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Synthesis of zinc oxide nanocrystalline powders for cosmetic applications

Chia-Liang Kuo [a], Cheng-Li Wang [b], Horng-Huey Ko [c], Weng-Sing Hwang [a], Kuo-ming Chang [b], Wang-Long Li [d], Hong-Hsin Huang [e], Yen-Hwei Chang [a], Moo-Chin Wang [c,*]

[a] *Department of Materials Science and Engineering, National Cheng Kung University, 1 Ta-Hsueh Road, Tainan 70101, Taiwan*
[b] *Department of Mechanical Engineering, National Kaohsiung University of Applied Sciences, 415 Chien-Kung Road, Kaohsiung 80782, Taiwan*
[c] *Department of Fragrance and Cosmetic Science, Kaohsiung Medical University, 100 Shih-Chuan 1st Road, Kaohsiung 807, Taiwan*
[d] *Institute of Nanotechnology and Microsystems Engineering, National Cheng Kung University, 1 Ta-Hsueh Road, Tainan 70101, Taiwan*
[e] *Department of Electrical Engineering and Department of Chemical and Materials Engineering, Cheng Shiu University, Kaohsiung 83347, Taiwan*

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Abstract

The synthesis of zinc oxide (ZnO) nanocrystalline powders for cosmetic applications by a coprecipitation process has been investigated. When the $Zn(OH)_2$ precipitates are calcined at 373 K for 10 min, the crystalline phases comprise the major phase of $Zn(OH)_2$ and the minor phase of ZnO. XRD pattern shows that only ZnO is present and no other phase is detected when the $Zn(OH)_2$ precipitates calcined at 413 K for 10 min. The nanocrystallite size of ZnO increases slightly from 32.3 to 44.3 nm when the calcination temperature increases from 413 to 873 K. The activation energy of ZnO nanocrystallite growth is 2.02 kJ/mol, which reveals that the nanocrystalline ZnO is easily grown at low temperature. The UV transmission of ZnO nanocrystallites in the wavelength range from 290 to 375 nm is about 35%, indicating that the ZnO nanocrystallites have an excellent UV-absorbing capability.

Keywords: Zinc oxide; Cosmetic; Nanocrystallites; Coprecipitation

1. Introduction

Ultraviolet (UV) radiation that reaches the earth and damages skin can be divided into three key wavelengths: (1) UVC (32–280 nm), (2) UVB (280–320 nm), and (3) UVA (320–400 nm). UVA radiation, is a major culprit in photoaging and skin cancers [1]. In addition, UVB, which primarily reaches the top-most layer of skin, is thought to be responsible for acute photodamage, including sunburn and some non-melanoma skin cancers [1]. Hence, protection against both UVA and UVB radiation is very important. Shaath [2] pointed out that sunscreens used for the protection of human skin against the harmful effects of solar radiation must contain certain amounts of UV-absorbing substances. Fine particles of various metal oxides, such as ZnO and TiO_2, are extensively used as agents to attenuate (absorb and/or scatter) the UV radiation, and have many desirable characteristics, such as a long history of topical use, broad spectrum absorption, high photostability and low irritancy [3].

Zinc oxide (ZnO) has a hexagonal wurtzite structure (space group $P6_3mc$) with lattice constants of a and c being 3.250 and 5.207 Å, respectively, a direct band gap of 3.37 eV (368 nm), and large excition binding energy of 60 meV at room temperature [4]. ZnO is used in solar cell windows, piezoelectric transducers, gas sensors, UV light emitting/detecting technology and devices with optoelectronic (UV) properties [5]. Moreover, ZnO is also used as a bright green luminescence phosphor in fluorescent devices [6].

Recently, ZnO nanoparticles have attracted much interest because of their various remarkable chemical and physical properties that are distinctive from those of conventional bulk materials. To date, various methods have been adopted for the preparation of ZnO crystallites including sol–gel method [7], evaporative decomposition of solutions [8], gas-phase reaction [9], wet chemical synthesis [10] and hydrothermal discharging-gas method [11]. However, these methods usually involve high temperatures and sometimes complicated processes, which might result in impurities in the final products [12].

* Corresponding author. Tel.: +886 7 3121101x2366; fax: +886 7 3210683.
E-mail address: mcwang@kmu.edu.tw (M.-C. Wang).

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However, in order to obtain ZnO nano-powders with appropriate chemical and optical properties for their intended applications, control of morphology, chemical composition, purity and particle size during synthesis are very important. Several studies have demonstrated that a coprecipitation process has many advantages in obtaining highly crystallized nano-powders with a narrow grain size distribution, high purity and low calcination temperature [13–16]. Specifically, the particle properties of ZnO, such as crystallinity and morphology, can be controlled by adjusting factors such as the source species, pH value, reaction temperature, time, and so on.

In the present study, $Zn(NO_3)_2{\cdot}6H_2O$ and NH_4OH have been used for the synthesis of ZnO nanocrystallites by a coprecipitation process. The main purpose of the present investigation is to examine the effect of various process parameters on the phase transformation and growth of ZnO by thermogravimetric and differential thermal analyses (TG/DTA), X-ray diffraction (XRD), transmission electron microscopy (TEM), electron diffraction (ED), and ultraviolet spectrometry (UVS).

This word will investigate: (i) the thermal behavior of $Zn(OH)_2$, (ii) the phase transformation and growth of nanocrystalline ZnO at various calcination temperatures, and (iii) the UV transmission at 290–400 nm.

2. Experimental procedure

2.1. Sample preparation

The starting materials were reagent-grade $Zn(NO_3)_2{\cdot}6H_2O$ (purity ≧ 98%, supplied by Alfa Aersar, USA) and 25.0 vol% ammonia solution (NH_4OH, supplied by Riedel-de Haën, Germany). 0.05 M and 1.0 vol% aqueous solutions were prepared from reagent-grade $Zn(NO_3)_2{\cdot}6H_2O$ and 25 vol% NH_4OH, respectively. The aqueous solution of 1.0 vol% NH_4OH was then added to $Zn(NO_3)_2{\cdot}6H_2O$ solution slowly at a rate of 0.05 cm^3/min, with vigorous agitation at room temperature. At the end of titration, a syringe was used to minimize the size of falling drops and reduce the local reaction effect. During the whole process, the pH value was kept in a range of 7–10 by adjusting the amount of NH_4OH. The mixed solution was stirred at room temperature for 24 h to obtain white precipitates. After precipitation, the precipitates were washed thoroughly two times with a large amount of ethanol (puirty ≧ 99.85%, supplied by J.T. Baker, USA) to remove NH_4NO_3. Subsequently, the precipitates were freeze dried at 218 K in a vacuum.

2.2. Sample characterization

TG/DTA analyses (SETARAM TGA24 Simultaneous Symmetrical Thermoanalyzer, France) were conducted on a 50 mg precipitate sample at a heating rate of 10 K/min in air with Al_2O_3 powders as a reference material. The calcination temperature was determined from the results of DTA. The crystalline phase was identified using an X-ray diffractometer (XRD, Model Rad IIA, Rigaku Co., Tokyo, Japan) with CuK_α radiation and a Ni filter, operated at 30 kV, 20 mA and a scanning rate of 0.25°/min. The microstructure of the ZnO powders was examined by transmission electron microscopy (TEM), operating at 200 kV. Electron diffraction (ED) was also conducted on the calcined samples. The UV-shielding was measured with a UV transmission spectrometer (Optomerics, SPF-290).

3. Results and discussion

3.1. Thermal behavior of the $Zn(OH)_2$ precipitates

Fig. 1 shows the TG/DTA curves of the precipitates, which were heated from 323 to 1473 K in static air at a heating rate of 10 K/min. The TG curve shows a minor weight loss from 323 to 381 K, followed by a major weight loss up to about 423 K, another weight loss extending up to 518 K, and a small weight loss up to 1273 K. Above 1273 K, there is no further weight loss until 1473 K. The first weight loss (−0.5%) is assigned to the vaporization of absorbed water. The first large weight loss (−8.4%) can be ascribed to the removal of most of the hydroxide radicals in the precipitates. The second large weight loss (−15.6%) between 423 and 518 K is mostly due to the decomposition of amino radicals. Finally, the small weight loss between 518 and 1273 K is due to the removal of residual hydroxide radicals involved in the intermediates.

The DTA result in Fig. 1 also indicates that there are two main endothermic peaks, at 401 and 483 K. The endothermic peak at 401 K is due to the dehydration of the precipitates, while that at 483 K is attributed to the decomposition of NH_2^- into N_2 and H_2 [17].

3.2. Phase evaluation of the $Zn(OH)_2$ precipitates at various calcination temperatures

The XRD patterns of the $Zn(OH)_2$ precipitated at various pH values and calcined at 413 K for 10 min are shown in Fig. 2,

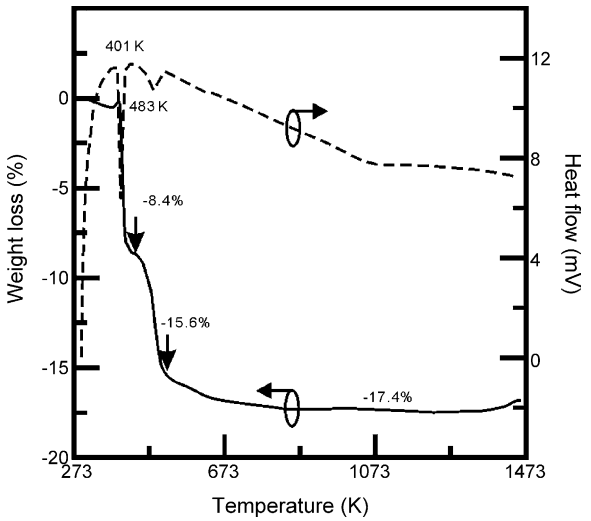

Fig. 1. DTA/TG curves of ZnO precursor powders precipitated at pH 9 with a heating rate of 10 K/min.