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Precipitation of ZnO particles and their properties

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Abstract

The aqueous suspensions obtained from zinc acetate solution neutralized with varying amounts of NH_4OH solution were hydrothermally aged at 160 °C. The precipitates were characterized by XRD, Raman, B.E.T. and TEM. ZnO particles were produced by dissolution/reprecipitation mechanism from the starting precipitate. The rate of this transformation increased with an increase in pH from 7 to 10. The sizes of these ZnO particles were in the micron range and their physical shape depended on pH. Ageing of the starting aqueous suspension for 7 months at pH 10 and room temperature yielded aggregates consisting of nanosize ZnO particles (~20 to ~60 nm). Nanosize ZnO particles were also synthesized by the sol–gel method based on fast hydrolysis of zinc 2-ethylhexanoate dissolved in 2-propanol. It was shown that nanosize particles induced distinct spectral changes in the standard Raman spectrum of ZnO.

Keywords: Precipitation; ZnO; XRD; Raman; TEM; B.E.T.

1. Introduction

Zinc oxide (ZnO) powders have found important applications in rubber and paint industries, catalysis, production of varistors etc. Microstructural and chemical properties of ZnO powders depend on the synthesis method of this material. Different synthesis methods were used to prepare ZnO particles of different size and morphology.

The precipitation of Zn^{2+} ions in aqueous solutions with decomposing urea was investigated [1,2]. Basic zinc carbonate ($Zn_5(OH)_6(CO_3)_2$) was the solid reaction product, and upon heating in air at 300 °C, or above 300 °C, it decomposed into ZnO. The process involving decomposing urea was also used in the synthesis of ZnO varistors [3]. The ZnO particles of varying morphologies were obtained by precipitation of Zn^{2+} ions in aqueous solutions with decomposing hexamethylenetetramine (HMTA) [4,5]. Triethanolamine (TEA) and ethylenediamine (EDA) were also used [6,7] for the precipitation of Zn^{2+} ions.

Taubert et al. [8,9] investigated the influence of water-soluble synthetic polymers on the crystallization of ZnO in aqueous solutions. Uniform and monodisperse ZnO particles were precipitated in the presence of starch [10].

The precipitation of ZnO particles under homogeneous conditions in aqueous solutions was reported [11]. The results of that work suggest that the organic ligand inhibited $Zn(OH)_2$ precipitation on one side and favoured the formation of ZnO particles on the other. The influence on particle morphology was also observed. Rataboul et al. [12] prepared nanoparticles of Zn^0 starting from a $Zn(C_6H_{11})_2$ precursor, then oxidized them by heating up to 600 °C in air to obtain ZnO particles. The microemulsion method was also used to prepare ZnO nanoparticles [13]. Komarneni et al. [14] used microwave irradiation of a $Zn(NO_3)_2$ solution neutralized at pH 8–12 to prepare ZnO powders. Tsuzuki and McCormick [15] applied mechanochemical processing in the synthesis of ZnO nanoparticles. ZnO particles were also prepared by adding LiOH powder [16], or the ethanolic solution of LiOH [17], to the ethanolic solution of zinc acetate.

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Many researchers extensively investigated the formation and properties of ZnO thin films [18–24] because of their wide applications. There are significant differences between the formation and properties of ZnO powders and films, because in the formation of ZnO thin films the surface interactions between the film and substrate play an important role.

We recently started a systematic investigation [25,26] of the relationship between the synthesis of ZnO powders and their properties. In the present work we report new results about the influence of chemical synthesis on the formation of ZnO particles and their properties. ZnO particles were obtained by hydrothermal treatment of the suspensions produced from zinc acetate solutions neutralized by varying amounts of the NH_4OH solution. A specific attention was focused on the influence of pH on the size and shape of ZnO particles formed. Nanosize ZnO particles were precipitated by fast hydrolysis of alcoholic solution of zinc 2-ethylhexanoate with tetramethylammonium hydroxide (TMAH) solution.

2. Experimental

Analytical pure chemicals, $Zn(CH_3COO)_2{\cdot}2H_2O$ and $NH_3{\cdot}$aq. (25%) supplied by Kemika were used. The 0.2 M $Zn(CH_3COO)_2$ solution was prepared by dissolving a proper amount of $Zn(CH_3COO)_2{\cdot}2H_2O$ salt. A transparent solution was obtained. It is recommended to use a fresh $Zn(CH_3COO)_2{\cdot}2H_2O$ salt, because with a long ageing of this salt it may undergo hydrolysis in the solid state. Zinc 2-ethylhexanoate containing 1% of ethylene glycol monomethylether supplied by Alfa Aesar was used. TMAH [$(CH_3)_4NOH$, 25% (w/w) aqueous solution, electronic grade, 99.99% (metal basis)] was also supplied by Alfa Aesar. Water free 2-propanol and absolute ethanol supplied by Kemika were used. Twice distilled water was prepared in own laboratory.

The experimental conditions for the hydrothermal synthesis of samples C1–C9 are given in Table 1. The procedure for the preparation of these samples was as follows: a proper volume of H_2O was added into 100 ml of the 0.2 M $Zn(CH_3COO)_2$ solution, then into this solution a proper volume of the concentrated NH_4OH solution was added with strong shaking. For a given time of autoclaving the solid products were separated from mother liquor using an ultra-speed centrifuge (Sorvall RC2-B). The solid products were subsequently washed with twice distilled water, then dried.

Sample C10 was prepared in a similar way as samples C7–C9; however, the corresponding aqueous suspension was aged at room temperature for 7 months. In adjusting a desirable pH value a small fluctuation in the volume of concentrated NH_4OH solution, given in Table 1, could be observed, due to the varying concentration of $NH_3{\cdot}$aq. solution (evaporation of NH_3) supplied by different vendors.

Sample C11 was prepared by fast hydrolysis of zinc 2-ethylhexanoate dissolved in 2-propanol with addition of TMAH solution. A 2.009 g of zinc 2-ethylhexanoate containing 1% of ethylene glycol monomethylether was dissolved into 36 ml of 2-propanol. A clear (transparent) solution was obtained. Into this solution 4 ml of TMAH solution was added under strong mixing. The so formed suspension was transferred into autoclave, then heated at 120 °C for 2 h. After a proper time of autoclaving, the precipitate was separated from the liquid phase using Sorvall RC2-B ultraspeed centrifuge. The precipitate was washed three times with ethanol and 2 times with twice distilled water, then dried at 60 °C.

pH readings of mother liquor were made with a pH meter (model: PHM-26) manufactured by Radiometer, using a combined glass electrode. X-ray powder diffraction measurements were performed using a Philips MPD 1880 counter diffractometer with monochromatized CuKα radiation. The B.E.T. measurements were performed using a Flow-Sorb II 2300 surface area analyzer (Micromeritics, Norcross, Ga). TEM observations were carried out by a Philips electron microscope. Raman spectra were recorded using a coherent Innova-100 argon laser with $\lambda = 514.5$ nm as excitation source. The scattered light was analysed by a Dilor Z-24 Raman spectrometer.

Table 1
Experimental conditions for hydrothermal synthesis of samples C1–C9 at 160 °C and the results of XRD and B.E.T. analyses

Sample	0.2 M $Zn(CH_3COO)_2$/ml	H_2O/ml	NH_4OH/ml	Time of autoclaving	pH (final)	XRD analysis	B.E.T. analysis/$m^2\ g^{-1}$
C1	100	7	3	15 min	7	Zn(II)-complex + ZnO (molar fraction 0.1–0.2)	
C2	100	7	3	2 h	7	ZnO	0.62
C3	100	7	3	72 h	7	ZnO	0.49
C4	100	5	5	15 min	8	ZnO + very small fraction of Zn(II)-complex	
C5	100	5	5	2 h	8	ZnO	1.15
C6	100	5	5	72 h	8	ZnO	1.07
C7	100	0	10	15 min	10	ZnO	1.52
C8	100	0	10	2 h	10	ZnO	1.82
C9	100	0	10	72 h	10	ZnO	1.45