



Fabrication and characterization of Zn–ZnO core–shell microspheres from nanorods

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ARTICLE INFO

Article history:

Received 13 May 2008

In final form 17 September 2008

Available online 15 October 2008

ABSTRACT

We present a new method to synthesize ZnO nanorods on zinc spheres to form a core–shell structure. Selective self-assembly growth of a shell with ZnO nanorods on a metallic Zn microsphere core has been accomplished via hydrothermal synthesis. The crystal structure, morphologies and chemical composition were characterized by X-ray diffraction, transmission electron microscopy, scanning electron microscopy and energy dispersive X-ray spectroscopy. The interfacial chemistry involved in the growth of ZnO nanorods on the Zn core and a possible growth mechanism are discussed. The specific structure of the highly oriented one-dimensional nanorods may find applications in nanoelectronics, nanophotonics and nanomedicine.

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1. Introduction

The controlled fabrication of functional nanoarchitected materials is an important objective of fundamental and applied research. In nanotechnology, it is important to synthesize specifically shaped nanostructures, which could serve as building blocks in the assembly process. There are different synthesis techniques that are used for the surface coating of an object, such as sol-gel coating, self-assembly and sonochemical processing.

Among all the nanomaterials, ZnO attracted a lot of attention with its various architectures [1,2], as an excellent candidate for self-assembly. ZnO is also promising for device applications due to its unique material properties such as wide and direct band gap and a large free exciton binding energy [3], high optical gain (300 cm^{-1}) [4,5] and high mechanical and thermal stabilities [6,7]. ZnO nanorods with their high carrier mobility serve as direct conduction pathways for excitons and they can represent different types of nanoscale building blocks that have been used to assemble functional devices [1–4,8–10]. Especially important for applications of these ZnO one-dimensional (1-D) nanorods are methods to assemble them into highly integrated and hierarchically organized nanostructures for device integration without using sophisticated equipment [4–8].

Core/shell type ZnO nano/microspheres have been studied due to their potential applications in nanocomposite materials. For example, Sulieman et al. [11] have reported a vapor transport synthesis of hollow-opened ZnO/Zn or Zn/ZnO microspheres on Si sub-

strate using high purity Zn and ZnO powder as sources. Duan et al. [12], employed an integrated autoclave and pyrolysis process to synthesize partially opened ZnO hollow microspheres. In both cases, high temperatures (600 °C or higher) were used to react the Zn powder with oxygen and the ZnO shells are consisted of multicrystalline domains or particulates.

Here, we report for the first time a simple hydrothermal synthesis of self-assembled ZnO nanorods into three-dimensional (3-D) spherical shells on a Zn microsphere. The ZnO nanorods are self-organized such that their *c*-axes are all perpendicular to the surface of the Zn microsphere and the length of the ZnO nanorods is equivalent to the thickness of the ZnO shell. We also propose a possible growth mechanism and discuss factors that influence the formation mechanism of the ZnO nanorods shell on Zn core.

2. Experimental

2.1. Synthesis

An appropriate quantity of zinc sulfate [$\text{Zn}(\text{SO}_4) \cdot 7\text{H}_2\text{O}$] and ammonium hydroxide [$\text{NH}_4(\text{OH})$] (Fisher Scientific, 99.9%) were mixed until they were completely dissolved. The molar ratio of $\text{Zn}^{2+}/\text{NH}_3$ was in the range 1:2 to 1:20. The pH of the system was 10.5. The aqueous solution was loaded into a reactor [13] and a piece of cleaned silicon wafer or cleaned glass substrate [14] was placed in the aqueous solution and 0.3–1.0 g of pure zinc powder (2–10 μm in diameter) was added. Then the reactor was transferred and positioned on a hot plate [13]. The system was heated to a preset temperature (95 °C) and held for 15 min.

Initially, zinc sulfate was dissolved in deionized water. Then by adding ammonia solution, it dissociated in water [15].

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