Non-Basic Solution Routes to Prepare ZnO Nanoparticles

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Abstract. Nanocrystalline ZnO particles were prepared from alcoholic solutions of zinc acetate dihydrate without using base such as NaOH or LiOH through a colloid process carried out at a low temperature of 60°C. A comparative study of chemical reactions from zinc acetate dihydrate to ZnO was made using different types of monool solvents, i.e. methanol, ethanol, and 2-methoxyethanol. It was revealed that layered hydroxide zinc acetate was formed as an intermediate and its transformation into ZnO was a key reaction step in any of the solutions. Reaction time necessary for the precipitation of ZnO was greatly influenced by the solvents used. Methanol was useful for the preparation of the ZnO nanoparticles, which were chemically pure in terms of cation impurities and exhibited green photoluminescence by the ultraviolet excitation.

Keywords: ZnO, nanoparticles, formation mechanisms, photoluminescence

1. Introduction

Semiconductor nanoparticles have attracted interests of many academic and industrial researchers because of their unusual optoelectronic properties based on quantum size effects [1]. Numerous reports are found in the literature regarding synthetic techniques as well as potential or practical applications of nanosized semiconductors such as CdS, CdSe, ZnS, TiO2, Fe2O3, and ZnO [2–7].

Wurtzite ZnO is an n-type semiconductor with a wide band-gap of 3.3 eV. Nanosized ZnO can be utilized in electrochemical fields including chemical sensors [8], photocatalysts [9], phosphors [10] and dye-sensitized solar cells [11–14]. Nanocolloids or nanopowders of ZnO have been prepared by adopting synthetic methods developed by Koch et al. [15], Bahnemann et al. [16], or Spanhel and Anderson [17]. Basically, zinc salts such as Zn(ClO4)2, Zn(NO3)2, Zn(CH3 COO)2·2H2O, or Zn(CH3COCHCOCH3)2·H2O (zinc acetylacetonate) are dissolved in alcoholic or other organic solvents to which basic solutions containing NaOH, LiOH or NH4OH are added [18–27]. It is believed that formation of colloidal ZnO follows several reaction steps, of which the last is transformation of zinc hydroxide to zinc oxide under basic solution conditions,

\[ \text{Zn(OH)}_2 \leftrightarrow \text{ZnO} + \text{H}_2\text{O} \quad (1) \]

This reaction is likely to be valid for the process using Zn(ClO4)2 because ClO−4 ions are inert in terms of ability of complex formation with Zn2+ in alcoholic solutions [28, 29] and do not impede the formation of zinc hydroxyl complexes. In contrast, Zn(Ac)2·2H2O (Ac = CH3COO) provides much more complicated reaction precursors for ZnO because of higher reactivity of Ac ions (CH3COO−) with Zn2+ [30]. In the presence of the Ac ions in the basic solutions, the precursors of ZnO are reported to be Zn10O4(Ac)12, Zn4O(Ac)6, or Zn5(OH)8(Ac)2·2H2O [7, 26, 31]. Hydrolysis and condensation of these

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precursors lead to the precipitation of ZnO in the presence of base.

In view of fundamental studies as well as industrial applications of nanoparticles, chemically pure or compositionally well-defined ZnO is required. This is because electrical and luminescent properties undergo dramatic changes by impurities doped in ZnO [32, 33]. Moreover the growth manner and kinetics of nanoparticles are also influenced by foreign cationic species. While effort has been made to remove alkali ions (Li⁺ or Na⁺) by washing in order to obtain pure ZnO [7], development of the process without addition of base is a prime requirement for future applications of the ZnO nanoparticles. Kumar et al. [34] reported sonochemical synthesis of nanosized ZnO from aqueous solutions of Zn(Ac)₂·2H₂O using a high-intensity ultrasonic horn under 1.5 atm of argon at room temperature. Very recently, Poul et al. [35] have suggested a possible synthesis of the nanoparticles through hydrolysis of zinc salts in polyol media (diethylene glycol or ethylene glycol).

In this study, nanocrystalline ZnO particles were successfully prepared through controlled hydrolysis of Zn(Ac)₂·2H₂O under moderate conditions such as neutral solutions, a low temperature of 60°C, an atmospheric pressure, and an ambient atmosphere. A comparative study was made to investigate reaction, nucleation and crystal growth mechanisms underlying the colloid process using different types of monool solvents, i.e. methanol, ethanol, and 2-methoxyethanol.

2. Experimental

2.1. Colloid Process

Zinc acetate dihydrate, Zn(Ac)₂·2H₂O, with 99.9% purity was obtained from Wako Pure Chemicals Co., Ltd., Japan. Methanol (MeOH), ethanol (EtOH), and 2-methoxyethanol (2-ME) were used as received from Taisei Chemical Co., Ltd., Imazu Chemical Co., Ltd., and Wako, Japan, respectively, without further purification.

Three kinds of Zn(Ac)₂·2H₂O solutions were prepared by using MeOH, EtOH, or 2-ME as solvents. For the MeOH solution, a 6.5853 g (0.03 mol) sample of Zn(Ac)₂·2H₂O was dissolved in 200 mL of MeOH under vigorous stirring at room temperature and atmospheric pressure and then ultrasonicated for 10 min. The clear, transparent solution was obtained. For the EtOH or the 2-ME solution, the same amount of Zn(Ac)₂·2H₂O was added to 196 mL of EtOH or 2-ME under the same conditions. In contrast to the MeOH solution, Zn(Ac)₂·2H₂O was not dissolved completely in these two solutions. Then 4 mL of water was added to each solution and the resultant mixtures were ultrasonicated for 10 min, leading to the clear, transparent solutions. Taking account of the hydration water in Zn(Ac)₂·2H₂O, a molar ratio, H₂O/Zn, calculated was 2 for the MeOH solution and 9.4 for the EtOH and 2-ME solutions.

The solutions were placed into 200 mL Erlenmeyer flasks and heated at 60°C under reflux for various periods of time using rotary evaporation apparatus. Careful attention was paid in order not to lose the solvents during heating. After white precipitates were observed, the solutions were removed from the apparatus and cooled to room temperature. The precipitates were then centrifuged at 13000 rpm for 10 min. Final products were dried at room temperature in the ambient atmosphere following the removal of supernatant.

For the precipitates prepared from the MeOH solution, washing was done with methanol by repeating centrifugation. As described later, washing was effective to remove by-products such as Zn₅(OH)₈(Ac)₂·2H₂O and obtain single-phase ZnO nanoparticles.

2.2. Analysis and Measurement

Crystal structure identification was made by X-ray diffraction (XRD) with a Rigaku model RAD-C diffractometer using Cu Kα radiation in the 2θ range 3–60°. Particle sizes were observed by high resolution transmission electron microscopy (HRTEM) with a Philips model TECNAI F20 microscope. Optical absorption spectra were recorded with a Hitachi model U-3300 ultraviolet (UV) visible spectrophotometer. Photoluminescence (PL) spectra were measured at room temperature with a Shimadzu model RF-5700PC using a Xe lamp (150 W) as a UV light source. Fourier transform infrared (FTIR) spectra were measured using the KBr method with a BIO-RAD model FTS-60A spectrophotometer. Thermal behavior was examined by thermogravimetry-differential thermal analysis (TG-DTA) with a Mac Science model 2020S thermal analyzer using a heating rate of 5°C/min in air. The pH value of the solution was measured by a Horiba model F-21 pH meter.