Available online at www.sciencedirect.com
ScienceDirect
Colloids and Surfaces A: Physicochem. Eng. Aspects 319 (2008) 130–135
COLLOIDS AND SURFACES A
www.elsevier.com/locate/colsurfa

A simple preparation technique for shape-controlled zinc oxide nanoparticles: Formation of narrow size-distributed nanorods using seeds in aqueous solutions

Tetsuo Kawano, Hiroaki Imai *

Department of Applied Chemistry, Faculty of Science and Technology, Keio University 3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223-8522, Japan

Received 14 September 2006; received in revised form 8 May 2007; accepted 14 May 2007
Available online 18 May 2007

Abstract

Various shapes of wurtzite-type ZnO nanoparticles were selectively produced in a simple aqueous system prepared by mixing $ZnSO_4$ and NaOH solutions. Ellipsoidal nanoparticles were obtained by the addition of an alkaline agent into an acidic zinc solution (acidic route), while nanorods were grown by mixing a zinc precursor into an alkaline solution (basic route). The aspect ratio and size distribution of the nanorods grown through the basic routes were controlled by the addition of nanoparticles prepared by the acidic route as seeds. On the other hand, micrometric branching rods were obtained by dilution of the reaction solution in the basic routes. The morphological variation of ZnO particles is ascribed to the balance of the nucleation and crystal growth depending on the degree of the supersaturation. We successfully prepared narrow size-distributed rods with a nanometric width and a submicrometric length using the seed particles, because the presence of the seeds suppressed additional nucleation and then controlled the degree of the supersaturation for steady growth of the crystalline particles.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Zinc oxide; Nanoparticle; Nanorod; Crystal growth; Seed

1. Introduction

Wurtzite-type zinc oxide (ZnO), a wide band-gap (3.37 eV) semiconductor with a large exciton-binding energy, is an attractive material because of its unique properties, such as optical transparency, electric conductivity, piezoelectricity and near-UV emission [1–4]. The size and morphology are important parameters to determine the physical and physicochemical properties of ZnO crystals. Various kinds of nanoscale morphologies, such as spherical particles [5], rods [6–9], whiskers [10], columns [11–13], wires [14], tubes [15], rings [16], disks [17] and other characteristic shapes [18–20], were fabricated. Wet chemical methods using aqueous solution-based systems have been widely applied for the preparation of the ZnO crystals with various morphologies. The size and shape of ZnO crystals grown in the solutions were controlled by the reaction conditions [21], selection of precursors [22] and addition of organic molecules including surfactants [21,22], amine [23], solvents [24,25] and polymers [26,27].

One-dimensional (1D) ZnO materials were prepared using various methods [6–10,14,15,28–33]. In particular, nanorods have been produced in basic solution systems at low temperatures [6–9,33] and under hydrothermal conditions [7]. The submicrometric control of the length of the nanorods in a range smaller than the wavelength of visible light is essential for applications to optically transparent materials, such as ZnO–polymer composite films for a component of recording media [4]. Although the aspect ratio varied in the range of 50–100 with a width of 10–30 nm by changing $[OH^-]/[Zn^{2+}]$ [6], preparation techniques for nanorods with submicrometric lengths have not been established.

We selectively produced nanoparticles and nanorods of ZnO crystals using a simple mixing technique of $ZnSO_4$ and NaOH solutions without any organic additives [9]. However, the size distribution of the nanorods broadened because the nucleation was not controlled in the mixtures. In the present study, we performed further control of nanometric shapes and size distribution of ZnO particles by addition of seeds into the simple system. The

* Corresponding author. Tel.: +81 45 566 1556; fax: +81 45 566 1551.
E-mail address: hiroaki@applc.keio.ac.jp (H. Imai).

0927-7757/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.colsurfa.2007.05.019

mechanism of morphological variation is discussed on the basis of the balance of the nucleation and crystal growth at a certain degree of supersaturation. This work would provide not only a simple method for selected fabrication of 1D ZnO particles with a nanometric width and a submicrometric length, but also fundamental information for shape control of nanoparticles prepared through the crystal growth in aqueous solutions.

2. Experimental

A stock solution (pH 5.3) of 0.2 M zinc sulfate ($ZnSO_4$) and an alkali solution (pH 13.8) of 4.0 M sodium hydroxide (NaOH) were prepared by dissolution of zinc sulfate heptahydrate ($ZnSO_4{\cdot}7H_2O$, 99.5%; Kanto Chemical) and NaOH (Junsei Chemical) into purified water, respectively. The reactions were fundamentally performed with stirring by mixing the stock solution of $ZnSO_4$, the alkali solution of NaOH and a certain amount of purified water. The final pH of the mixture was fixed to ca. 13 because a highly basic condition is suitable for the direct preparation of wurtzite-type ZnO crystals [12]. Precipitation occurred at 60 °C for 2 h after the mixing of the solutions. The products obtained by centrifugation were washed with purified water and then dried at 60 °C in air. However, the shape and size of resultant particles depended on the mixing procedure of the solutions.

As an acidic route, 25.0 cm^3 of the alkali solution (4.0 M NaOH) was dropped at an approximate rate of 5 cm^3/min into an acidic mother solution (pH 5.6) prepared from 25.0 cm^3 of the stock solution (0.2 M $ZnSO_4$) and 50.0 cm^3 of purified water. As a basic route, 25.0 cm^3 of the stock solution (0.2 M $ZnSO_4$) was dropped at an approximate rate of 5 cm^3/min into a basic mother solution (pH 13.6) obtained by mixing the alkali solution (4.0 M NaOH) and purified water. Typically, 25.0 cm^3 of the stock solution was added into a mixture of 25.0 cm^3 of the alkali solution and 50.0 cm^3 of purified water (basic route 1). The final concentrations of $ZnSO_4$ and NaOH for the acidic route and basic route 1 were 0.050 and 1.0 M, respectively.

Seed-mediated crystal growth was performed using the basic route to modify the morphology of resultant ZnO crystals. Initially, seed particles of ZnO crystals were prepared via the above-mentioned acidic route and washed with abundant purified water. Then, 12.5 cm^3 of the stock solution (0.2 M $ZnSO_4$) was dropped at an approximate rate of 5 cm^3/min into a seeded mother solution produced from 12.5 cm^3 of the alkali solution (4.0 M NaOH), 25.0 cm^3 of purified water and 50.0 cm^3 of a seed suspension (basic route 2). The amount of seeds varied from 0 to 0.077 g in 100 cm^3 of the final solution by changing the concentration of the seed suspension. The degree of supersaturation was lowered during the formation of ZnO crystals by subsequent dilution (basic route 3). A mother solution for basic route 1 was initially prepared by mixing 12.5 cm^3 of the stock solution, 12.5 cm^3 of the alkali solution and 25.0 cm^3 of purified water. After being stirred for 5 min, the reaction solution was diluted by addition of an excessive amount of water with a volume of 50.0 cm^3. The concentrations of $ZnSO_4$ and NaOH in the resultant solution for basic routes 2 and 3 were 0.025 and 0.5 M, respectively. The preparation conditions are listed in Table 1.

The precipitated particles were characterized by $\theta/2\theta$ X-ray diffractometry (XRD; Rigaku RAD-C and Bruker D8 Advance) using Cu Kα radiation. The morphologies of the particles were observed with a field-emission scanning electron microscope (FESEM, Hitachi S-4700) at 5 kV accelerating voltage and a field-emission transmission electron microscope (FETEM, Philips TECNAI F20). The size of the ZnO particles was estimated from the FESEM images.

3. Results

According to the XRD patterns (Fig. 1), the precipitates were assigned to wurtzite-type ZnO regardless of the preparation routes. However, the shape of the products was obviously influenced by the preparation route as shown in Figs. 2 and 3, and listed in Table 2. Ellipsoidal nanoparticles with an average width of 32 nm and a length of 44 nm were grown at pH 12.8 through the acidic route (Fig. 2(a) and (b)). On the other hand, ZnO nanorods with a high aspect ratio were obtained at pH 12.8 through basic route 1 (Fig. 2(c) and (d)). The lattice image indicates that the ZnO rods were single-crystalline and were elongated along *c* axis (Fig. 4). Fig. 5 shows cumulative undersize distribution of ZnO particles estimated from FESEM images. The median width and length of the rods pre-

Table 1
Conditions for the preparation of wurtzite-type ZnO particles

Route	Mother solution	Additional solution	Final concentrations		
			$ZnSO_4$ (M)	NaOH (M)	Seed (g/100 cm^3)
Acidic	0.2 M $ZnSO_4$ 25.0 cm^3; H_2O 50.0 cm^3	4.0 M NaOH 25.0 cm^3	0.050	1.0	0
Basic 1	4.0 M NaOH 25.0 cm^3; H_2O 50.0 cm^3	0.2 M $ZnSO_4$ 25.0 cm^3	0.050	1.0	0
Basic 2–1	4.0 M NaOH 12.5 cm^3; H_2O 75.0 cm^3	0.2 M $ZnSO_4$ 12.5 cm^3	0.025	0.5	0
Basic 2–2	4.0 M NaOH 12.5 cm^3; H_2O with seeds 75.0 cm^3	0.2 M $ZnSO_4$ 12.5 cm^3	0.025	0.5	0.019
Basic 2–3	4.0 M NaOH 12.5 cm^3; H_2O with seeds 75.0 cm^3	0.2 M $ZnSO_4$ 12.5 cm^3	0.025	0.5	0.077
Basic 3	4.0 M NaOH 12.5 cm^3; H_2O 25.0 cm^3	First 0.2 M $ZnSO_4$ 12.5 cm^3; second H_2O 50.0 cm^3	0.025	0.5	0

Stock solution: 0.2 M $ZnSO_4$, Alkali solution: 4.0 M NaOH.

Download English Version:

https://daneshyari.com/en/article/596899

Download Persian Version:

https://daneshyari.com/article/596899

Daneshyari.com