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Characterization and antibacterial activity of nanostructured ZnO thin films synthesized through a hydrothermal method

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ABSTRACT

Nanostructured ZnO films have been successfully synthesized on Zn substrates by a simple hydrothermal method at 120 °C in 24 h. The morphologies of the products were controlled by the following alkaline precursor solutions: NaOH, LiOH and NH_4OH, which played a role in the crystallization process by generating rod-like, pencil-like and star-like particles, respectively. The phase and crystallinity of the nanostructured films were characterized by X-ray diffraction and selected area electron diffraction, the vibrational modes were determined by Fourier transform infrared spectrometry and Raman spectroscopy, and their morphologies were visualized by scanning electron microscopy and transmission electron microscopy. The photoluminescence of the products exhibited a strong, green–yellow band emission at 540 nm. By using the inhibition zone method, the as-synthesized ZnO nanostructures were observed to inhibit bacterial activity.

1. Introduction

Nanostructured materials have a variety of different properties compared to bulk materials, due to their surface features, quantum size and macroscopic quantum tunneling effects [1,2]. These materials exhibit an interesting size-dependence based on electrical, optical, magnetic and chemical properties that bulk materials are unable to achieve [1,3]. Thus, the synthesis of uniformly sized nanomaterials is of key importance. The physical and chemical properties are strongly dependent on their dimension and are broadly referred to as size effects [3]. The most important requirement in the synthesis of nanomaterials is the ability to control their size and shape, including the maintenance of their uniformity [3,4]. The size of the nanocrystals also significantly influences the electronic diffusion process [4]. The most popular demonstration of the size-dependent characteristics of nanomaterials is a continuous fluorescent emission from semiconducting nanomaterials [5]. Their shapes can play a critical role in determining such properties as the energy gap (E_g) [4]. The shapes of nanomaterials can be simply classified based on their dimensionality [4]: one-dimensional (1D) nanorods and nanowires [4] exhibit superior optical and electrical properties that originate from scaling down their dimensions to the length scale by comparing them to the de Broglie wavelength of the carriers [6].

Among the prominent metal-oxide materials, ZnO has been intensively investigated for potential applications in piezoelectric [7], electronic [7,8], gas sensing [9], photocatalysis [8,9], optoelectronic devices [6–8] and, especially, as materials for room temperature ultraviolet (UV) laser diodes [6] and data storage units [8]. ZnO has the well-known specific electrical and optoelectronic properties of II–VI semiconductors [2,9] with a wide band gap of 3.37 eV and a large exciton binding energy of 60 meV at room temperature [2,8–10] that is greater than its thermal energy at room temperature (26 meV) [6]. In recent years, 1D ZnO nanostructured arrays on a variety of substrates have attracted considerable interest because of their specific optoelectronic and field-emission characteristics originating from their unique heterogeneous crystalline structures, leading to promising applications in the fabrication of functional nano-/micro-devices [11]. Films with well-aligned ZnO nanorods or nanowires may exhibit much larger surface areas than ZnO films synthesized from randomly oriented nanoparticles [11]. Moreover, these nanorods are packed notably densely, enabling the fast and effective diffusion of electrons, and they are used for lasers and solar cells [11]. Recently, ZnO films of nanostructures have been fabricated on a variety of substrates, including Si [6,9], glass [7,10] and indium tin oxide (ITO) [12,13], by several different methods: chemical vapor deposition (CVD) [6], thermal evaporation [6], sol–gel [7], etching [8], hydrothermal [11]/solvothermal routes [14] and electrodeposition [13,15].

In this research, nanostructured ZnO films on Zn substrates were hydrothermally synthesized in solutions containing NaOH, LiOH and

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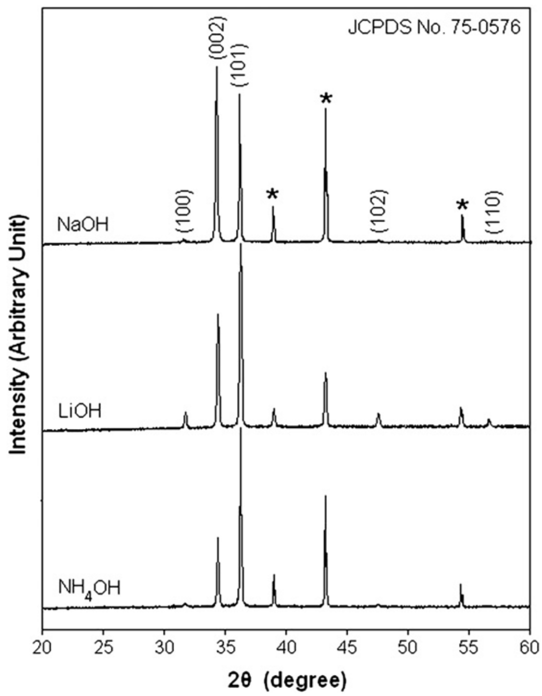

Fig. 1. XRD patterns of ZnO synthesized in NaOH, LiOH and NH_4OH alkaline precursor solutions.

NH_4OH without using any catalysts or templates through a common, simple, safe and low-cost method. The effects of the as-synthesized ZnO with different morphologies were studied and reported with respect to their properties and applications for photoluminescence and antibacterial activity.

2. Experimental methods

Zinc foils (15 mm × 15 mm × 0.25 mm), used as both a solid reagent and as substrates for the direct growth of nanostructured ZnO films, were carefully cleaned in 99% ethanol and DI water containing ultrasound baths. Concurrently, NaOH, LiOH and NH_4OH solutions with the same concentration of 5 M were added to 20 ml DI water to form precursor solutions until the pH values were 12, 12 and 10, respectively. The precursor solutions were put in Teflon-lined stainless steel autoclaves, and the clean Zn foils were added to each solution. The autoclaves were tightly closed, heated at 120 °C for 24 h and left to cool down to room temperature. The as-synthesized films on Zn substrates were rinsed with DI water and ethanol several times and dried at 70 °C for 48 h.

The crystallinity and phases of the products were characterized by an X-ray diffractometer (XRD, Philips X'Pert MPD) using Cu-K_α radiation at 45 kV and 35 mA in the range of 20–60 deg, and the surface morphologies were characterized by both a field emission scanning electron microscope (FE-SEM, JEOL JSM-6335F) operating at 35 kV and a transmission electron microscope (TEM, JEOL JEM-2010) equipped with a selected area electron diffractometer (SAED) operating at 200 kV. The atomic vibrations were measured by a Fourier transform infrared (FTIR, RX Perkin Elmer) spectrometer operating in the range of 400–4000 cm^{-1} at room temperature with ZnO tablets diluted 40-fold with KBr and by a Raman spectrometer (T64000 HORIBA Jobin Yvon) using 50 mW and a 514.5 nm wavelength Ar green laser. The emission wavelength was measured by a photoluminescence (PL, LS 50B Perkin Elmer) spectrometer using a 215 nm excitation wavelength at room temperature, including the investigation of antibacterial activities by different film morphologies.

In this research, two types of bacteria–gram-positive (*Staphylococcus aureus*) and gram-negative (*Escherichia coli*)–were used to study the antibacterial activity of ZnO thin films by the inhibition zone method. Both strains were transferred into flasks containing nutrient broth (NB) with an initial optical density (OD) of 0.1 at a 660 nm orange wavelength; and the bacteria were cultured at 37 °C under aerated conditions until reaching an OD of 0.3. Agar was then added to the flasks. Modified agar diffusion assays (testing disks) were used to determine the antibacterial activity of the ZnO thin films after 24 h incubation at 37 °C by observing the formation of clear zones around the foils.

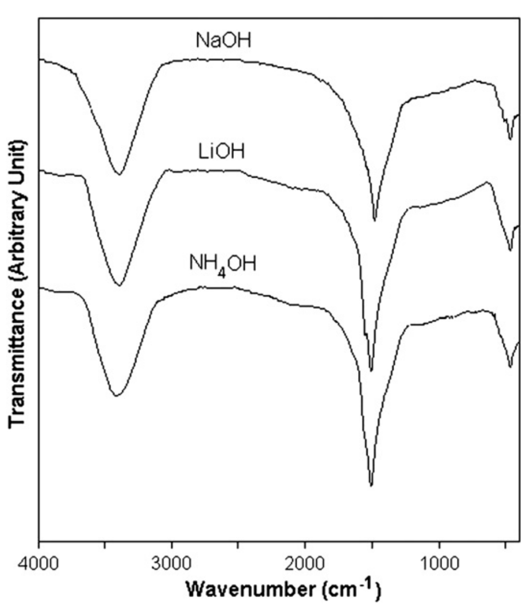

Fig. 2. FTIR spectra of ZnO synthesized in NaOH, LiOH and NH_4OH alkaline precursor solutions.

3. Results and discussion

3.1. XRD

The XRD patterns (Fig. 1) of the ZnO films synthesized in NaOH, LiOH and NH_4OH solutions on Zn substrates were very sharp, indicating the existence of products with good crystalline structure. All diffraction patterns can be indexed to possess a hexagonal wurtzite structure, compared to JCPDS No. 75-0576 [16], including additional peaks marked with asterisks indexed to be Zn substrates compared to JCPDS No. 04-0831 [16]. No characteristic peaks of other impurities were

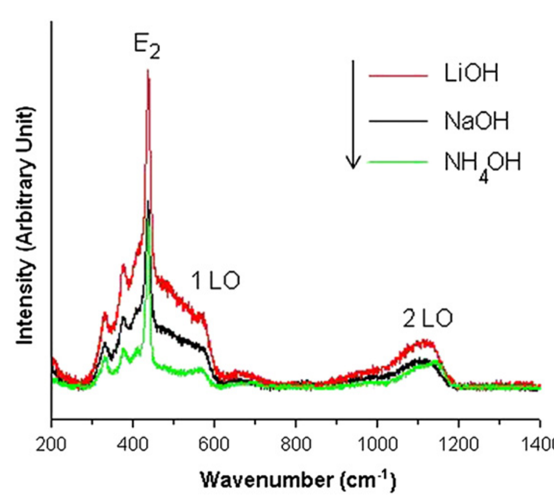

Fig. 3. Raman spectra of ZnO synthesized in NaOH, LiOH and NH_4OH alkaline precursor solutions.