zn(NO_3)\cdot 6H_2O$ aqueous solution (0.1 mol/L) and 100 mL of NaOH aqueous solution (0.1 mol/L) were mixed to obtain zinc hydroxide ($Zn(OH)_2$) precipitate. The precipitate was separated from the solution by centrifuge at 3000 rpm for 5 min. The obtained $Zn(OH)_2$ was dispersed into distilled water and was again separated by the centrifuge. This procedure was repeated 3 times. The $Zn(OH)_2$ was then dispersed in 50 mL of H_2O_2 aqueous solution whose concentration was 1 mol/L, 0.1 mol/L, or 0 mol/L. From this point, the concentration of H_2O_2 aqueous solution is referred to as "$[H_2O_2]$". The dispersed solution was heated at 348 K for 2 h in a closed vessel. The resultant solution was either a translucent sol or a solution with an aggregated precipitate. The obtained sols and precipitates were dried at 348 K for 6 h. The structure of the dried sol powder was characterized by means of X-ray diffraction (XRD) (Cu Kα 40 kV, 200 mA, Mac Science MXP-18) and Raman spectroscopy (JASCO NRS1000). The particle shape was observed by field emission-SEM (FE-SEM Hitachi S4700). The obtained powder was fired at one of the following temperatures for 2 h to prepare ZnO particles: 453 K, 473 K, 493 K, 573 K, and 773 K.

Figure 1 shows the XRD patterns of the dried sol powder and the precipitate. The XRD pattern of the sample prepared by using of $[H_2O_2]$ = 0 mol/L solution in Figure 1a can be identified as pure ZnO. The state of the obtained ZnO was aggregated precipitate, which is not suitable for the preparation of ZnO films and nanoparticles. When the amount of $[H_2O_2]$ is 0.1 mol/L or 1 mol/L, the XRD patterns correspond to zinc peroxide (ZnO_2) as shown in Figures 1b and 1c. After the reaction between $Zn(OH)_2$ and H_2O_2 aqueous solution, the resultant solution appears as a stable translucent sol without precipitate. The crystalline size was calculated using Scherrer's equation and the fwhm of zinc peroxide (200) plane. The crystalline sizes of the $[H_2O_2]$ = 0.1 mol/L and $[H_2O_2]$ = 1 mol/L samples were 13.3 nm and 12.0 nm, respectively.

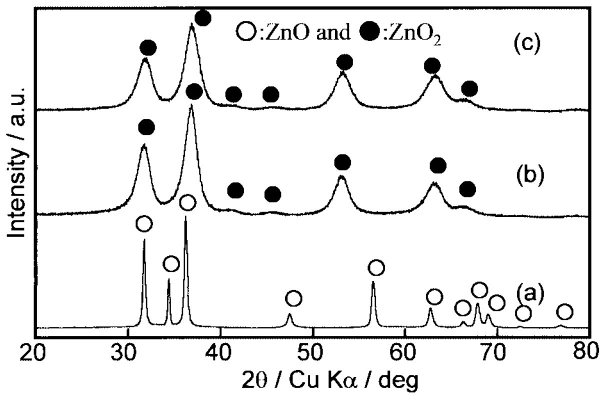

Figure 1. X-ray diffraction patterns of the powders prepared by drying the sols and precipitates obtained by the reaction between $Zn(OH)_2$ and H_2O_2 aqueous solution. $[H_2O_2]$: (a) 0 mol/L, (b) 0.1 mol/L, and (c) 1 mol/L.

It is known that zinc peroxide consists of Zn^{2+} and peroxo ion(O_2^{2-}).[6] Zinc peroxide also has a NaCl-type structure[6]. In order to examine whether or not the obtained compounds contained peroxo ion, the Raman spectra were measured as shown in Figure 2. Figure 2a shows the spectrum of ZnO powder, used as a reference. The stretching band of Zn^{2+}–O^{2-} at 435 cm^{-1} is shown as peak A. Peaks B and C in Figures 2b and 2c correspond to the stretching bands of O–O bond of peroxo ion and that of CO_3^{2-}, respectively.[7,8] Peak A was not observed in Figures 2b and 2c. Peak C indicates that CO_2 in the air formed zinc carbonate. These Raman spectra and XRD patterns show that the primary compound obtained by using H_2O_2 aqueous solution ($[H_2O_2]$ = 0.1 mol/L and 1 mol/L) was zinc peroxide. Other methods of preparation of zinc peroxide have been reported. However, the morphology of prepared zinc peroxide to date has been aggregated precipitate. No method of preparation of zinc peroxide sol has yet been reported.

Figures 3a and 3b show the FE-SEM images of zinc peroxide particles. The size of the particles prepared by using the

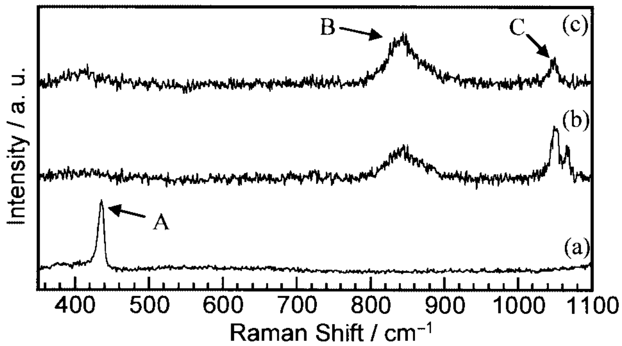

Figure 2. Raman spectra of the powders prepared by drying the obtained sols. (a) ZnO (reference), (b) $[H_2O_2] = 0.1$ mol/L, and (c) $[H_2O_2] = 1$ mol/L.

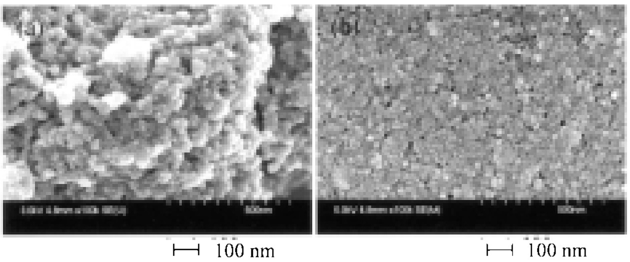

Figure 3. FE-SEM images of the powders obtained by drying the zinc peroxide sols.
(a) $[H_2O_2]=0.1$ mol/L and (b) $[H_2O_2]=1$ mol/L.

$[H_2O_2]$ = 0.1 mol/L solution fell within the range of 10 nm to 50 nm as shown in Figure 3a, while the size of the particles prepared by using the $[H_2O_2]$ = 1 mol/L solution fell within the range of 15 nm to 20 nm as shown in Figure 3b. The formation of zinc peroxide particles depends on the cleavage process of oxo and hydroxo bridges in $Zn(OH)_2$ by coordination of peroxo ion to Zn^{2+}.[9] With a solution of $[H_2O_2]$ = 1 mol/L, the cleavage process of oxo and hydroxo bridges in $Zn(OH)_2$ effectively occurs; compared with a solution of $[H_2O_2]$ = 0.1 mol/L. Thereby, when H_2O_2 aqueous solution of higher concentration was used, the smaller zinc peroxide particles were obtained. Using this method, it is possible to obtain almost monodispersed zinc peroxide nanoparticles. The stable zinc peroxide sols described here are expected to be a precursor of ZnO films and nanoparticles.

Figure 4 shows the XRD patterns of the fired zinc peroxide nanoparticles prepared using an H_2O_2 solution ($[H_2O_2]$ = 1 mol/L). The XRD pattern shown in Figure 4a indicates the presence of zinc peroxide. The XRD patterns in Figure 4b and 4c correspond to ZnO. Thus, ZnO was obtained by firing zinc peroxide sols at a temperature higher than 473 K.

Figure 5 shows the FE-SEM images of ZnO particles prepared by firing zinc peroxide nanoparticles ($[H_2O_2]$ = 1 mol/L). The average particle size of ZnO prepared by firing at 573 K and 773 K was 19 nm and 41 nm, respectively. Almost monodispersed ZnO nanoparticles can be obtained by firing zinc peroxide nanoparticles. As the firing temperature becomes higher, the larger sizes of ZnO nanoparticle are obtained due to grain growth of the ZnO particles; in other words, the firing temperature is critical in controlling the particle size.

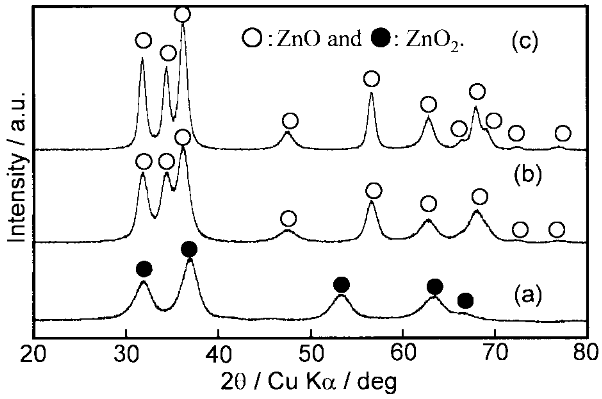

Figure 4. The XRD patterns of the powderes prepared by firing the zinc peroxide powder ($[H_2O_2]$=1 mol/L).
The firing temperature : (a) 453 K, (b) 473 K, and (c)493 K.

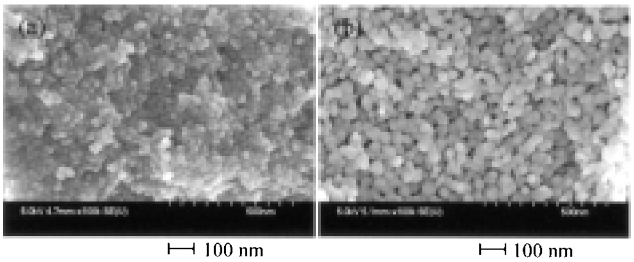

Figure 5. FE-SEM images of the powders obtained by firing the zinc peroxide powders ($[H_2O_2]$=1 mol/L)
The firing temperatures are (a) 573 K and (b) 773 K.

In summary, zinc peroxide nanoparticles can be obtained by peptization of $Zn(OH)_2$ with the aid of H_2O_2 aqueous solution. The process of firing zinc peroxide nanoparticles at temperatures of more than 473 K produces ZnO, which was almost monodispersed nanoparticles.

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References

1 Z. M. Jarzębski, in “Oxide Semiconductors,” Pergamon Press, Oxford (1973), Chap. 13, pp. 228–239.
2 T. N. Rao and L. Bahadur, *J. Phys. Chem.*, **144**, 179 (1997).
3 S. Monticone, R. Tufeu, and A. V. Kanaev, *J. Phys. Chem. B*, **102**, 2854 (1998).
4 L. C. Corrie and J. K. Kenneth, *Langmuir*, **16**, 3764 (2000).
5 V. Brunere, J. Kalina, and G. Ozolinš, *Latv. PSR Zinat. Akad. Vestis, Kim. Ser.*, **6**, 657 (1986).
6 N. G. Vannerbeng, *Arkiv für Kemi*, **14**, 119 (1959).
7 D. A. Long, in “Raman spectroscopy,” McGraw-Hill (1977), Chap. 7, pp. 204–205.
8 K. Nakamoto, in “Infrared and Raman Spectra of Inorganic and Coordination Compounds,” John Wiley & Sons, New York (1986), Chap. 2, p. 105.
9 J. Livage, M. Henry, and C. Sanchez, *Prog. Solid State Chem.*, **18**, 259 (1988).