Synthesis of zinc oxide nanorods with different aspect ratios by solvothermal method

Lijuan Wan1,2, *, Ming Yang3

1Nanjing Vocational Institute of Transport Technology, Nanjing, China
2Jiangsu Engineering Technology Research Center for Energy Conservation and Emission Reduction of Transportation, Nanjing, China
3School of Transportation, Southeast University, Nanjing, China

*Corresponding author e-mail: bartty_ym@163.com

Abstract. The ZnO nanorods with different aspect ratios have been synthesized by solvothermal method. The as-prepared ZnO samples were characterized by BET surface area measurements, SEM and etc. By modulating the different reaction temperatures and the different precursors, the as-prepared ZnO samples with nanorods morphology and different radius were prepared and the influence of the reaction conditions are investigated. Also the different morphologies may influence the potential applications of the as-prepared ZnO.

1. Introduction
Zinc oxide (ZnO) with different shape and orientation has attracted considerable attention as a versatile material due to its potential wide ranging applications, including light-emitting diodes, dye-sensitized solar cells, catalysis, biosensor, piezoelectric nanogenerators and so forth [1–4]. Recently, ZnO, which is expected as a good photocatalyst, has been documented that the microstructures have effects on the applications such as orientation and morphological characters. To get various ZnO nanostructures such as rods, wires, combs, belts, cables, many strategies such as the wet-chemistry route [5] and vapor transport process [6, 7] have been proposed. Solvothermal or hydrothermal techniques [8, 9] are more economic than vapor phase route owing to the flexible adjustment of experimental parameters and mild synthesis conditions, which have been widely used as the effective approaches to prepare ZnO with various morphologies. In previous reports, the synthetic conditions have great effects on the microstructure of ZnO such as reaction conditions or medium and morphology-directing agents, and the morphologies of ZnO have been manipulated by some surfactants, such as PSS and etc [10–11]. Particularly, as an anion surfactant for the morphology modulation, the PSS has been widely used in the synthesis of metal oxides with different morphologies [12].

Also, with hydroxyl groups, organic solvents for the synthesis of ZnO have an important effects on the nucleation and growth of ZnO. With various morphologies, well-defined ZnO nanostructures such as nanowires, rods, tetrapods, stars, flowers and high-symmetry hierarchical nanostructures, for example, under a solvothermal treatment with zinc acetate, ZnO has been obtained with rod-like morphology and different aspect ratios by changing organic solvents with different hydroxyl groups, and compared with various low-dimensional ZnO nanostructures, the ZnO with different morphologies such as the core–shell ZnO, ZnO assemblies, those hollow three-dimension, ZnO spheres, may show large...
light-harvesting efficiencies, high photocatalytic activity, and superior collective properties. [13,14]. In this work, the ZnO nanorods with different aspect ratios have been synthesized by solvothermal method.

2. Experimental
The starting materials utilized are zinc nitrate hexahydrate(Zn(NO$_3$)$_2$·6H$_2$O, analysis purity grade) or zinc chloride, 26~28% NH$_3$·H$_2$O, absolute ethanol (Nanjing Chemical Reagent Co. Ltd.). F127 triblock polymer was purchased from Alfa Aesar and used as received without further purification. Distilled water was used throughout the experiment.

In a typical process, zinc nitrate hexahydrate or zinc chloride and F127 was dissolved in the solution containing water and ethanol with a proportion at room temperature, then the NH$_3$·H$_2$O was dropped in it. The mixture was stirred for 30 min, then transferred into Teflon-lined stainless steel autoclave, and heated at different temperatures for 6 h. These samples were treated by centrifugation and thoroughly rinsed with ethanol and water for several times, and then dried at 60 °C in an oven, and calcined at 500 °C for 4 h for subsequent characterization.

Characterization of samples: The products were characterized by X-ray diffraction (XRD) for phase identification on a Rigaku Ultima III diffractometer with Cu Kα radiation (λ = 0.154 nm, 40 kV, 40 mA) and a scan rate of 10 °·min$^{-1}$. The specific surface area of the as-prepared powders was obtained on a Micromeritics TriStar 3000 instrument (USA) at 77 K and Brunauer–Emmett–Teller (BET) equation were used to calculate the specific surface area. The morphology and microstructure were observed using a field emission scanning electron microscope (FE-SEM; NOVA NanoSEM230, FEI Ltd.) with accelerating voltage of 5 kV.

3. Results and discussion
The SEM image provides information on the morphology of as-prepared ZnO samples. From Figure 1, it can be observed that ZnO nanorods are synthesized and the radius of the ZnO nanorods is about 50~100 nm. And, the diffraction peaks from the XRD result are in good agreement with a typical wurtzite-type ZnO crystal, JCPDS No.36-1451, (hexagonal, $P6_3mc$). There were no impurity phases which were detected.

![Figure 1. SEM image of the as-prepared ZnO sample prepared using zinc chloride as the precursor.](image)

To study the influence of the reaction temperature on the morphologies of the as-prepared ZnO samples, the ZnO samples prepared at 160 or 180 °C are synthesized. From Figure 2 and Figure 3, the ZnO samples prepared at 160 °C show the nanorod morphology and the radius is about 500 nm, while the ZnO samples prepared at 180 °C show the nanorod morphology and the radius is about 900 nm and the hexagonal morphology is more obvious.
4. Conclusion
In summary, the as-prepared ZnO samples with nanorods morphology and different radius were synthesized due to the different reaction temperatures and the different precursors. The influence of the reaction conditions are studied. And the different morphologies may influence its potential applications.

Acknowledgments
This work was financially supported by Natural Science Research Projects of Universities in Jiangsu Province (19KJB610014), and High-level Scientific Research Foundation for the Introduction of Talent of Nanjing Vocational Institute of Transport Technology.
References

[1] Z.W. Zhao, X.J. Chen, B.K. Tay, J.S. Chen, Z.J. Han, K.A. Khor, A novel amperometric biosensor based on ZnO: Co nanoclusters for biosensing glucose, Biosens. Bioelectron. 23 (2007) 135–139.

[2] M.H. Huang, S. Mao, H. Feick, H.Q. Yan, Y.Y. Wu, H. Kind, E. Weber, R. Russo, P.D. Yang, Room-temperature ultraviolet nanowire nanolasers, Science 292 (2001) 1897–1899.

[3] S.W. Liu, C. Li, J.G. Yu, Q.J. Xiang, Improved visible-light photocatalytic activity of porous carbon self-doped ZnO nanosheet-assembled flowers, CrystEngComm 13 (2011) 2533–2541.

[4] Y. Qin, X. Wang, Z.L. Wang, Microfibre–nanowire hybrid structure for energy scavenging, Nature 451 (2008) 809–813.

[5] J. Zhang, S.R. Wang, M.J. Xu, Y. Wang, B.L. Zhu, S.M. Zhang, W.P. Huang, S.H. Wu, Hierarchically porous ZnO architectures for gas sensor application, Cryst. Growth Des. 9 (2009) 3532–3537.

[6] Z.L. Wang, Self-assembled nanoarchitectures of polar nanobelts/nanowires, J. Mater. Chem. 15 (2005) 1021–1024.

[7] W. Ogasawara, W. Shenton, S.A. Davis, S. Mann, Template mineralization of ordered macroporous chitin-silica composites using a cuttlebone-derived organic matrix, Chem. Mater. 12 (2000) 2835–2837.

[8] J.G. Yu, X.X. Yu, Hydrothermal synthesis and photocatalytic activity of zinc oxide hollow spheres, Environ. Sci. Technol. 42 (2008) 4902–4907.

[9] B. Cheng, E.T. Samulski, Hydrothermal synthesis of one-dimensional ZnO nanostructures with different aspect ratios, Chem. Commun. 8 (2004) 986–987.

[10] X.L. Zhang, R. Qiao, R. Qiu, J.C. Kim, Y.S. Kang, Fabrication of hierarchical ZnO nanostructures via a surfactant-directed process, Cryst. Growth Des. 9 (2009) 2906–2910.

[11] Z. Liu, X.D. Wen, X.L. Wu, Y.J. Gao, H.T. Chen, J. Zhu, P.K. Chu, Intrinsice dipole-field-driven mesoscale crystallization of core–shell ZnO mesocrystal microspheres, J. Am. Chem. Soc. 131 (2009) 9405–9412.

[12] J.G. Yu, C. Li, S.W. Liu, Effect of PSS on morphology and optical properties of ZnO, J. Colloid Interface Sci. 326 (2008) 433–438.

[13] Z.W. Pan, Z. Dai, Z.L. Wang, Nanobelts of semiconducting oxides, Science 291 (2001) 1947–1949.

[14] S.K.N. Ayudhya, P. Tonto, O. Mekasuwandumrong, V. Pavarajarn, P. Praserthdam, Solvothermal synthesis of ZnO with various aspect ratios using organic solvents, Cryst. Growth Des. 6 (2006) 2446–2450.