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The growth mechanism and PL performance of Bat-like ZnO Nanorods

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Abstract. Bat-like ZnO nanorods were prepared by evaporation of Zn powders without any catalyst. The length of nanorods ranged from several micrometers to tens of micrometers. Growth mechanism of the nanorods was discussed combining field emission scanning electron microscopy and high-resolution transmission electron microscopy results. The photoluminescence spectrum was measured by using a He-Cd laser as the excitation source (325 nm) and all the results indicated the product had perfect crystal quality.

Introduction

Integrated nanostructures of ZnO enable it to be one of the most oxide nanomaterials for investigating nanoscale physical and chemical properties, therefore, many efforts have been made to control the structure of nanocrystals by anisotropic crystal growth [1-3]. Over the pass few years, ZnO crystals with multifarious shape and size seem to emerge endlessly, such as nanopropeller arrays[4], fibers with periodic junctions[5], comblike ZnO [6], tetrapod-like ZnO nanocrystals [7, 8]. Due to the noncentral symmetry and surface polarization, more and more complicated structures of ZnO will be found in the future.

Various methods have been explored for the synthesis of diversiform ZnO nanomaterials. Among them, evaporating pure zinc powder in different conditions is a typical one. In this work, we develop an effective method for fabricating novel ZnO nanostructures, that is, bat-like ZnO nanorods and self-assembly of them. It have been found that the diameter of bat-like nanorods can be modulated from nanometers to the microscales, which may be found applications in nanoelectronics and photonics.

Experimental Details

In a typical synthesis, about 5g zinc powders (99.999%) were placed in a ceramic boat. After the boat and powders were transferred into a furnace quipped with a quartz tube, the furnace was heated to 650-700 ℃ at a rate of 35℃/min and was kept at the temperature about 2 hours. Then the furnace was cooled to room temperature. No inert gas was flow into the tube and the tube was not sealed, so the tube was filled with air.

Results and Discussion

Fig. 1 shows the representative FE-SEM images of the obtained ZnO structures. Microcrystal shaped like the bat of baseball and assembled in the form. (Fig. 1a). The diameter of the "handgrip" arranged from 100nm to 300nm while the diameter of the thick head was about 1μm to 2μm. And the length of the "bat" was several micrometers (Fig. 1b), thereby the length-diameter ratio of the ZnO bat was near

that of a real bat (~ 10). In addition to the single bat-like rods, assemblies of these crystals were also found (Fig. 1b, c). The approximate sixfold array composed of bat-like nanorods was very similar to the three-dimensional self-assembled ZnO-based heterostructure[9]. The thick head of the "bat" was hexagonal and cylindrical though the handle was not very clear. Compared to the other familiar nanostructures, the difference was that the diameters of the nanorods and the arms of the nanostructures are not uniform. Moreover, the connection way between the nanorods is also different, which may reflect the growth mechanism of the ZnO bat. We also inferred that the ZnO bat grow from the "handle" rather than the "head" by the integrated bats instead of the single bat. In most case, especially for the so-called tetrapod ZnO(T-ZnO), the nucleate point locates at the intersection of the four arms of T-ZnO. And the diameter of the arms is invariable or become narrow. It can be interpreted by the variation of supersaturation of zinc vapor. In general, the flow of oxygen is a definite value, while the supply of znic vapor is not steady. At the beginning the znic powder largely evaporated created high supersaturation ratio while the reaction went along, znic powder was used up after some time, which leads to the diameter of the arms become thinner. In this paper, our experiment may provide a new route to preparation ZnO nanorod with periodically nanostructure.

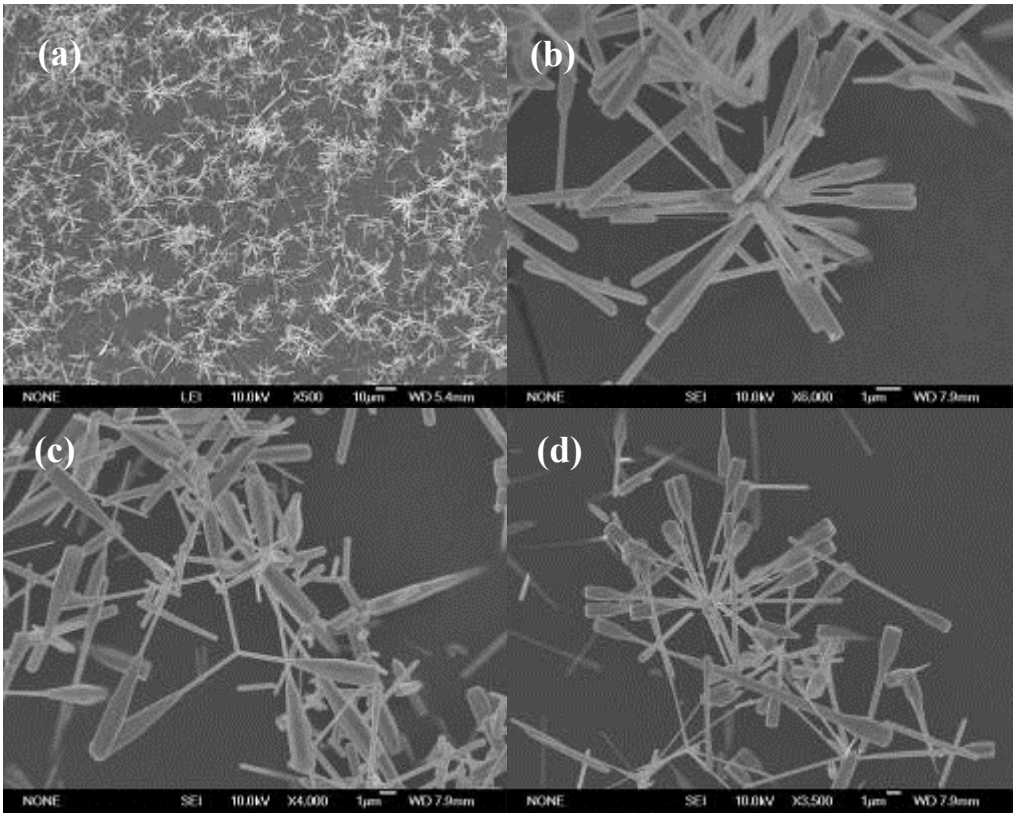

Fig. 1 Typical FE-SEM images of the bat-like ZnO crystals on carbon cloth. a) Low magnification. b), c) High magnification of self-assembly bat-like crystals. d) tripod like ZnO nanostructure.

Further structural characterization of the bat-like ZnO rods was performed using TEM. Both single bat-like ZnO crystal and ZnO bat assemble are all shown in Fig. 2. From Fig. 2a, it can be seen that a perfect ZnO "bat" with a diameter from 130nm to 240nm and a length of 3μm formed. In Fig. 2b, dendrite ZnO nanorod with broken arm was observed. We speculate that the structure was very frangible and it could not survive from the ultrasonic bath in preparing the TEM sample. The ZnO "bats" shown in Fig. 1 and Fig. 2b were jointed through the handle, while in some literature the thicker joint is a well known/familiar structure [10, 11].

A high-resolution TEM image (Fig. 2c) at the joint of the tripod shows the interface between two arms, where the boundary between the arm and core with the same wurtzite structure can be seen. Selected area electron diffraction (SAED) (Fig. 2d) on the joint and the arms of ZnO assemble shows that all the structure are single-crystalline and grow along the <001> direction. There is no znic-blende structure core observed which is consistent with early reports [12,13].

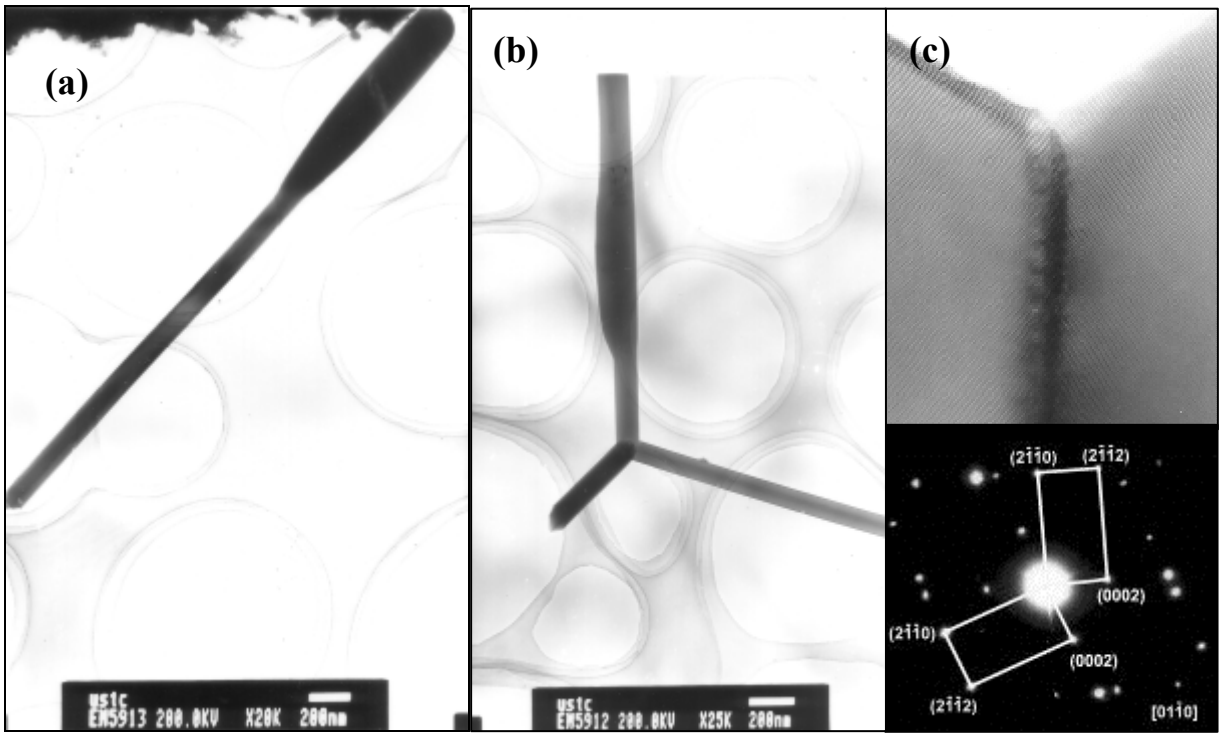

Fig. 2 TEM images and SAED of the bat-like ZnO crystals. (a) a single ZnO nanobat, (b) ZnO nanorod, (c) High resolution image of the junction of the ZnO nanorod and (d) SAED of the junction.

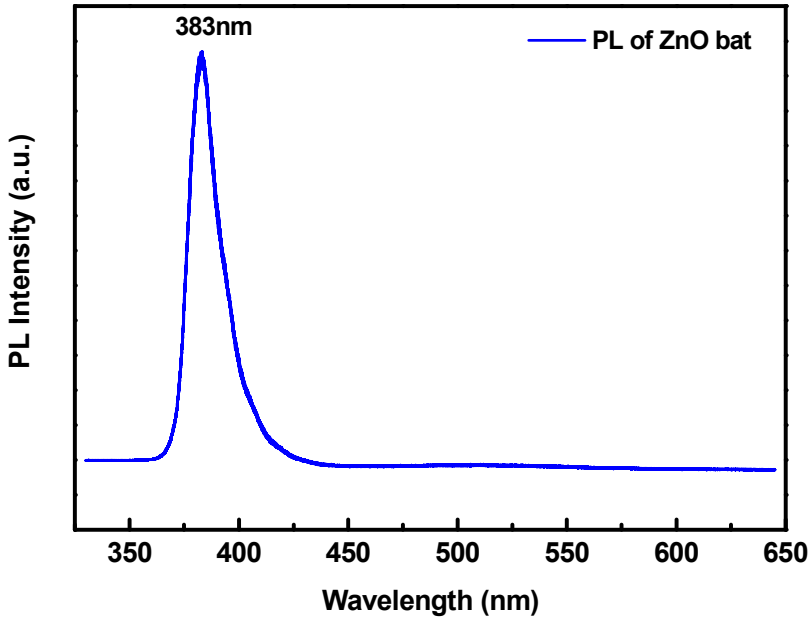

Fig. 3 PL spectrum of the bat-like ZnO nanorods.

The PL spectrum of the product was shown in Fig. 3. An strong UV emission peak at ~383 nm was observed, which generally originated from the direct recombination of the free excitons through an exciton–exciton collision process[7]. The visible emission reported in many literatures was almost disappearance indicating the ZnO bats had good crystal quality which accorded with the TEM results.

In conclusion, uniform bat-like nanocrystals were fabricated by evaporating pure zinc powder in air. HRTEM and PL experiment results indicate the nanocrystals have perfect qulity. The growth mechanism of the bat-like crystals was also discussed and the synthesis method could be used for preparing other semiconductors.

Acknowledgements

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