Self-Assembled Growth of Tail-Like Cluster Composed of Flower-Shaped ZnO Microwires by Chemical Vapor Deposition Method

Qingyi Wang[1], Yu Qiu[1,2,*], Jiming Bian[1], Bing Li[1], ShanChun Zhang[1] and Jiacheng Luo[1]

[1]*School of Physics, Dalian University of Technology, Dalian 116024, People's Republic of China*

[2]*The Key Laboratory for Micro/Nano Technology and System of Liaoning Province, Dalian University of Technology, Dalian 116024, People's Republic of China*

Abstract: A self-assembled ZnO tail-like cluster (TC) had been successfully synthesized by a simple chemical vapor deposition method. Scanning electron microscopy observations show that ZnO TC is composed of bushy ZnO microwires with flower-shaped cross sections. Long and narrow furrows can be clearly observed on the surface of the ZnO TC. A possible growth model is proposed to discuss the formation mechanism. The analytical result indicates that the flower-shaped ZnO microwires are formed by the lateral coalescence of ZnO wires at high temperature. The room temperature PL spectrum shows a prominent UV emission band around 380 nm, and no green emission is found, implying that the unique flower-shaped ZnO microwires have high optical quality. This controlled growth of ZnO TC may have implication for potential applications in novel optoelectronic micro/nanodevices in the near future.

Keywords: ZnO, cluster, flower-shaped, coalescence.

1. INTRODUCTION

Obtaining novel morphology of micro/ nanostructures is vital for studying structure-physical property relationships as well as for realizing the novel functional micro/nanodevices, since the physical and chemical characteristics of these materials are strongly connected with their structures [1]. As a wide and direct band gap (3.37 eV) semiconductor with large exciton binding energy (60 meV), ZnO has been the main subject of current studies for its superior optical and electronic properties. These properties make it an excellent material for important applications, including solar cells [2, 3], surface acoustic waveguides [4], light emitting devices [5, 6], piezoelectric devices [7], gas sensors [8, 9] and so on. In the past decade, much effort has been invested to study one-dimensional (1D) ZnO nano/microstructures and their self-assembled novel structures [10-13] because of their unique properties, and extensive applications in electronic and optoelectronic devices. Up to now, however, no report could be found on synthesizing self-assembled ZnO tail-like cluster (TC) composed of flower-shaped ZnO microwires, which is quite important in exploiting novel properties as well as constructing novel photoelectric devices.

In this letter, we report the synthesis of self-assembled ZnO TC by a simple chemical vapor deposition (CVD) method. Studies indicated that the ZnO TC was composed of bushy flower-shaped ZnO microwires coalesced from ZnO fine wires at high temperature. The novel ZnO microwires may be applicable for the fabrication of optoelectronic devices in the near future.

2. EXPERIMENTAL PROCEDURE

2.1. Synthesis of ZnO Tail-Like Cluster (TC)

In our study, a unique ZnO TC was synthesized by a simple and reproducible CVD method in a horizontal tube furnace, consisting of a quartz tube (Ø 30 mm×40 cm), temperature controller, gas control system, and so on. A mixture of ZnO powder (purity: 99.99%) and graphite powder (with a molar ratio of 1:1) was used as the source material, which was placed at one end of the quartz tube. Then the prepared quartz tube was put in the center of the horizontal tube furnace where the temperature reaches the maximum. Then, the furnace was heated up in a constant flow of N_2. As the temperature reached up to 600°C, O_2 was then introduced into the furnace to participate in the reaction. The furnace was held at the growth temperature of 1000°C for 60 min in the constant flow of N_2 and O_2 with a flow rate of 80 and 60 sccm, respectively. At last, the furnace was turned off and cooled in air to the room temperature. After these steps, we can obtain a bridge-shaped product, as shown in the downstream zone (2~3 cm away from the source material), shown in the inset of Figure **1**.

*Address correspondence to this author at the The Key Laboratory for Micro/Nano Technology and System of Liaoning Province, Dalian University of Technology, Dalian 116024, People's Republic of China;
E-mail: yuqiu@dlut.edu.cn

E-ISSN: 2410-4701/17

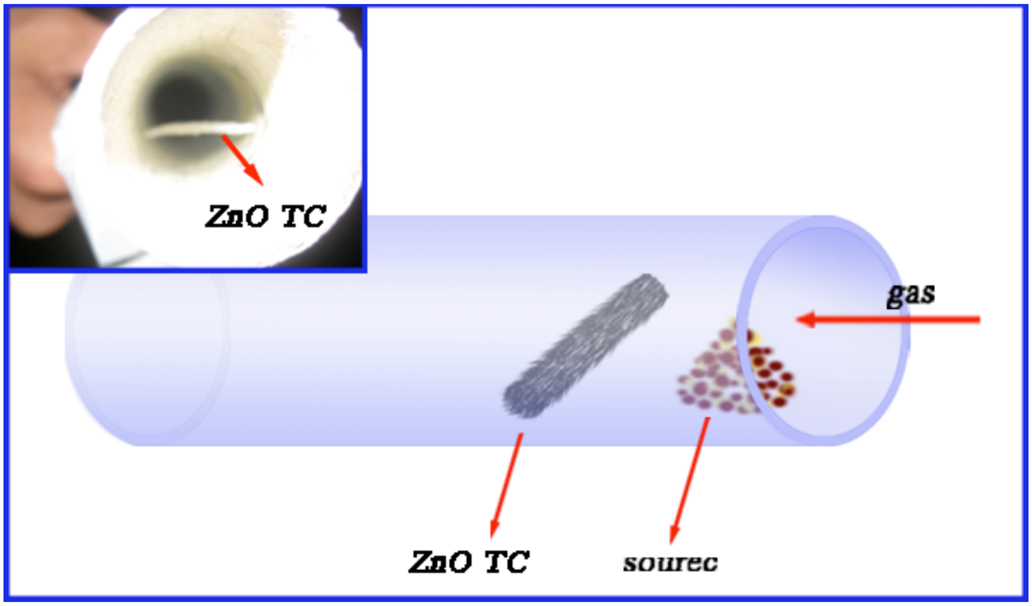

Figure 1: Schematic diagram of a ZnO TC grown inside the quartz tube; the inset displays its digital camera photograph.

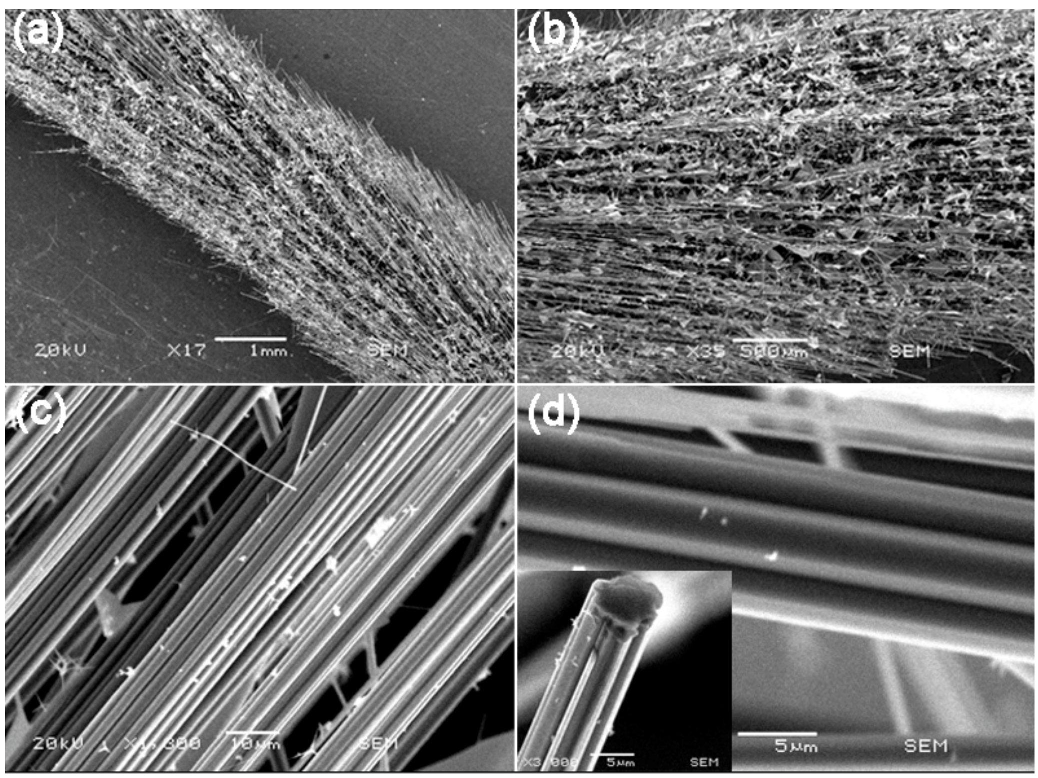

Figure 2: (**a-c**) SEM images of the as-synthesized ZnO tail-like cluster product under different magnifications; the inset of (**d**) is the SEM image of cross section of single ZnO microwire.

2.2. Characterizations

Morphological analyses were carried out by scanning electron microscopy (SEM; JEOL-6360LV). The photoluminescence (PL) measurement was also conducted with excitation at 325 nm at room temperature.

3. RESULTS AND DISCUSSIONS

Figure **2** shows SEM images of the as-synthesized ZnO tail-like cluster product under different magnifications. From Figure **2**(**a**), we can see that the as-grown product extremely resembles a tail covered with bushy “hairs”. The ZnO TC has a diameter ranging

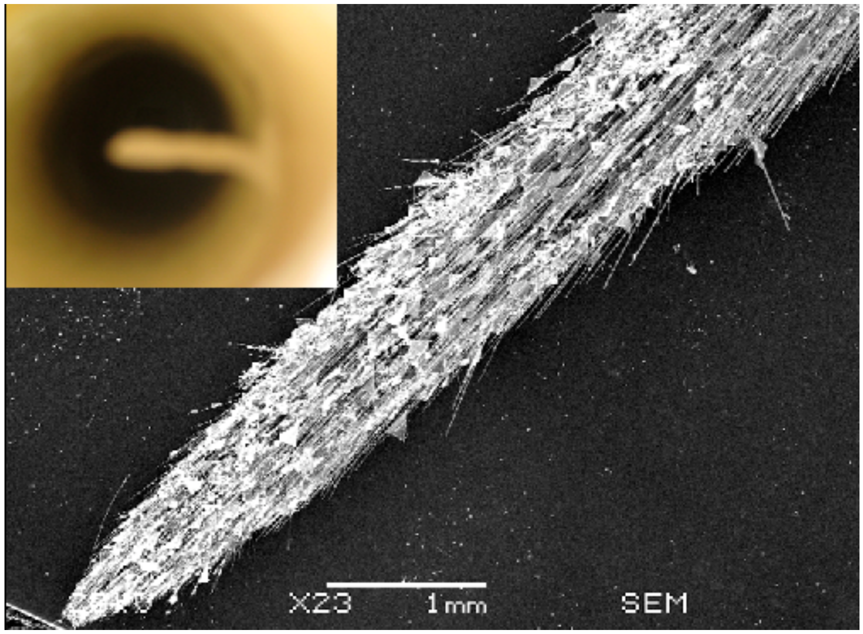

Figure 3: SEM image of the ZnO TC grown for 30 min at 1000^{o}C, the inset displays the optical picture of the ZnO TC.

from 2.5 mm to 3 mm, and a length of about 30 mm. Long and narrow furrows can be clearly observed on the surface of ZnO TC as shown in Figure **2**(**c**). Figure **2**(**d**) shows the high-magnification SEM images of the "hairs", which clearly show that the "hairs" are actually ZnO microwires with the diameter ranging from 10 μm to 15 μm. It is also interesting to see that these ZnO microwires grown from ZnO TC have deep grooves on their lateral sides, as shown in Figure **2**(**b**). To further study the structural characteristic of these unique ZnO microwires, the corresponding cross sections are also analyzed using SEM. The inset of Figure **2**(**d**) shows a typical SEM image of single ZnO microwire, from which we can see that the cross sections of the microwires are mainly flowered-shaped rather than hexagonal [14, 15]. The novel ZnO microwires reveal different structural characteristics from previous reported ZnO hexagonal microwires. The possible growth mechanism of the unique ZnO microwires and the ZnO TC will be discussed in a later section.

To understand the growth mechanisms involved in the formation of ZnO TC, another experiment was conducted. The reaction time of the experiment was reduced to 30 minutes from 60 minutes, while other reaction conditions held constant. A free-standing ZnO TC (ZnO FSTC) was observed rather than a bridge-shaped structure across the reactive tube. Figure **3** presents SEM image of the ZnO FSTC, which reveals information regarding the growth mechanism. First, ZnO TC starts from one side of the quartz tube and extends to the opposite side. Second, continuous reaction leads to growing up of ZnO TC along both the axial and lateral directions. It is obvious that the ZnO FSTC is the only product at the middle growth stages. If sufficient reactants were kept in growth atmosphere during growth, the ZnO FSTC would further develop into a bridge-shaped structure across the reactive tube as seen in Figure **1**. According to the analyses above, the possible growth mechanisms of ZnO TC can be deduced as followed: (1) nucleation on internal wall of the reacting tube; (2) the rapid growth of 1D microwires *via* vapor-solid growth process; (3) second nucleation and growth on the microwires; and (4) repeating the growth process as Step (3), which facilitates the formation of the ZnO TC and its growing up from one side of the tube to the opposite side. This process will not stop until the reactants are insufficient. The reason why the tail-like product is constructed rather than a dispersed tree-like one can be attributed to the high reaction temperature, which may be a key factor to accelerate the growth and coalescence of the ZnO microwires [16]. Figure **4** shows typical SEM image of coalesced microwires. The schematic illustration in dashed frame of Figure **4** displays the possible growth mechanism of the coalesced microwires. As the reaction time increases, ZnO fine microwires constantly grow up. The growth of the fine wires both in the axial and lateral directions easily results in the adjacent ZnO wires coalesce into a flower-shaped structure which has been clearly shown in inset of Figure **2**(**d**). And several adjacent flower-shaped microstructures may also coalesce with each other, which may account for the long and narrow furrows observed on the surface of ZnO TC. The "coalescence" phenomenon at high temperature is also detected in others' reports. Jeong

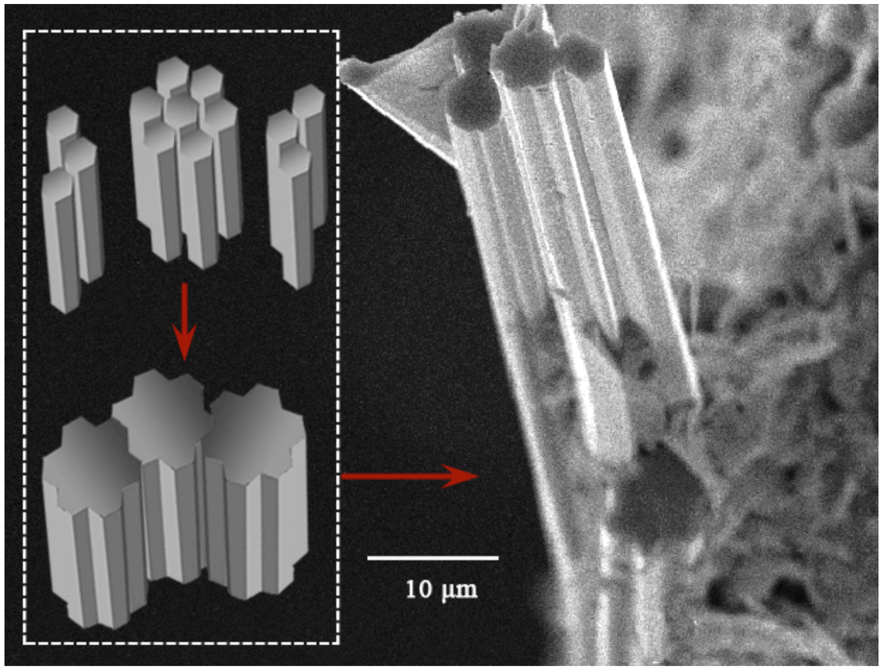

Figure 4: SEM image of the coalesced microwires; the inset in dashed frame displays schematic illustration for the possible growth mechanism of coalesced microwires.

et al. [16] synthesized single-crystalline ZnO microtubes, and suggested that the ZnO microtubes were formed by the coalescence of ZnO nanowires at a high reaction temperature. However, the exact growth mechanism is still under investigation. This controlled growth of ZnO TC may have implication for potential applications in novel optoelectronic devices in the near future.

The PL property of single ZnO microwires taken from ZnO TC and ZnO FSTC were examined respectively using a He-Cd laser (325 nm) as the excitation source at room temperature. And no obvious difference can be seen in both cases. Figure **5** shows the typical room temperature PL spectrum of both cases. Clearly, only a prominent UV emission at about 389 nm has been observed from the room-temperature PL spectrum. As we known, the UV emission, which is also called near band edge (NBE) emission, is attributed to the recombination of free excitons through an exciton–exciton collision process [17, 18]. No deep-level emission was found. Generally, the deep-level emission can be attributed to the impurities and structural defects in the crystal such as oxygen vacancies, zinc interstitials, etc., [19, 20]. Vanheusden *et al*. [21] proposed the mechanism of green emission and reported that green emission corresponds to the singly occupied oxygen vacancies in ZnO and that the emission results from the recombination of a photo-generated hole with an electron occupying the oxygen vacancies. Therefore, the photoluminescence spectrum shown in Figure **5** indicates that the ZnO microwires from ZnO TC have high optical quality.

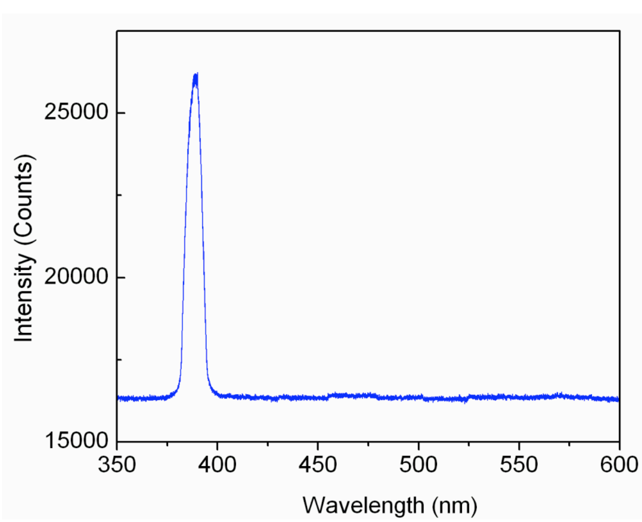

Figure 5: The typical RT PL spectrum of single ZnO microwires.

CONCLUSIONS

In summary, a self-assembled ZnO tail-like cluster (TC) has been successfully synthesized by a simple chemical vapor deposition method at a high temperature. SEM observations show that the ZnO TC with deep grooves on their lateral sides has the diameter ranging from 2.5 mm to 3 mm, and length about 30 mm, which is composed of bushy ZnO microwires with flower-shaped cross sections. The possible growth mechanism of the ZnO TC has been proposed. It was suggested that the flower-shaped microwires growth from ZnO TC was formed by the coalescence of neighboring ZnO wires due to the high temperature. The photoluminescence spectrum indicated that the ZnO microwires from ZnO TC had high optical quality, which may be applicable for the fabrication of novel optoelectronic devices in the near future.

ACKNOWLEDGMENTS

This work was supported by the NSFC (Project No. 61504018), Foundation of Key laboratory for Micro/Nano Technology and System of Liaoning and Province (20140405).

REFERENCES

[1] Hu JT, Odom TW, Lieber CM. Chemistry and physics in one dimension: Synthesis and properties of nanowires and nanotubes. Acc Chem Res 1999; 32: 435-445. https://doi.org/10.1021/ar9700365

[2] Baxter JB, Walker AM, Van Ommering K and Aydil ES. Synthesis and characterization of ZnO nanowires and their integration into dye-sensitized solar cells. Nanotechnology 2006; 17: S304-S312. https://doi.org/10.1088/0957-4484/17/11/S13

[3] Baxter JB and Aydil ES. Dye-sensitized solar cells based on semiconductor morphologies with ZnO nanowires. Sol Energy Mater Sol Cells 2006; 90: 607-622. https://doi.org/10.1016/j.solmat.2005.05.010

[4] Emanetoglu NW, Gorla C, Liu Y, Liang S and Lu Y. Epitaxial ZnO piezoelectric thin films for saw filters. Mater Sci Semicond Process 1999; 2: 247-252. https://doi.org/10.1016/S1369-8001(99)00022-0

[5] Ryu YR, Lee TS, Lubguban JA, White HW, Kim BJ, et al. Next generation of oxide photonic devices: ZnO-based ultraviolet light emitting diodes. Appl Phys Lett 2006; 88: 241108. https://doi.org/10.1063/1.2210452

[6] Hwang DK, Kang SH, Lim JH, Yang EJ, Oh JY, et al. p-ZnO/n-GaN heterostructure ZnO light-emitting diodes. Appl Phys Lett 2005; 86: 222101. https://doi.org/10.1063/1.1940736

[7] Wang ZL. The new field of nanopiezotronics. Mater. Today 2007; 10: 20-28. https://doi.org/10.1016/S1369-7021(07)70076-7

[8] Suchea M, Christoulakis S, Moschovis K, Katsarakis N and Kiriakidis G. ZnO transparent thin films for gas sensor applications. Thin Solid Films 2006; 515: 551-554. https://doi.org/10.1016/j.tsf.2005.12.295

[9] Roy S and Basu S. Improved zinc oxide film for gas sensor applications. Bull Mater Sci 2002; 25: 513-515. https://doi.org/10.1007/BF02710540

[10] Gao PX and Wang ZL. Self-assembled nanowire-nanoribbon junction arrays of ZnO. J Phys Chem B 2002; 106: 12653-12658. https://doi.org/10.1021/jp0265485

[11] Lao JY, Wen JG and Ren ZF. Hierarchical ZnO nanostructures. Nano Lett 2002; 2: 1287-1291. https://doi.org/10.1021/nl025753t

[12] Liu F, Cao PJ, Zhang HR, Li JQ and Gao HJ. Controlled self-assembled nanoaeroplanes, nanocombs, and tetrapod-like networks of zinc oxide. Nanotechnology 2004; 15: 949-952. https://doi.org/10.1088/0957-4484/15/8/013

[13] Fang Z, Tang KB, Shen GZ, Chen D, Kong R, et al. Self-assembled ZnO 3D flowerlike nanostructures. Mater Lett 2006; 60: 2530-2533. https://doi.org/10.1016/j.matlet.2006.01.034

[14] Hu JQ, Li Q, Wong NB, Lee CS and Lee ST. Synthesis of uniform hexagonal prismatic ZnO whiskers. Chem Mater 2002; 14: 1216-1219. https://doi.org/10.1021/cm0107326

[15] Wang LS, Zhang XZ, Zhao SQ, Zhou GY, Zhou YL, et al. Synthesis of well-aligned ZnO nanowires by simple physical vapor deposition on c-oriented ZnO thin films without catalysts or additives. Appl Phys Lett 2005; 86: 24108. https://doi.org/10.1063/1.1851607

[16] Jeong JS, Lee JY, Cho JH, Suh HJ and Lee CJ. Single-crystalline ZnO microtubes formed by coalescence of ZnO nanowires using a simple metal-vapor deposition method. Chem Mater 2005; 17: 2752-2756. https://doi.org/10.1021/cm049387l

[17] Kong YC, Yu DP, Zhang B, Fang W and Feng SQ. Ultraviolet-emitting ZnO nanowires synthesized by a physical vapor deposition approach. Appl Phys Lett 2001; 78: 407-409. https://doi.org/10.1063/1.1342050

[18] Thongtem T, Phuruangrat A and Thongtem S. Characterization of nanostructured ZnO produced by microwave irradiation. Ceram Int 2010; 36: 257-262. https://doi.org/10.1016/j.ceramint.2009.07.027

[19] Sun Y, Ketterson JB and Wong GKL. Excitonic gain and stimulated ultraviolet emission in nanocrystalline zinc-oxide powder. Appl Phys Lett 2000; 77: 2322-2324. https://doi.org/10.1063/1.1316069

[20] Ong HC and Du GT. The evolution of defect emissions in oxygen-deficient and -surplus ZnO thin films: the implication of different growth modes. J Cryst Growth 2004; 265: 471-475. https://doi.org/10.1016/j.jcrysgro.2004.02.010

[21] Vanheusden K, Seager CH, Warren WL, Tallant DR, Caruso J, et al. Green photoluminescence efficiency and free-carrier density in ZnO phosphor powders prepared by spray pyrolysis. J Lumin 1997; 75: 11-16. https://doi.org/10.1016/S0022-2313(96)00096-8

Received on 24-12-2017 Accepted on 28-12-2017 Published on 31-12-2017

DOI: http://dx.doi.org/10.15377/2410-4701.2017.04.1