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Preparation of zinc oxide/silica nanocomposite particles via consecutive sol–gel and flame-assisted spray-drying methods

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HIGHLIGHTS

- Water glass was used as a silica source to prepare ZnO/SiO_2 nanocomposite.
- The mixed $ZnO–SiO_2$ colloids were dried by flame-assisted spray-drying methods.
- The addition of SiO_2 to ZnO resulted in the increase of the particles photoluminescence intensity.
- Silica content of the nanocomposites is significantly affected the particles characteristics.

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ABSTRACT

ZnO/SiO_2 nanocomposites were prepared using consecutive sol–gel and flame-assisted spray-drying methods. Zinc oxide and silica sols were prepared individually from zinc acetate and water glass, respectively, via a sol–gel method. Subsequently, zinc oxide sol, silica sol, and a mixture of both were spray dried in a flame reactor to generate powder of pure zinc oxide, pure silica, and a ZnO/SiO_2 nanocomposite, respectively, in order to compare the characteristics. The generated particles were characterized via luminescence spectrophotometer, Fourier Transform Infrared (FTIR), X-ray diffraction (XRD), and scanning electron microscopy (SEM) to obtain the photoluminescence spectra, chemical bonding, crystallinity, and morphology of the particles, respectively. The photoluminescence emission recorded at 250 nm excitation showed a peak at approximately 400 nm that was characterized by a violet band. The highest intensity was shown by a 75 mol% ZnO sample followed, in order, by 50 mol% ZnO, 25 mol% ZnO, and pure ZnO.

1. Introduction

New energy-conserving light sources have generated a tremendous amount of interest due to increasing energy demands and concerns of global warming. Solid-state light emitting diodes (LEDs) are now receiving increased attention as energy-saving sources, particularly phosphor-converted LEDs due to their high luminescence efficiency. Phosphors are usually limited to monochromatic emissions. Therefore, to generate white light, a blend of phosphors that emits in blue, green and red wavelengths is required. Zinc oxide is a wide-band-gap semiconductor that exhibits a strong and stable broad-band emission. ZnO has been considered as an alternative source to replace expensive GaN-based LEDs [1], because they have semiconducting properties that compare favorably to those of relatively expensive phosphor materials. Other applications of zinc oxide particles include the following: high-density data storage systems, transparent electrodes, gas sensing, bio-detection, UV light emitters, window material for displays, solar cells, and lasers [2].

Aerosol or wet processes can be utilized to synthesize ZnO nanoparticles. Particles on the nano scale are preferred due to the unique and improved properties that are a result of their size, composition and structure [3]. ZnO nanoparticles were synthesized using an integrated pulse combustion-spray pyrolysis process [4]. The fluctuations in the flow of hot gasses in pulse combustion systems enhance energy transfer and promote an increase in crystalline nanoparticles compared with the micron-sized particles that are produced by conventional spray pyrolysis. Other methods include gel-template combustion [5] and flame spray pyrolysis [6]. An aerosol-based spray-drying system for producing particles with a controlled morphology has been described in detail [7].

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Besides aerosol processing, the synthesis of ZnO nanoparticles through wet-chemical processing is also an area of particular interest, because it provides an economical alternative using moderate temperatures and pressures. Particle size is controlled by the rate of nucleation and coagulation that is highly influenced by synthesis conditions such as temperature, precursor concentration, and solvent type. A synthesis of ZnO colloidal nanoparticles with sizes that range from 3 to 6 nm has been demonstrated via a sol–gel approach [8]. However, an increase in particle size after aging resulted in a significant color shift in the photoluminescence spectra [9]. Nanoparticles tended to coagulate and form larger particles, which led to a decrease in their functional characteristics. In an attempt to maintain the characteristics of nanoparticles, they were mixed with inert material to generate a nanocomposite. Furthermore, trapping the particles in a solid matrix hindered the growth of ZnO nanoparticles, and the properties of the particles would not change. Nanocomposite structures are formed by incorporating functional nanoparticles into a transparent matrix material, which stabilizes the particle size and growth and maintains the enhanced nanoparticles [10].

Transparent silica nanoparticles are well suited for use in a matrix because they have almost no effect on the embedded nanoparticles. Variations in synthesis methods cause ZnO nanoparticles to exhibit different optical properties when embedded into amorphous silica nanoparticles by varying the particle size and composition [11]. A matrix of silica particles can play an important role in determining the controllable luminescence position of ZnO nanoparticles. Zinc oxide–silica nanocomposites have been prepared by sol–gel and spray-combustion methods using tetraethoxysilane (TEOS) and hexamethyldisiloxane (HMDSO), respectively [12,13]. However, TEOS and HMDSO are relatively expensive and toxic organic precursor materials. Zinc oxide nanoparticles embedded in a silica nanoparticle matrix were investigated by consecutive sol–gel and spray-drying methods by using commercial colloidal silica [14,15]. Water glass is a promising candidate for the synthesis of silica colloidal nanoparticles, and it is both relatively inexpensive and plentiful. The preparation of colloidal silica nanoparticles from water glass has been accomplished under both acidic and basic conditions [16]. Silicic acid was generated before the formation of colloidal silica nanoparticles. In addition, silicic acid can be synthesized from biomass that is abundant in tropical regions.

The objective of this work was to synthesize a ZnO/SiO_2 nanocomposite using a flame-assisted spray drying method with mixed colloidal ZnO and silica precursors synthesized by sol–gel methods. Colloidal ZnO and silica were synthesized from zinc acetate and water glass, respectively. The use of water glass as a silica source was a novel attempt in a ZnO/SiO_2 nanocomposite. The silica content in the colloidal precursor was studied for its effect on the characteristics of the generated particles.

2. Material and methods

Zinc acetate ($Zn(CH_3COO)_2{\cdot}2H_2O$, p.a. 99.5%, Merck), lithium hydroxide (LiOH, 98%, Merck), ethanol (absolute, Merck), potassium hydroxide (KOH, Merck), and water glass ($Na_2O{\cdot}nSiO_2{\cdot}mH_2O$, 8% Na_2O, 27% SiO_2, Merck) were used as received. Colloidal zinc oxide particles were prepared based on a method established by Spanhel and Anderson using 0.1 M zinc acetate and 0.14 M lithium hydroxide with ethanol as a solvent [8]. By using the correlation between average particle diameter (d_p) and the absorption shoulder ($\lambda_{1/2}$), based on the UV–Vis absorbance measurement (spectrophotometer, Thermo Scientific Genesys), at the wavelength where the absorption was half of the excitonic peak, the size of the colloidal ZnO was 3.75 nm. The correlation was as follows [17]:

$$\frac{1240}{\lambda_{1/2}} = 3.301 + \frac{294.0}{d_p^2} + \frac{1.09}{d_p} \qquad (1)$$

Colloidal silica particles were prepared by diluting water glass into distilled water to generate a 0.1 M colloidal solution at a temperature of 60 °C. After the temperature was decreased to room temperature, the water glass solution was passed through a cation exchange resin to form a silicic acid solution. To the silicic acid solution, 0.1 M KOH was added drop-by-drop while the solution was stirred rigorously to adjust the pH to 8. Under these conditions, the solution was polymerized to form colloidal silica particles [16]. The particle size distribution of the prepared colloidal silica, as measured by Malvern Particle Size Distribution, is depicted in Fig. 1. The average geometric particle size (d_g) and its geometric standard (σ_g) deviation were 11.25 and 1.29, respectively. The surface charges of colloidal silica and colloidal ZnO particles were −13.10 and −5.00 mV, respectively, by measuring their zeta potentials (Zetasizer, Malvern).

The colloidal zinc oxide and silica were mixed to obtain 25, 50, and 75 mol% ZnO. For comparison, pure colloidal zinc oxide and silica were also used as precursors. The mixed colloidal solution was used as a precursor for the flame-assisted spray-drying system, as shown in Fig. 2. In the flame reactor, propane gas was used as a fuel and air was used as an oxidizer. The flow rate of the fuel was 0.50 L/min and the flow rate of the oxidizer was 10-fold greater. In order to carry uncharged droplets from the nebulizer (ultrasonic nebulizer, NE-U17, Omron) to the flame reactor, air with a flow rate of 2 L/min was used as the carrier gas.

In order to examine the water content of pure ZnO and pure silica samples, thermogravimetry analysis (TGA, Mettler Toledo) was used to measure the change in weight of the generated particles by increasing the temperature at a heating rate of 10 °C/min. Scanning electron microscopy (SEM, Zeiss) at 20 kV was used to examine the morphology of the generated particles. An X-ray diffractometer (XRD, Philips) using filter CuKα radiation (λ = 1.54 Å) operated at 40 kV and 30 mA was used to record the diffraction spectra with 2θ from 10° to 60°. The Fourier Transform Infrared (FTIR, Perkin Elmer) spectrum was analyzed for wave numbers ranging from 4000–500 cm^{-1}. FTIR was used to characterize the type of chemical bonding by evaluating the chemical bond's vibrating energy that was altered by the absorbance of infrared radiation. A luminescence spectrometer (Perkin Elmer) equipped with a xenon source was used to examine the excitation and emission luminescence spectra.

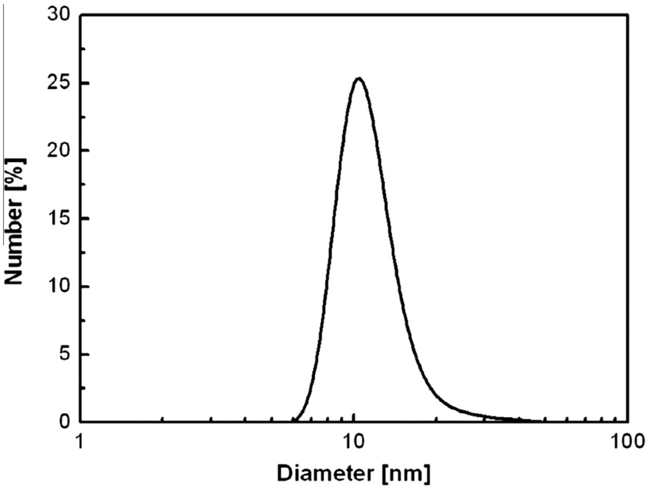

Fig. 1. Particle size distribution of as-prepared colloidal silica.