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# Controlled growth of semiconducting oxides hierarchical nanostructures

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## Abstract

Semiconducting ZnO hierarchical nanostructure, where ZnO nanonails were grown on ZnO nanowires, has been fabricated under control experiment with a mixture of ZnO nanopowders and Sn metal powders. Sn nanoparticles are located at or close to the tips of the nanowires and the growth branches, serving as the catalyst for the vapor–liquid–solid growth mechanism. The morphology and microstructure of ZnO nanowire and nanonail were measured by scanning electron microscopy and high-resolution transmission electron microscopy. The long and straight ZnO nanowires grow along [0001] direction. ZnO nanonails are aligned radially with respect to the surface the ZnO nanowire. The long axis direction of nanonails forms an angle of ~30° to the [0001] direction.

*Keywords:* Hierarchical structure; Controlled-growth; Nanowire; Nanonail; Semiconducting oxide

## 1. Introduction

Research in quasi-one-dimensional (Q-1D) nanomaterials has attracted a great deal of attention because they are abundant and of potential application in semiconductor and electronic technologies, especially for nanoelectronics and optoelectronics [1–4]. Binary semiconducting oxides have distinctive properties and are now widely used as functional and smart devices, such as chemical and biological sensors. The electrical conductivity of these oxides depends sensitively on the type and concentration of molecules adsorbed on their surfaces. Q-1D nanobelts and nanowires of semiconducting oxides, such as ZnO, $SnO_2$, $Ga_2O_3$, $In_2O_3$, CdO, and $PbO_2$ materials for sensor and fuel cell applications have been synthesized [5–7]. ZnO has a wide band gap of 3.37 eV and a large exciton binding energy of 60 meV, and displays excellent piezoelectric and optical properties. Recent study indicates that the ZnO nanostructures are rich in morphology. ZnO nanostructures with different morphologies, such as nanowires (or nanorods) [3,8–10], nanobelts (nanoribbons) [5,11], nanowires array [12], comb-like nanowires array [13], nanoneedles arrays [14,15], nanorings [16], and tetrapods (or dendrites) [17] have been successfully synthesized. For example, single crystalline ZnO nanobelts and nanorings have been prepared by thermal evaporation ZnO powder [5,16]. Large-scale synthesis of ZnO nanowires has been achieved on Au-coated silicon substrates by physical evaporation of the mixture of ZnO and graphite powders [3,10] and polycrystalline ZnO nanowires have been fabricated within the nanochannels of porous alumina [12]. Using metal-organic chemical vapor deposition (MOCVD) method, vertically well-aligned ZnO nanoneedles on Si substrates also has been reported [15]. By simply adjusting the reaction temperature and the partial pressure of oxygen within the system, tetrapods and dendrites of ZnO nanostructure have been successfully synthesized [17].

In the last few years, there has been an increasing interest on the hierarchical nanostructures. Several authors have prepared the hierarchical nanostructures of semiconducting oxide [18–20], silica [21], and HgS

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[22]. In this paper, we report ZnO hierarchical nanostructures, where ZnO nanonails were grown on ZnO nanowires, which have been successfully synthesized using the mixture of Sn metal powder and ZnO nanopowders as the source material. ZnO nanowires are straight and long, the tip of a nanowire has a large head, which is identified as a Sn metal particle that served as the catalyst for the growth. A large number of ZnO nanonails were found to form on the outer shells of ZnO nanowires. Every ZnO nanonail has a large head, and another tip exhibits sharp morphology. A high density of ZnO nanonails is vertically aligned over the surface of the ZnO nanowire in the radial direction. Therefore, the method may suggest a way of making a heterojunction between a nanowire and a nanowire for so-called bottom-up manufacturing techniques.

## 2. Experimental section

The experimental set-up used for the synthesis consists of a horizontal tube furnace, an alumina tube, an argon gas supply and a control system. ZnO nanonails were grown on the surface of ZnO nanowire in the presence of a Sn catalyst, suggesting that vapor–liquid–solid (VLS) mechanism is applicable for the current growth process through thermal evaporation. Sn metal powder with a purity of 99.99% and ZnO nanopowder with weight ratio of 1:2 (5 g in total) were fully mixed and then used as the source material. The mixture powders were placed at the center of an alumina crucible. A silica plate was typically placed at 5–10 cm from the center of the crucible, which acted as a substrate for collecting the growth products. Then the crucible was inserted into the alumina reactor, and this alumina was then placed inside a horizontal electronic resistance furnace with the center of the crucible positioned at the center of the furnace and the substrate placed downstream of the gas flow. The temperature of the furnace was rapidly increased to 1200 °C from room temperature and kept at 1200 °C for 2 h under a constant flow gas of argon. Argon was introduced into the alumina tube through a mass-flow controller at rates of 50 standard cubic centimeters per minute (sccm). After the furnace was slowly cooled down to room temperature the Ar flow was turned off. A layer of wool-like products was formed on the walls of the crucible and the surface of the substrate.

The as-prepared products were characterized and analyzed by scanning electron microscopy (SEM) (JEOL JSM-5610LV), high-resolution transmission electron microscopy (HRTEM) (JEOL 2010, 200 kV), and energy-dispersive X-ray (EDX) spectrometer (JEOL EX-54145 JMH) attached to the SEM instrument. For SEM observations, the product was pre-sputtered with a conducting layer of noble Pt metal. The specimens for HRTEM were prepared by putting the as-prepared products in ethanol and immersing them in an ultrasonic bath for 5 min, then dropping a few drops of resulting suspension containing the synthesized materials onto a Cu grid coated with a holey carbon film.

## 3. Results and discussion

SEM observation shown in Fig. 1(a) reveals that the products consist of a large quantity of wire-like nanostructures with typical lengths in the range of several tens to several hundreds of micrometers; some of them even have lengths in the order of millimeters. A typical magnified SEM image of the as-prepared products is given in Fig. 1(b). A long and straight wire has a large head and there are many branches on the surface of the wire. A magnified SEM image is shown in Fig. 1(c) from the box in Fig. 1(b). It can be clearly seen that a large number of nanonails were grown on the surface of the long and straight wire. Every nanonail has a head and the typical widths of the head are in the range of several tens of nanometers to several hundred nanometers as shown in Fig. 1(d). Another tip of the nanonail exhibits sharp morphology. A high density of the nanonails is vertically aligned over the surface of the long and straight nanowire in the radial direction. XRD patterns shown in Fig. 1(e) reveal the overall crystal structure and phase of the hierarchical nanostructures. Miller indices are indicated on each diffraction peak. It can be seen that a set of peaks with strong intensity can be indexed in peak positions to a crystalline ZnO phase. XRD patterns show hexagonal structure with lattice constants $a_o = 0.32$ nm and $c_o = 0.519$ nm, which are consistent with those of bulk ZnO crystal [23] (JCPDS 5-664). The other peaks in this pattern can be indexed as metal Sn (peaks marks with asterisks). From the relation intensity of these peaks, we can deduce that in the product ZnO is the main phase, whereas Sn is minor phase.

Further structural and elemental analyses of the ZnO nanonails and the ZnO nanowires were performed using HRTEM. TEM image [shown in Fig. 2(a)] of a single ZnO nanowire provided further structural information about this material. The bright-field TEM image showed that a linear segment was crystalline with a uniform diameter of 30 nm. The HRTEM image shown in Fig. 2(c) was recorded along the $\langle 001 \rangle$ zone axis. The clear lattice fringes in this image indicated a single crystal structure of the nanowire. The spacing of 0.256 nm between adjacent lattice planes corresponds to the distance between two (0002) crystal planes, indicating $\langle 0001 \rangle$ as the growth direction for the ZnO nanowires. Selected-area electron diffraction (SAED) patterns [inset in Fig. 2(c)] of the same nanowire also confirmed that it was a single crystal and the [0001] direction was a common growth direction in the long and straight ZnO nanowires.

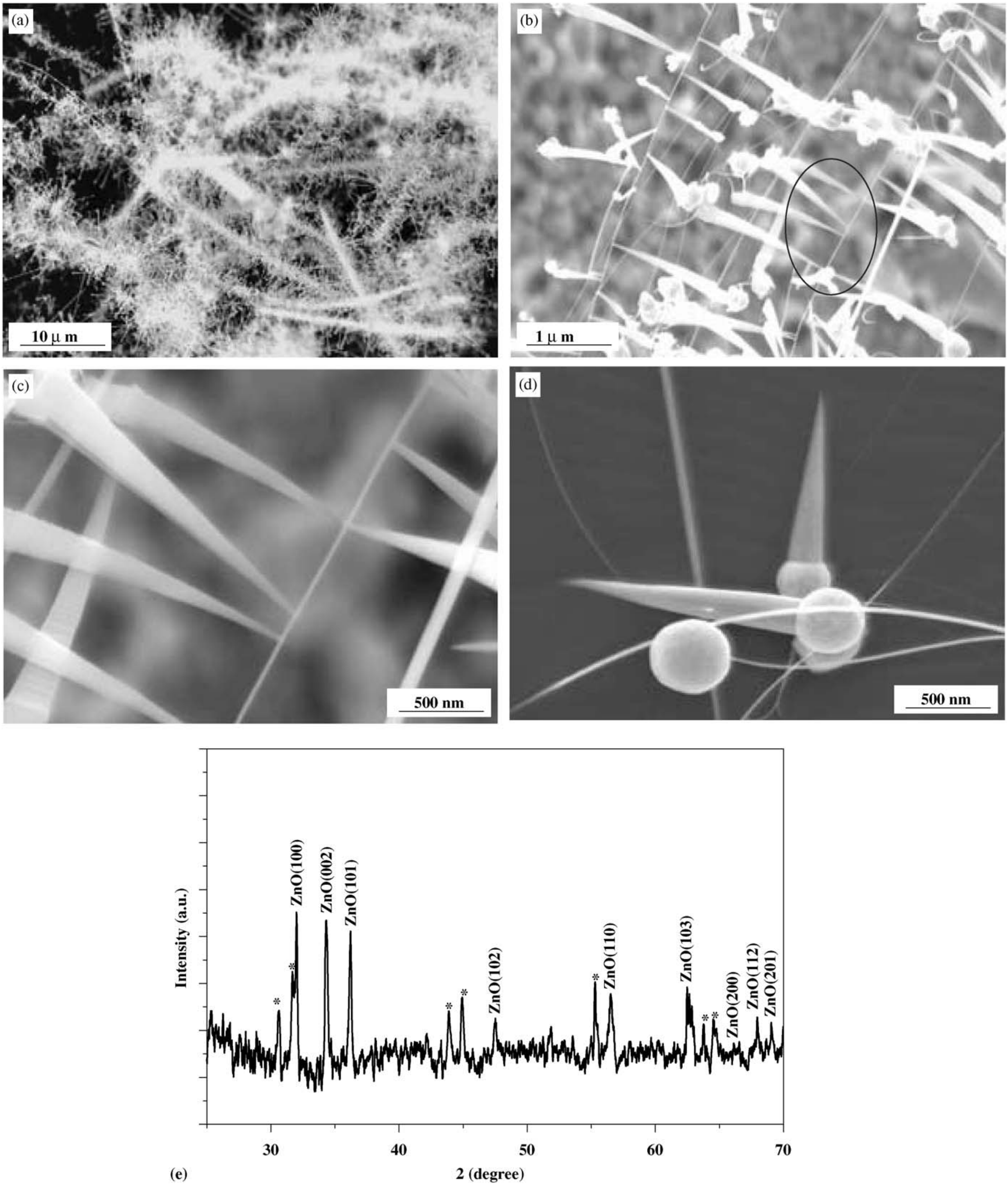

Fig. 1. (a) A SEM image of the as-synthesized products. (b) A typical high magnification SEM image of the ZnO nanonails grown on the ZnO nanowires. (c) A magnified SEM image from the marked area (black circle) in Fig. 1(b). (d) A SEM image of ZnO nanonails: They have a large head and the tips exhibit sharp morphology. (e) XRD patterns recorded from the as-prepared product.

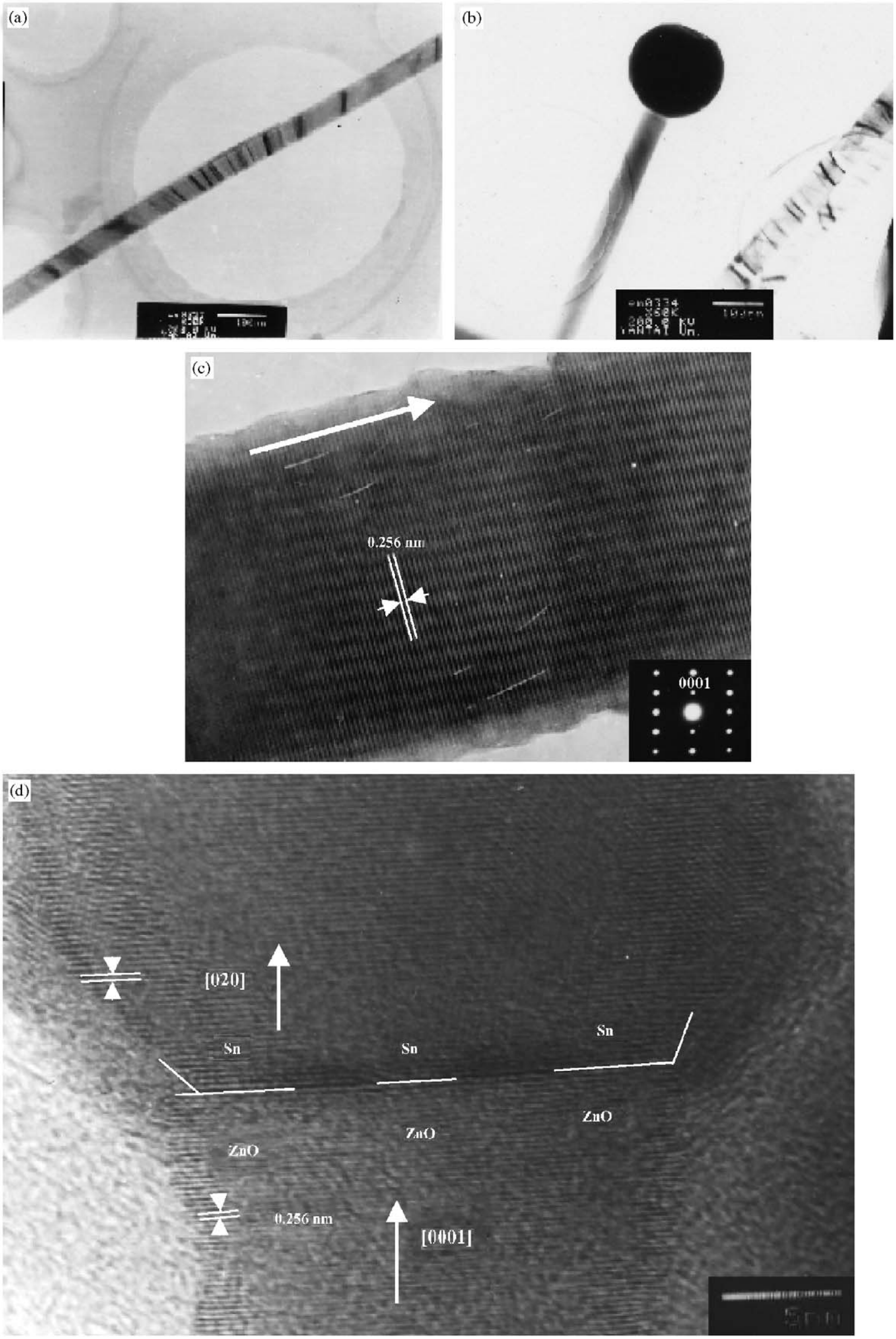

Fig. 2. (a) A TEM image of an individual ZnO nanowire. The image shows that the nanowire has a uniform diameter of 30 nm along its entire length. (b) The tip of the ZnO nanowire shown in (a) has a large head, which is identified as a Sn metal particle that served as the catalyst for the growth of the VLS mechanism. (c) HRTEM image from the crystalline ZnO nanowire (as shown in Fig. 2a). The (0002) planes (spacing, 0.256 nm) are perpendicular to the growth direction (white arrow labeled with [0001]). The inset is the corresponding electron diffraction pattern. (d) HRTEM image from the interface region between the Sn and ZnO (as shown in Fig. 2b).

A TEM image shown in Fig. 2(b) of the tip of the nanowire has a large head that is identified as a Sn metal particle that served as the catalyst for the growth. The diameter of the solidified spherical droplet at the tip is bigger than the width of the nanowire. The diameter of the ZnO nanowire is about 20 nm and the diameter of the Sn particle is about 60 nm. A HRTEM on the knot of ZnO nanowire and Sn nanoparticle is shown in Fig. 2(d). Note that the interface between the Sn particle and the ZnO nanowires is flat. Fig. 2(d) depicts the interface structure between the ZnO nanowire and the Sn particle. It is clear that [0001](ZnO) is the growth direction of the ZnO nanowire. After measuring the Sn lattice spacing, the [020](Sn) direction of the Sn particle corresponds to ZnO growth direction [0001](ZnO).

TEM image shown in Fig. 3(a) reveals that the geometrical shape of individual ZnO nanonail. In the image, it has a large head and the stem gradually tapers down from several hundred nanometers to several tens of nanometers and its tip exhibits the extreme sharp morphology. To further reveal the structure of the ZnO nanonail and see lattice fringes of the ZnO nanonail, a HRTEM image is shown in Fig. 3(b) that comes from the boxed region in Fig. 3(a). In the image, the long-axis direction of the nanonail is indicated by an arrow and the space of about 0.257 nm between arrowheads corresponds to the distance between two (0002) planes. Further examination shows that the long-axis direction of the nanonail forms an angle of ~30° to the [0001] direction. In addition, Fig. 3(c) shows that two nanonails can join into one branch at the tip.

EDX measurements made on the tip [arrows in Fig. 4(a)] indicates that the tip is composed only of Sn [shown in Fig. 4(b)]. The stem is composed mainly of Zn and O [shown in Fig. 4(c)]. The molecular ratio of Zn/O of the nanowire (or nanonail) calculated from the EDX quantitative analysis data is close to that of a bulk ZnO crystal. Therefore, EDX microanalysis shows that the products are large quantities of ZnO nanowires and ZnO nanonails. Because of the low melting point, the Sn droplets are still liquid while the sample is cooled to below the growth temperature [24]. Therefore, the Sn droplets can slip off the tip, and lie at the side of the wire [arrows in Fig. 4(a)]. Pt signals are generated from a conducting layer for SEM observation.

These data from SEM, TEM, and HRTEM altogether reveal that the growth of the ZnO hierarchical nanostructures may be dominated by the VLS process [25]. It is well known that the presence of a liquid drop is essential for the effective operation of the VLS mechanism. The solidified spherical droplets (equal or more than the diameter of a nanowire) at the tips of the nanowires are commonly considered to be the evidence for the operation of the VLS mechanism. In VLS growth process, the droplet is located at the growth front of the wire and acts as the catalytic active site. From the experimental results demonstrated above, the Sn particles are liquid droplets at the growth temperature due to their low melting point (232 °C), and serve as the sites for adsorption of ZnO vapor. As the main wires grow

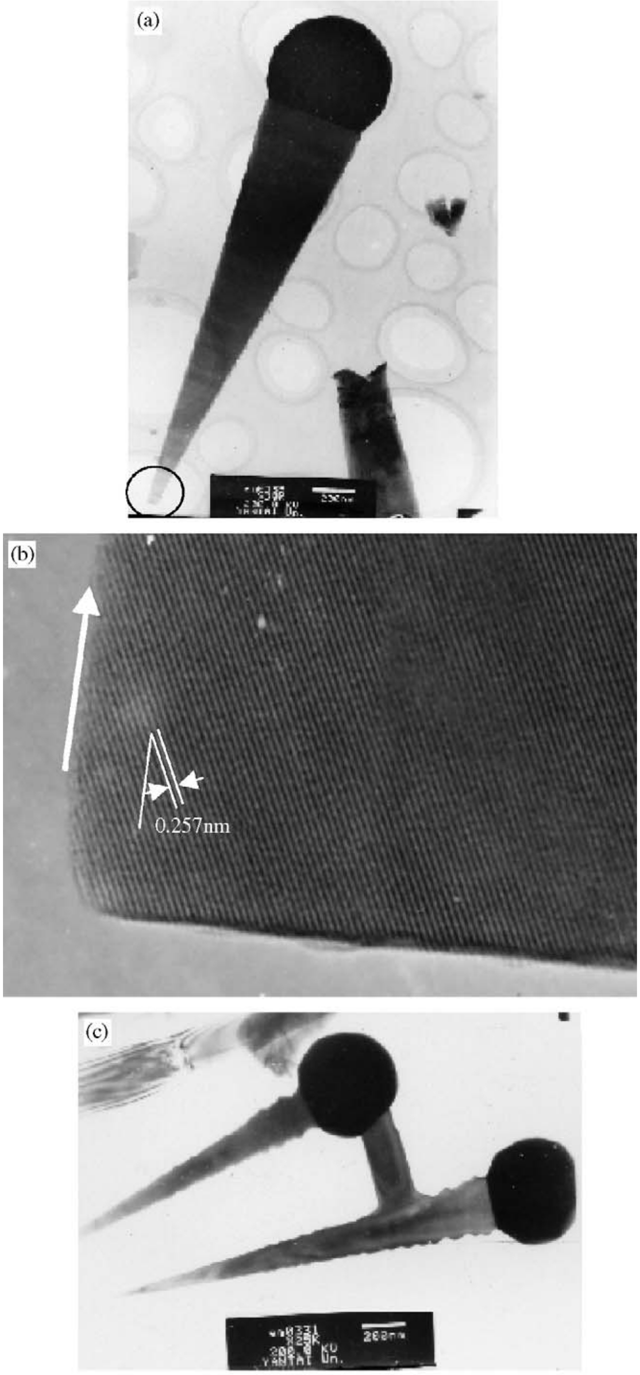

Fig. 3. (a) A TEM image of an individual ZnO nanonail. The image shows that the nanonail has a large head with diameter about several hundred nanometers and another tip exhibits the extreme sharp morphology about several tens of nanometers. (b) HRTEM image of the ZnO nanonail from the box in (a). The examination shows that the long-axis direction of the nanonail forms an angle of ~30° to the [0001] direction. (c) A TEM image shows that two nanonails can join into one branch at the tip.

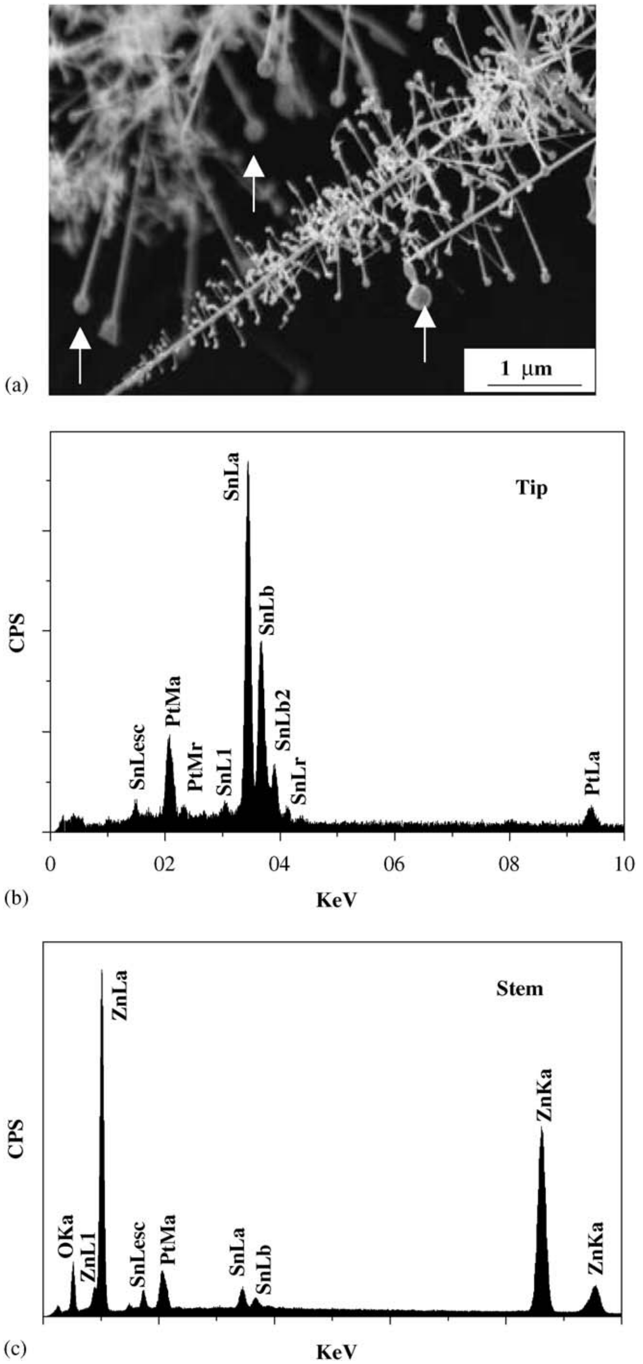

Fig. 4. (a) SEM images of the as-synthesized ZnO nanonails grown on the surfaces of the ZnO nanowires, showing several growth features of the branches. (b) A typical EDX spectrum taken from the tips of the ZnO nanowires and ZnO nanonails, suggesting that the tip contains Sn only. (c) A typical EDX spectrum taken from the stems of the ZnO nanowires and ZnO nanonails, suggesting that the stem contains Zn and O. The stem is also composed of Sn. The reason is the arrival of the tiny Sn droplets onto the stems of ZnO nanowire surface and nanonail surface. Pt signals are generated from a conducting layer for SEM observation.

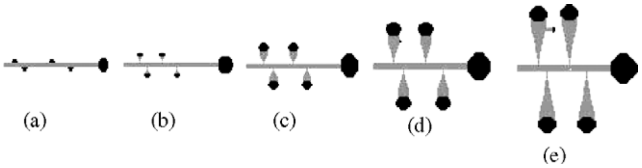

Fig. 5. A proposed model for describing the growth process of the hierarchical nanostructure: ZnO nanonails grown on the surfaces of the ZnO nanowires.

along [0001] with Sn particles at the tips (Fig. 5a), smaller droplets of Sn particles can be formed on the surface of the ZnO nanowire, which leads to the growth of ZnO branches, resulting in the formation of the perpendicular branches (Fig. 5b). All of the grown branches are likely to be confined in the (0001) plane because the entire piece is a single crystalline structure as shown in Fig. 3(b). As the tip of the branch grows bigger and bigger, the more ZnO vapor will be adsorbed by the catalytic active site, the bigger the diameter of the branches will become (as shown in Figs. 5c–e). While the lower parts of the branches show extreme sharp morphology, its tip exhibits a large head. As the side branches grow longer and longer, smaller droplets of Sn particles can be formed on the ZnO nanonail surface (Fig. 5e). This fact leads to the growth of smaller ZnO branches, resulting in the formation of the perpendicular branches. The experimental result shown in Fig. 3(c) also has been demonstrated.

It is very interesting why the shape of wires and nails is different when the ZnO is formed by the same mechanism. The growth of the hierarchical nanostructures presented in the present study can be separated into two stages [18]. The first stage is a fast growth of the ZnO nanowire along [0001] with Sn as the catalyst. The growth rate is so high that a slow increase in the size of the Sn droplet has little influence on the diameter of the nanowire; thus, the axial nanowire has a fairly uniform shape along the growth direction. The second stage of the growth is the nucleation and epitaxial growth of the nanonails due to the arrival of the tiny Sn droplets onto the ZnO nanowire surface. This stage is much slower than the first stage because the lengths of the nanonails are much shorter than that of the nanowire. Since Sn is in liquid state at the growth temperature, it tends to adsorb the newly arriving Sn species and grows into a larger sized particle. Therefore, the width of the nanonail increases as the size of the Sn particle at the tip becomes larger, resulting in the formation of the tadpole-like structure observed in SEM and TEM. In addition, it is noted that the stem is also composed of Sn, shown in Fig. 4(c). The reason is the arrival of the tiny Sn droplets onto the ZnO nanowire surface and nanonail surface.

When Au served as the catalyst for growth of the ZnO nanostructures under control experiment without Sn powder in the starting materials, the experimental results of Yang's group [10] and ours altogether have demonstrated that the product are large ZnO nanowires. Hierarchical nanostructures of ZnO were not fabricated. The reason is possibly that Au catalyst has higher melting point than that of Sn catalyst. This fact also indicates the importance of Sn catalyst on formed hierarchical ZnO nanostructures. In addition, the presence of a large ball tip shown in Figs. 2(b), 3(a) and 4(a) is indicative of a growth process by the VLS mechanism. However, we also note that the EDX results of the tips shown in Fig. 4(b) mainly consisted of Sn and Pt elements. The tips were not composed of Sn–Zn alloy or Sn–ZnO alloy. An important question here is how the growth mechanism of Sn metal particles served as catalyst. Therefore, further investigation into specific catalytic function and growth mechanism for Sn metal particles that served as the catalyst for the growth is underway.

## 4. Conclusions

In summary, by mixing of Sn metal powder and ZnO nanopowder as source material, a hierarchical ZnO nanostructure in which ZnO nanonails grown on ZnO nanowires has been successfully synthesized. ZnO nanowires are straight, smooth, and every tip has a large head. A high density of ZnO nanonails is vertically aligned over the surface of the ZnO nanowire in radial direction. Every ZnO nanonail has a large head and its tip exhibits sharp morphology. HRTEM images of the as-prepared products show that the ZnO nanowire and ZnO nanonail are pure, structurally uniform, and single-crystalline. EDX analysis shows that the products are large quantities of ZnO nanowires and ZnO nanonails. Therefore, the hierarchical nanostructure has multi-outlets and are ideal objects for the fabrication of nanoscale functional devices.

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