

Haitao Niu
Tong Lin
Xungai Wang

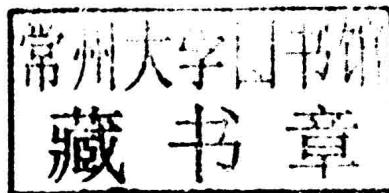
Electrospinning of Polymers for Functional Nanofibres

Fibre generators, Fibre morphologies and properties

Haitao Niu
Tong Lin
Xungai Wang

Electrospinning of Polymers for Functional Nanofibres

**Fibre generators, Fibre morphologies and
properties**



Impressum / Imprint

Bibliografische Information der Deutschen Nationalbibliothek: Die Deutsche Nationalbibliothek verzeichnet diese Publikation in der Deutschen Nationalbibliografie; detaillierte bibliografische Daten sind im Internet über <http://dnb.d-nb.de> abrufbar.

Alle in diesem Buch genannten Marken und Produktnamen unterliegen warenzeichen-, marken- oder patentrechtlichem Schutz bzw. sind Warenzeichen oder eingetragene Warenzeichen der jeweiligen Inhaber. Die Wiedergabe von Marken, Produktnamen, Gebrauchsnamen, Handelsnamen, Warenbezeichnungen u.s.w. in diesem Werk berechtigt auch ohne besondere Kennzeichnung nicht zu der Annahme, dass solche Namen im Sinne der Warenzeichen- und Markenschutzgesetzgebung als frei zu betrachten wären und daher von jedermann benutzt werden dürften.

Bibliographic information published by the Deutsche Nationalbibliothek: The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available in the Internet at <http://dnb.d-nb.de>.

Any brand names and product names mentioned in this book are subject to trademark, brand or patent protection and are trademarks or registered trademarks of their respective holders. The use of brand names, product names, common names, trade names, product descriptions etc. even without a particular marking in this works is in no way to be construed to mean that such names may be regarded as unrestricted in respect of trademark and brand protection legislation and could thus be used by anyone.

Coverbild / Cover image: www.ingimage.com

Verlag / Publisher:

LAP LAMBERT Academic Publishing

ist ein Imprint der / is a trademark of

AV Akademikerverlag GmbH & Co. KG

Heinrich-Böcking-Str. 6-8, 66121 Saarbrücken, Deutschland / Germany

Email: info@lap-publishing.com

Herstellung: siehe letzte Seite /

Printed at: see last page

ISBN: 978-3-659-31906-8

Zugl. / Approved by: PhD, Geelong, Deakin University, 2010

Copyright © 2013 AV Akademikerverlag GmbH & Co. KG

Alle Rechte vorbehalten. / All rights reserved. Saarbrücken 2013

Haitao Niu
Tong Lin
Xungai Wang

Electrospinning of Polymers for Functional Nanofibres

Dedication

This work is dedicated to my parents, Mr. Ximing Niu and Mrs. Guihua Zhang, and my wife, Hua Zhou, and my son Zichen Niu, for their endless love and support!

Acknowledgements

A lot of people have supported my research work. First and foremost, I would like to express my sincerest gratitude to my supervisor, Professor Tong Lin, for his indefatigable guidance and encouragement from the first day of my study. His support is so important that I would not have accomplished this book without it.

I also would like to thank another supervisor, Professor Xungai Wang, for giving me such a marvellous opportunity to study at Deakin and lots of helpful suggestions to my works.

I would like to thank Dr Jian Fang and Mr Xin Wang for assisting my project and for providing the opportunity for me to contribute to their projects, which has resulted in joint publications.

My special thanks go to Mr. Chris Hurren, Mr. Graeme Keating, and Dr. Xin Liu. Their knowledge and patience were very helpful to me. Without their help I couldn't have obtained many of my results.

I also thank Dr. Wendy Tian and Dr. Zongli Xie from CSIRO for the DSC and BET analysis, Mr. Rod Mackie and Mr. Finlay Shanks from Monash University for XRD and Raman analysis, Dr. Robert Jones from La Trobe University for XPS analysis, my fellow researchers Dr Yan Zhao and Miss Yaqiong Zhou for TG and mechanical analysis, and visiting student Mr Yuhua Xue from Zhejiang University for some of the TEM analysis.

I wish to thank all my friends in the Centre for Material and Fibre Innovation at Deakin University. I really enjoyed the wonderful time with them.

Finally, I wish to express my gratitude to my dear parents and my wife and lovely son for their support and trust for my study and life.

Abstract

Electrospinning is very useful method to produce polymeric nanofibres with controlled fibre fineness and morphology. Electrospun nanofibre membranes can be used in diverse applications due to their porous structure, high surface area and tuneable functionality. In spite of big improvements in this technology, some problems associated with electrospinning still remain unsolved. Needle electrospinning typically has a low production rate, which has been the main obstacle to the commercialisation of electrospun nanofibres. Needleless electrospinning has much higher nanofibre productivity than needle electrospinning. However, how the spinneret shape affects the electric field profile in needleless electrospinning, the electrospinning process, fibre morphology and productivity has not been fully elucidated. Sylgard 184 has been regarded as a highly useful polydimethylsiloxane (PDMS) elastomer, but the successful electrospinning of Sylgard 184 elastomer remains a challenge, because its curing process requires 48 hours at room temperature or 10 hours at 60 °C. Will the core-shell electrospinning technique be able to produce PDMS fibres? Electrospun carbon nanofibres, showing porous structure and large surface area, find good applications in catalysis, filtration, energy storage, and battery. However, there has been no report on the morphology and properties of carbon nanofibres from bicomponent polymer nanofibres. How to use side-by-side nanofibres to produce inter-bonded fibrous network has not yet been demonstrated. Ag containing nanofibres endow the fibres with good catalytic and antivirus properties. However, the controlled growth of Ag crystals on electrospun nanofibres hasn't been reported. It remains unclear if the Ag nanoparticles within PAN nanofibres can be induced to undergo an *in-situ* reduction so that Ag can be formed just on the surface of PAN fibres.

The objectives of this project are:

- a) to elucidate the influence of spinneret shape on needleless electrospinning process, fibre morphology and productivity;
- b) to produce Sylgard 184 PDMS fibres from a co-electrospinning process and examine the influences of post-electrospinning treatment on the resultant PDMS fibre morphology and elasticity;
- c) to produce inter-connected carbon nanofibres using side-by-side co-electrospinning followed by carbonisation treatment and examine their properties and electrochemical performances; and
- d) to produce PAN core-Ag sheath electrospun fibres through a post-electrospinning treatment, and examine the influence of treatment conditions on the morphology of Ag sheath layer.

Table of Contents

DEDICATION	1
ACKNOWLEDGEMENTS	2
ABSTRACT	3
LIST OF FIGURES.....	9
LIST OF TABLES	16
CHAPTER 1.....	17
LITERATURE REVIEW.....	17
1.1 Electrospinning and electrospun nanofibres	17
1.2 Needle electrospinning.....	25
1.3 Needleless electrospinning	35
1.4 Fibre collecting modes.....	38
1.5 Material Aspects	44
1.5.1 Thermoplastic nanofibres	44
1.5.2 Elastic nanofibres.....	49
1.5.3 Metal-containing polymer nanofibres	51
1.5.4 Carbon nanofibres.....	53
1.5.5 Inorganic nanofibres	56
1.6 Summary	57
CHAPTER 2.....	59

EXPERIMENTAL PART	59
2.1 Materials.....	59
2.2 Electrospinning.....	59
2.2.1 Preparation of polymer solutions.....	59
2.2.2 Needleless electrospinning	60
2.2.3 Needle electrospinning	61
2.3 Carbonisation and activation.....	64
2.4 UV light treatment of Ag-containing nanofibres	67
2.5 Growth of nano-structured Ag	67
2.6 Finite Element Analysis	68
2.7 Characterisations	69
CHAPTER 3	74
NEEDLELESS ELECTROSPINNING USING DIFFERENT SPINNERETS	74
3.1 Experimental part.....	74
3.2 Electrospinning of PVA nanofibres	75
3.2.1 Cylinder electrospinning.....	75
3.2.2 Ball electrospinning	83
3.2.3 Disk electrospinning	85
3.2.4 Needle electrospinning	90
3.2.5 Comparisons	91
3.3 Electric field analyses	92
3.3.1 Needle electrospinning setup	92
3.3.2 Cylinder electrospinning setup	93

3.3.3 Ball electrospinning setup.....	99
3.3.4 Disk electrospinning setup.....	101
3.4 Discussion	106
3.4.1 Needle electrospinning	107
3.4.2 Analysis of experimental and calculation results	109
3.5 Conclusions	110
CHAPTER 4.....	114
BICOMPONENT ELECTROSPINNING	114
4.1 Experimental part	114
4.1.1 Core-sheath electrospinning of PDMS-PVP core-sheath fibres...	114
4.1.2 Selective removal of PVP from PDMS-PVP core-sheath fibres..	115
4.1.3 Electrospinning of PVP-PAN side-by-side nanofibres	115
4.1.4 Carbonisation of PVP-PAN nanofibres.....	116
4.2 Highly elastic PDMS fibrous membrane from core-sheath bicomponent fibres.....	116
4.2.1 Preparation of PDMS fibres.....	116
4.2.2 Physical properties of PDMS fibre membranes	119
4.3 Inter-bonded carbon fibrous membranes from side-by-side bicomponent nanofibres	124
4.3.1 Carbonisation and activation of nanofibres	124
4.3.2 Fibre morphology	126
4.3.3 Characterisations of carbon nanofibres	133
4.3.4 Electrochemical performance	149
4.3.5 Porous properties	153
4.3.6 The relationship between surface properties and electrochemical performance	159

4.4 Conclusions	161
CHAPTER 5.....	162
METAL-CONTAINING COMPOSITE FIBRES	162
5.1 Experimental part	162
5.2 Photoreduced AgNO ₃ /PAN fibres.....	162
5.2.1 Fibre morphology	162
5.2.2 Characterisations of photoreduced AgNO ₃ /PAN fibres	169
5.2.3 Formation mechanism	173
5.3 Conclusions	174
CHAPTER 6.....	176
CONCLUSIONS AND FUTURE WORKS	176
6.1 Main conclusions.....	176
6.2 Future works.....	181
REFERENCES.....	183

List of figures

Figure 1. 1 Schematic illustration of the basic setup for electrospinning, the Taylor cone, and a SEM image of electrospun nanofibres [3]	18
Figure 1. 2 (a) Instability region in an electrified PEO-water jet; (b) Instability region in an electrified PEO-water jet, superposition of the whipping jet (exposure time =18 ns) and the envelope (exposure time = 1/250 s), the whipping jet can be seen as a dark line; diameter of circle =15 mm; (c) Instability region in an electrified PEO-water jet, exposure time =18 ns and a trace of the jet is shown, vertical distance = 20 cm [116].....	27
Figure 1. 3 (a) Core-sheath electrospinning and a SEM image of core-sheath nanofibres [120], (b) modified core-sheath electrospinning process to produce hollow nanofibres (1 electrospinning setup; 2 electrospun hollow nanofibres) [121].	29
Figure 1. 4 (a) Side-by-side electrospinning [124], (b) electrospinning setup for electrospinning of side-by-side bicomponent nanofibres [114], (c) a SEM image of side-by-side bicomponent nanofibres with one fibre side removed [114].....	30
Figure 1. 5 Schematics of a multi-compartmental electrospinning setup and fibres (Scale bar 20 μm) [125]	31
Figure 1. 6 AC electrospinning (a) and a SEM image of as-spun nanofibres (b), (scale bar 2 microns) [126].....	31
Figure 1. 7 Schematic illustration of two melt-electrospinning setups and the SEM images of the electrospun fibres, (a) [128], (b) [130].....	32
Figure 1. 8 Jet repulsion in a multiple-needle electrospinning [131]	33
Figure 1. 9 Electrospinning with a cylindrical electrode and SEM image [132]	34
Figure 1. 10 Electrospinning using tubular foam spinneret and a SEM image of nanofibres electrospun [133]	35

Figure 1. 11 Aligned tube electrospinning setup and a SEM image of electrospun nanofibres [134].....	35
Figure 1. 12 (a) A two-layer-fluid electrospinning setup; (b) multiple jets ejected towards the counter-electrode, (c) an image of as-spun fibres (scale bar is 50 mm) [135]	36
Figure 1. 13 Schematic illustration of a linear cleft electrospinning setup and electrospinning process [137]	37
Figure 1. 14 Roller electrospinning, and commercialised NanospiderTM [138]	38
Figure 1. 15 Setup for electrospinning aligned nanofibres and obtained nanofibres, (a) [139], (b) [140], (c) [142], (d) [141].....	39
Figure 1. 16 Fibre collection with auxiliary counter electrode and SEM image [144]	40
Figure 1. 17 “House of Santa Claus” motif written by PAN nanofibres (distance = 2.2 mm, Voltage = 0.47 kV) [145].....	41
Figure 1. 18 (a) Schematic illustration of fibrous tubes electrospun using 3D columnar collectors. (①: 3D columnar collectors and ②: fibrous tubes; w, working collector; pa, plane assistant collector; sa, stick assistant collector), (b) Fibrous tube electrospun (diameter, 500 μm , inset is the cross-section image), (c) a SEM image of fibres assemblies in the fibrous tube [146]	41
Figure 1. 19 An electrospinning setup using a water reservoir as collector to produce nanofibre yarns and a SEM image of the yarn collected [147]	42
Figure 1. 20 Dural disk fibre collector and a SEM image of the twisted nanofibre yarn [148].....	43
Figure 1. 21 A schematic electrospinning setup (a) and collected nanofibre yarn (b) [149]	43
Figure 2. 1 Schematic illustrations of three needleless electrospinning setups (a: disk, b: cylinder,c: ball spinnerets)	61

Figure 2. 2 Apparatus for conventional needle electrospinning	62
Figure 2. 3 Core-sheath electrospinning of PDMS-PVP core-sheath nanofibres	63
Figure 2. 4 Illustration of a microfluidic spinneret for electrospinning side-by-side nanofibres	63
Figure 2. 5 Photo of the tubular furnace used for carbonisation and activation of nanofibres. This tube furnace can heat up to 1100 °C. All the samples were carbonised in a quartz tube in N ₂ atmosphere.	64
Figure 2. 6 A photo of UV light source	67
Figure 2. 7 Geometry of cylinder spinneret, ball spinneret and disk spinneret systems	68
Figure 2. 8 SUB4000 UV-VIS spectrometer and the DH2000-BAL UV light source	70
Figure 2. 9 CAM101 KSV Contact Angle Meter	71
Figure 3. 1 Illustration of a cylinder electrospinning process.....	75
Figure 3. 2 SEM images of PVA nanofibres electrospun by cylinder spinneret at different applied voltages (Cylinder diameter = 80 mm, fillet radius = 2 mm, PVA concentration = 9.0 wt%, collecting distance = 13 cm). (At 47 kV and 52 kV the fibres were only generated from the cylinder ends).....	77
Figure 3. 3 Dependencies of average fibre diameters on (a) applied voltage and (b) PVA concentration. (Collecting distance = 13 cm, cylinder diameter = 80 mm, fillet radius = 2 mm).....	78
Figure 3. 4 Dependencies of productivity on (a) applied voltages and (b) PVA concentrations. (Collecting distance = 13 cm, cylinder diameter = 80 mm, fillet radius = 2 mm)	79
Figure 3. 5 SEM images of nanofibres electrospun from cylinder spinneret with different fillet radii (PVA concentration = 9 wt%, applied voltage = 57 kV, collecting distance = 13 cm)	81

Figure 3. 6 The influences of cylinder fillet radius on (a) fibre diameter and (b) productivity (Cylinder diameter = 80 mm, applied voltage = 57 kV, collecting distance = 13 cm)	82
Figure 3. 7 SEM images from cylinder spinneret with different diameters (PVA concentration = 9 wt%, applied voltage = 57 kV, collecting distance = 13 cm, cylinder fillet radius = 10 mm,)	82
Figure 3. 8 The influences of cylinder diameter on (a) fibre diameter and (b) productivity (Fillet radius = 10 mm, applied voltage = 57 kV, collecting distance =13 cm)	83
Figure 3. 9 Illustration of a ball electrospinning process.....	84
Figure 3. 10 (a) SEM image of PVA nanofibres produced by a ball spinneret (Applied voltage = 57 kV, collecting distance = 13 cm, PVA concentration = 9 wt%), (b) the comparison of fibre diameter and productivity between the ball spinneret and cylinder spinneret (fillet radius = 2 mm)	84
Figure 3. 11 Illustration of a disk electrospinning process	85
Figure 3. 12 SEM images of PVA nanofibres electrospun by disk spinneret under different applied voltages (Disk thickness = 2 mm, PVA concentration = 9.0 wt%, collecting distance = 13 cm).....	86
Figure 3. 13 Dependences of fibre diameter on (a) applied voltage and (b) PVA concentration. (Collecting distance = 13 cm, disk thickness = 2 mm)	87
Figure 3. 14 Dependencies of productivity on (a) different applied voltages and (b) different PVA concentrations. (Collecting distance = 13 cm, disk thickness = 2 mm)	88
Figure 3. 15 SEM images of fibres from disk spinnerets with different thicknesses (PVA concentration = 9%, applied voltage = 57 kV, collecting distance =13cm, disk diameter = 80mm)	89