

### http://researchspace.auckland.ac.nz

#### ResearchSpace@Auckland

#### **Copyright Statement**

The digital copy of this thesis is protected by the Copyright Act 1994 (New Zealand).

This thesis may be consulted by you, provided you comply with the provisions of the Act and the following conditions of use:

- Any use you make of these documents or images must be for research or private study purposes only, and you may not make them available to any other person.
- Authors control the copyright of their thesis. You will recognise the author's right to be identified as the author of this thesis, and due acknowledgement will be made to the author where appropriate.
- You will obtain the author's permission before publishing any material from their thesis.

To request permissions please use the Feedback form on our webpage. <u>http://researchspace.auckland.ac.nz/feedback</u>

#### General copyright and disclaimer

In addition to the above conditions, authors give their consent for the digital copy of their work to be used subject to the conditions specified on the <u>Library Thesis Consent Form</u> and <u>Deposit Licence</u>.

#### **Note : Masters Theses**

The digital copy of a masters thesis is as submitted for examination and contains no corrections. The print copy, usually available in the University Library, may contain corrections made by hand, which have been requested by the supervisor.

# CONTROLLABLE FABRICATION OF ZINC OXIDE FUNCTIONAL NANO-/MICRO-STRUCTURE IN AQUEOUS SOLUTION

Xiaodong Yan

A thesis submitted in partial fulfillment

of the requirements for the degree of

Doctor of Philosophy in Chemical and Materials Engineering

The University of Auckland

August, 2010

Copyright 2010 by XIAODONG YAN

#### ABSTRACT

Nanostructures of ZnO show intriguing chemical, electrical, and physical properties and are promising for a broad range of applications in catalysis, electronics and photonics. Cost-effective techniques that can be used to prepare structures with controllable compositional, structural, and functional properties are fundamental to the utilization of ZnO in small scale devices with enhanced performance. Although many methods have been developed to fabricate ZnO nanostructures, systematic research on functional materials development based on ZnO is still needed as this fascinating material probably has the richest family of low-dimensional nanostructures.

The research reported in this thesis aims to develop ZnO-based nanostructural materials using a facile and low-temperature aqueous solution growth approach, to analyze their compositional, mechanical, structural, and functional properties using advanced characterization techniques, to get a better understanding of the mechanisms behind nanostructure growth, and to explore their potentials in catalytic, optical, and electronic applications.

In the first part of this thesis, low-dimensional ZnO nano-/micro-rods with tailored structural property (growth direction, aspect ratio, and surface distribution density) were grown glass substrates in aqueous solutions containing zinc salt on and hexamethylenetetramine at temperatures generally lower than 95°C. The substrates were pre-deposited with a thin layer of ZnO seeds using a magnetron sputter. The potential influences of growth conditions, typically including concentration, pH, type of zinc salt, solution temperature, reaction duration, and inorganic or organic additive, have been subjected to systematic investigation. This led to an improved understanding of the chemical reactions and nucleation/growth processes involved in the morphological evolution of ZnO-based hierarchical nanostructures.

The second part of the thesis, ZnO nano-/micro-rod arrays with controllable distribution density have been successfully synthesized by adjusting the initial pH of the weak acidic growth solution. ZnO arrays with a large inter-rod space provide a good opportunity for

I

characterizing the property of an individual rod. In this research, mechanical property tests have been successfully performed directly on a single rod without the need of any complicated sample preparation. The electronic properties of these aligned ZnO nanorod arrays have also been explored by studying the I-V characteristics of both heterojuction and homojuction p-n devices.

In next two chapters, complex ZnO structures, including nanotubes and three-dimensional ball-shaped clusters have been presented and disscussed, respectively. The morphology and microstructure of these structures were characterized by scanning electron microscopy, transmission electron microscopy, and *in-situ* cathodoluminescence. The corresponding growth mechanisms were proposed based on the analysis of the characterization results.

Chapter 7 describes that aligned ZnO nano-rod arrays were further used as templates to prepare a novel composite nanostructure. By coating these ZnO nanorods with TiO<sub>2</sub> nanowires using magnetron sputtering technique, a ZnO/TiO<sub>2</sub> core-brush structure has been successfully achieved. Their morphology and microstructure have been investigated using scanning electron microscopy, transmission electron microscopy, powder X-ray diffractometer, energy-dispersive X-ray spectroscopy and X-ray Photoelectron Spectroscopy. This composite nanostructure shows a significantly enhanced photocatalytic activity in decomposition of a typical organic dye under UV and sunlight irradiation. This new structure has many other interesting properties and may have great potential in other optoelectronic applications.

In the last part of this thesis, conclutions and future works are addressed according to the synthesis, characterization and application results.

Π

#### ACKNOWLEDGEMENTS

I would like to express my great appreciation to my supervisor, Professor Wei Gao, for giving me the opportunity to study such a fundamentally interesting and purposeful research project. I have great admiration for him and feel fortunate to work under his supervision. I would also like to thank Dr. Michael A. Hodgson for being my co-supervisor and Dr. Zhengwei Li for the great help he gave me in the early stage of my PhD study.

Special thanks are given to the members in our research group. They are: Dr. Chongwen Zou, Mr. Ray Chen, Mr. Weiwei Chen, and Ms. Jie Han, who have helped me throughout my research at the University of Auckland.

I owe gratitude to so many people that have contributed to this thesis in many different ways. The following researchers and organizations mentioned here for their valuable collaboration, technical assistance and discussion.

- Prof. Mathew R. Philips and Dr. Steven Moody, University of Technology Sydney (UTS), Australia (CL)

- Drs. Chris Glover, Lisa Giachina and Bernt Johannessen, Soft X-ray Beamline (XAS), Australia Synchrotron, Australia (XPS)

- Dr. Xiangdong Gao, Shanghai Institute of Ceramics, Chinese Academy of Sciences (SICCAS), China (DSSC)

- Prof. Jiming Bian, Dalian University of Technology, China (PL)

- Prof. Toshio Maruyama and Assoc. Prof. Shi Ji, Tokyo Institute of Technology, (Japan) (HRTEM)

- Drs. Sang Yeol Lee and Yong-Won Song, Korea Institute of Science and Technology (KIST), Korea (micro-PL)

- Dr. Michelle E. Dickinson\* and Mr. Jeffrey P. Schirer, Hysitron, Inc. U. S. A. (\* now with the University of Auckland) (Nanoindentation)

- Ms. Catherine Hobbis, (RCSMS), the University of Auckland (SEM & ESEM)

- Dr. E Emma AC Emanuelsson-Patterson and Mr. Arshid Mahamood Ali, Faculty of Engineering, the University of Auckland (UV)

- Dr. K. C. Aw and Ms. Noviana T. Salim, Faculty of Engineering, the University of Auckland (IV)

- Dr. Andrian Turner, Faculty of Science, the University of Auckland (TEM)

- Ms. Hilary Holloway, Faculty of Medical and Health Sciences, the University of Auckland (TEM)

- Dr. Hui Peng, Polymer Electronics Research Centre (PERC), the University of Auckland (EC)

- Technicians, Chemical & Materials Department, the University of Auckland

I gratefully acknowledge the Doctor Scholarship from the University of Auckland

Finally, thanks to my family, especially my wife and lovely daughter. I couldn't have done the study without their continuous and unwavering support. What more can I say but thank you for always being there with me.

# **Table of Contents**

ABSTRACT	I
ACKNOWLEDGEMENTS	III
Table of Contents	V
List of Figures	IX
List of Tables	XIV
Chapter 1. Introduction	1
1.1 Background	1
1.2 ZnO in General	2
1.2.1 Basic Properties	2
1.2.2 Crystal Structure	4
1.3 Synthesis of ZnO Nanostructures	5
1.3.1 General Growth Methods	5
1.3.1.1 Gas-phase Deposition Techniques	
<ul><li>1.3.1.2 Solution-phase Growth Methods</li><li>1.3.2 Aqueous Solution Growth</li></ul>	
<ul><li>1.3.2.1 Solution Chemistry</li><li>1.3.2.2 Growth Mechanism</li></ul>	
1.3.2.3 Limitations of Current Techniques	
1.4 Electronic, Optical and Mechanical Properties	
1.4.1 Electronic Properties	19
1.4.2 Optical Properties	21
1.4.3 Mechanical Properties	23
1.5 Application	25
1.6 Aims and Objectives of This Study	
1.6.1 Aims	
1.6.2 Objectives	
Reference	

Chapter 2. Experimental Methods	45
2.1 Growth of nanostructures	45
2.1.1 Template preparation	45
2.1.2 Growth of ZnO nano-/micro-structures	46
2.2 Structure and property characterization	47
Chapter 3. Fabrication of ZnO Nano-/Micro-Rod Arrays	49
3.1 Introduction	49
3.2 Controllable growth of ZnO nanostructures	49
3.2.1 Influence of pH on the growth of ZnO nano-/micro-rods with tunable distributed density	
<ul> <li>3.2.1.1 Experimental procedure</li></ul>	51 55 57
<ul><li>3.2.2.1 Results and discussions</li></ul>	60
<ul><li>3.2.3.1 Results and discussions</li><li>3.2.4 Influence of concentration</li></ul>	
<ul><li>3.2.4.1 Results and discussions</li><li>3.2.5 Influence of the type of zinc salt</li></ul>	
3.2.6 Influence of additive	67
3.2.7 Influence of substrate	69
3.2.8 Summary	71
Reference	72
Chapter 4. Property Characterization of ZnO Nano-/Micro-Rods	74
4.1 Mechanical property of ZnO nano-/micro-rods – Nanoindentation of individual nano-/micro-rod	74
4.1.1 Introduction	74
4.1.2 Experimental	75
4.1.3 Results and discussions	76

4.1.4 Summary	83
4.2 Photoluminescence property and electronic application $-p$ - $n$ juction device	
4.2.1 Photoluminescence property of ZnO nano/microrods	
4.2.2 Integration of ZnO nano-/micro-rods based <i>p-n</i> juction devices	
<ul><li>4.2.2.1 Device integration and characterization</li><li>4.4.3 Summary</li></ul>	
Reference	
	95
Chapter 5. ZnO Nano-/Micro-Tubes	97
5.1. Introduction	97
5.2 Experimental	98
5.3 Results and discussions	100
5.4 Summary	
Reference	
Chapter 6. Three-Dimensional ZnO Architecture - from Nano-/Micro-Rods to Ball-S Clusters	-
6.1 Introduction	
6.2. Experimental	
6.2.1 Materials preparation	
6.2.2 Materials characterization	
6.3 Results and Discussions	
6.3.1 Morphological and compositional characterization	
6.3.2 Cathodoluminescence property	114
6.3.3 Renucleation and sequential growth mechanism	114
6.3.4 Role of Al <sup>3+</sup> in renucleation and secondary growth	118
6.4 Conclusion	121
Reference	
Chapter 7. ZnO/TiO <sub>2</sub> Core-Brush Nanostructure	
7.1 Introduction	
7.2. Experimental	

7.2.1 Sample preparation	127
7.2.2 Sample characterization	
7.2.3 Photocatalysis	128
7.3. Results and Discussions	129
7.3.1 Morphology and Structure	129
7.3.2 EDS analysis	135
7.3.3 X-ray Photoelectron Spectroscopy (XPS)	136
7.3.4 Photoluminescence	137
7.3.5 UV-vis Spectrophotometry	138
7.3.6 Growth Mechanism of ZnO/TiO <sub>2</sub> Core-Brush Nanostructure	139
7.3.7 Photocatalytic Activity	141
7.4. Conclusions	145
Reference	147
Chapter 8. Conclusion and Further work	
8.1 Conclusions	152
8.2 Further works	154
Appendix	156
List of publication	147

## **List of Figures**

Figure 1-1. Crystal structure of wurtzite ZnO, (A) 3-D representation and (B) 2-D representation.

**Figure 1-2**. Relationship between supersaturation in deposition solutions, growth rate and morphology of crystallites.

**Figure 1-3**. (a) AFM image of a ZnO nanowire FET combined with the schematic of the measurement circuit. (b) *I-V* curves of a ZnO nanowire FET from  $V_g = -6$  V to 6 V; (c) Change of the transfer characteristics of two nanowires grown in different synthesis conditions. Nano wire A has a mobility of 80 cm<sup>2</sup>/V·s and carrier concentration ~10<sup>6</sup> cm<sup>-3</sup>; and nanowire B has a mobility of 22 cm<sup>2</sup>/V·s and carrier concentration ~10<sup>7</sup> cm<sup>-3</sup>. (d) A demonstration of periodic modulation of the nanowire conductance by a scanning probe. The inset is a schematic of the measurement set up.

**Figure 1-4**. a) CL image of a pure ZnO nanobullet acquired using a 385 nm emission window. CL spectra were acquired at various locations along the nanobullet as marked in the image and are plotted in (b); c) Plots showing the variations of the luminescence peak positions within a single nanobullet along its length, observed at two different accelerating voltages.

Figure 2-1. Unbalanced magnetron sputter system.

**Figure 2-2**. Containers and oven for aqueous solution growth. (A) Telflon-lined autoclave, (B) 500 ml and (C) 150 ml sealable glass bottles.

**Figure 3-1.** Typical XRD pattern of ZnO nano-/micro-rod arrays formed in acid condition (pH 3-5).

**Figure 3-2**. SEM images of as-grown ZnO nano/microrods with various density: (a) initial pH = 3; (b) initial pH = 4; (c) initial pH = 5; (d) initial pH = 6; (e) initial pH = 7; and (f) 0.1 mol/L Zn(NO<sub>3</sub>)<sub>2</sub> + 0.1 mol/L HMT at pH 6.

**Figure 3-3.** Surface distribution density of ZnO nano-/micro-rods as a function of the initial pH of the solution  $(0.025 \text{ mol/L Zn}(NO_3)_2 + 0.025 \text{ mol/L HMT})$ ; solution temperature = 95°C, growth time = 4 h.

Figure 3-4. Top view of ZnO seed template deposited by magnetron sputtering for 30min.

Insert is the cross-sectional image.

**Figure 3-5**. SEM images showing the morphological evolution of ZnO seed layers grown on Si wafers with immersion time in reaction solution. (a) 0 min; (b) 15 min; (c) 30 min; (d) 60 min; (e) 90 min and (f) 120 min. Insert are corresponding cross-section images. All scale bars are 1  $\mu$ m.

**Figure 3-6.** Changes of length (triangles) and diameter (squares) of ZnO nano/microrods versus reaction time. Error bars represent standard deviation.

**Figure 3-7**. SEM images of ZnO grown on the glass template at different temperatures: (a) 70 °C, (b) 90 °C, (c) 120 °C, (d) 150 °C, (e) 170 °C, and (f) 200 °C. Inserts are corresponding cross-section images at higher magnifications. All scale bars are 2  $\mu$ m.

**Figure 3-8**. Variation of length (triangles) and diameter (squares) of ZnO nano/microrods versus reaction temperature. Error bars represent standard deviation.

**Figure 3-9**. SEM images of ZnO grown on the glass template with different concentrations of  $Zn^{2+}$  + HMT: (a) 0.01 mol/L, (b) 0.02 mol/L, (c) 0.03 mol/L, (d) 0.04 mol/L, (e) 0.05 mol/L, and (f) 0.06 mol/L. All scale bars are 5  $\mu$ m.

**Figure 3-10**. Variation of length (triangles) and diameter (squares) of ZnO nano-/micro-rods versus solution concentration. Error bars represent standard deviation.

**Figure 3-11**. SEM images of ZnO grown on glass templates from solutions containing zinc salt and HMT (1:1): (a) Zn(NO<sub>3</sub>)<sub>2</sub>, (b) ZnCl<sub>2</sub>, (c) Zn(CH<sub>3</sub>COO)<sub>2</sub> and (d) ZnSO<sub>4</sub>.

**Figure 3-12**. SEM images and corresponding aspect ratio distributions of ZnO rods arrays: (a) and (b) formed without additive  $(Zn^{2+} + HMT)$ , (c) and (d) with citrate  $(Zn^{2+} + HMT + citrate)$ , and (e) and (f) with PEI  $(Zn^{2+} + HMT + PEI)$ .

**Figure 3-13**. SEM images of ZnO grown on different substrates: (a) cross-section and (b) top-view on ITO substrates; (c) cross-section and (b) top-view on Si; (e) high magnification image and (f) low magnification image on polymer (PPE).

**Figure 4-1**. SEM images of solution grown ZnO nano/micro-rods: (a) cross section view, and (b) top view.

**Figure 4-2**. A typical XRD pattern of as-grown ZnO nano/micro-rods showing preferential growth along the *c*-axis direction.

**Figure 4-3**. *In-situ* SPM images of topographical (0001) faces of an individual ZnO rod: (a) before indentation, (b) 2-D post-indentation, (c) 3-D post-indentation, and (d) typical load-displacement curve from indentation test.

**Figure 4-4**. In-situ SPM topographical images of  $(01\overline{1}0)$  face of an individual ZnO nano/micro-rod: (a) 2-D and (b) 3-D before indentation; (c) user-specified indent locations on a 2-D topographical *in-situ* SPM image of the  $(01\overline{1}0)$  face of a selected ZnO nano/microrod prior to testing; (d) 2-D and (e) 3-D post-indentation SPM images; (f) typical load-displacement curve.

**Figure 4-5**. SEM images of ZnO rods and corresponding room-temperature PL: (a)  $L/D \approx 4.5$  and (b) PL spectrum, (c)  $L/D \approx 3.2$  and (d) PL spectrum.

**Figure 4-6**. SEM cross-section view of the heterojuction structure: (a) after coating insulator film, (b) after deposition of top Au electrode film.

Figure 4-7. *I–V* characteristics of the Au contact on ZnO.

**Figure 4-8**. The heterojunction p-n device structures and corresponding *I-V* characteristics: (a) and (b) p-Si/n-ZnO, (c) and (d) p-GaN/n-ZnO.

Figure 4-9. *I–V* characteristics of the Au contact on p-Zn(As)O.

Figure 4-10. The homojunction p-n device structures (a) and *I-V* characteristics (b).

Figure 4-11. A semilog plot of *I-V* curve of Fig. 4-10b at forward bias.

**Figure 5-1**. (a) SEM image of ZnO nanotubes. Insert is the high magnification SEM image of an individual ZnO nanotube. (b) TEM image of a ZnO nanotube. Insert is the corresponding electron diffraction pattern for ZnO.

**Figure 5-2**. SEM images of the tubular morphology formed after different etching periods: (a) A ZnO nanorod before etching, (b) A ZnO nanorod with a pit-like top after 1 hr of etching; (c), (d) and (e) partial dissolution of the rod core after a longer etching time (2-3 hours); (f) a ZnO nanotube obtained after 4 hours of KOH (0.05 M) etching.

**Figure 5-3**. TEM images of the tubular structure at different etching period: (a) a ZnO nanorod with a hollow top, (b) ZnO tubular structure with the inner plans (correspond to Fig. 5-2c), (c) ZnO tubular structure with the partial dissolved inner plans (rectangular areas highlight), and (d) a single ZnO nanotube.

**Figure 5-4**. (a) Room temperature CL spectra obtained from the top and side surfaces of the ZnO nanotube, (b) monochromatic CL image recorded from the top surface of a nanorod, and (c) monochromatic CL image recorded from the side surface of a nanotube.

**Figure 6-1**. The sequential growth process of a ball-shaped ZnO crystal cluster: (a) a primary hexagonal ZnO nano-/micro-crystal (arrow indicate the joint section), (b) renucleation and secondary growth started from the twin section of the primary rod, (c) new branches growing along the primary rod, (d) to (f) formation of 2-D structures, (g) and (k) formation of 3-D structures, (i) all new branches grew into a similar size at the later growth stage, and (j) a final ball-shaped cluster.

**Figure 6-2**. SEM and EDS analysis results: (b) and (c) were obtained from S1 and S2, respectively, on the intermediate ZnO rod at the early growth stage (a); (e) and (f) were obtained from S3 and S4, respectively, on the 3-D cluster at the later growth stage (d). All scale bars are 2  $\mu$ m.

**Figure 6-3**. CL spectra and corresponding monochromatic CL images recorded on various ZnO crystals formed at different growth stages: (a) CL spectra, CL image of a primary rod (b), an intermediate product (c) and a final ball-shaped crystal (d), respectively. Insert are SEM images.

**Figure 6-4**. SEM images of renucleation and sequential growth of ZnO arrays perpendicular to the substrate: (a) & (b) at the early renucleation and growth stage; (c) & (d) at the intermediate growth stage, and (e) & (f) at the later growth stage.

Scheme 6-1. Illustration of the re-nucleation and sequential growth process of ZnO 3-D cluster.

**Figure 6-5**. Absorption of Al(OH)<sub>3</sub> on ZnO crystals at different growth stages: (a) the early growth stage, (b) and (c) top view of intermediate growth stages, (d) the final growth stage. (e) a typical EDS spectrum obtained from the positions where absorption of Al(OH)<sub>3</sub> precipitation was found ( as arrows indicated in a-d). All scale bars are 2  $\mu$ m.

Figure 7-1. SEM cross-sectional image of solution growth ZnO nanorods.

**Figure 7-2.** SEM images of  $ZnO/TiO_2$  core-brush nanostructures prepared with different sputtering times: (a) 30 min, low magnification; (b) 30 min, high magnification; (c) 60 min, low magnification; (d) 60 min, high magnification; (e) 90 min, low magnification; (f) 90 min, high magnification.

**Figure 7-3.** (a) TEM image of ZnO nanorods (NR), (b) the corresponding SAED pattern, (c) and (d) HRTEM images of ZnO NR.

**Figure 7-4.** TEM/HRTEM images of fine structures of  $ZnO/TiO_2$  composite structures: (a)  $ZnO/TiO_2$  nanostructure after 30 min sputtering of  $TiO_2$ , (b) 60 min, (c) 90 min, (d)  $ZnO/TiO_2$  core-brush (CB) structure with a low magnification, (e) and (f) HRTEM images of CB; inset in (f) is the corresponding SAED pattern.

**Figure 7-5.** Schematic illustrations of the 2-step preparation process of the  $ZnO/TiO_2 CB$  nanostructure.

Figure 7-6. XRD patterns of the ZnO NR and the ZnO/TiO<sub>2</sub> CB nanostructure.

Figure 7-7. EDS spectra of the ZnO NRs and the ZnO/TiO<sub>2</sub> CB nanostructures.

**Figure 7-8**. XPS spectra: (a) the ZnO NR and ZnO/TiO<sub>2</sub> CB (90 min), and (b) fine scan of Ti2p peaks.

**Figure 7-9**. Room temperature PL spectra from: (a) the ZnO NRs sample, (b) the ZnO/TiO<sub>2</sub> core-brush samples with deposition time of 60 min, and (c) with deposition time of 90 min. The insert is the curve fitting for the PL spectra of the 60 min sample.

**Figure 7-10**. UV-vis spectra of the  $TiO_2$  film,  $TiO_2/ZnO$  composite film and TiO ZnO CB nanostructures.

**Figure 7-11**. (a) UV-vis spectra of B-PGR solutions with  $ZnO/TiO_2$  CB (90 min sputtering) as a function of irradiation time; (b) photo-decomposition rate of B-PGR over different photocatalysts under UV light irradiation.

**Figure 7-12**. The linear fitting of  $\ln(C/C_0)$  vs. time for degradation curve shown in Fig. 6-9b (the blank sample is not included).

Figure 7-13. Cyclic photodegradation test using ZnO/TiO<sub>2</sub> CBs.

**Figure 7-14.** Degradation of B-PGR using different photocatalysts (insert photo) under sunlight irradiation for 3 h and the UV-vis absorption spectral change of B-PGR solution over the  $ZnO/TiO_2$  CBs (90 min) as a function of sunlight irradiation time.

# **List of Tables**

Table 1-1 Basic Chemical Properties of ZnO

 Table 1-2 Basic Physical Properties of ZnO

Table 1-3. Methodologies for ZnO deposition and growth

**Table 1-4**. Summary of different methods and results of aqueous solution growth of ZnO nano-/micro-structure

Table 3-1. Summary of experimental conditions for synthesis of ZnO nano-/micro-structure

**Table 4-1**. Hardness and Young's modulus measured on (0001) and ( $01\overline{1}0$ ) faces of an as-grown ZnO nano/micro-rod, and on nanowire/belt, epitaxial film and bulk single crystal from references (Refs.14, 26, 27)

Table 4-2. Results of Hall Effect measurement of ZnO film before and after As diffusion