

Controllable growth of zinc oxide micro- and nanocrystals by oxidization of Zn–Cu alloy

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Abstract

A simple and fast, controllable gas vaporization of alloy method for producing various micro- and nanostructures of ZnO in air atmosphere with a large yield was presented in this paper. The presence of Cu was proved to strongly affect the growth morphology of the synthesized ZnO through the control of the partial pressure of zinc, which could be fulfilled by changing the composition of Zn and Cu for the used reactants. Given the simplicity of the procedure, and the economic advantages, the method described here is likely to be of interest in industrial-scale applications.

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1. Introduction

Zinc oxide (ZnO) has received great attention in recent years for its potential applications in photonic material. It possesses a direct bandgap of 3.37 eV at room temperature with a large exciton binding energy of 60 meV. The strong exciton binding energy, which is much larger than that of GaN (25 meV) and the thermal energy at room temperature (26 meV) can ensure an efficient exciton emission at room temperature under low excitation energy [1]. As a consequence, ZnO is recognized as a promising photonic material in blue-UV region. For example, as a UV laser it can allow reading compact disks with much more information, greatly increasing the amount of data stored. Room-temperature UV emission properties have recently been demonstrated from ZnO epitaxial films, microcrystalline thin

films, and nanoclusters [2]. In addition, low cost, high chemical flexibility and low threshold intensity make ZnO nanostructures an ideal candidate for commercial miniaturized laser light sources [3].

Owing to these promising applications, one-dimensional ZnO nanostructures such as nanowires [3], nanobelts [4,6], nanotubes [5], and nanodendrites [6] have been synthesized by a variety of methods. However, most methods are relatively complicate and have low yield, not suitable for commercial production. The traditional approaches to synthesize one-dimensional ZnO nanostructures are usually by means of a vapor-phase transport process with the assistance of metal catalysts or a template-assisted growth [3–6]. Furthermore, considering that electrical and optical properties of nanomaterials depend sensitively on both shape and size, it is important to obtain the expected shape and size in a controllable way. In this work, we describe a method to synthesize high-purity ZnO micro- and nanocrystals and nanowires in air by a controllable gas vaporizing by alloy (CGVA) method, which only includes a simple, fast process, and may be applied for commercial production.

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2. Experimental

ZnO micro- and nanocrystals were synthesized using a chemical vapor transport and condensation system developed in our lab. In a typical synthesis processes, 5 g of pure metal Zn (99.99%) or Cu–Zn (99.99%) mixed powders at certain weight ratio (Cu/Zn = 2/8, 4/6, 5/5, 6/4, 7/3, and 9/1, respectively) were put in a small alumina boat to serve as the source material. The alumina boat was then pushed to the central of the alumina tube in air atmosphere at 1250 °C and held for several minutes. After the reaction, a large amount of white powder could also be collected at the alumina boat and the downstream area of this alumina tube. A representative yield for the reactions of Cu/Zn = 6/4 was ~7.0%.

ZnO nanowires were synthesized in the same manner by oxidizing a block of brass (41.51 wt% of Zn) with the weight of 46 g. The furnace was first heated to 1250 °C and held for 30 minutes under the protection of an argon flow of 80 standard cubic centimeters per minute. Followed let the melted brass exposed to the air atmosphere and reacted for several minutes. After the reaction, the alumina tube was clogged up with a cotton-like ZnO product. The collected product in the tube weighted ~4.0 g and the yield was ~8.7%. Small brass bean remained in the alumina boat.

Morphology, structure and chemical composition of the samples were examined using an X-ray diffraction (XRD, D/max-rB, CuK α radiation), a scanning electron microscopy (SEM, Hitachi X-650) equipped with an EDS, and transmission electron microscopy (TEM, JEM-100C).

3. Results and discussion

Fig. 1 shows a typical XRD pattern of the as-synthesized white powder sample (Cu/Zn = 4/6, weight ratio). The diffraction peaks can be indexed to a hexagonal structure of ZnO with cell constants of $a = 3.24$ and $c = 5.19$ Å. No diffraction peaks produced from Cu and CuO could be found from the pattern, though there are some weak peaks from small amount of A: zinc that has not been oxidized and B: zinc nitride from the reaction of zinc and nitrogen in the air.

Further structural characterization of the products was performed using TEM and SEM. Fig. 2 shows typical SEM images of the ZnO micro- and nanocrystals. When pure Zn was used as reactant, uniform sprout-like ZnO tetrapod microstructures were obtained (Fig. 2a). When Cu was added to the Zn with the weight ratio 2/8, bullet-like product with hexagonal cylinder microstructures was achieved (Fig. 2b). However, when more proportion of Cu was added, the ZnO with tetrapod micro- and nanostructure appeared (Fig. 2c

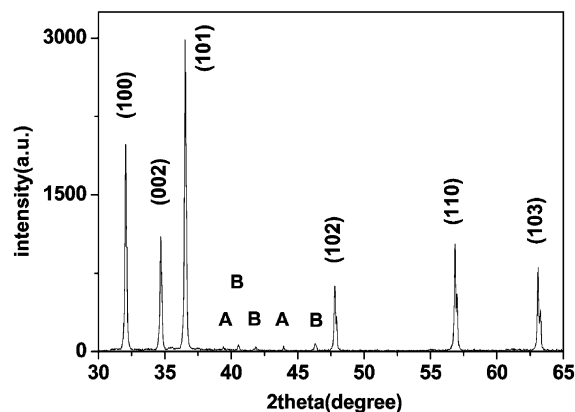


Fig. 1. XRD pattern of the as-synthesized dendrite ZnO nanocrystals (Cu/Zn = 4/6 weight ratio). Indices of the peaks are specified above the peaks (A) peaks of purity of zinc, (B) peaks of purity of zinc nitride).

Cu/Zn = 4/6, Fig. 2d Cu/Zn = 5/5, and Fig. 2e Cu/Zn = 6/4). The diameter of the arms in the tetrapod structure decreases with increasing Cu content. The thin tetrapods generally have the needle-shaped arms (Fig. 2d), while the thick ones have two kinds of uniform structures: special edge-like arms (Fig. 2c) and hexagonal cylinder arms (Fig. 2e and the inset), which are unique morphologies of ZnO nanocrystals compared to that reported previously [6]. Furthermore, while a further higher Cu proportion was used, microwires with a radiation flower (Fig. 2f, Cu/Zn = 7/3) and chrysanthemum petal-like microcrystals (Fig. 2g, Cu/Zn = 9/1) were obtained.

High yield of ZnO nanowires can be produced by oxidation of melted brass with a commercial purity (41.51 wt% of Zn) using the same CGVA method. Fig. 3 shows the typical SEM and TEM images of these ZnO nanowires. Determined from TEM images (Fig. 3b), the diameter of the ZnO nanowires varied from 10 to 150 nm. The observed variation in diameter may be related to the inhomogeneous sizes of the nuclei of the oxide nanowires [7]. The lengths of these nanowires distributed from 3 to 10 μ m. The nanosheets and nanoscale tripods, as by-products, often appear in the products (Fig. 3a). XRD pattern confirms a hexagonal structure of ZnO (Fig. 3c). Some weak peaks from small amount of zinc and zinc nitride are also detected, same as those in Fig. 1.

Understanding the growth mechanism will be important in order to control and design nanostructures. All experiments in this study were carried out in air atmosphere. It is apparent that the synthesis of ZnO nanostructures discussed here is based on the oxidation of thermal evaporation of Zn powder under the controlled conditions. The crystal growth may be dominated mainly by the following two growth

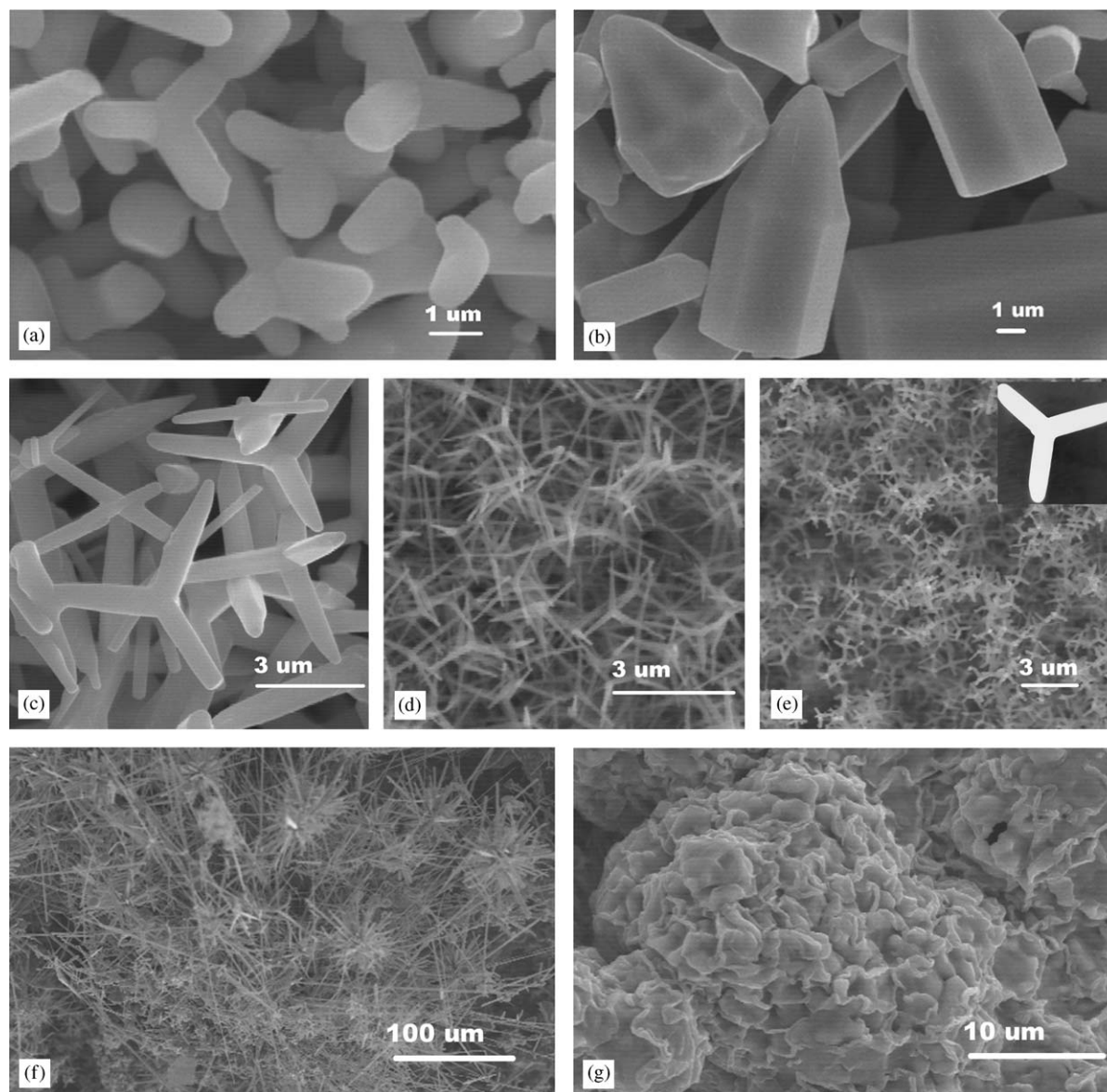


Fig. 2. SEM images of ZnO micro- and nanocrystals synthesized by (a) pure zinc and by Cu–Zn alloy at certain weight ratio of (b) 2/8, (c) 4/6, (d) 5/5, (e) 6/4, where the inset image is a TEM image of single tetrapod, (f) 7/3, and (g) 9/1—see text for details.

mechanisms: vapor–solid (VS) and catalyst-based vapor–liquid–solid (VLS) mechanism.

In the cases of the pure Zn and the Zn mixed with a small or medium proportion of Cu, there is no catalyst particles observed at the tips of arms of ZnO tetrapod structure, indicating that the growth of ZnO micro- and nanostructure cannot be dominated by the catalyst-based VLS mechanism but basically by a VS mechanism. In fact, the additive Cu functions more likely a releasing controller of metal zinc gas rather than a catalyst as reported by other groups [8].

According to the Cu–Zn binary phase diagram [9], the Cu addition increase the boiling point of Cu–Zn alloy,

therefore, Zn vapor can be released from the liquid Cu–Zn alloy slowly and continuously at the reaction temperature. In addition, because CuO can be reduced to pure Cu by Zn vapors and then be re-oxidized again, the CuO, coming from the oxidation of Cu on the surface, also helped absorb a part of Zn vapor and depressed the releasing of Zn vapor, working well in situ as an effective controller of metal gas. Previous work on the growth of ZnO gains proved a possible shape control by adjusting the ratio of the oxygen partial pressure [3,6]. Though some researches highlight the importance of Zn vapor pressure, it is actually hard to search for a simple and effective method to control

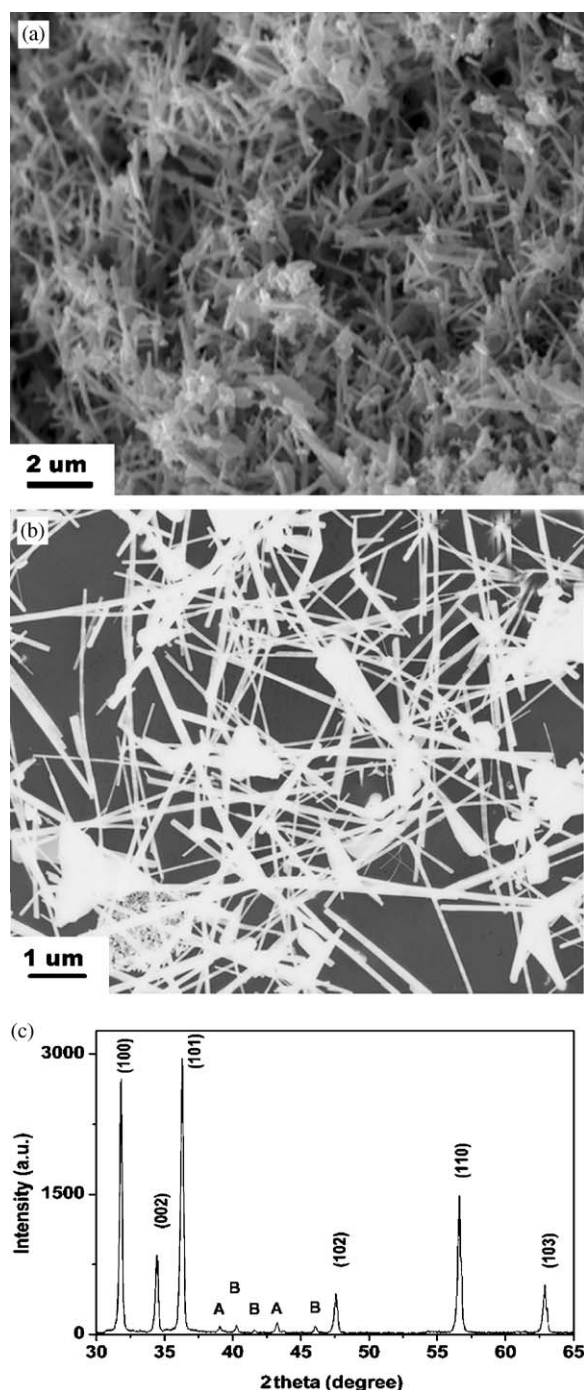


Fig. 3. (a) SEM, (b) TEM micrograph and (c) typical XRD pattern for the as-synthesized product of ZnO nanowires (A: peaks of purity of zinc, B: peaks of purity of zinc nitride).

vapor generation. However, here the presence of Cu realizes the control of Zn vapor pressure and then strongly confines the growth of the finally synthesized ZnO with various sizes and shapes by appropriately adjusting vaporization ratio during the reactions. Furthermore, experiments results show that there is a big difference of morphology of products of the

experiment of Cu/Zn = 6/4 and the experiment of brass (41.45 wt% of Zn) (as shown in Fig. 2e and Fig. 3b), though these two kinds of reactants have approximately the same proportion of Zn. We believe the difference of morphology of products is caused by the difference of alloy melting degree. Brass has higher alloy melting degree than the mixed powders of Cu/Zn and this leads to a difference of control in the releasing of metal gas and then the difference in the morphology of final products. Further detailed investigation is needed.

In addition, for the cases of Zn mixed with a large proportion of Cu, according to Cu–Zn binary phase diagram it is much difficult to form a liquid Cu–Zn alloy at this experimental temperature. We only collected some radiation-flower-like microwires with a large diameter (Fig. 2f). This morphology often exists in the microwires or nanowires synthesized in the presence of catalyst via a CVD method, which may be attributed to a catalyst-assisted VLS growth [10].

We also collected some bubble-like compact crusts at the alumina boat after the reaction when Cu–Zn alloy was used as reactant. The compositional and morphological studies for the byproducts can help us to further understand the proposed CGVA method. XRD analysis indicates that the byproducts mainly consist of ZnO and little Zn. Moreover, SEM examination shows a three-tiered structure of the compact oxide crust (Fig. 4a). The exterior of the compact crust was covered by a large amount of white ZnO micropods with a uniform diameter about 1 μm (Fig. 4b), possibly caused by the oxidation of little Zn vapor at the surface of brass. Fig. 4c shows the morphology appearing in the middle layer of the compact crust, which consists of large ZnO microcrystal particles with a regular shape. We believe that the growth of ZnO nuclei from the oxidation of a liquid Zn layer at high temperature may result in these ZnO microcrystals. Much Zn gas aggregates inside the compact oxide crust and forms the fungus-like morphology (Fig. 4d). Based on above experimental results, it is reasonable to suppose an enrichment of Zn vapor content at the surface of brass and a slow releasing of Zn vapor at the reaction temperature. Actually, when using the brass as reactant, we need to break the bubble-like crust, which obstructs the supply of oxygen, appearing at the surface at initial reaction stage to meet with the latter growth of ZnO. However, in the latter reaction, the presence of Cu seems helpful to cease the formation of the crust.

According to the TEM observation (Fig. 5), we find some un-developed ZnO multiply twinned structure [11], which explicitly shows that the following growth process: each grain within the ZnO multiply twinned particles develops to a thick branch (Fig. 5a) at the first step and then forms three thin nanowires (Fig. 5b) by the incorporation of atoms at a whisker side surface and the diffusion of atoms along the lateral surface confined

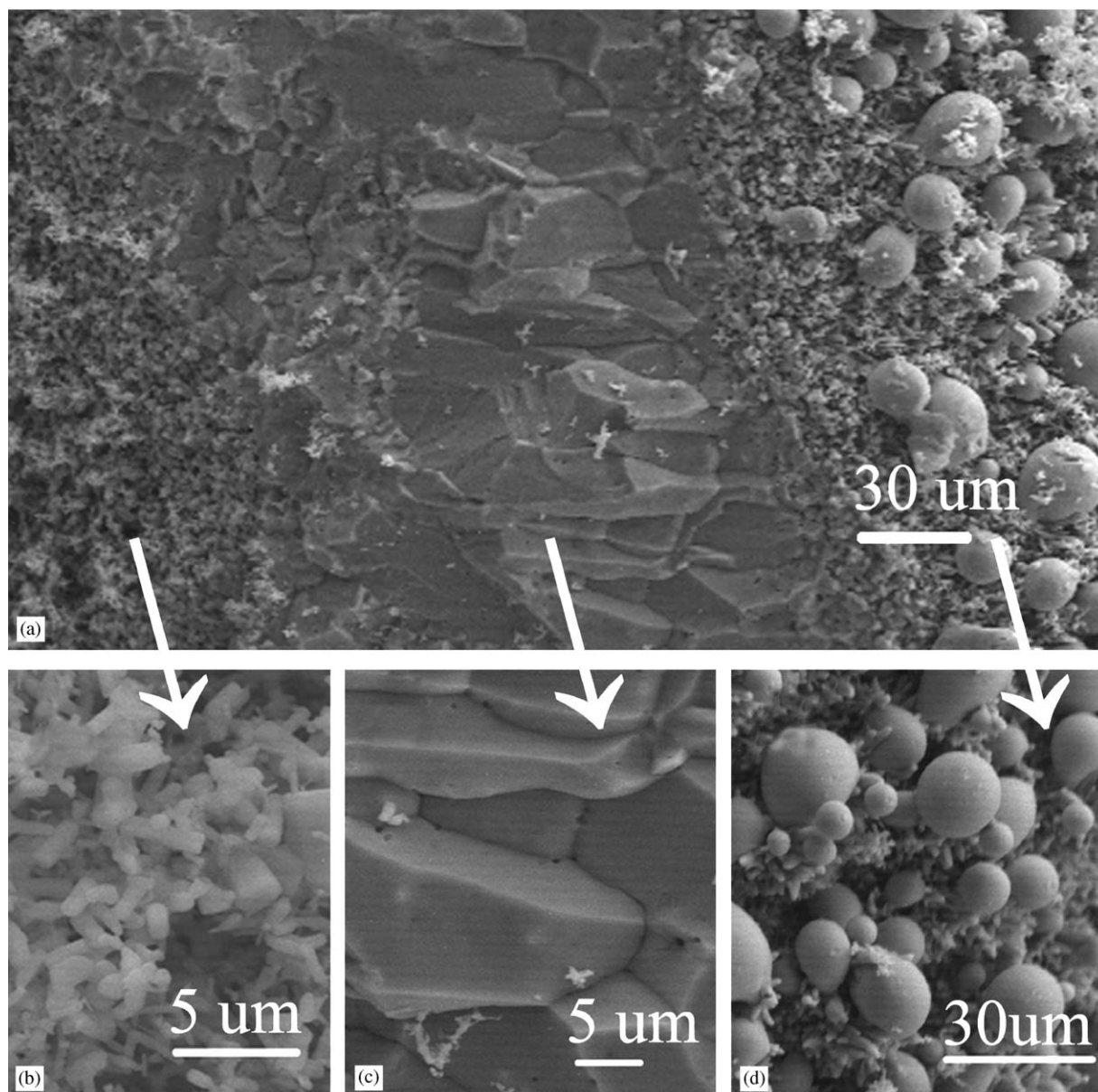


Fig. 4. SEM analysis of the compact oxide crust: (a) A three-tiered structure, (b) the exterior, (c) the middle layer and (d) interior of the compact crust.

by the fine tip. The process is in agreement with the VS whisker growth mechanism proposed by Sears [12]. Then the nanowires with a uniform diameter growing from the same ZnO twinned particles will separate at the multiply twinned joints (Fig. 5c). The dendrite nanostructures in Fig. 5 give a direct evidence for VS growth of nanowires. We believe that the diameter and length of ZnO nanowires can be controlled by the size of twinned particles [12].

It is noteworthy that our reaction process provides a fast route to synthesize ZnO nanostructures with the controlled morphology by continually transporting the vapors to the reaction area. Furthermore, because the

experiment is carried out in air atmosphere, the process of supplying reactant vapors should be feasible in a large scale. We believe the CGVA method can be well extended to other synthetic technology of nano-materials.

In summary, a simple CGVA method for producing several micro- and nanostructures of ZnO in air atmosphere in a large scale is presented. The partial pressure of the reactant metal vapors can be adjusted by varying the proportion between Zn and Cu. The presence of Cu actually has a key effect on the control of the sizes and shapes of the finally synthesized ZnO, so that a confined growth is achieved easily. Given the

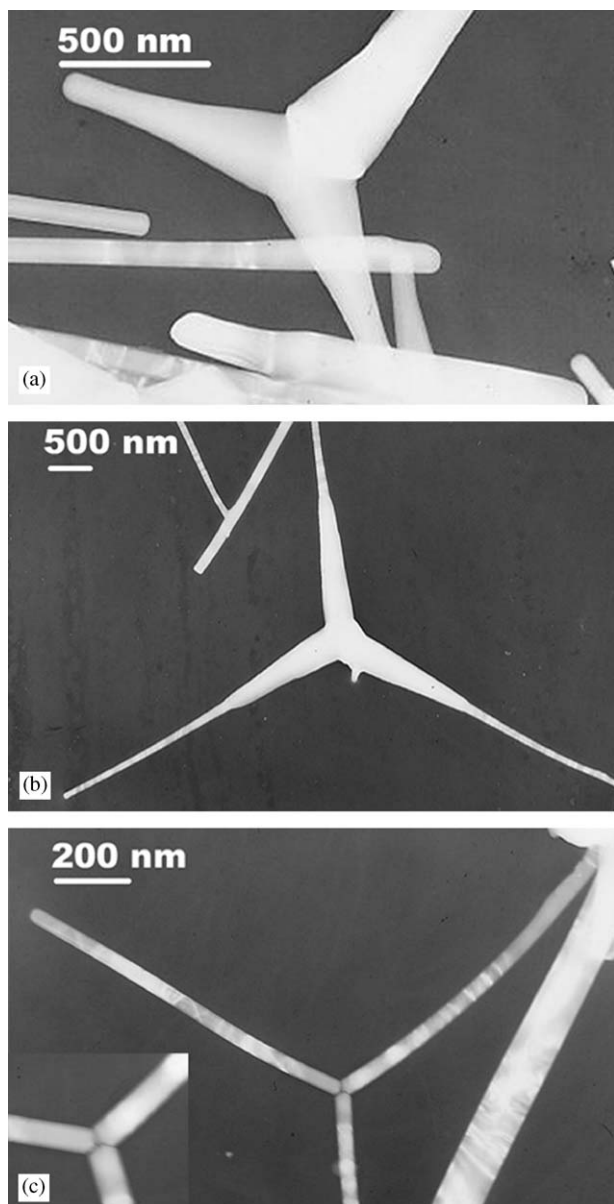


Fig. 5. TEM analysis of (a–c) several nanoscale tripods of different growth progress found in product, see text.

simplicity of the procedure and the economic advantages the materials utilized, the method described here is likely to be of interest in industrial-scale applications.

Acknowledgments

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