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# The synthesis and photoluminescence of multipod-like zinc oxide whiskers

Tao Gao<sup>1</sup>, Yanhong Huang and Taihong Wang

Institute of Physics, Chinese Academy of Sciences, PO Box 603, Beijing 100080,  
People's Republic of China

E-mail: tgaoztian@163.net

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## Abstract

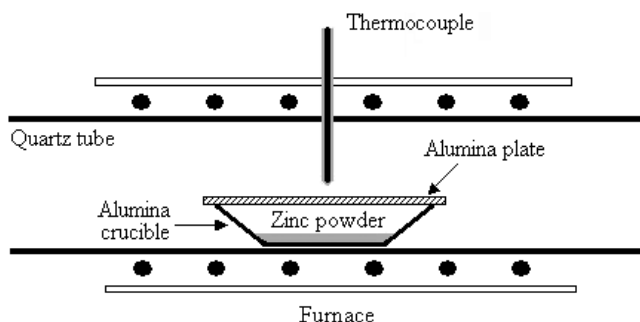
Multipod-like zinc oxide (M-ZnO) whiskers were produced in bulk quantity by the thermal oxidation of metal Zn powders that had been etched by an NiSO<sub>4</sub> aqueous solution. X-ray diffraction, scanning electron microscopy and energy dispersive x-ray analysis investigations showed that the M-ZnO whiskers had pure hexagonal structure with several needle-like legs united at a common junction. A weak photoluminescence emission band peak around 380 nm and an intensive one around 495 nm were observed in the M-ZnO whiskers, which have been attributed to the near band-edge emission and the deep-level emission related to oxygen vacancy, respectively.

## 1. Introduction

Technological applications in different areas such as catalysis, sensors, photoelectron devices, and other highly functional and effective devices are driving forces of the investigations on nanostructured semiconductors [1]. Zinc oxide (ZnO), a II–VI compound semiconductor with a wide direct band gap of 3.37 eV, has been the subject of scientific interest for a long time because of its low cost, unique electrical, optoelectronic and luminescent properties, and many important practical applications [2]. Recently, the synthesis and characterization of ZnO whiskers (or nanorods) have received great attention due to their high-temperature strength and excellent chemical stability, and promising industrial applications [3–7]. For example, it has reported that ZnO whiskers with a high aspect ratio could be used as a probing tip to develop high-resolution imaging techniques for atomic force microscopy and scanning tunnelling microscopy [8, 9].

For the synthesis of ZnO whiskers with controllable geometrical characters, many methods have been developed [3–7]. The conventional growth process of ZnO whiskers involves vapour-phase oxidation of metallic Zn powders [7, 10]. For example, Kitano *et al* [11] have

<sup>1</sup> Author to whom any correspondence should be addressed.



**Figure 1.** The apparatus employed for the synthesis of the M-ZnO whiskers. A Pt–Rh thermal couple was used to control the heat rate and temperature.

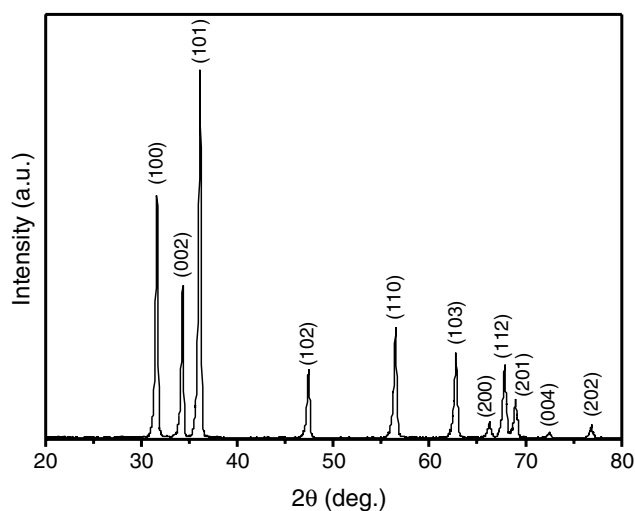
reported previously the synthesis of ZnO whiskers by oxidizing Zn particles coated with a ZnO layer mixed with zeolite as a reaction catalyst. It should be noted that the ZnO whiskers produced via the vapour-oxidation process of Zn powders possess a quite characteristic morphology, which consists of four needle-like legs united at a common core to form a tetrapod structure [10–12]. Due to their three-dimensional symmetry and the needle-like legs, tetrapod-like ZnO whiskers with radical shapes have potential applications such as enforcement when dispersed in rubbers or ceramics [10–12]. Moreover, by introducing either Sn–Zn alloy powder [13] or surface etched Zn powders [14] as starting materials, a new shape of ZnO whiskers with ‘multi-legs’ form has been fabricated. However, the nucleation and growth mechanism, and the properties of these ZnO whiskers with novel structural characteristics, are still underdeveloped, and investigations on the new synthetic methods by which the size and shape of ZnO materials can be easily varied are also necessary.

We report in this paper the synthesis and photoluminescence of multipod-like ZnO (M-ZnO) whiskers by thermal oxidation of metal Zn powders that have been etched by an  $\text{NiSO}_4$  aqueous solution. The M-ZnO whiskers, having more than four (even tens of) legs united at a common junction, have distinct morphological characteristics from the tetrapod-like ZnO whiskers reported previously [10, 11]. Since the size and morphology of materials are of great significance for their properties and consequent applications, M-ZnO whiskers with a high surface-to-volume ratio are expected to have possible applications for electro-optical devices and chemical sensors.

## 2. Experimental details

The method used for the preparation of the M-ZnO whiskers was somewhat similar to that described in [13, 14].  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  and Zn powder both of analytical grade without further purification were used as starting materials. First, 5.25 g  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  was dissolved in 200 ml de-ionized water to obtain an  $\text{Ni}^{2+}$ -containing solution. Then 6 g of zinc powder was put into the solution. After the suspension was vigorously stirred for 10 min, the precursors were filtered, washed with de-ionized water, and dried at 70 °C in air for 3 h; this was then followed by the thermal oxidation process.

The thermal oxidation apparatus used in the present work is shown in figure 1; it consisted of an electronic resistance furnace and a 25 mm inner-diameter quartz tube reactor mounted horizontally inside. The etched Zn powders (about 3 g) were placed in an alumina crucible. The crucible was covered by an alumina plate and placed inside the quartz tube at the centre of the furnace. The furnace was heated to 920 °C at a rate of 100 °C  $\text{min}^{-1}$  and held at this



**Figure 2.** XRD patterns of the produced M-ZnO whiskers. All the diffraction peaks were indexed according to the data of hexagonal ZnO (JCPDS Card No.: 36-1451).

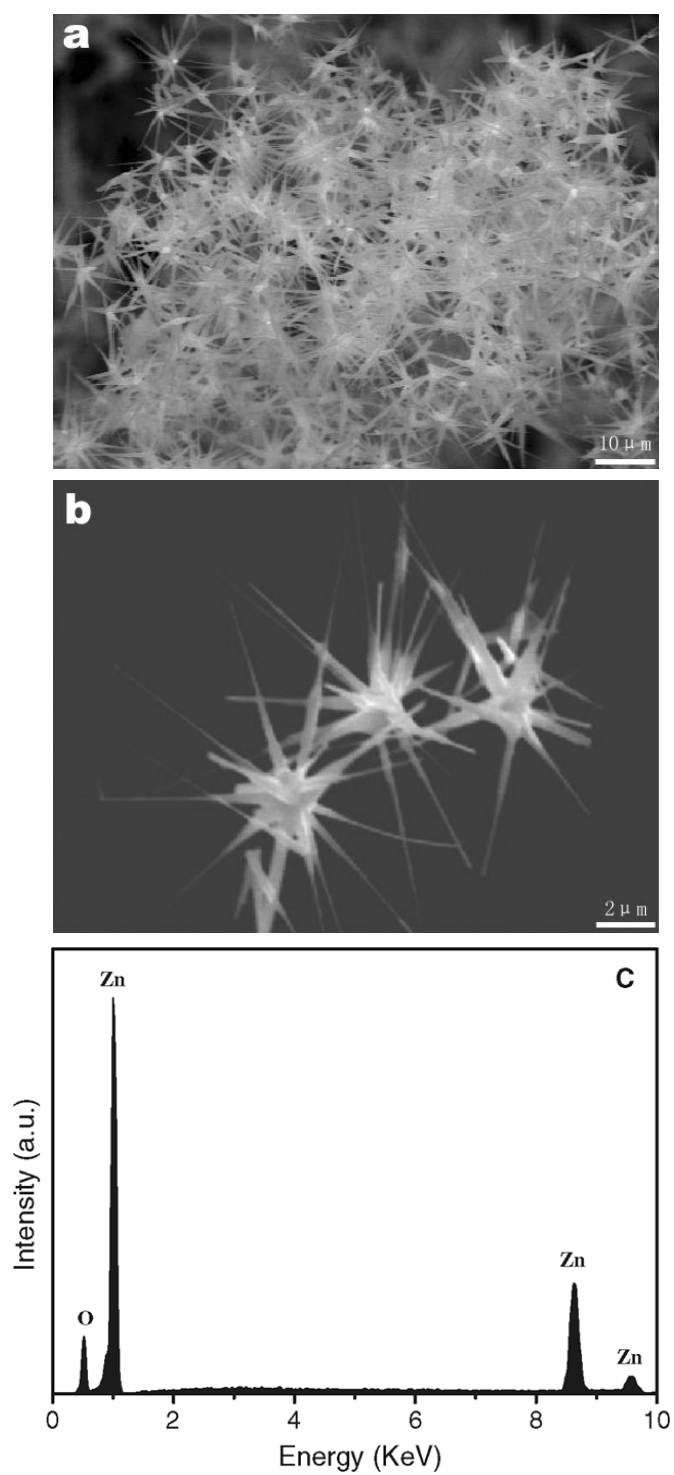
temperature for 30 min to oxidize the Zn powders. After the thermal oxidation process, the furnace was cooled naturally to room temperature. Some white wool-like products in high yield were formed on the alumina plate and the inner wall of the crucible.

The products were characterized by x-ray diffraction (XRD, D/Max-2400, Cu  $K\alpha$ ,  $\lambda = 0.1542$  nm) and scanning electron microscopy (SEM, HITACHI S-4200) equipped with energy-dispersive x-ray spectroscopy (EDX). Photoluminescence (PL) measurements were carried out on an RPM 2000 Vis-UV spectrophotometer using the He-Cd laser line of 325 nm as an excitation source at room temperature.

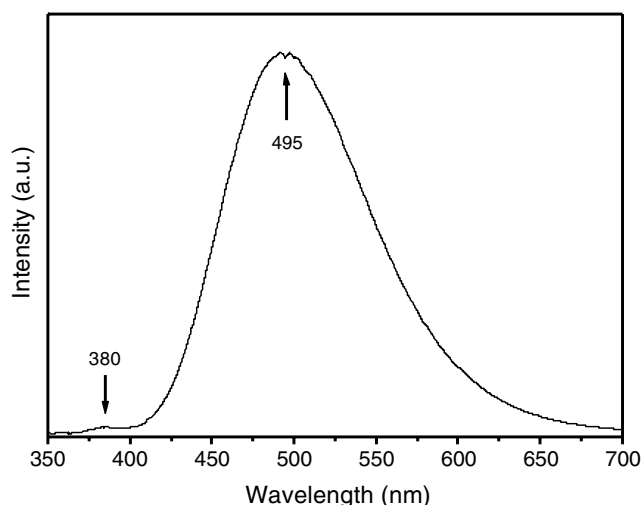
### 3. Results and discussions

The XRD pattern shown in figure 2 reveals the overall phase composition and purity of the products. All the diffraction peaks can be indexed to the hexagonal structure of ZnO with cell constants of  $a = 0.324$  nm and  $c = 0.519$  nm, which are well within the standard values for bulk ZnO (JCPDS Card No.: 36-1451). No diffraction peaks from the other crystalline forms such as Zn, Ni or nickel oxide were detected in our samples, indicating that the products are pure crystalline ZnO.

The general morphology of the products was observed by SEM and shown in figure 3(a). It can be seen that the accumulated ZnO whiskers are formed in high yield. No particles were produced and very few secondary growth components were observed. The high-resolution SEM image (figure 3(b)) shows that the produced ZnO whiskers exhibit a multipod-like morphology and more than four, that is, up to tens of needle-like legs unite at the same junction. The centring nucleus of the multipod ZnO (M-ZnO) is about 1  $\mu\text{m}$ . The length distribution of the M-ZnO whiskers' legs was measured during the SEM observation. The results reveal that most of the M-ZnO whiskers have typical leg lengths about 10  $\mu\text{m}$ , while a small number of M-ZnO whiskers having leg lengths about 20  $\mu\text{m}$  are also observed. The chemical composition of the M-ZnO whiskers was characterized by using energy dispersive x-ray analysis (EDX) as shown in figure 3(c). It is found that the M-ZnO whiskers are composed of only elemental Zn and O with molecular ratio of 55:45, implying that the obtained products



**Figure 3.** SEM images of the M-ZnO whiskers: (a) image of mass-produced M-ZnO whiskers; (b) magnified image of the M-ZnO whiskers; (c) EDX spectrum of the M-ZnO whiskers.



**Figure 4.** Room temperature photoluminescence spectrum of the M-ZnO whiskers. The excitation wavelength was 325 nm.

are pure ZnO with some localized defects, i.e. excess Zn atoms. A lot of whiskers' tips and junctions were carefully measured, and no detectable elemental Ni was found, which was similar to that reported previously by Sun *et al* [14]. However, why the elemental Ni is not detectable in the M-ZnO whiskers is still under discussion.

It is known that the potential applications of 1D nanostructures rely on their physical or chemical properties that are greatly influenced by their microstructures. A photoluminescence (PL) spectrum of the M-ZnO whiskers at room temperature was measured and is shown in figure 4. In addition to the emission in the ultraviolet (UV) region around 380 nm, an intensive broad visible emission band peak around 495 nm can be observed. The UV emission peak around 380 nm has been well understood and is attributed to the near band-edge emissions of the M-ZnO whiskers, which is similar to the other ZnO nanostructures reported previously [2, 10, 15]. The intensive broad PL emission peak at 495 nm, observed previously in the tetrapod ZnO whiskers [10, 15], has been suggested to be mainly due to the presence of various point defects such as the oxygen vacancy, which can easily form recombination centres [2, 10, 15].

However, there is no consensus in the literature on the positions of the visible emission peaks in the PL spectrum of ZnO nanostructures and their origin [16]. For example, Vanhausden *et al* [16] have assigned green emission at 510 nm to the radiative recombination of a photogenerated hole with an electron occupying the single ionized oxygen vacancy in ZnO. This transition has also been given as an explanation for the green emission at 495 nm of the tetrapod ZnO whiskers [10, 15]. On the other hand, since the luminescence properties of semiconductors are very sensitive to their surface structures [17], the surface states have also been identified as the possible cause of the visible emission in ZnO nanowires [18] and nanoparticles [19]. In the present work, it is reasonable to assume that the increase of the number of legs (multipod ZnO whiskers) would further enhance the interaction between the ZnO and the external environment, and make the luminescence more sensitive to their surface structures. Hence, it is likely that the green emission at 495 nm would be attributed to the existence of surface oxygen vacancies in the M-ZnO whiskers. During the EDX characterization, we found that there were excess Zn atoms in the M-ZnO whiskers (see figure 3(c)), which provides indirect evidence for the existence of

oxygen vacancies in the M-ZnO whiskers. Additionally, it should be pointed out that, under the same optical pumping conditions, the green emission from the M-ZnO whiskers is stronger than that from the tetrapod ZnO whiskers prepared under the same conditions by using the surface oxidized Zn powders as precursor. Such an enhancement in the green emission is attributed to the high quantity of the surface oxygen vacancies in the M-ZnO whiskers owing to their high surface-to-volume ratio compared with that of the tetrapod ZnO whiskers. Similar results have also been reported in Yang's work [2], in which the strong green emission from thicker ZnO nanowires is suggested to be due to the high concentration of surface oxygen vacancies.

It still remains an open question as how the multipod-like ZnO whiskers are formed. Owing to the similarity of their radical shapes, growth of the M-ZnO whiskers would be similar to the tetrapod ZnO whiskers [10–14]. We repeated the same thermal oxidation process several times. It was found that, when the Zn powders, which were not treated by the Ni<sup>2+</sup>-containing solution, were used as precursor, only the tetrapod ZnO whiskers were obtained, implying that the Ni<sup>2+</sup> etching treatment of the Zn powders plays an important role in the formation of the M-ZnO whiskers. During the etching process, Ni<sup>2+</sup> reacted with Zn at the solution/powder interfaces, and consequently, Zn powders with Ni or NiO particles on their surfaces would be obtained. In the subsequent thermal oxidizing process, under the present experimental conditions, Zn powders were heated above boiling temperature (about 907 °C), while the melting point of the other materials such as Ni was extremely high (about 1453 °C). It is reasonable that a small amount of the Ni or NiO particles formed during the etching treatment would be carried into the vapour phase along with the evaporation of Zn vapour, be deposited on some facets of polyhedral ZnO nuclei, and thereby serve as catalysts for the growth of needle-like ZnO legs. This process would be governed by a vapour–liquid–solid (VLS) mechanism which was similar to that reported previously for the formation of ZnO nanorods on Si substrate [20]. The growth process for the M-ZnO whiskers proposed herewith is different from that reported previously [13, 14], of which details will be discussed in a forthcoming paper.

#### 4. Conclusions

We have prepared multipod-like zinc oxide (M-ZnO) whiskers in bulk quantity by thermal oxidation of metal Zn powders that have been etched by an Ni<sup>2+</sup>-containing solution. Investigation results show that the M-ZnO whiskers having radical shapes are pure crystalline ZnO with hexagonal structure. A vapour–liquid–solid (VLS) growth mechanism has been proposed for the formation of the M-ZnO whiskers. An intensive photoluminescence emission band peak around 495 nm and a weak one around 380 nm were observed in the M-ZnO whiskers, which have been attributed to the deep-level emission related to oxygen vacancies and the near band-edge emission, respectively. These M-ZnO whiskers with a high surface-to-volume ratio are expected to have possible applications for electro-optical devices and chemical sensors.

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