

Controllable Assembly of Aligned ZnO Nanowires/Belts Arrays

Hongbo Huang, Shaoguang Yang,* Jiangfeng Gong, Hongwei Liu, Junhong Duan, Xiaoning Zhao, and Rong Zhang

National Laboratory of Microstructures, Nanjing University, Nanjing 210093, China

Yinglin Liu and Yichun Liu

Center for Advanced Optoelectronic Functional Material Research, Northeast Normal University, Changchun 130024, China

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We describe a simple method to assemble ZnO nanowires/belts into highly ordered arrays. ZnCu₂ alloy was used as the Zn source, which reacted with water vapor to generate ZnO nanocrystals. The reaction was performed in a mild way, which facilitated the easy control of the reaction conditions. By simply controlling the water bath temperature and carrier gas flux in our experiments, we obtained ZnO nanowires/belts aligned to form ordered arrays. The highly ordered nature of the ZnO arrays is suggested to be related both with the polarities of the H₂O molecule and the ZnO (0001) surface. Photoluminescence (PL) microscopy revealed that the comblike structures had waveguide properties, where green light enhancement was observed at the tips of the branches. The light enhancement property reveals their promising applications as light source arrays.

Introduction

Zinc oxide has received great attention in recent years for its potential applications in electronics and photonics. Many attempts have been made to develop ZnO-based luminescent devices in the visible–UV region due to its low cost, environmental friendliness, high chemical flexibility, and low threshold intensity.^{1,2} Owing to their interesting properties and attractive applications, multiform ZnO nanostructures have been synthesized by a variety of methods.^{3–6} These days, the focus is on moving to the fabrication of aligned nanostructures because of their practical applications in many fields. Although some success has been shown on making aligned nanowires, experiments show that it is difficult to controllably align the nanostructures (such as nanowires and nanobelts). Hence finding a controllable method to orderly align nanostructures represents a significant challenge in the field of controllable assembly of nanostructures.

Some researches have highlighted that the partial pressure of zinc, as well as that of oxygen, plays an important role in ZnO crystal growth to form various nanostructures.^{7–9} This implies that controlling zinc or oxygen in the reaction is a key factor in realizing a controllable assembly of ZnO nanostructures. In view of which, we design here a simple method to assemble ZnO nanowires/belts to highly ordered arrays by a controllable vaporizing method, in which ZnCu₂ alloy was used as the Zn source to control the Zn evaporation rate, and the O source was provided by water vapor, which was carried out from the water bath by N₂ gas into the reaction region. The relative mild reaction condition maintained in our trials favored the controllable ZnO crystals growth.

Experimental Section

In our experiments, the assembly of aligned ZnO nanowires/belts arrays was realized through two-step process: growth of ZnO nanobelts and assembly of ZnO nanowires/belts arrays. Both steps were carried out by reaction of zinc with water in a horizontal tube furnace simply by controlling the water bath temperature and carrier gas flux. ZnCu₂ alloy was used as the Zn source, and several ZnCu₂ alloy wires (diameter 0.1 mm, about 3 mm high above the alloy) were used as substrate to collect the products. Water vapor was used as the oxidizer, which was carried into the reaction region by nitrogen gas through a water bath upstream. The system was purged by nitrogen gas for 20 min before heating. In the first step, the temperature of the system was raised to 900 °C within 20 min from room temperature and held for 30 min. A steady N₂ flow of 150 sccm through 20 °C water bath was introduced into the ZnCu₂ alloy region. After the reaction, bunches of white whiskers were wrapped around the alloy wires upstream of the source material. These white whiskers were ZnO nanobelts, which were further illustrated. Subsequently, in the second step, the N₂ flow and water bath temperature was respectively raised to 300 sccm and 30 °C while holding the other conditions constant. After another 30 min of reaction, the morphologies of the white whiskerlike products changed from nanobelts to comblike structures.

The as-synthesized products were characterized and analyzed by scanning electron microscopy (SEM, SEM Philips XL30) and transmission electron microscopy (TEM Philips Tecnai F20). Inductively coupled plasma (ICP) spectrometry (Jarrell-Ash, J-A1100) was used to estimate the element contents of the products. Microphotoluminescence (PL) was measured by an UV spectrophotometer (JY Company) excited by the 325 nm He–Cd laser, and the PL microscopy was characterized by a fluorescence microscope (Nikon E800) excited by the

* Corresponding author. E-mail: sgyang@nju.edu.cn.

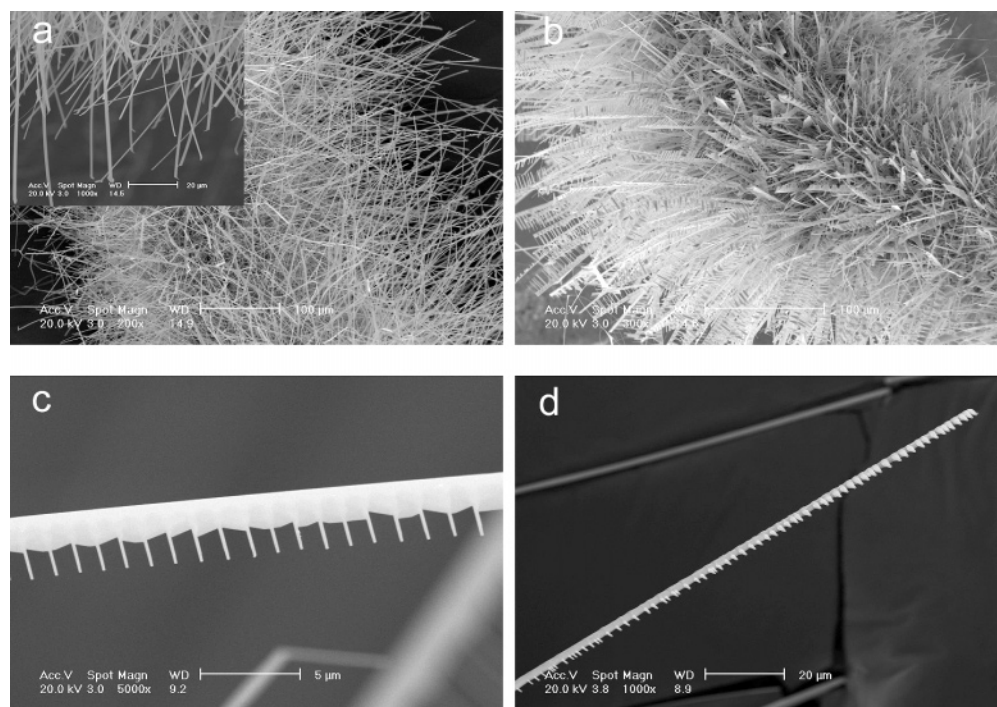


Figure 1. SEM images of the products. Key: (a) fairly uniform belts, (b) comblike structures bunches, (c) a typical comblike nanostructure, and (d) sprouts on a nanobelt.

320–380 nm light from halogen lamp. Laser Raman spectrometry (LRS, JY HR800), equipped with argon ion laser (488 nm), was performed to investigate the oxygen vacancies in the nanowires/belts samples.

Results and Discussion

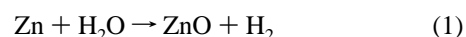
After the first step, a large number of belt bunches covered the ZnCu₂ alloy wires, although a slight amount of small comblike nanostructures less than 5% was also found in the products. Scanning electron microscopy (SEM) image (see Figure 1a) revealed that the belts have a uniform size along their length, with a typical width of 1 μ m, and extend over 0.1 mm in length. Energy-dispersive X-ray spectrometry (EDX) analysis results revealed that the belts mainly consist of Zn and O species. The only impurity observed, Cu of less than 0.1%, was found by inductively coupled plasma (ICP) spectrometry. These impurity atoms come from the evaporation of the ZnCu₂ alloy. The lattice spacings, measured by high-resolution transmission electron microscopy (HRTEM), between adjacent lattice planes perpendicular and parallel to growth direction were found to be 0.26 and 0.28 nm, respectively, which corresponds to the (0002) and (01 $\bar{1}$ 0) crystal planes in wurtzite ZnO. Along with indexing of electron diffraction pattern, it can be concluded that the belts grow along the [01 $\bar{1}$ 0] direction, with its side surfaces $\pm(0001)$ and top/bottom surface $\pm(2\bar{1}\bar{1}0)$, in agreement with other work on ZnO belts.^{10,11}

In the second step, nanowires/belts were assembled on the belts prepared in the first step. Figure 1b shows the SEM image of the products formed in this step. On any one belt, the nanowires/belts array can only distribute on one side to form a comblike structure as a result. Although few nanowires/belts emerged in the sample, a significant yield of the comblike structures is estimated—over 95%. Figure 1c shows details of a typical comblike nanostructure, in which the branches have uniform length about 2 μ m, distributed with an ideal periodicity of 1.3 μ m. The SEM image shows that the branches of a comblike nanostructure are uniform across the entire length,

even near the top of the stem, which reveals that all of the branches grow synchronously without the growth of the stem. Hence, we suggest that the belts and the branches of comblike nanostructures grew respectively in two distinct steps and that the belts prepared in the first step acted as the stems on which the new nanowires/belts grew to form the comblike morphology. This is further evidenced by the sprout structures formed at the very beginning of the second step, shown in Figure 1d. These sprouts align in an orderly manner on the same side of the nanobelt, and they can be regarded as the starting points of the branches in the following growth of the comblike structure. The mechanism of two-step growth has been proposed previously in the research on complex hierarchical nanostructures, where sets of central axial ZnO nanowires were surrounded by radially distributed nanobranches.¹²

Further characterization of the comblike structures was carried out. The TEM image is shown in Figure 2a, while the inset shows a selected area electron diffraction (SAED) pattern on the whole nanocomb, which reveals the single crystalline nature of the nanostructure. Figure 2b is an enlargement of the TEM image of a branch. The trapezoidal shape of the branch top is different to the previous cuniform or quadrate respectively reported in refs 2 and 13. The lower-left and upper-right insets of Figure 2b are HRTEM images of the marked parts recorded along the [2 $\bar{1}\bar{1}$ 0] direction. They show clearly the (01 $\bar{1}$ 0) (d = 0.28 nm) and (0002) (d = 0.26 nm) fringes, which agree with that of the belts of the first step. HRTEM as well as SAED analysis confirms that the growth front of the ZnO branches is along c axis, with side surfaces $\pm(01\bar{1}0)$, and top/bottom surfaces $\pm(2\bar{1}\bar{1}0)$.

The ZnO products are formed by the reaction of zinc atoms with water vapor at high temperature



which is well-known as a main way to prepare hydrogen gas by decomposing hot water by zinc. In the present work, this

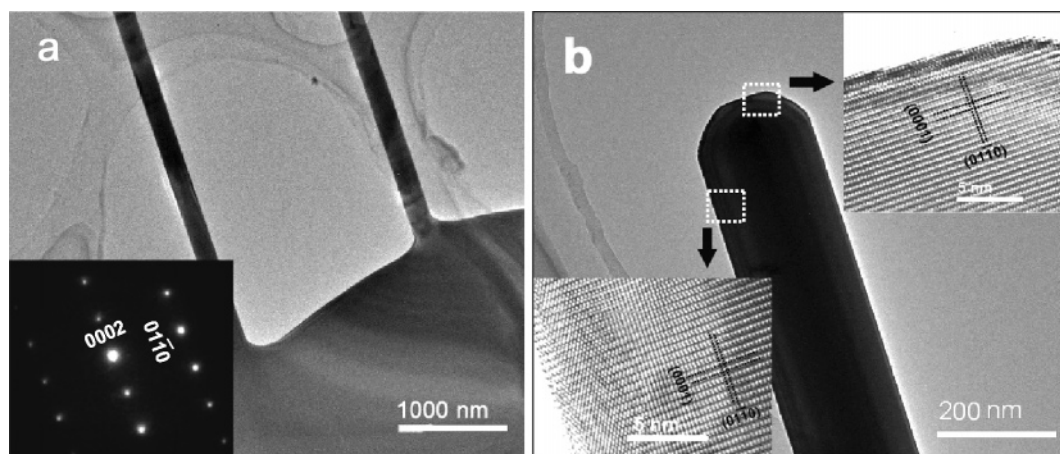


Figure 2. (a) TEM image with an insert of SAED of comb like structure. (b) Enlargement of TEM image of a branch. Insets are HRTEM images of the marked parts.

reaction is designed to be controllable in a mild way. As ZnCu_2 alloy is used as the precursor, Cu helps to control the zinc vapor to release from the alloy slowly and continuously at the reaction temperature. Additional, since overabundant O in the reaction system will obstruct the zinc atoms in evaporating from the alloy to grow ZnO nanostructures, the oxygen source is provided by H_2O molecule through substitution reaction. Compared with the other oxygen sources, such as air, water vapor can control the performance of the reaction under mild conditions, which satisfies the controllable ZnO crystal growth. Because the formation of ZnO nanostructures are very sensitive to the concentration of oxygen in the growth system, the method used to control the crystal growth was focused on the oxygen source in previous works, such as to oxidize zinc in low vacuum instead of in air^{14,15} or to react zinc with oxides.^{16,17} In this study, the method was extended to control both zinc and oxygen sources, and by control of these growth kinetics parameters, the growth behavior of ZnO nanobelts can be changed. In the first step, the fast growth rate is along the $[01\bar{1}0]$ direction and $\pm(0001)$ planes are formed as small side surfaces to form the ZnO belts. In the subsequent second step, more water vapor was introduced into the reaction region by increasing the water bath temperature and the carrier gas flux rate. At the same time, the zinc partial pressure was also influenced by the carrier gas flux. This change of growth kinetics leads to the fast growth direction shifting to the $[0001]$ direction. From the thermodynamic point of view, the $\pm(2\bar{1}10)$ planes act as the relative low energy surfaces in the reaction conditions of both two steps and finally survive as the top/bottom surface in the belts and the branches.

Furthermore, we have utilized the polarity of the H_2O molecule and ZnO in order to make the assembled nanowires/belts arrays ordered. As described previously, the side surfaces of the ZnO belts formed in the first step are $\pm(0001)$, which are polar planes. In the second step, the positively charged Zn-(0001) surface absorbs H_2O strongly due to the polarity of the water molecule. The electric field of the Zn-(0001) surface will be periodically modulated by the charge neutrality of Zn^{2+} and O^{2-} respectively from the belt surface and H_2O molecule. This may lead to an ordered absorbance of water molecule on the Zn-(0001) surface, which results in the consequent growth of ZnO crystals to form the ordered sprouts by the continuous reaction of Zn with the water molecule absorbed on the ZnO nanobelt surface. The ordered sprouts on the nanobelts, as the origin of nanowires/belts, will grow to form a comblike ZnO nanostructure as observed in the present work. Previously, a self-catalyzed process was regarded as one mechanism for the

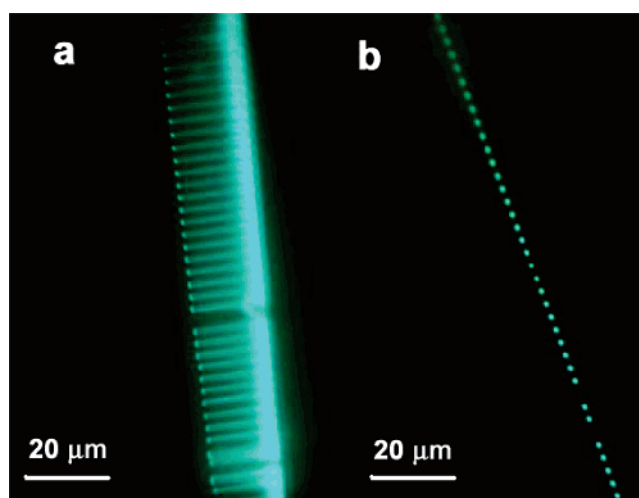


Figure 3. (a) Side view and (b) top view of PL microscopy of a ZnO comblike nanostructure.

growth of ZnO in the formation of comblike ZnO by evaporating ZnO powder in a vacuum,¹³ and our experiments suggest that the polar charged surface of ZnO belts is likely to play an important role in the assembly of nanowires/belts to comblike ZnO structures in the present process.

PL microscopic images were taken under the stimulation of a wavelength of 380 nm. Figure 3a shows a side view of a single ZnO comblike structure, which reveals its strong green PL emission property. The green PL intensity of the stem is evidently stronger than the branches. Moreover, it is interesting that an enhancement of green PL emission can be observed at the tips of the branches of the nanocomb. The top view of a nanocomb, which is shown in Figure 3b, shows an ordered light array. This property suggests a promising application as a light source array. The stronger green PL emission of the stem than the branches is caused by the larger width of the stems compared to the branches. That means a larger quantity of ZnO are excited on the stem by the exciting light, more green emission leads that a stronger green PL intensity is observed compared to the branches in the PL microscopy. However the enhancement at the tips is likely to be related to a waveguide property. Our following experimental evidence taken from PL spectra and Raman spectra further elucidate this matter. Further studies were taken at room temperature on a micro-PL spectrometer under the stimulation of He-Cd laser with wavelength of 325 nm. The spectrum obtained from the comb away from the branch

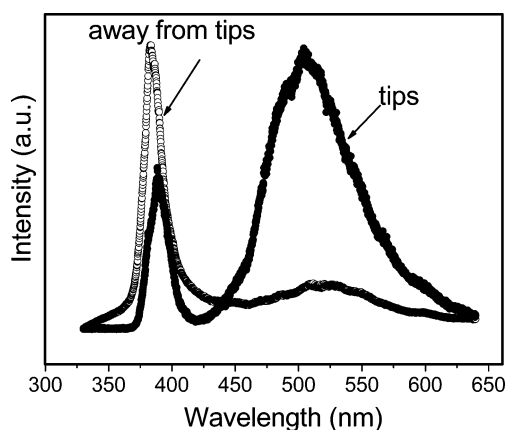


Figure 4. PL spectra of belts away from and near branch tips.

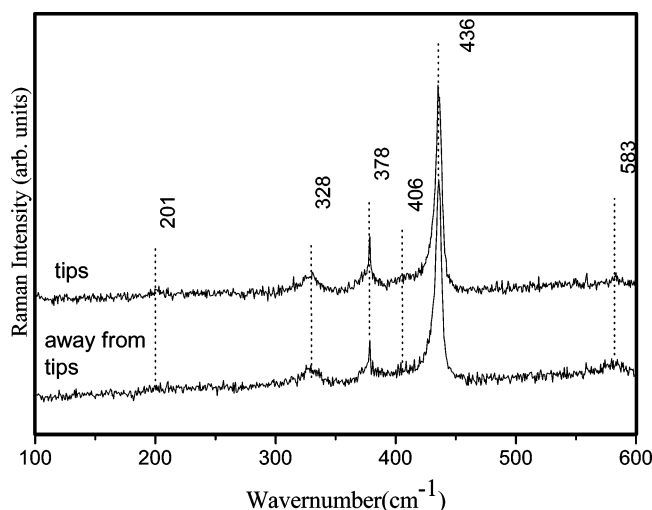


Figure 5. Raman spectra of laser focusing on branch tip and area away from branch tips.

tips consists of an intensive UV peak at 383 nm and a weak green band around 510 nm. The spectrum focused on the branch tips shows a large enhancement of the green band. It is generally accepted that the UV peak at 383 nm results from free excitonic emission of ZnO,^{18,19} while the green band arises from the recombination of a shallow trapped electron with a deep trapped hole.^{20,21}

Raman spectra focused on the tips and areas away from the tips showed no evident difference. Peaks at 378 ($A_1(\text{TO})$), 406 ($E_1(\text{TO})$), 436 (E_2), and 583 cm^{-1} ($E_1(\text{LO})$) (marked in Figure 5) are expected for bulk ZnO.^{22,23} The peaks that appear at 201 and 328 cm^{-1} have been assigned as second-order modes.²⁴ However, oxygen vacancies in ZnO nanobelts may cause the peaks at 221 and 556 cm^{-1} .²⁵ This result has been confirmed by postannealing ZnO nanobelts for 1 h in a pure oxygen atmosphere at 900 °C.²⁶ The absence of these two peaks indicated that there were oxygen vacancies in the tips or the area away from the tips. Raman spectra therefore exclude the possibility of the enhancement of the green light emission being attributed to oxygen vacancies. Our results suggest that the inhomogeneous PL emission of green light along the branches, which was characterized by the PL microscopic images and micro-PL spectrum, should instead be mainly attributed to the waveguide property as shown in nanobelts and periodic ZnO microfibers.^{27,28} When the combs were excited by UV light, a major portion of the green fluorescence was reflected by the branch surfaces and transported along them and emitted from the tips.^{29–31} Therefore, the origin of the green light enhance-

ment at the tips of the branches is structure-related rather than induced by oxygen vacancy effects.

Conclusion

In summary, we describe a simple two-step method for assembling ZnO nanowires/belts into highly ordered arrays. ZnCu₂ alloy was used as the Zn source reacting with water vapor to generate ZnO nanocrystals. The reaction was performed in a mild way, which facilitated the easy control of the reaction conditions. Simply by control of the water bath temperature and carrier gas flux in our experiments, the ZnO nanowires/belts were aligned to form ordered arrays. The highly ordered nature of the ZnO arrays is suggested to be related to both the polarities of the H₂O molecule and the ZnO (0001) surface. PL microscopy revealed that waveguide property occurred in the comblike structures, where green light enhancement was observed at the tips of the branches. The light enhancement property reveals their promising applications as light source arrays.

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