Synthesis of ZnO nanorods based on electrospinning technology

Xiuzhen Lu¹,², a, Yongqian Sun¹, *, Ziwei Jiang¹, b, Maomao Zhang¹, c, Yang Lin¹

¹SMIT Center, School of Mechatronic Engineering and Automation, Shanghai University, Shanghai, 200072, China
²Key Laboratory of Advanced Display and System Applications, Ministry of Education, Shanghai University, Shanghai, 200072, China

*Corresponding author e-mail: Email: sunyongqian@i.shu.edu.cn, a xzlu@shu.edu.cn, b ziweij@126.com, c zmm101341@163.com

Abstract. A new method for fabrication of ZnO nanorods was reported. ZnO nanorods were synthesized by electrospinning technology and heat treatment with polyvinyl alcohol (PVA) and Zinc acetate as precursor. After heat treatment of ZnO electrospun nanofibers, ZnO nanorods were obtained. Morphology of ZnO nanorods was characterized by Scanning electron microscopy (SEM). Various morphologies, such as sphere, flower and plane composed of ZnO nanorods were observed. Transmission electron microscopy (TEM) images demonstrated ZnO nanorods are a single crystalline structure with a diameter of 100-180 nm. The hexagonal wurtzite structure of ZnO nanorods was determined by X-ray diffraction (XRD) pattern and Raman spectra.

1. Introduction
ZnO 1D nanostructure have attracted remarkable attention in research because of its unique physical properties and wide range of potential applications in functional devices such as optoelectronics devices, sensors, solar cell [1-4] etc. Various synthesis methods have been utilized to fabricate ZnO nanorods including hydrothermal method, vapour deposition process, aqueous solution method, arc discharge method, electrochemical deposition and microwave deposition technology [5-10]. However, these methods lack suitability for large area or mass production of ZnO nanorods. Therefore, it is desirable to develop a new technology for mass and large area fabrication of ZnO nanorods.

Electrospinning technology was explored to be used in textile field firstly. However, it becomes a promising technique for functional devices and biomedical engineering due to its physical scale in recent years. Moreover, it is considered to be a simple and economical technique and suitable to produce large area materials. It is also hoped to be used in electronic devices fabrication because of its good compatibility with IC process [11]. Studies on electrospun ZnO nanofibers have been performed with different applications in sensors, solar cells and detectors [12-14] in these years.

In the present work, electrospinning technology was employed for synthesis ZnO nanorods. ZnO nanorods with different morphologies were obtained after heat treatment of electrospun ZnO nanofibers.
2. Experimental details
Polyvinyl alcohol (PVA) and Zn (CH$_3$COO)$_2$·2H$_2$O were used as the precursor for electrospinning of ZnO nanofibers. A PVA aqueous solution was prepared firstly by solving PVA in distilled water with a weight ratio of 10%. Then 0.6 g Zn (CH$_3$COO)$_2$·2H$_2$O was added into the PVA solution with constant stirring until the transparent solution was gained. Electrospinning was carried out at a voltage of 20 kV with distance of 20 cm between the tip of capillary and the Aluminum foil at room temperature. After dried at 120 °C for 1 hour, the composite nanofibers were calcined at 500 °C in air to obtain ZnO nanofibers. In order to get ZnO nanorods, ZnO electrospun nanofibers were squeezed and then subjected to heat treatment in air at 100, 300 and 500 °C for 1, 3, 5, 7, 9 hours respectively. SEM, TEM, XRD and Raman spectra were used for analysis of microstructure, and morphology of ZnO nanorods.

3. Results and discussion
Figure 1 shows the SEM images of as-spun ZnO/PVA nanofibers and ZnO nanofibers after calcination at 500 °C. The network structure of nanofibers was still retained after calcination of as-spun ZnO/PVA nanofibers. The surface of the ZnO nanofibers was no longer smooth resulting from the burn-out of PVA and crystallinity of ZnO. The SEM images showed clearly that the fibers were composited of connected ZnO grains along the fibers.

SEM results of ZnO nanorods gained after subjected to heat treatment of ZnO electrospun nanofibers are shown in figure 2. ZnO nanorods instead of nanofibers were observed in all samples after heat treatment. The morphologies of these materials were various. Some of them were demonstrated as a sphere composed of nanorods, shown in figure 2 (a); some of them looked like a flower, shown in figure 2 (b, c); some of them was a plane consisting of nanorods arranged tightly or loosely, shown in figure 2 (d-f). The samples were composed of several structures. Figure 2 (g, h) shows the SEM images of electrospun ZnO nanostructure after heat treatment at 500 °C for 3 and 9 hours. Some region of the two samples, region 1 and 4, looked like ZnO balls. Some region of them, region 2 and 3, demonstrated as flowers or plane.

Crystalline structure of ZnO nanorods was investigated by XRD. All the diffraction peaks, (100), (002), (101), (102), (110), (103), (200), (112), (201), (004), (102), (104), (203), in the XRD pattern shown in figure 3 (a) can be indexed to the hexagonal wurtzite ZnO. There is not obvious difference demonstrated in the XRD pattern of ZnO nanorods, such as orientation of certain plane, with that of ZnO bulk material, which resulted from the disordered array of ZnO nanorods. The Raman scattering was performed to investigate the vibrational properties of ZnO nanorods. The peaks at 330, 380, 437, and 580 cm$^{-1}$ were appeared in the Raman spectra of ZnO nanorods shown in figure 3 (b). The mode at 437 cm$^{-1}$ corresponds to E$_{2}$H phonon scattering mode, which is related to the band characteristic of wurtzite phase [15]. Therefore, the appearance of E$_{2}$H confirmed the wurtzite crystal structure of ZnO nanorods, which was in excellent agreement with XRD and SAED results. The peak at 580 cm$^{-1}$ is assigned to E$_{1}$L, which was attributed to the formation of oxygen deficiency, interstitial Zn and free
carrier [16]. The peak of E2H-2L at 330 cm\(^{-1}\) was ascribed to the multiple phonon scattering [17]. The peak at 380 cm\(^{-1}\) corresponds to A1 symmetry with TO mode.

![Figure 2](image_url)

**Figure 2.** SEM images of ZnO nanorods obtained after heat treatment. (a) ZnO ball made of nanorods. (b, c) ZnO flower made of nanorods. (d-f) ZnO plane made of nanorods. (g) ZnO nanorods annealed at 500 °C for 3 hours. The morphology of region 1 is similar with that shown in (a); The morphology of region 2 is as same as that shown in (b, c). (h) ZnO nanorods annealed at 500 °C for 9 hours. The morphology of region 3 is similar with that shown in (f); The morphology of region 4 is as same as that shown in (a).

To examine the microstructure of ZnO nanofibers and nanorods in detail, TEM observation was carried out. The results are shown in figure 4. Polycrystalline structure of a single ZnO electrospun nanofiber was demonstrated obviously in figure 4 (a, b). The fiber was composed of a large number of grains with a size ranging from 20-60 nm. And there was not a certain orientation of those grains. The selected area electron diffraction (SAED) pattern of figure 4 (b) shown in figure 4 (c) indicated the polycrystalline and wurtzite structure of the ZnO nanofibers too. The low-magnification TEM image in Figure 4 (d) showed a bunch of ZnO nanorods with a diameter ranging approximately from 100-180 nm. HRTEM image of a single ZnO nanorod is shown in figure 4 (e). The inset of figure 4 (e) is the SAED pattern of ZnO nanorod, indicating that the obtained ZnO nanorods was single-crystal structure. The lattice spacing of 0.26 nm between adjacent lattice planes gained from HRTEM of ZnO nanorod...
shown in figure 4 (f) corresponds to d spacing of the (002) planes. Therefore, the [0002] direction was the growth direction of the ZnO nanorods obtained in this study.

**Figure 3.** (a) XRD pattern of ZnO nanorods by electrospinning. (b) Raman spectra of ZnO nanorods based on electrospinning.

**Figure 4.** TEM results of ZnO nanofibers and ZnO nanorods. (a, b) Electrospun ZnO nanofibers; (c) SEAD of Electrospun ZnO nanofibers; (d) A cluster of ZnO nanorods; (e) A single ZnO nanorod, inset: SEAD of a single ZnO nanorod; (f) HRTEM image of the edge of ZnO nanorod.
4. Conclusion
ZnO nanorods with various morphologies were successfully synthesized by electrospinning technology. After subjected to heat treatment, the ZnO electrospun nanofibers with polycrystalline structure were transformed into ZnO nanorods with hexagonal wurtzite single crystalline structure. The TEM results showed that the diameter of the nanorods was approximately 100-180 nm and the growth direction of them was [0002]. This method is a well-established, low cost, large area and mass production technology for preparation of 1D nanomaterial, which has a broad prospect of applications of sensors, solar cell etc.

Acknowledgments
This work was financially supported under the National Natural Science Foundation of China (NSFC) under Grant No. 51102161. We would also like to thank Min Shao for XRD measurement and analysis and Instrumental Analysis and Research Center of Shanghai University for TEM and SEM measurement.

References
[1] Tai-You Chen, Huey-Ing Chen, Chi-Shiang Hsu et al. IEEE Electro Device Letters 2012; 33: 1486-1488.
[2] Yong Qin, Xudong Wang, Zhong Lin Wang, Nature 2008; 451:809-815.
[3] M Willander, O Nur, Q X Zhao et al. Nanotechnology 2009, 20: 332001.
[4] Noha Samir, Dina S. Eissa, Nageh K. Allam, Mater. Lett. 2014; 137: 45-48.
[5] Masood Mehrabian, Kavoos Mirabbaszadeh et al. Phys. Scr. 2013, 88: 065303.
[6] Hsin-Ming Cheng, Hsu-Cheng Hsu, Song Yang et al, Nanotechnology 2005; 16: 2882-2886.
[7] A Kathalingam, V Senthilkumar S Valanarasu and Jin-Koo Rhee, Semicond. Sci. Technol. 2012; 27: 105006.
[8] F Fang, J Futter, A Markwitz and J Kennedy, Nanotechnology 2009; 20: 245502.
[9] Chien-Te Hsieh, Shu-Ying Yang, Jia-Yi Lin, Thin Solid Film 2010; 518: 4881-4889.
[10] Y. T. Lim, J. Y. Son, J. –S. Rhcc, Ceram. Int. 2013; 39: 887-890.
[11] Björn Carlberg, Teng Wang, Johan Liu, Langmuir 2010; 26: 2235-2239.
[12] Andrzej Stafiniak, Boguslaw Boratynski et al. Sens. Actuators B 2011; 160: 1413-1418.
[13] Il-Doo Kim, Jae-Min Hong, Byong Hong Lee et al. Appl. Phys. Lett. 2007; 91: 163109.
[14] Wei Wang, Zhenyu Li, Wei Zheng et al. Sens. Actuators B 2010; 143: 754-758.
[15] Jae Young Park and Sang Sub Kim, J. Am. Cera. Soc. 2009; 92: 1691-1694.
[16] Ji Nan Zeng, Juay Kiang Low, Zhong Min Ren et al. Appl. Surf. Sci. 2002; 197-198: 362-367.
[17] Puneet Singh, Kunal Mondal, Ashutosh Sharma, J. Colloid and Interface Sci. 2013; 394: 208-215.