Low-Temperature Synthesis of ZnO Nanoparticles by Heating of Zn(OH)$_2$ in a Neutral Mixed Solution of Ethanol and H$_2$O

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Zinc oxide particles were prepared by heating zinc hydroxide precipitate in a mixed solution of H$_2$O and ethanol at 348 K for 2 h. When the molar fraction of ethanol in the solution increased, the particle size of the obtained zinc oxide decreased. The band-gap absorption edge of the UV–VIS spectra of the obtained zinc oxide particles also shifted to the shorter wave length with an increase of ethanol molar fraction in the mixed solution. When zinc hydroxide was heated in pure ethanol, zinc oxide nanoparticles whose average diameter was 41 nm were obtained. The zinc oxide nanoparticles can be obtained by heat treatment of zinc hydroxide in the neutral solution at 348 K.

Key-words: Zinc oxide, Nanoparticles, Dissolution-precipitation process, Zinc hydroxide, Neutral solution

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1. Introduction
Zinc oxide (ZnO) is a n-type semiconductor and photo-luminescent, and these characteristics have been applied in various kinds of electrical devices. In recent years, the applications of ZnO in developing a transparent electrode-ductive film have been intensively investigated.\(^1\),\(^2\) Furthermore, ZnO thin films are used in the electrodes of dye-sensitized solar cells.\(^3\),\(^4\) Thus, it is extremely important to be able to prepare ZnO nanoparticles using a simple and low-temperature process; specifically, the development of a means of preparing a stable sol with dispersion of ZnO nanoparticles is essential because these nanoparticles can easily form ZnO thin films. Corrie and Kenneth has reported a method of synthesis of nanocrystalline ZnO by hydrolysis of zinc alkoxide under controlled conditions,\(^5\) and Eric et al. prepared ZnO nanoparticles by the addition of LiOH to an ethanolic zinc acetate solution.\(^6\) In a previous paper, we reported that ZnO whisker can be obtained by heating an aqueous solution of Zn(OH)$_2$ ions at 348 K for 2 h.\(^7\) Furthermore, it is well known that Zn(OH)$_2$ easily crystallizes to ZnO under basic conditions.\(^8\) Nevertheless, it is preferred that the formation of ZnO particles occur in a neutral and low-temperature process. In the present study, we investigated a synthetic method of preparing ZnO nanoparticles by heating Zn(OH)$_2$ in a neutral solution at 348 K.

2. Experiments
2.1 Preparation of ZnO particles
The ZnO particles were prepared as follows: 100 ml of an aqueous solution (0.1 mol/l) of Zn(NO$_3$)$_2$·6H$_2$O and 100 ml of NH$_3$ aqueous solution (0.2 mol/l) were prepared. The NH$_3$ aqueous solution was added to the zinc nitrate aqueous solution and the obtained Zn(OH)$_2$ precipitate was separated by centrifuge at 3000 rpm for 5 min. The obtained Zn(OH)$_2$ was dispersed into distilled water and was again separated by centrifuge. This procedure was repeated 3 times, and the impurities in the precipitate were removed. The obtained pure Zn(OH)$_2$ was then dispersed in 100 ml of H$_2$O. The solution with the dispersed Zn(OH)$_2$ was heated at 348 K for 2 h in a closed glass vessel (200 ml), and the obtained precipitate was then filtered with suction and dried at 348 K for 12 h. The heating procedure of Zn(OH)$_2$ in the solution was carried out using ethanol (EtOH) and the mixed solutions of EtOH and H$_2$O instead of H$_2$O. Furthermore, 0.01 mol/l of the ethylene diamine-N,N’,N’-tetaacetic acid disodium salt (EDTA·2Na) aqueous solution was also used for heating Zn(OH)$_2$.

2.2 Characterization
The Zn$^{2+}$ concentration in the solution heated with Zn(OH)$_2$ was measured by absorbimetric analysis with xylanol orange. All of the chemicals used in this preparation were of reagent grade (Wako Pure Chemical Industries, Ltd., Osaka). The structure of the obtained powder was characterized by X-ray diffraction (XRD) (Cu K$\alpha$, 40 kV, 200 mA, MXP-18, Bruker AXS Co., Ltd., Kanagawa). Particle shape was observed by field emission scanning electron microscopy (FE–SEM, JSM–6330, JEOL, Tokyo). The ultraviolet–visible (UV–VIS) spectra of the ZnO powders were measured by integrating sphere (JASCO U–best210, Jasco, Tokyo).

3. Results and discussion
Figures 1(a)–(d) show the XRDR patterns of the obtained particles prepared by heating Zn(OH)$_2$ in the mixed neutral solution of ethanol and H$_2$O at 348 K for 2 h. All XRDR patterns can be assigned to crystallized ZnO. When the molar fraction of EtOH in the mixed solution increased, the half-width of the XRDR peaks also increased, indicating that the crystallite size decreases with an increase of the molar fraction of EtOH in the mixed solution. In general, it is well known that crystallization from Zn(OH)$_2$ to ZnO occurs under basic conditions (pH 9), however, the present experimental
results show that this also occurs in a neutral solution.

FE-SEM images were examined in order to determine the morphology and size of the obtained ZnO particles. The average particle sizes shown in Figs. 2(a)-(c) are 4.5 μm, 0.52 μm and 41 nm, respectively. Thus, the average particle size decreased with an increase of the fraction of EtOH in the mixed solution. Specifically, when Zn(ΟH)₂ was heated in pure EtOH, ZnO nanoparticles whose diameter was less than 100 nm were obtained. The solution used for heating and dispersion of Zn(ΟH)₂ greatly affected the morphology and particle size of the obtained ZnO. These differences in ZnO particle morphology indicate that the formation and crystallization process from Zn(ΟH)₂ to ZnO particles depends greatly on the solution used for heating Zn(ΟH)₂. It is considered that the crystal growth of ZnO was inhibited in the EtOH solution. Furthermore, the change of the morphology of the obtained particles indicates that the crystal habit during depended on the EtOH content in the solution. The adsorption of EtOH molecules on the growing surface of the ZnO crystal particle changed the crystal habit of the obtained particles.

Figure 3 shows the UV–VIS spectra of the obtained ZnO powder; the UV–VIS absorption curve of the ZnO powder prepared by heating Zn(ΟH)₂ in H₂O is shown in Fig. 3(a). The wave length λ₁/₂ at which absorption was 50% of that at the excitonic shoulder was 393 nm. On the other hand, the λ₁/₂ of the ZnO particles prepared by heating in EtOH was 380 nm. Thus, the absorption edge shifted to a shorter wave length when EtOH was used for heating Zn(ΟH)₂. In general, the absorption edge of ZnO particles shifts to a shorter wave length when particle size decreases. Therefore, the results shown in Fig. 3 are consistent with the fact that the obtained ZnO particle size decreased when EtOH was used for the solution.

As mentioned in the previous section, the crystallization of Zn(ΟH)₂ to ZnO generally occurs under basic conditions. Under the present reaction conditions, ZnO formation occurred in a neutral solution, which raises interesting questions about the formation mechanisms of such ZnO particles. Zn(OH)₂ in a solution dissociates to form Zn²⁺ ions and OH⁻ ions. Thus, it is believed that the area near the surface of the Zn(OH)₂ precipitate in the solution was under basic conditions due to the presence of OH⁻ ions produced by the dissociation of Zn(OH)₂, even though the solution as a whole was neutral. In the literature, Zn(OH)₂⁻ ions formed in basic solution easily change to form ZnO since the coordinated state of OH⁻ to Zn²⁺ is quite similar in both ZnO and Zn(OH)₂⁻. The ZnO particle formation process thus depends greatly on the dissociation of Zn(OH)₂ and the formation of Zn(OH)₂⁻ in the solution.

In order to investigate the formation process of ZnO in the mixed solution of EtOH and H₂O in greater detail, it is im-

![Fig. 1. XRD patterns of the ZnO particles prepared by heating Zn(ΟH)₂ in the mixed solution of H₂O and EtOH at 348 K for 2 h. The molar fraction EtOH/(H₂O + EtOH) of the mixed solution was: (a) 0, (b) 0.4, (c) 0.7 and (d) 1.](image)

![Fig. 2. FE-SEM images of the ZnO particles prepared by heating Zn(ΟH)₂ in the mixed solution of H₂O and EtOH at 348 K for 2 h. The molar fraction EtOH/(H₂O + EtOH) of the mixed solutions were (a) 0, (b) 0.6 and (c) 1, respectively.](image)

![Fig. 3. UV–VIS spectra of the ZnO powder prepared by heating Zn(ΟH)₂ in the solution at 348 K for 2 h. The used solution was: (a) H₂O and (b) EtOH.](image)
important to estimate the degree of the dissociation of the Zn(OH)$_2$ in the solution. In the present study, the concentration of Zn$^{2+}$ ion in the solution after heating at 348 K for 2 h ([Zn$^{2+}$]) was measured and plotted against the molar fraction of EtOH in the solution ([EtOH]) (Fig. 4). As shown in Fig. 4, [Zn$^{2+}$] was around 0.5 mmol/l in the [EtOH] molar fraction range from 0 to 0.3. When [EtOH] increased from 0.3 to 1, [Zn$^{2+}$] greatly decreased from $5 \times 10^{-4}$ mol/l to $3 \times 10^{-3}$ mol/l. As shown in Fig. 2, the particle size of the obtained ZnO decreased with a decrease in [Zn$^{2+}$], whose level depends on the degree of the dissociation of Zn(OH)$_2$. The [Zn$^{2+}$] which can be estimated by the solubility product $K_{sp}$ of Zn(OH)$_2$ was $2.02 \times 10^{-7}$ mol/l. This [Zn$^{2+}$] in the solution is much greater than the estimated value. Then, the Zn$^{2+}$ and OH$^{-}$ ions on the basic surface layer make it possible for Zn(OH)$_2$ to be formed, and this Zn(OH)$_2$ can then transform to ZnO. When Zn(OH)$_2$ was heated in EtOH in the present study, the [Zn$^{2+}$] in the solution was quite low compared to that of H$_2$O. When the [EtOH] increased, the ZnO crystal growth rate decreased. Therefore, the [EtOH] affected the size of the obtained ZnO particles. If the ZnO formation occurred by the dissolution and precipitation process as discussed above, it would be expected that the masking agent of Zn$^{2+}$ ions inhibited the ZnO crystal growth process and reduced the obtained particle size. Figures 5(a) and (b) show the FE-SEM images of the ZnO particles prepared by heating Zn(OH)$_2$ in H$_2$O and 0.01 mol/l of the EDTA-2Na aqueous solution, respectively. When the EDTA-2Na aqueous solution was used instead of H$_2$O, the average particle size of the obtained ZnO decreased from 4.5 µm to 0.51 µm. The masking effect of EDTA molecules by coordination to Zn$^{2+}$ ions formed by dissolution of Zn(OH)$_2$ reduced the ZnO formation rate. Therefore, this result indicates that the formation of ZnO particles from Zn(OH)$_2$ precipitate occurred by the dissolution–precipitation process.

4. Conclusion

We were able to obtain crystallized ZnO particles using a very simple process, specifically, by heating Zn(OH)$_2$ precipitate in a neutral solution of either H$_2$O or EtOH at 348 K for 2 h. When EtOH was used for the solution, ZnO nanoparticles were obtained. The particle size was able to be controlled by the ethanol concentration of the mixed solution of ethanol and H$_2$O. The formation of ZnO particles occurred by dissolution–precipitation process.

References