Fibre-shaped Electronic Devices:
Preparation, Characterization and Modelling

By
Yang Zhou
(B.Eng.)

Submitted in fulfilment of the requirements for the degree of
Doctor of Philosophy (Engineering)

Deakin University
September, 2017
I am the author of the thesis entitled

*Fibre-shaped Electronic Devices: Preparation, Characterization and Modelling*

submitted for the degree of Doctor of Philosophy (Engineering)

This thesis may be made available for consultation, loan and limited copying in accordance with the Copyright Act 1968.

*‘I certify that I am the student named below and that the information provided in the form is correct’*

Yang Zhou

Full Name: ........................................................................................................

(Please Print)

Signed: ........................................................................................................

Signature Redacted by Library

Date: ........................................................................................................

12-09-2017
I certify the following about the thesis entitled (10 word maximum)

_Fibre-shaped Electronic Devices: Preparation, Characterization and Modelling_

submitted for the degree of  Doctor of Philosophy (Engineering)

a) I am the creator of all or part of the whole work(s) (including content and layout) and that where reference is made to the work of others, due acknowledgment is given.

b) The work(s) are not in any way a violation or infringement of any copyright, trademark, patent, or other rights whatsoever of any person.

c) That if the work(s) have been commissioned, sponsored or supported by any organisation, I have fulfilled all of the obligations required by such contract or agreement.

d) That any material in the thesis which has been accepted for a degree or diploma by any university or institution is identified in the text.

e) All research integrity requirements have been complied with.

_I certify that I am the student named below and that the information provided in the form is correct_

Yang Zhou

Full Name: .................................................................................................................................

(Please Print)

Signed: ......................................................................................................................................

Signature Redacted by Library

Date: ...........................................................................................................................................

12-09-2017
PROGRESSES ARISING FROM THIS THESIS


2) Book chapter: “Fibres as Electronic Devices” in Handbook of Fibres as Advanced Materials, Wiley. (Accepted, June, 2017)


4) Zhou Y., Fang J., Zhao Y., Wang H. X., Zhou H., Dai L. M., Lin T., Motion Sensors from Conducting Polymer–Metal Schottky Contact (to be submitted)

**Conference presentation**

5) Zhou Y., Fibre Shaped Electronic Devices, NanoWorld Conference, Boston, USA, 2017


**Conference poster**


8) Zhou Y., Electrochromic/Supercapacitive Dual Functional Fibres, IFM Annual Research Conference, Geelong, Australia, 2014
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>TABLE OF CONTENTS</td>
<td>V</td>
</tr>
<tr>
<td>Abbreviations</td>
<td>XXI</td>
</tr>
<tr>
<td>Acknowledgments</td>
<td>XXII</td>
</tr>
<tr>
<td>Abstract</td>
<td>XXIII</td>
</tr>
<tr>
<td>1 Introduction</td>
<td>1</td>
</tr>
<tr>
<td>1.1 Research Background</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Knowledge gaps and specific aims</td>
<td>3</td>
</tr>
<tr>
<td>1.3 Thesis Outline</td>
<td>8</td>
</tr>
<tr>
<td>2 Literature Review</td>
<td>10</td>
</tr>
<tr>
<td>2.1 Introduction</td>
<td>10</td>
</tr>
<tr>
<td>2.2 Categories of fibre-shaped electronic devices</td>
<td>12</td>
</tr>
<tr>
<td>2.2.1 Twisted fibre devices (TFDs)</td>
<td>13</td>
</tr>
<tr>
<td>2.2.2 Fibre electrode wrapped fibre devices (FEWFDs)</td>
<td>14</td>
</tr>
<tr>
<td>2.2.3 Sheath-core single fibre devices (SCSFDs)</td>
<td>16</td>
</tr>
<tr>
<td>2.2.4 Parallel coil fibre devices (PCFDs)</td>
<td>18</td>
</tr>
<tr>
<td>2.3 Electrode materials</td>
<td>19</td>
</tr>
<tr>
<td>2.3.1 Metals and metal oxides</td>
<td>20</td>
</tr>
<tr>
<td>2.3.2 Carbon-based materials</td>
<td>21</td>
</tr>
<tr>
<td>2.3.3 Conducting polymers</td>
<td>24</td>
</tr>
<tr>
<td>2.4 Applications of wearable electronic devices</td>
<td>24</td>
</tr>
</tbody>
</table>
2.4.1 Electrochromic devices ................................................................. 25
2.4.2 Motion sensors ........................................................................... 31
2.4.3 Energy harvesters ................................................................. 36
2.4.4 Energy storage ........................................................................ 47
2.4.5 Transistors .............................................................................. 56
2.4.6 Electroluminescent device ....................................................... 58

3 Materials and Characterization Approaches ........................................... 60

3.1 Materials ..................................................................................... 60
3.1.1 Chemicals ................................................................................. 60
3.1.2 Other materials .......................................................................... 61
3.2 Experimental details ..................................................................... 61
3.2.1 Preparation of fibre with PCFD structured electrode .............. 61
3.2.2 Preparation of gel electrolyte .................................................... 63
3.2.3 COMSOL Finite element method (FEM) analysis .................... 63
3.3 Experimental instruments ......................................................... 65
3.3.1 Surface and cross-section morphology ..................................... 65
3.3.2 Gold electrode preparation ...................................................... 66
3.3.3 Electrochromic performance characterization ......................... 67
3.3.4 Electrochemical properties characterization ............................ 68
3.3.5 Raman Spectrum .................................................................... 68
3.3.6 Controllable movement of aluminium tip ................................. 69
3.3.7 Electrical signal recording ............................................................... 70

4 Electrochromic/Supercapacitive Dual Functional Fibres ....................... 71

4.1 Experimental ........................................................................................ 71

4.1.1 Electrodeposition of PEDOT in electrochromic fibre ..................... 71

4.2 Results and Discussion ........................................................................... 73

4.2.1 Surface morphology ......................................................................... 73

4.2.2 Energy dispersive X-ray analysis ....................................................... 73

4.2.3 FTIR and Raman Spectrum .............................................................. 74

4.2.4 Electrochromic properties ................................................................. 75

4.2.5 Supercapactive properties ............................................................... 84

4.2.6 FEM analysis ................................................................................. 88

4.3 Conclusion ............................................................................................ 92

5 Multicolour Electrochromic Fibre with Helix-patterned Electrode .......... 93

5.1 Experimental ........................................................................................ 93

5.1.1 Overview of multi-coloured electrochromic fibres preparation ....... 93

5.1.2 Electrodeposition of WO3 in electrochromic fibre ......................... 94

5.1.3 Electrodeposition of P3MT in electrochromic fibre ........................ 94

5.2 Results and Discussion .......................................................................... 95

5.2.1 Cyclic voltammetry curves of WO3 coating .................................... 95

5.2.2 Energy dispersive X-ray analysis of WO3 coating ......................... 96

5.2.3 Surface morphology of WO3 coating .......................................... 97
7.2.1 Improvement on stability and durability of electronic devices with PCFDs structure ................................................................. 144
7.2.2 Combination of electrochromic fibre and PEDOT-based DC generator .......................................................................................... 144
7.2.3 Motion sensors with mapping functions ........................................ 145
7.2.4 Comprehensive study on finite element method (FEM) analysis of fibre with PCFD structure ................................................................. 145
8 References ........................................................................................................ 148
TABLE OF FIGURES

Figure 1.1 An overview of wearable electronic devices. (Source: Beecham Research) ........................................................................................................................................................................2

Figure 1.2 Illustrations of a comparison between PCFD structure and FEWFD structure: (a) 3D schematic of device with PCFD structure; (b) Cross-section view of device with PCFD structure; (c) 3D schematic of device with FEWFD structure; (d) Cross-section view of device with FEWFD structure .......... 5

Figure 2.1 Overview of application fields of fibre-shaped electronic devices..... 12

Figure 2.2 Typical structure of fibre-shaped electronic devices ...................... 13

Figure 2.3 Fibre-shaped solar cell with FEWFD structure before bending at (a) low and (b) high magnifications, respectively. The twisted, wire shaped polymer solar cell with the silver wire as the electrode after bending at (c) low and (d) high magnifications, respectively. 16

Figure 2.4 Cross-sectional comparison between fibre-shaped supercapacitor with twisting (left) and coaxial (right) structures with identical amount of electrode materials. 17

Figure 2.5 Illustration of a typical electrochromic device. 101 ............................... 26

Figure 2.6 Illustration of electrochromic application of composite fibres: (a-e) Digital photographs of electrochromic performance of fibres in various forms (f) colour gradient of electrochromic fibre. (g) Reflectance of composite fibres at different working potential. 30

Figure 2.7 (a) Electrochromatic transitions during the charge–discharge process; (b) An electrochromic fibre-shaped supercapacitor at various potential. 31

Figure 2.8 Mechanical–electric properties of the sensor unit. (a) Optical image of a typical sensor unit; (b) Schematic illustration of the cross contact point of the
piezoresistive rubber sensor unit. (A is the contact area and d is the thickness of the pizeoresistive rubber layers between the silver electrodes); (c) The equivalent circuit of the sensor unit; (d) Schematic illustration of the shape deformation at the contact point of the sensor unit under press, stretch, and flexion. \(A_p\) and \(d_p\) are the contact area and thickness under press, \(d_s\) is the thickness under stretch, and \(A_f\) is the contact area under flexion; (e–g) The plots of relative resistance change \((\Delta R/R_0)\) of the sensor unit as a function of loading force, tensile strain, and bending angle. \(^{135}\) .................................................................35

Figure 2.9 (a) Schematic of alternative coating of thermoelectric fibres. (b) Illustration of fibre with thin film deposited on one side. (c) Schematic of experimental setup for applying a temperature gradient and measuring the induced open circuit voltage. (d) Power per couple vs. the segment length for different hot junction temperatures. \(^{136}\) ..........................................................................................................................37

Figure 2.10 Structure and performance of TE textiles. A–f) Schematic illustrations (a–c) and photographs (d–f) of realized zigzag-stitch, garter-stitch, and plain-weave TE textiles, respectively. The scale bars are 2 mm long. G–i) The output power per textile area and per TE couple, measured as a function of the temperature difference \((\Delta T)\) for zigzag-stitch, garter-stitch, and plain-weave TE textiles, respectively. The inset of (i) shows the output power of a plain-weave TE textile for a \(\Delta T\) of up to 200 °C. \(^{137}\) ..................................................................................................................39

Figure 2.11 (a) Schematic of fibre perovskite solar cell; (b) Performance decay under bending states; (c) Performance decay under twisting states; (d) Fluorescence spectrum of devices with pristine perovskite and perovskite/CNT electrodes. \(^{17}\) .................................................................................................................................43
Figure 2.12 (a) Schematic of ZnO nanowires fibre-shaped piezoelectric device and electricity generating processes; (b) The short circuit output current and (c) the open-circuit output voltage of a double-fibre nanogenerator measured by applying an external pulling force at a motor speed of 80 r.p.m. 78 ........................................... 45

Figure 2.13 (a) Schematic of ZnO paper-based piezoelectric device; (b) output voltage and (c) current of multi-fibre based piezoelectric generator subjected to repeated cycles of FP and FR under forward-connected mode. 155 ......................... 46

Figure 2.14 Electrochemical properties of supercapacitor wires; (a) Cyclic voltammogram of a supercapacitor with 24% PANI weight; (b) Galvanostatic charge–discharge curves of a supercapacitor with 24% PANI weight; (c) Dependence of specific capacitance and Coulomb efficiency on cycle number of a supercapacitor with 34% PANI weight; (d) Dependence of specific capacitance on the PANI weight percentage; (e) Schematic of the unbending and bending morphologies; (f) Dependence of the specific capacitance of a supercapacitor with 34% PANI weight on bending cycle number. 68 .................................................... 50

Figure 2.15 Schematic of (a) preparation process of a stretchable supercapacitor; 160 (b) self-healing supercapacitors. 161 ................................................................. 52

Figure 2.16 Electrochemical properties of the cable battery with hollow anode compared with a device with a dense anode; (a) Images of the cable batteries with dense and hollow anode system; (b) First charge and discharge profiles of cable batteries; (c) Capacity retention of cable batteries; (d) AC impedance spectra of cable battery after one cycle in the frequency range from 100 kHz to 1 Hz. 162 ... 53

Figure 2.17 Schematic and electrochemical performance; (a) Schematic of a simplified structure showing only the two hybrid electrodes; (b) Charge and discharge curves under increasing current rates (1C = 183 mA g⁻¹); (c) Energy
and power densities compared with previous energy storage systems; (d) Rate performance at increasing current rates from 10 to 100C and long-term stability test at a current rate of 10 C. 79 .................................................................54

Figure 2.18 (a-c) Scanning electron microscopy (SEM) images of a spring-like fibre at different magnifications; (d–f) SEM images of a fibre at different strains (d) 0 %, (e) 50 % and (f) 100 %; (g) Evolution of resistances of the fibre during a stretching and releasing process with a strain of 100 %; (h) Tensile stress–strain curve of a fibre. 171 ........................................................................................................56

Figure 2.19 Working schematic of (a) OFET and (b) OECT with respect to their “ON” and “OFF” states. 172 ........................................................................57

Figure 2.20 (a) The dependence of luminance on the observation angle for a “luminescent fibre”. Here L0 and L correspond to the luminance measured at 0 and at other observation angles; (b–d) Images of woven “luminescent fibres” being selectively lightened. 173 ........................................................................59

Figure 3.1 Chemical structures of (a) poly(3,4-ethylenedioxythiophene)(PEDOT) and (b) poly(3-methylthiophene) (P3MT). ........................................................................60

Figure 3.2 (a) Schematic of the preparation of parallel coil fibre device; (b) Digital photo of parallel coil fibre device with fishing line substrate; (c) Digital photo of parallel coil fibre device with PVC wire substrate. .................................................62

Figure 3.3 AFM characterization of coating roughness and thickness: (a) Planar coating profile; (b) 3D coating profile; (c) Thickness difference between uncoated and coated areas. ..................................................................................63

Figure 3.4 Scanning electron microscopy (Supra 55 VP). .................................66

Figure 3.5 Leica EM ACE600. ........................................................................67

Figure 3.6 Experimental setup for optical properties characterization. ..........67
Figure 3.7 CHI 760D electrochemical workstation.............................................. 68
Figure 3.8 Renishaw InVia Raman spectrometer............................................. 69
Figure 3.9 NLS4 Series precision linear stage with self-made holder. .......... 69
Figure 3.10 Experimental setup for piezoelectric signal collecting and monitoring. ............................................................................................................................... 70
Figure 4.1 Schematic of preparation routine of electrochromic/supercapacitive
dual functional fibre.......................................................................................... 72
Figure 4.2 SEM images of dual functional fibre: (a) Surface morphology of
PEDOT coated area and uncoated area; (b) Magnified view of PEDOT coated
area.................................................................................................................... 73
Figure 4.3 EDX spectrum of PEDOT-coated area and uncoated blank gap area. 74
Figure 4.4 (a) FTIR of PEDOT coating; (b) Raman spectrum of PEDOT coating. ......................................................................................................................... 75
Figure 4.5 (a) Digital photos to show the single fibre device at colourized and
decolourized states; (b) Electrochromic transition when the device at a bending
state.................................................................................................................... 76
Figure 4.6 Optical absorbance spectra of the single fibre device at the
electrochromic colouration and decolouration states. ..................................... 76
Figure 4.7 Coordination of colour at decolourized (0.46, 0.44) and coloured (0.28,
0.25) states (obtained through CIE1931 chromaticity diagram). ................... 77
Figure 4.8 Monitored variation of reflectance and corresponding current of fibre-
based device at applied potential switching between -0.6 V and +0.6 V. .......... 78
Figure 4.9 Variation of reflectance of the device during repeated colouration and
decolouration for 250 cycles............................................................................. 80
Figure 4.10 Loss of $\Delta \rho$ value during the repeated colouration/decolouration cycles. .................................................................................................................... 81

Figure 4.11 SEM image of surface morphology of dual functional fibre substrate (a) before cyclic voltammetry scan; (b) after 1000 cyclic voltammetry scans from -1 to +1 V. .................................................................................................................... 82

Figure 4.12 SEM-EDX spectrums of dual-functional fibre with and without 1000 cycles potential stimuli at 1 V. .............................................................................................................. 83

Figure 4.13 Relationship between applied potential and $\Delta \rho$. ......................................................... 84

Figure 4.14 (a) Cyclic voltammetry curves of the fibre-based device at different potential scan rates; (b) Relationship between specific capacitance and scan rate. .................................................................................................................................................. 85

Figure 4.15 (a) Galvanostatic charge-discharge profile at various currents; (b) Relationship between specific capacitance and current.......................................................... 86

Figure 4.16 (a) Specific capacitance loss after 1000 charging and discharging cycles; (b) CV curves of the first and 1000th cycle at a scan rate of 0.1 V/s. ............ 87

Figure 4.17 Loss of reflectance difference of fibre-based dual functional devices under galvanostatic charge-discharge test. .................................................................................. 87

Figure 4.18 (a) CV curves of the device under various bending angles at 0.1V/s; (b) Stability of capacitance after 1000 bending cycles at 90° bending angle. ....... 88

Figure 4.19 (a) Electric potential distribution of single counter electrode model (Model I) obtained by COMSOL Multiphysics; (b) Simulated potential distribution along x-axis (Model I). .................................................................................................................. 89

Figure 4.20 (a) Electric potential distribution of double counter electrode model (Model II); (b) Simulated potential distribution along x-axis (Model II)......... 90

XV
Figure 4.21 (a) Experimental data of the relationship between applied potential and colouration width (x-axis value), (b) Simulated data of the relationship between applied potential and colouration width (x-axis value).

Figure 5.1 Schematic of preparation process of (a) PCFD electrodes; (b) WO₃|electrolyte|WO₃; (c) P3MT|electrolyte|P3MT; (d) WO₃|electrolyte|P3MT electrochromic fibres and their working states.

Figure 5.2 Cyclic voltammetry curves of electrodeposited WO₃ film in three-electrode system of 0.1 M lithium perchlorate electrolyte solution.

Figure 5.3 Cyclic voltammetry curves of the as-prepared device (a) at a various scan speeds; (b) at 0.1 V s⁻¹ before and after 1000 times cycles.

Figure 5.4 EDX-SEM spectra of the WO₃-coated gold electrode.

Figure 5.5 SEM images of WO₃ coating layer deposited at various potentials: (a) to (c) WO₃ deposited under -0.5 V with high, medium, and low magnifications respectively; (d) to (f) WO₃ deposited under -1 V with high, medium, and low magnifications respectively; (g) to (i) WO₃ deposited under -2 V with high, medium, and low magnifications respectively.

Figure 5.6 (a) SEM image of WO₃ coated Au interdigital electrodes and the uncoated gap; (b) Magnified SEM view of WO₃ covered surface.

Figure 5.7 Digital photos to show the colouration and decolouration of WO₃|electrolyte|WO₃ electrochromic fibre.

Figure 5.8 Reflectance spectrum variation of WO₃|electrolyte|WO₃ fibre under bleaching and colouring status.

Figure 5.9 Monitored variation of reflectance at applied potential switching between +1.5 and -1.5 V.
Figure 5.10 3D mapped colour space of colours appeared of WO3|electrolyte|WO3 electrochromic fibre. ............................................................................................ 103

Figure 5.11 Digital photos to show the colouration and decolouration of P3MT|electrolyte|P3MT electrochromic fibre. ................................................................. 104

Figure 5.12 Reflectance spectrum variation of P3MT|electrolyte|P3MT fibre under bleaching and colouring status................................................................. 105

Figure 5.13 Reflectance spectrum to show the colouration and decolouration of P3MT|electrolyte|P3MT electrochromic fibre. ................................................................. 106

Figure 5.14 3D mapped colour space of colours appeared of P3MT|electrolyte|P3MT electrochromic fibre. ................................................................. 106

Figure 5.15 Digital photos of reversible colouration of WO3|electrolyte|P3MT fibre under +1.5 and -1.5 V bias ................................................................. 107

Figure 5.16 3D chromaticity of colours originated from the corresponding two status of WO3 and P3MT respectively................................................................. 108

Figure 5.17 Stability test of electrochromic performance of WO3 and P3MT electrodes. ................................................................................................. 109

Figure 5.18 Device geometry (inset: digital photo of actual device). ............... 110

Figure 5.19 Mesh features applied on the established model............................ 113

Figure 5.20 Electric potential distribution within the entire fibre. .................... 114

Figure 5.21 Electric potential at the interface between electrode and electrolyte along X-axis direction................................................................. 115

Figure 5.22 Concentration distribution within the entire fibre.......................... 116

Figure 5.23 Li+ concentration at the interface between electrode and electrolyte along X-axis direction ................................................................. 117
Figure 5.24 Time-dependent Li⁺ concentration in electrolyte within marginal area (point A) and central area (point B) of one coil electrode. ........................................ 118

Figure 6.1 FTIR spectrum of PEDOT layer. .......................................................... 121

Figure 6.2 (a) Schematic of experimental setup; (b) specification of aluminium rod. .................................................................................................................. 122

Figure 6.3 SEM imaging of (a) surface morphology of PEDOT sensor; (b) magnified view of PEDOT coated surface; (c) cross-sectional view of PEDOT coated device. ........................................................................................................ 123

Figure 6.4 AFM imaging of PEDOT samples deposited at different times: (a) 30 s; (b) 60 s and (c) 120 s. .............................................................................................................. 123

Figure 6.5 Output curve of Al rod repeatedly attaching and detaching at three different locations of the PEDOT film. ................................................................. 125

Figure 6.6 Output curve when Al rod attaching and detaching PEDOT surface at different pressures at the same location. ....................................................... 126

Figure 6.7 I–V plots for (a) Au/PEDOT/Al and (b) Au/PEDOT/Au devices with 100 and 200 grams load. ......................................................................................... 127

Figure 6.8 Voltage change when pressing the PEDOT film at different pressures. .............................................................................................................. 128

Figure 6.9 Long time output profile when Al rod constantly connecting to PEDOT. (at the same location) ................................................................. 129

Figure 6.10 Typical signals generated by sliding movement. .............................. 130

Figure 6.11 Electric output generated at different movement speeds. .............. 131

Figure 6.12 Electric output generated with different acceleration modes. ........ 132

Figure 6.13 Electric output generated at different pressure levels (sliding speed at 0.18 cm s⁻¹). ......................................................................................... 133
Figure 6.14 Repeatability of output signals generated at same location and
different locations. ............................................................................................... 134

Figure 6.15 AFM imaging of PEDOT film deposited at 120 s: (a) 2D and (b)
corresponding 3D profile of surface profile from location A; (c) 2D and (d)
corresponding 3D profile of surface profile from location B......................... 135

Figure 6.16 Experiment setup of using Al coved pencil as tip......................... 136

Figure 6.17 Influence of (a) speed and (b) pressure on output signals generated by
6B and 6H pencils.................................................................................................. 137

Figure 6.18 Schematic of patterned PEDOT film. ............................................. 138

Figure 6.19 Influence of gap width on output signals when the tip was right above
the device surface. ............................................................................................... 138

Figure 6.20 Voltage profiles generated by pencil at (a) 0.18 cm s⁻¹ (b) 0.53 cm s⁻¹
and (c) 1.4 cm s⁻¹ speed at same location. ............................................................ 139

Figure 6.21 Integration of PEDOT sensor onto (a) fibre device with whole
electrode without gap; (b) fibre device with coil electrode and gaps in between.
..................................................................................................................................... 141
LIST OF TABLES

Table 2.1 Structure parameters and feature of the fibre shaped electronic devices ................................................................. 18
Table 2.2 Summary of typical electrode materials used in wearable electronic devices. .............................................................. 23
Table 2.3 Recent development on fibre-shaped solar cells. ............................................................................................... 40
Table 2.4 Recent progress on fibre-shaped supercapacitors. .............................................................................................. 47
Table 5.1 Electrochromic properties of the three fibre devices. ......................................................................................... 103
Abbreviations

AFM - Atomic force microscopy
ATR - Attenuated total reflectance
EDX - Energy dispersive X-ray spectroscopy
FEWFDs - Fibre electrode wrapped fibre devices
FTIR - Fourier transform Infrared spectroscopy
H$_2$O$_2$ - Hydrogen peroxide
H$_2$SO$_4$ - Sulphuric acid
LiClO$_4$ - Lithium perchlorate
P3MT - Poly(3-methylthiophene)
PEDOT- Poly(3,4-ethylenedioxythiophene)
PC - Polycarbonate
PCFDs - Parallel coil fibre devices
SCSFDs - Sheath-core single fibre devices
SEM - Scanning electron microscopy
TFDs - Twisted fibre devices
UV - Ultraviolet
WO$_3$ - Tungsten oxide
XRD - X-ray Diffracti

XXI
Acknowledgments

Firstly, I would like to express my sincerest gratitude to Deakin University for providing HDR scholarship. I sincerely appreciate my principal supervisor Professor Tong Lin for accepting me to work in his team and for the great support, guidance and supervision to my study. I would like to specially thank my associate supervisors Dr. Jian Fang and Dr. Yan Zhao. The experiments would not have been finalized without their support, encouragement and caring throughout these years.

I am extremely grateful to Dr. Zhiguang Xu for his support while conducting the AFM characterization. I also want to personally thank Dr. Hao Shao and Mr. Guilong Yan for conducting SEM and other characterizations.

I want to thank Mr. Graeme Keating, Ms Andreea Voda and Mr. Patrick Phillips for their time and patience in providing technical assistance and instrument training on Instron, FTIR and Raman spectrum tests.

Special thanks to my group members, Dr. Hongxia Wang, Dr. Hua Zhou, Dr. Haitao Niu, for their kindly help and assistance during my PhD study.

Finally, I would like to express my gratitude to my family for their understanding and advice during my PhD study. Without their encouragement, I would not have finished this thesis.
Abstract

Fibre-shaped electronic devices are superior to other flexible devices in terms of size, stability and versatility, which are favourable in the development of wearable electronics. This PhD project aims to develop a novel fibre-shaped electronic device with various functions. The thesis covers the following experimental works.

A fibre shaped electronic device that have two parallel coil electrodes on fibre substrate have been developed for the first time. To prove working of the device, PEDOT, a conducting polymer, was electrodeposited on the coil electrodes. The fibre device shows simultaneous electrochromic and supercapacitive properties, and the two functions work without interference each other. To further prove the advantages of the parallel coil fibre devices, two types of electrochromic materials (i.e., P3MT and WO3) were deposited separately onto the two coil electrodes in the same device. The devices show either alternative colour patterns or same colour on single fibre substrate. Theoretical studies related to electric potential and electrochromic properties have also been conducted using a finite element method.

In addition, a motion sensor was developed based on a novel semiconducting polymer-metal Schottky contact mechanical to electric conversion mechanism. Using a flexible film as model, the ability of the device to sense sliding and touching has been demonstrated. The film-shaped sensor was then transformed into coil electrodes to prove the feasibility of using this novel Schottky contact for device fibre shaped motion sensors.

This PhD thesis is innovative in the follow aspects: 1) It is the first time to prove a novel fibre shape electronic device that have parallel coil electrodes on a
fibre substrate; 2) Electrochromic-supercapacitve, multicolour electrochromic properties were formed on the fibre device, 3) A Schottky contact was for the first time used for detection of sliding and touching, and the feasibility of this novel concept for making fibre shaped device was proven. They will be useful for development of novel multifunctional fibre electronics.

In addition, this thesis contains a comprehensive literature review to summarize recent progresses in fibre-shaped electronic devices. Future works in the research directions studied are proposed.
1 Introduction

1.1 Research Background

With the advancement of modern technology, “wearable electronics” have sprung out of scientific laboratories and being seen in the market. (Figure 1.1) The integration of electronic functions and artificial intelligence into clothing textiles changes human lives and improves our health and fitness. Giant leaps have been made in this field, and recent commercialization of wearable devices for entertainment and communication (e.g., Google Glasses, LG G Watch, Samsung Gear Live, Apple Watch) are typical examples. Fashion companies are keen to add electronic functions to their fashion design. Levis and Philips have added smart phones, LEDs and music players into clothing, and Nokia has also integrated their mobile phone into snow jackets. ¹
It is highly desirable that electronic features are incorporated into textiles in a simple, low-cost way and electronics textiles are comfortable to wear with stable performances. However, most of conventional electronic devices cause issues when they are incorporated into fabrics and clothes due to the structure, hardness and moisture sensitive features. To this end, directly building electronics on fibres is highly promising. Fibres are basic part of fabrics and textiles. Endowing fibres with electronic functions will naturally make the fabrics have the same function. Fibres are often flexible, which is very important for the application of wearable electronics. Both natural fibres (e.g., cotton, silk, hemp) and synthetic fibres (e.g., nylon, Kevlar) are low-cost with sufficient supply. This helps to reduce the
manufacturing cost and maintain the affordability of wearable electronic devices. Multi-functional fibres have been developed and used in military and information technology fields. Therefore, there has been rapidly increasing research interest in fibre-shaped electronic devices. Although the wide development of nanotechnology and nanomaterials has accelerated the research progress in fibre-shaped electronic devices, the small size and non-flat structure of fibres increase the complicity and difficulty of device fabrication. The existing fibre-shaped electronic devices are typically built using two separate fibres. Fibre shaped electronics fabricated just on single fibre have been less demonstrated.

1.2 Knowledge gaps and specific aims

Based on recent development in fibre-shaped electronic devices, knowledge gaps have been identified as described below:

Knowledge gap 1: Limited device structures were developed for making fibre shape electronics.

Three device structures have been reported so far for making fibre-shaped electronic devices, namely twisted fibre devices (TFDs), fibre electrode wrapped fibre devices (FEWFDs) and sheath-core single fibre devices (SCSFDs). TFDs and FEWFDs require multiple fibres to be either twisted together or wrapped onto a substrate. The devices fall in the scope of yarns, rather than single fibres. The multi-fibres structures are not as compact as single fibre structures in terms of size and incomplete contact between electrodes and electrolyte may occur, leading to unstable performance and cracking after repeated bending and other physical
deformations. SCSFDs resemble the configuration of sandwich structured planar electronic device with multi-layered active materials deposited on a single core fibre substrate. Due to multilayer structure and outer electrode layer, SCSFDs have low transparency, which affects functionality and performance in certain situations (e.g., being used as solar cells or display devices). Evidently, device structure plays a crucial role in deciding the device performance. Single fibre devices with more reasonable device structure are highly desirable, but have been seldom reported.

Depositing two coil-shaped electrodes onto a single fibre substrate possesses advantages of both FEWFDs and SCSFDs: Two electrodes will be deposited onto substrates rather than being wrapped or twisted altogether, which leads to a more compact and stable structure than FEWFDs and TFDs. Electrodes will be horizontally arranged along fibre axial direction to eliminate overlaps and low transparency issues occurred in SCSFDs.

In addition, the electric field of parallel coil fibre devices (PCFDs) can be formed in the direction along the fibre surface, which is different to that in FEWFDs. For example, when loaded with electrochromic substances, both the electrodes contribute to the device colour. This is different to the FEWFDs, where the coil electrode and the central electrode form an electric field with the direction perpendicular to the fibre surface. In this case, the colouration zone, where electrochromic reaction occurred most intensively, was shaded by the coil electrode. (See Figure 1.2)
Figure 1.2 Illustrations of a comparison between PCFD structure and FEWFD structure: (a) 3D schematic of device with PCFD structure; (b) Cross-section view of device with PCFD structure; (c) 3D schematic of device with FEWFD structure; (d) Cross-section view of device with FEWFD structure.

Owing to above-mentioned superiorities of PCFDs, the first aim of my PhD project is:

**Aim 1: Find an approach to effectively integrate two parallel coil electrodes onto a fibre substrate.**

**Knowledge gap 2: The development of multiple functional fibre-shaped electronic devices is limited.**

Electrochromic materials can change their optical properties via the electricity-driven redox reactions. For example, the colour of electrodeposited PEDOT will switch from transparent blue to dark blue if a bias of -0.6 V is applied. Hence, depositing electrochromic materials can be a straightforward way to investigate the working state (e.g., potential, current) of electrodes. For example,
the occurrence of electrochromic phenomenon can be viewed as a proxy to indicate the completed circuit has been established.

To date, fibre-shaped electronic devices have been predominately applied in supercapacitors and solar cells. These devices merely serve as planar devices in miniature and exhibit identical functions with those planar counterparts. However, the fibre-shaped substrate is different from conventional planar substrates in a variety of aspects, indicating potential opportunities for unique applications. The existing applications of fibre-shaped electronic devices fail to completely utilize the novelty of fibre substrate and the resulting application scope is expected to be enlarged.

Aside from demonstrating the feasibility of electrode structure, electrochromic materials also show appealing features when applied on fibre devices. For example, multiple colour patterns can be achieved on a single fibre by utilizing the synergy of two or more electrochromic materials. Electrochromic fibre with WO$_3$ and P3MT on each electrode is expected to exhibit blue|blue and transparent|red colour patterns at -1.5 and +1.5 V bias respectively. These tuneable colour patterns show potential applications in optical modulators such as optical fibre communications, where dynamic changes in optical properties are required. Accordingly, the second aim of my PhD project is:

**Aim 2: Find an effective method to prepare multifunctional electrochromic fibre device and multicolour electrochromic fibre device based on the parallel coil fibre device structure.**
Knowledge gap 3: Single fibre devices with motion sensing function has never been reported.

Motion sensors are important in wearable applications (e.g., flexible touch screen, pressure mapping) where recognizing motions such as sliding and touching from human body is needed. A variety types of motion sensors such as resistive, capacitive, triboelectric nanogenerator (TENG) and piezoelectric nanogenerator (PENG) sensors have been widely reported and applied in wearable electronics. Endowing motion sensing function in fibre electronics is favourable in terms of several emerging areas such as human-machine interface applications and microrobots. However, motion sensing function has never been applied on single fibre substrates to date.

In PCFDs, the continuous electrode-gap arrangement along fibre axial direction can lead to the formation of alternative circuit connection-disconnection when another conducting objective moves along the fibre. One can utilize this arrangement to achieve motion sensing function by integrating materials that are responsive to movement by generating electricity.

Previously, our group has reported a PPy-based polymer-metal Schottky contact energy harvester that can convert mechanical energy to DC output. Preliminary results have shown that PEDOT-based devices can achieve Schottky contact as well and can linearly response to speed and pressure by generating DC output. Inspired by this, it is expected to achieve this configuration on single fibre with coil electrodes. Accordingly, the third aim of my PhD project is:

Aim 3: Use Schottky contact to prepare motion sensor and prove its feasibility to make single fibre device.
1.3 Thesis Outline

This thesis consists of seven chapters as listed below:

- Chapter 1: Brief introduction of the whole thesis, including significance, knowledge gaps, and specific aims of this PhD project.

- Chapter 2: Literature review of fibre-shaped electronic devices, including basic concepts, structure and electrode materials of existing fibre-shaped electronic devices, recent progress and future trends of wearable electronics.

- Chapter 3: Experimental methodology of materials used in this project, device preparations, characterization instruments, approaches and finite element analysis methods.

- Chapter 4: Research chapter that presents detailed results about the preparation of fibre-shaped electrochromic/supercapacitive dual functional devices with parallel coil electrodes. The electrochromic performance and supercapacitive properties were characterized, followed by a finite element analysis on electric field distribution of the devices.

- Chapter 5: This chapter shows the results on multi-colour single fibre electrochromic devices. A comprehensive finite element analysis was conducted to study the distribution of electric potential and ion concentration in the device.
➢ Chapter 6: This chapter illustrates the preparation, characterization of a motion sensor that can response to sliding movement and pressure by generating DC output. The device was firstly prepared on a film substrate to prove the feasibility of using conducting polymer-metal Schottky contact to sense motions. Then, the concept was applied onto fibre devices.

➢ Chapter 7: A summary of all results that have been achieved in this PhD project and some suggestions for future work in this area.
2 Literature Review

2.1 Introduction

Wearable electronic devices are designed to be soft, flexible and even stretchable, to adapt to bodies’ shape and movement.\textsuperscript{8-11} Wearable electronics are very useful in the areas like health monitoring, activity tracking, military garments, energy conversion, and next-generation personal communication.

Early wearable electronic devices were prepared by mounting electronic components on clothes or accessories. Some of the devices such as smart glasses, watches and wristbands have been commercialised and used in sports and health monitoring equipment. However, they are mostly based on silicon electronics and are unsuitable for use in textiles due to the rigidity. Recently, great attention has been paid towards integrating functional components (e.g., integrated circuits, electrodes) into flexible planar substrates, e.g. PET films, through coating methods. These flexible devices, however, still have poor wear comfort and some substrates are impermeable to air and moisture.\textsuperscript{12-13} An alternative way to fabricate wearable electronics is to incorporate electronic functions into textile substrates, e.g. fibre, yarn and fabric. The wearable electronic textiles prepared in this way possess high air permeability. Among them, fibres are considered as a promising type of material owing to the advantageous features, such as high aspect ratio (> 50) and flexibility. It also allows to prepare multifunctional devices simply through assembling the fibres with different functional components into the same fabric.\textsuperscript{14-16} Compared with yarn- or fabric-based electronics, fibre-based electronic devices have higher
integration ability, versatility in forming multiple functions into a yarn or fabric through conventional braiding, weaving or knitting technique for instance.

Considerable efforts have been made over the last decade to prepare fibre-shaped electronics. Various electronic devices have been shaped into fibres, including energy generators,\textsuperscript{17-18} energy storage devices,\textsuperscript{19-20} electrochromic fibres\textsuperscript{21} and transistors\textsuperscript{22}. The fibre-based energy generators are able to generate electricity from various energy sources such as solar energy and mechanical vibration. They are expected to supply power to personal electronic devices and develop self-powered smart textiles. Electrochromic fibres can change colour upon an applied electric potential.\textsuperscript{23}

Although significant progresses have been made in fibre-based electronics, most of the existing fibre-shaped electronic devices show interior performance to their conventional counterparts. Challenges still exist in making flexible fibre-shaped devices: The working environment requires the devices to withstand repeated squeezing or bending deformations which are accompanied with body movements. The durability against wearing and washing is also critical. Besides, it remains difficult in the fabrication of fibre-shaped electronics owing to the delicate nature. The small size and non-flat structure of fibre substrates increase the complicity as well.

In this chapter, typical device structures that have been widely employed in fibre-shaped electronics are enumerated, along with a summary of electrode materials and recent progresses in fibre electronics. The development trend of fibrous smart electronics has been discussed as well.
2.2 Categories of fibre-shaped electronic devices

So far, there have been four major types of structures of fibre shaped electronic devices in previous reports. They all consist of two or more electrodes with functional layers. According to structure features, these devices can be named as fibre electrode wrapped fibre devices (FEWFDs), twisted fibre devices (TFDs), sheath-core single fibre device (SCSFDs) and parallel coil fibre devices (PCFDs). The details about the device structures are described below:
2.2.1 Twisted fibre devices (TFDs)

TFDs are prepared by twisting two fibrous electrodes together. The fibrous electrodes can be made either by intrinsic conductive fibres (e.g., carbon fibre or metal wire) or polymer fibres with conducting coating. The twisting feature endows the TFD devices with sufficient specific surface area and interaction for electrochemical reactions. TFDs do not require an external substrate to hold electrodes. Hence, the fabrication process of TFDs is simple and the device dimension can be minimized. The performance and stability of TFD devices are significantly affected by twisting parameters (e.g. twisting tightness, pitches), fibre diameters and thickness of the active coating layers. Zhang et al.\textsuperscript{24} reported the influence of twisting features on the performance of a TFD solar cell, where Ti wire and MWCNT fibre were used as two electrodes. It has been revealed that a TFD with an optimal pitch distance of 750 \( \mu \text{m} \) can achieve the highest efficiency.

Figure 2.2 Typical structure of fibre-shaped electronic devices.
Reducing pitch distance increases the possibility of blocking the incident light by MWCNT fibres whereas increasing pitch distance will reduce the contact area between two electrodes. It was mentioned as well that either over-twisted or under-twisted electrodes could affect device stability. A further investigation on twisting tightness has been conducted by Chen et al. \(^\text{25}\), where they reported that the twist tightness played a crucial role in deciding the performance of fibre-shaped solar cells. Increasing the tightness would increase the twisting stress and the possibility of short circuit within the device, whereas the efficiency will be reduced when the twists become loosed due to the decreased intimate contact. The major concern of TFDs is the susceptibility to physical deformation. For example, frequent fold, rub or bending could result in loosing or untwisting the structure, or motion between two electrodes. To obtain better stability, fibrous electrodes for TFDs usually have similar diameters and mechanical properties.

### 2.2.2 Fibre electrode wrapped fibre devices (FEWFDs)

FEWFDs are prepared by wrapping a fibre electrode on another central fibre electrode. The two electrodes in FEWFDs are set asymmetrically and the mechanical stretchability and elasticity of the devices can be tuned through the choice of the central fibre material. Electroactive materials are deposited onto either one or both fibrous electrodes. For example, Wang et al. \(^\text{26}\) deposited a layer of TiO\(_2\) on Ti wire electrode to improve the power conversion efficiency of a fibre solar cell. The TiO\(_2\) layer provided a pathway for charge transport and it served as a separator to avoid short circuit which could be caused by the close contact between two electrodes. In most cases, electron and charge transport occur within the effective
area defined by two electrodes and the surrounded electrolyte. The effective area in the FEWFDs can be adjusted by varying the angle and density of the wrapping fibres, which are key parameters to affect performance. Chen et al.\textsuperscript{25} discussed the influence of various screw pitches on the performance of a FDRFD solar cell. The device with 0.8 mm pitch distance had the highest current density whereas the device showed the lowest current density when the pitch distance was 1.4 mm. It was explained that shorter screw distance increased the number of contact point which facilitated charge transport and increased the short-circuit current density. In addition, increasing the coil density could block the incident light captured by the central electrode, resulting in decrease in light harvesting performance. Besides, exfoliation of the coating layer might occur when high friction was introduced during wrapping the electrode.

Bending could lead to disconnection of the electrode. As shown in Figure 2.3, disconnection occurred between two electrodes after repeated bending. The power conversion efficiency (PCE) reduced from 0.48\% to 0.14\% after 50 cycles of bending the device.
Figure 2.3 Fibre-shaped solar cell with FEWFD structure before bending at (a) low and (b) high magnifications, respectively. The twisted, wire shaped polymer solar cell with the silver wire as the electrode after bending at (c) low and (d) high magnifications, respectively.\textsuperscript{24}

The wrapping electrode offers a possibility to hold liquid electrolyte in the device. Liu et al.\textsuperscript{27} reported a FEWFD solar cell using liquid electrolyte, and the capillary effect originated from the gap between the two fibre-shaped electrodes enabled the liquid to be stored in the space.

### 2.2.3 Sheath-core single fibre devices (SCSFDs)

SCSFDs have a multiple layer structure. They have a similar configuration to sandwich structured flat electronic device. In general, the two electrodes are separated by active layers in between. Unlike FEWFDs and TFDs where two fibres are used as electrodes, SCSFDs have a sheath-core structure which reduces device dimension because all components are integrated into a fibrous substrate. Because
of the intimate contact among materials, SCSFDs have higher utilization and better physical stability than FEWFDs and TFDs.\textsuperscript{28} Zhang et al.\textsuperscript{29} reported a SCSFD structured DSSC with Ti wire and CNT film electrodes. They indicated that the compact contact between two electrodes facilitated ion diffusion towards counter electrode. This allows electrons accumulated at the counter electrode to be captured timely by triiodide ions. Since the electrolyte is infiltrated between the two electrode layers, leakage of the electrolyte substance is eliminated. In addition, the compact electrode layers avoid potential physical disconnection between the electrode and the active layer. Peng\textsuperscript{28} highlighted superior volume utilization in SCSFDs by suggesting that the cross-sectional area of a SCSFD (\(2\pi r^2\)) was two times larger than that of TFDs (\(4\pi r^2\)) when other parameters were controlled same (See the illustration in Figure 2.4),

![Cross-sectional comparison between fibre-shaped supercapacitor with twisting (left) and coaxial (right) structures with identical amount of electrode materials.\textsuperscript{28}](image)

Chen et al.\textsuperscript{30} indicated that the SCSFD supercapacitor showed better performance than those with TFD structure. Based on Nyquist plot results, they concluded that the internal resistance of the SCSFD was lower than that of TFD.
The galvanostatic charge-discharge plot also suggested that SCSFD required less time for a charging-discharging cycle.

A limitation for SCSFDs is the low transparency of the external electrode layer. This affects device performance when used as solar cells, touch screens and display. Since incident light is blocked by multiple layers of active substances, SCSFD-structured solar cells allow less light to reach electroactive layer.31-32

2.2.4 Parallel coil fibre devices (PCFDs)

PCFDs were developed later than other types of fibre devices. They combine the structure features of FEWFDs and SCSFDs. However, PCFDs differ from FEWFDs and SCSFDs in that the fibre in PCFDs functions like a substrate. Two electrodes cover around the fibre substrate in the shape of parallel coils. The electrodes on the fibre substrate can be formed using a coating or deposition technology. This makes the parallel coils look like a structured sheath. Therefore, PCFDs have higher structure stability than FEWFDs and TFDs. Important structure parameters, their advantages and disadvantages of above-mentioned structures are summarized in Table 2.1.

Table 2.1 Structure parameters and feature of the fibre shaped electronic devices

<table>
<thead>
<tr>
<th>Structure Parameters</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>TFDs Twisting tightness Screw pitch</td>
<td>High specific surface area Miniature in size Large incident area</td>
<td>Possibility of short circuit Ineffective contact Twisting stress</td>
<td>24-25, 33</td>
</tr>
</tbody>
</table>
### 2.3 Electrode materials

Electrode materials play an essential role in deciding device properties. The electrode materials are often required to have following features:

1. Be electrically conductive to complete the circuit;
2. Provide sufficient surfaces for connection with electroactive materials;
3. Can form effective contact with active substances;
4. Be stable in both physical and chemical properties.

The commonly used electrode materials for fibrous electronic devices include metal/metal oxides, carbon nanomaterials and conducting polymers.


2.3.1 Metals and metal oxides

Metals are the most extensively used electrode material because they are widely available and have high electrical conductivity. For making fibre shaped electronic devices, the metal electrode can be prepared either in the form of metallic wires or a thin coating on a fibre substrate. The techniques to fabricate metal electrodes for fibre electronics include wrapping metal wires on the fibrous substrate or twisting them with another fibre electrode. In some cases, the metallic wires are coated with a layer of electroactive materials, such as TiO$_2$, to enhance their light absorbing performance in DSSC.$^{26}$

For substrates that are intrinsically poor in conductivity, a wide range of coating techniques can be used, including sputter coating, thermal evaporation, electrodeposition and dip coating. Sputter coating and thermal evaporation are suitable mainly for flat surfaces whereas wet chemical methods could suit both curve and flat surfaces.

Apart from metallic wires, indium tin oxide (ITO) is also widely employed owing to high transparency. Thermal evaporation, sputter coating, chemical vapour deposition, spray pyrolysis and plating have been used to apply ITO on various substrates. Most coating methods can be performed at room temperature, and they are cost effective and environmentally friendly as well.$^{36-37}$

Metal and metal oxides in the form of nanowire possess both good transparency and conductivity. Lee et al.$^{38}$ reported the preparation of ITO nanowires and the conductive coating had an optical transmittance up to 90% and
sheet resistance of 89 Ohm sq$^{-1}$. Kim et al.$^{39}$ prepared a transparent electrode based on Ag nanowires. The sheet resistance of the coating was less than 100 Ohm sq$^{-1}$ and the optical transmittance was around 90%. By optimising the nanowire diameter and length, the nanowire coatings could be transparent in near-infrared region.$^{40}$

In addition, some transition metal oxides like zinc oxide (ZnO), manganese dioxide (MnO$_2$) and ruthenium dioxide (RuO$_2$) have been used as electrode materials as well. They show great potential in making anode in lithium batteries and supercapacitors owing to the reversible redox reactions and high charge storage capacity.$^{41}$ When they are processed into nanostructures, their electrical conductivity can be substantially improved. The synthesis of such transition metal oxides requires low working temperature and can be applied on a variety of surface especially on textiles and fabrics.$^{42-44}$

2.3.2 Carbon-based materials

Carbon-based materials such as carbon nanotubes (CNTs), carbon nanofibres and graphene have high carrier mobility, conductivity, and mechanical properties.$^{45-46}$ Despite they have relatively lower electrical conductivity than metals, their chemical stability is much higher and the conductivity can be improved by the addition of conducting components.$^{47}$

The mechanical properties of CNTs were found to have a tremendous effect on device performance. Liu et al.$^{34}$ reported that the PCE of a fibrous polymer solar cell can be improved from 0.8% to around 2% when silver wire electrode was
replaced with CNT fibre. Firstly, high flexibility of CNTs led to superior performance by providing better-fitted contact area. The stability was improved since CNT films maintained their continuous morphology and adhered to substrate when the fibre substrate was under bending status. Secondly, the possibility of short circuit caused by the penetration of rigid metal wires on functional polymer layers can be reduced. The outstanding mechanical stability of CNTs allow them to be used to develop elastic electrodes. For example, a rubber fibre wrapped by a thin layer of CNTs sheet was used to prepare a fibre-shaped supercapacitor. Such a device can be stretched over 400% of its original length, and still maintains the specific capacitance at 79.4 F g⁻¹.⁴⁸

CNT sheets are usually prepared by layer by layer cross-stacking of aligned CNTs.⁴⁹ The number of layers and stack direction can be used to modify the properties. When CNTs were doped with nitrogen, defects developed on the tube walls. The presence of these defects facilitated the diffusion of ions in batteries.⁵⁰ This improved not only battery performance but also the capacitance when used as electrode material for supercapacitors.⁵¹

Since electrode transparency is an important factor for wearable solar cells and organic light emitting diodes, the transparency of carbon-based materials has been improved by many methods. For example, optimisation of rod coating or spin coating methods allowed to prepare an electrode with the transparency as high as 85%⁵²-⁵⁴ and electrode from hybrid CNTs, fin-like Fe/CNTs for instance, have an optical transmittance of 88%.⁵⁵

Graphene possesses high strength (0.1 - 0.5 GPa), excellent electrical conductivity (10⁴ S m⁻¹) and wide potential window. Graphene has attracted
intensive interest for making electrode. Graphene-based materials can be used either in a conventional two-dimensional form or three-dimensional structures (e.g., aerogels and foams). Table 2.2 summarizes typical electrode materials reported for wearable electronic devices.

### Table 2.2 Summary of typical electrode materials used in wearable electronic devices.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Type</th>
<th>Features</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti wire</td>
<td>Metal</td>
<td>Suitable for TiO$_2$ modification</td>
<td>60-64</td>
</tr>
<tr>
<td>Stainless wire</td>
<td>Metal</td>
<td>Anti-corrosion</td>
<td>65-66</td>
</tr>
<tr>
<td>Aligned CNTs sheet</td>
<td>Carbon-based</td>
<td>Good electrical and thermal conductivity</td>
<td>67-69</td>
</tr>
<tr>
<td>Graphene/Graphene oxide</td>
<td>Carbon-based</td>
<td>High specific surface area</td>
<td>70-72</td>
</tr>
<tr>
<td>Carbon</td>
<td>Carbon-based</td>
<td>High theoretical specific capacitance</td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td>Carbon-based</td>
<td>Thermal conductivity</td>
<td></td>
</tr>
<tr>
<td>PANI/PEDOT</td>
<td>Conducting polymers</td>
<td>Redox reactions</td>
<td>72, 74-76</td>
</tr>
<tr>
<td>MnO$_2$</td>
<td>Metal oxide</td>
<td>High charge storage capacity for solar cell</td>
<td>20</td>
</tr>
<tr>
<td>ZnO</td>
<td>Metal oxide</td>
<td>Morphology can be precisely controlled</td>
<td>77-78</td>
</tr>
<tr>
<td>LiMn$_2$O$_4$/Li$_4$Ti$<em>5$O$</em>{12}$</td>
<td>Metal oxide</td>
<td>High working voltage</td>
<td>79-80</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Little volume changes</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Excellent ion transport</td>
<td></td>
</tr>
</tbody>
</table>
2.3.3 Conducting polymers

Conducting polymers possess large conjugated structure. The electrical conductivity, solubility, optical properties and stability of conducting polymers can be tailored by modifying the polymer structure. For example, the electrical conductivity and solubility of PEDOT can be improved by doping the polymer with polystyreesulfonate (PSS), which enables the easy applying of PEDOT on various substrates through dip-coating. Hou et al. 81 prepared PEDOT:PSS electrode which had a high conductivity of 109 S cm\(^{-1}\). Besides, the morphology of conducting polymers (e.g., nanofibres, nanotubes) also affects performance. Huang et al. 82 reported that PPy nanofibres with a diameter of 60 to 100 nm exhibited excellent conductivity (20–130 S cm\(^{-1}\)) at ambient temperature. Oh et al. 83 synthesised PPy nanowires via electrodeposition and the PPy nanowires in aqueous dispersion had excellent electrochemical activity and strong emission.

2.4 Applications of wearable electronic devices

Wearable electronics, which are clothing or fibre assemblies incorporated with electronic function, have exhibited great potential for applications in healthcare, personal electronics, communications, industry and defense. 16, 19, 46, 84 They can be divided into two main categories as aesthetic enhancement and performance oriented, with each of the categories showing their own characteristics and application fields. Aesthetic enhancing wearables often have a colour changing or light emitting feature, designed to improve aesthetic appearance and visual impact. 85-89 They are useful for making fashion clothing, decorations, information
monitoring or personal devices where visual indication is needed. \(^{90-92}\) Performance oriented wearables focus on various electronic functions such as logic circuiting, computing, remote signal exchange, energy conversion or storage\(^{17, 79, 93-99}\). Fibre shaped electronic devices have shown application potential in above-mentioned fields as well. The device structure and application performances of electronic devices for wearable applications are detailed below:

### 2.4.1 Electrochromic devices

The term electrochromic is defined as the phenomenon that colour of electrochromic material (EM) changes reversibly when a potential difference is applied. The first electrochromic device (ECD) was reported in 1969 using tungsten trioxide (WO\(_3\)) film as the electrochromic material \(^{100}\). From then on, electrochromic materials and devices have been intensively investigated. In this section, electrochromic devices will be described with great details since electrochromic materials will be employed as a proof of concept for the PCFD structure which is widely described in this PhD project.

#### 2.4.1.1 Basic concepts

Electrochromic materials can change their optical properties by switching among various redox states that present different colours under an applied voltage. A typical electrochromic device consists of four main components: substrate, electrode, electrochromic material and electrolyte. Figure 2.5 illustrates a typical layered ECD. Electrolyte and electrochromic material are sandwiched between two
conductive layers that are connected to the positive and negative electrodes of a power source, respectively. Generally, optically transparent electrodes (OTEs) are incorporated into the ECD since the colour change needs to display. Electrochromic performance can be affected by power supply. Typically, a potential difference less than 3 V is sufficient for electrochromic operation, which leads to the change of state of either $\pi$ or d electrons.

![Illustration of a typical electrochromic device](image)

Figure 2.5 Illustration of a typical electrochromic device. 101

To have a comprehensive understanding of ECD, it is of great importance to describe and clarify the following terms:

(1) Substrate: The substrate, which is designed to protect whole device and prevent electrolyte from leaking, usually is made of epoxy and glass in conventional planar structure. Substrate material is usually transparent so the electrochromic effect of the function layer is visually observable. Device encapsulation is one of the most crucial processes for a commercialized ECD. Defective encapsulation will lead to serious damage of an ECD. For example, gas bubbles of hydrogen produced by reduction of hydrogen ions due to moisture will challenge physical stability of the device and insulate ion transfer of ECD. Besides, ECDs, especially some miniature
ECDs, are so delicate that even slight damage or leaking of electrolyte will result in the invalidation of the whole system.

(2) Conducting film: Conducting films, which are conductive materials (e.g., metal, carbon nanotube, and graphene) or insulating materials (e.g., polymer) with conductive coating as mentioned in previous section, function as the electrodes and are connected to a power supply to form a complete circuit. A low electrical resistance is desirable for the conducting film to achieve high device efficiency.

(3) Electrolyte: Electrolyte in an ECD has to be ionically conductive, but electronically insulating. High ionic conductivity facilitates the ion transfer between two electrodes while high electric resistance can avoid short circuit. Besides, for a transmissive ECD, the electrolyte must meet two requirements: (1) being a separation layer between cathode and anode; (2) being transparent in the given spectrum region. Electrolytes can be divided into four catalogues: (1) polymer electrolytes; (2) liquid electrolytes; (3) ceramic electrolytes; (4) solid inorganic electrolytes. Each of them has specific advantages and disadvantages. Among those types of electrolytes, polymer electrolytes have been studied and utilized extensively for flexible electrochromic applications based on following reasons: (1) easy fabrication; (2) physical stability; (3) excellent charge separating and ions conducting ability; (4) endurance.

(4) Electrochromic materials: Electrochromic materials (EM), which are usually coated or grown on electrodes, can change their optical properties by switching among various redox status that present different colours under an applied voltage, as shown in the following equation:

\[ \text{Oxidised form (O) + electron (e)} \rightarrow \text{Reduced form (R)} \]
Reduced form (R) - electron (e) → Oxidised form (O)

2.4.1.2 Important parameters of electrochromic devices

A few key factors need to be taken into consideration when evaluating electrochromic performance of an ECD:

Optical density (OD): OD is a mathematic expression of the optical transmittance of an electrochromic material at a certain wavelength spectrum \( \lambda \) (where \( T \) is the transmittance of the electrochromic material):

\[
\text{OD} (\lambda) = \log_{10} \frac{1}{T}
\]

Colouration efficiency (CE): CE is a term to correlate optical property to energy cost per unit area. It is defined as follows:

\[
\eta = \frac{\Delta A}{Q} \text{ (cm}^2/\text{C)}
\]

where \( \Delta A \) is optical absorbance difference before and after colouration, and \( Q \) is the charge injected per unit area during electrochromic process. Besides, CE can be also described at a certain wavelength \( \lambda \) by replacing \( \Delta A \) with optical density (OD). Under this circumstance, \( Q \) refers to charge passed per cm\(^2\) during colouration. Therefore, CE can be written as follows:

\[
\text{CE} (\lambda) = \eta = \frac{\Delta A}{Q} \text{ (cm}^2/\text{C)}
\]

Response time: Response time represents how fast the EC device can response to an electrical stimulation. Response time is the time required by electrochromic material to switch from bleached state to coloured state and vice versa.
Quantitatively, it is calculated by the time for the electrochromic material to achieve 90% change of optical property from its original state. A number of factors have influence on response time, including ionic conductivity of electrolyte, electric resistance of electrodes, potentials, area and thickness of electrochromic layers, morphology, etc.

Life cycle: Life cycle, represents the longevity of an ECD, is the time for an ECD to repeatedly switch between coloured and bleach state till dysfunction caused by irreversible physical damage.

2.4.1.3 Recent progress on wearable electrochromic devices

Electrochromic fibres are expected to be used for fashionable clothing, safety and communication purposes. Early electrochromic fibre was made of polydiacetylene (PDA) and CNTs. It could switch colour between blue and red by electrical stimulation. The fibre turned from blue to red when an electric potential was applied, and the blue colour restored once the applied voltage was removed. The CNT/PDA fibres possessed high electrical conductivity and fast switching rate of $1 \times 10^3$ S cm$^{-1}$ and 1 s, respectively. Colour changing was attributed to the interaction between CNTs and PDA. Current induced electrons hopped among nanotubes within a fibre and led to the polarization of -COOH groups and PDA backbones. As a result, delocalization of $\pi$-electrons was decreased by above polarization, which corresponded to colour changes.

Electrochromic fibres where colour variation originated from switch among multiple redox states were later reported. Such electrochromic fibres were prepared by electrodepositing electrochromic materials onto fibre substrates. Li et al. 65
reported a set of electrochromic fibres with multiple colours when woven into fabrics. (Figure 2.6) A thinner stainless-steel wire electrode was wrapped onto a coarse stainless-steel wire, followed by electrodeposition of PEDOT, poly(3-methylthiophene) (P3MT), and poly(2,5-dimethoxyaniline) (PDMA). Multiple colours can be observed due to intrinsic optical properties of deposited conducting polymers. Colour response in millisecond at a relatively low voltage was observed. By manipulating the operating potential, colour gradient ranging from grey to blue occurred, which was caused by the different intercalation level of dopant.

![Figure 2.6 Illustration of electrochromic application of composite fibres: (a-e) Digital photographs of electrochromic performance of fibres in various forms (f) colour gradient of electrochromic fibre. (g) Reflectance of composite fibres at different working potential.](image)

Aside from aesthetic enhancement, electrochromic fibres can be utilized as a potential sensor since electrochromic behaviour is dependent on the potential applied. In addition, electrochromic polymers have pseudocapacitance features intrinsically and can be made as dual functional fibres. PEDOT-based dual functional fibre was reported. (See Figure 2.7(a)) Au was selectively coated onto fibrous substrate with the help of a helix-shaped mask, followed by
electrodeposition of PEDOT. Uncoated blank space separated the continuous Au layer, resulting two electrodes integrated onto a single fibre substrate. Electrochromic performance can be observed on the helix electrodes directly without colour overlap which occurred in a traditional core-sheath structure and supercapacitor worked well without interference. Chen et al. 48 utilized this feature to monitor the working statues of a fibre-shaped supercapacitor. PANI coated CNT electrodes were deposited onto elastic substrate, and the resulting substrate was further woven into a supercapacitor network, where PANI acted as both monitor and pseudo capacitor. The fibre exhibits various colours depending upon the potential of supercapacitor. (Figure 2.7(b)) The direction and working potential can be known through different colours.

Figure 2.7 (a) Electrochromatic transitions during the charge–discharge process; 23 (b) An electrochromic fibre-shaped supercapacitor at various potential. 48

### 2.4.2 Motion sensors

Motion detection has wide applications in the fields of robots104-105, automobile106-108, sport109-111, health/ageing care112, human-machine communication and manufacture industry113. They can be prepared based on a variety of principles including optics, acoustics, microwave, resistivity and
capacitance, depending on the application purposes. For example, a passive IR sensor is able to detect people’s movement according to the mid-infrared radiation emitted from human body. Microwave sensors (also known as Doppler radar) can detect outdoor human activities such as walking and running. Resistive or capacitive touchscreens are broadly used in computer, smartphone and other digital devices where a command is issued simply by pressing or sliding of finger on the screen.

With the advancement of microelectronics and wireless communication, the demand for movement detection that is suitable for wearable electronics has increased significantly over recent years. To this end, conventional sensing principles exhibited limitations in terms of portability and sensitivity. For instance, capacitive touchscreens use human body as an electrical conductor to distort the electrostatic field on the screen and the capacitance change. However, capacitive sensors fail to detect insulating materials. Resistive sensors suffer from low contrast and insufficient sensitivity. Additionally, the structural complexity and high cost rise problems in large scale production.

Recently, sensors based on mechanical-to-electrical energy conversion (e.g., triboelectric nanogenerator (TENG) and piezoelectric nanogenerator (PENG)) have been intensively reported since they are especially desirable candidates for wearable sensors. TENGs generate triboelectric charges when two materials with opposite electric negative feature contact and separate frequently. Fan et al. prepared a pressure sensor using polydimethylsiloxane (PDMS) and polyester as active substances. The device was able to detect the impact from dropping water (3.6 Pa) or falling feather (0.4 Pa) on the surface, with a low-end detection limit of ~13 mPa. Zhu et al. reported a polymer nanowire TENG sensor which showed a
pressing sensitivity up to 44 mV/Pa and touch sensitivity of 1.1 V/Pa. Yang et al. \(^{127}\) prepared self-powered movement sensors using a single-electrode mode TENG mechanism, which requires the moving objects to be connected with an electrode and wires. PENGs can convert mechanical energy, vibration energy and hydraulic energy into electrical signals useful for the development of wearable sensors.\(^ {128}\) Chun et al. \(^ {129}\) prepared a self-powered sensor for detection of motion. The sensor devices consisted of piezoelectric hemispheres embedded PDMS. It generated an output of 4 V and 0.13 μA cm\(^{-2}\) and the device can be mounted onto wrist to sense wrist movement in various directions. Proto et al. \(^ {130}\) compared two piezoelectric transducers, i.e., lead zirconate titanate (PZT) and polyvinylidene fluoride (PVDF), for sensing body movement. The power output generated by a single transducer in common activities was in the range of 2-46 μW/cm\(^3\), and it can be further amplified by using a group of the devices. The PVDF device was more favourable than PZT because of the higher folding parameter. Wang et al. \(^ {131}\) reported a biocompatible body movement sensor with a combination of PENG and TENG, using aluminium/zinc oxide, polyvinylidene fluoride trifluoroethylene and PDMS as transparent electrode, piezoelectric layer, and friction layer, respectively. This TENG-PENG hybrid device can distinguish slight body movements from neck, finger, elbow, and ankle. Kalantarian et al. have reported smart watch and piezoelectric sensor integrated necklace to monitor eating habits of human being.\(^ {132-133}\) As-prepared smart necklace was able to classify food into solid and liquid categories and identify swallowing and food intake with high accuracy. Gereon et al. utilized a piezoresistive and stretchable fabric to making smart gloves with pressure sensing function.\(^ {134}\) Pressure measurements ranging from 1kPa to 500kPa can be performed in all fingers and palmar area of the gloves through a grasp. In
addition, Ge et al. produced a multifunctional sensor fabric which could response to normal pressure, lateral strain and flexion. A polyurethane yarn was used as substrate, followed by the wrapping of a nylon fibre. This basic fibre component was further treated with 3-triethoxysilylpropylamine in order to form hydrogen bonds between the interface. Ag nanowires and pizeoresistive rubber were used afterwards to construct a core-sheath structure. Figures 2.8 (b) and (c) illustrate the working principle and the equivalent circuit of the mechanical sensor. The resistance of sensor could change under various operation modes and be viewed as a function of input signal (e.g., loading force, tensile strain and bending angle). They have further achieved force mapping by weaving a number of fibre sensors into a fabric, which could detect the position of the object placed on the fabric and quantify mechanical stress through pressure, strain and flexion changes. (Figures 2.8 (e) to (f))
Figure 2.8 Mechanical–electric properties of the sensor unit. (a) Optical image of a typical sensor unit; (b) Schematic illustration of the cross contact point of the piezoresistive rubber sensor unit. (A is the contact area and d is the thickness of the piezoresistive rubber layers between the silver electrodes); (c) The equivalent circuit of the sensor unit; (d) Schematic illustration of the shape deformation at the contact point of the sensor unit under press, stretch, and flexion. Ap and dp are the contact area and thickness under press, ds is the thickness under stretch, and Af is the contact area under flexion; (e–g) The plots of relative resistance change ($\Delta R/R_0$) of the sensor unit as a function of loading force, tensile strain, and bending angle. 135
In sum, motion sensors based on mechanical-to-electrical energy conversion principles generate electricity with high sensitivity to human movement, pressure, vibration and gestures. They exhibit promising prospects in emerging areas such as human behaviour monitoring, smart skin and robotics man-machine technology, where seamlessly covering all shapes of nature surfaces is required.

2.4.3 Energy harvesters

Over the past several decades, global effort of converting renewable energy sources (i.e., mechanical, solar and water energy) to electricity has never been ceased. Especially in recent years, the urgency has been strengthened with the booming development of wearable electronics, which are hardly drivable using traditional power suppliers. Considerable work that focus on flexible energy conversion devices have been reported (e.g., solar cells, supercapacitors, batteries).60-61, 64, 136-138 These next-generation devices have exhibited both high flexibility and reasonable power conversion efficiency compared with their conventional predecessors.

2.4.3.1 Thermal energy harvesters

Thermoelectric devices convert temperature differences into electrical signal based on temperature gradient. Although the output voltage of thermoelectric devices remains small, the ability to convert heat energy, which is ubiquitous but usually cannot be effectively utilized, to electricity is favourable. Being as wearable
electronics, thermoelectric devices can utilize the intrinsic temperature gradient from human body, which is a promising feature over other electricity generators.

A thermoelectric device consists of thermoelectric material and two electrodes that used to conduct generated current. As early as 2008, Yadav et al.\textsuperscript{136} reported a yarn-based thermoelectric generator as shown in Figure 2.9(a), where Bi\textsubscript{2}Te\textsubscript{3} and Sb\textsubscript{2}Te\textsubscript{3} served as n- and p-type semiconductors, respectively. Silicon fibre of diameter 710 μm was used as the substrate. Silver and nickel were deposited via thermal deposition in an alternating pattern onto the fibre substrate as metal hosts for heating. This fibre generator exhibited a maximum power of 2 nW for 7 couples when ΔT was 6.6 K. Investigation on structure-performance relationship was conducted via finite element method analysis (FEM analysis), indicating that the power generated per couple increased firstly then decreased along with the increase of segment length. (Figure 2.9(b)) Before the maximum value was reached, the improvement of power output was attributed to the increase of temperature gradient caused by elongated segments. Afterwards, the increasing resistance caused by excess length dominates, leading to a decline in final output.

![Figure 2.9](image)

Figure 2.9 (a) Schematic of alternative coating of thermoelectric fibres. (b) Illustration of fibre with thin film deposited on one side. (c) Schematic of
experimental setup for applying a temperature gradient and measuring the induced open circuit voltage. (d) Power per couple vs. the segment length for different hot junction temperatures. 136

It has been known that the integration of electronics into textile will result in lower performance than theoretical value. To obtain an in-depth understanding of thermoelectric effects under practice scenario, Jae et al. 137 compared the output signals under various stitches, as shown in Figure 2.10. Flexible yarns were obtained by twisting basic n-type Bi$_2$Te$_3$ and p-type Sb$_2$Te$_3$ components. The yarns were then woven into zigzag stitch, garter stitch and plain weave structures. The zigzag structure was easy to fabricate, whereas had the lowest performance of 0.166 $\mu$W per couple since the requirement of insulating yarns reduced thermoelectric couples within a certain area. The garter stitch did not need the presence of insulating yarn. The insulating yarns in the garter stitch were used to control junction location during hand weaving process. The plain wave structure was used to provide thermoelectric materials connected in-series. The resulting thermoelectric textile had an outstanding output power up to 8.56 W cm$^{-2}$ when a temperature difference of 200 °C was applied towards textile thickness direction.
Figure 2.10 Structure and performance of TE textiles. A–f) Schematic illustrations (a–c) and photographs (d–f) of realized zigzag-stitch, garter-stitch, and plain-weave TE textiles, respectively. The scale bars are 2 mm long. G–i) The output power per textile area and per TE couple, measured as a function of the temperature difference ($\Delta T$) for zigzag-stitch, garter-stitch, and plain-weave TE textiles, respectively. The inset of (i) shows the output power of a plain-weave TE textile for a $\Delta T$ of up to 200 °C. 137
2.4.3.2 Solar cells

The research on fibre-shaped solar cells focuses on three cell types: dye sensitized solar cells, polymer solar cells and perovskite solar cells. Although the exact mechanism varies from type to type, they all convert solar energy into electricity via photovoltaic effect. In general, dye sensitized solar cells exhibit higher PCE than polymer cells, while require the use of liquid electrolyte. Hence, most fibre-shaped dye sensitized solar cells employ quasi-solid electrolyte or a tube infiltrated with electrolyte to protect the device. The key merit of polymer solar cell is the all-solid-state device feature where no liquid electrolyte is used. The all-solid-state feature is specifically suitable for wearable electronics. As an emerging type of solar cell, the possession of both solid state and high efficiency have made perovskite solar cells in the spotlight.

In general, fibre-shaped solar cells consist of stainless steel or titanium (Ti) wires coated with a layer of titanium dioxide (TiO$_2$) as working electrode and CNT sheet as counter electrode.\textsuperscript{139} Electroactive materials such as sensitizer and electrolyte surround the two electrodes in the form of gel or solid states. Table 2.3 lists recently reported fibre-shaped solar cells and their performance features.

Table 2.3 Recent development on fibre-shaped solar cells.

<table>
<thead>
<tr>
<th>Year</th>
<th>Structure</th>
<th>Electrode</th>
<th>PCE</th>
<th>Feature</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2013</td>
<td>SCSFD</td>
<td>Ti/TiO$_2$/CNT</td>
<td>4.10%</td>
<td>Stability during deformation</td>
<td>$^{60}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ultrathin</td>
<td></td>
</tr>
<tr>
<td>2013</td>
<td>SCSFD</td>
<td>Ti/TiO$_2$/CNT</td>
<td>2.6%</td>
<td>High thermal stability and flexibility</td>
<td>$^{61}$</td>
</tr>
<tr>
<td>Year</td>
<td>Source</td>
<td>Material Structure</td>
<td>Performance</td>
<td>Comment</td>
<td></td>
</tr>
<tr>
<td>------</td>
<td>--------</td>
<td>--------------------</td>
<td>-------------</td>
<td>---------</td>
<td></td>
</tr>
<tr>
<td>2014</td>
<td>SCSFD</td>
<td>Ti/TiO₂/CNT</td>
<td>6.83%</td>
<td>Core-sheath structured CNT/graphene nanoribbon fibrous electrode</td>
<td></td>
</tr>
<tr>
<td>2014</td>
<td>FEWFD</td>
<td>Ti/TiO₂/CNT</td>
<td>5.64%</td>
<td>Investigation on a set of carbon-based materials</td>
<td></td>
</tr>
<tr>
<td>2014</td>
<td>FEWFD</td>
<td>Ti/TiO₂/CNT</td>
<td>7.13%</td>
<td>Elastic and stretchable</td>
<td></td>
</tr>
<tr>
<td>2014</td>
<td>TFD</td>
<td>Ti/TiO₂/P3HT:PCBM/PEDOT:PSS/CNT</td>
<td>1.78%</td>
<td>Sealing free Scalable production</td>
<td></td>
</tr>
<tr>
<td>2014</td>
<td>SCSFD</td>
<td>Stainless steel/TiO₂/MAPbi₃/OMeTAD/CNT</td>
<td>3.3%</td>
<td>All solid flexible</td>
<td></td>
</tr>
<tr>
<td>2015</td>
<td>SCSFD</td>
<td>Stainless steel/ZnO/MAPbi₃/OMeTAD/CNT</td>
<td>3.8%</td>
<td>Facile preparation Obelisk-like ZnO layer</td>
<td></td>
</tr>
<tr>
<td>2015</td>
<td>FEWFD</td>
<td>Ti/TiO₂/CNT</td>
<td>5.47%</td>
<td>Stretchable Ultradurable</td>
<td></td>
</tr>
<tr>
<td>2015</td>
<td>FEWFD</td>
<td>Ti/TiO₂/CNT</td>
<td>5.22%</td>
<td>Stable under both stretching and bending</td>
<td></td>
</tr>
</tbody>
</table>

In 2001, Baps et al.¹⁴⁰ reported a fibre-shaped solar cell with SCSFD structure where a TiO₂ coated stainless wire served as internal electrode and conducting polymer as external electrode. The device can generate a potential around 0.3 V. This prototype has inspired more researchers to transform conventional planar device into a single fibre. Later on, investigation on fibre-based...
solar cells have been burgeoning over the past decade. Liu et al.\textsuperscript{141} reported a fibre-shaped polymer solar cell with a PCE of 0.6%. Fan et al.\textsuperscript{142} reported a TFD structured DSSC in 2008. The working electrode was made of TiO$_2$ coated stainless steel fibre and the counter electrode was a polymer protective layer coated Pt wire. The twisting structure enabled that incident light from all directions and angles can be captured by the electrodes. Polymer protective layer was employed to release local stress between two electrodes via elastic deformation. Hence, the back-transfer of carriers can be reduced. The optimal thickness of the protective layer was achieved at 3.5 $\mu$m. This device with 5 cm length achieved 610 mV open circuit voltage and 0.06 mA short circuit current, respectively. The fibre-shaped perovskite solar cell was first reported in 2014. Qiu et al. reported a SCSFD structured fibrous solar cell\textsuperscript{31}. Stainless steel wire was adopted as internal electrode, followed by the deposition of perovskite electroactive material CH$_3$NH$_3$PbI$_3$. Aligned CNT sheet with high transparency was used as external electrode. The all-solid-states perovskite fibre showed promising future for wearable applications with a PCE of 3.3%, which was higher than fibre-shaped dye sensitized solar cells and polymer cells reported at that time.

Afterwards, numerous efforts have been made to improve PCE and mechanical properties. The PCE of fibre-shaped solar cells can be improved by optimization of electrode in transparency and conductivity. For example, fibre-shaped solar cell with a PCE of 7.1% was produced recently.\textsuperscript{143} The aligned CNT electrode exhibited a transmittance over 80% and a conductivity of 500 S cm$^{-1}$. Low-dimensional metal such as Au, Ag and Cu nanowires, which possess both high transparency and conductivity, have been incorporated into fibre substrate.\textsuperscript{144-146}
Based on scattering effect, Li et al.\textsuperscript{147} reported a strategy to capture more light by controlling the thickness of TiO\textsubscript{2} layer.

Additionally, considerable efforts have been made to enhance electrode properties. For instance, the alignment of CNTs can enhance both mechanical and electrical properties.\textsuperscript{148-150} Alignment of CNTs leads to lower contact resistance, less defects, efficient load transfer and larger surface area when compared with unaligned CNTs.\textsuperscript{151} Additionally, aligned CNTs were condensed into thin films, serving as both effective hole extraction layers that eliminated the hole transport layer. Benefited from aligned CNTs, Qiu et al.\textsuperscript{17} reported a perovskite solar cell with high PCE up to 9.49\%. (Figure 2.11) It was stable under both bending and twisting operation modes. Significant decrease of fluorescence intensity in non-CNT contained perovskite indicated that CNTs could facilitate the effective ion extraction process.

![Figure 2.11](image)

Figure 2.11 (a) Schematic of fibre perovskite solar cell; (b) Performance decay under bending states; (c) Performance decay under twisting states; (d) Fluorescence spectrum of devices with pristine perovskite and perovskite/CNT electrodes.\textsuperscript{17}
Apart from CNTs, silicon-based p-i-n photodiode junction fibre can be produced via high pressure chemical vapour deposition (HPCVD). The fibre device possessed a coaxial p-i-n structure where amorphous silicon n⁺, i and p⁺ layers were deposited, followed by crystallization process. The p-i-n photodiodes endowed the fibres with high quantum efficiency, which is desirable in solar cell. Zhang et al. produced a SCSFD structured solar cell based on CuInSe₂ (CIS) and cadmium sulfide (CdS) deposited Mo wire. The wire electrode was further coated with ZnO and ITO layers. The solar cell had a PCE of 2.31% under various working conditions. Due to the core-sheath structure where each layer was stacked firmly onto the substrates, only 8% efficiency loss was observed when operating at 360 degree bending angle.

2.4.3.3 Mechanical energy harvesters

Mechanical energy harvesters can generate electricity from mechanical vibrations, which are particularly applicable for smart textiles because of the regular motions of wearers. Among many different types of mechanical energy harvesters, piezoelectric devices have attracted most of research interest. A piezoelectric device normally contains a layer of piezoelectric material and two electrodes on both sides. Piezoelectric outputs are generated under external force when the piezoelectric material experiences physical deformation. Qin et al. reported a TFD structured nanogenerator as elucidated in Figure 2.12. Two fibres coated with ZnO and ZnO/Au were twisted together to form a piezoelectric device. Relative sliding and deflection of two fibre resulted in charge generation, where the uncoated ZnO produced potential difference across width direction and ZnO with
gold coating was used for charge collection and transport. Figure 2.12(b) and (c) depict the short circuit current and the open-circuit output voltage of the twisting nanogenerator. When as-prepared fibre generators were integrated into textile fabrics, an output density of 20–80 mW m⁻² was observed.

Figure 2.12 (a) Schematic of ZnO nanowires fibre-shaped piezoelectric device and electricity generating processes; (b) The short circuit output current and (c) the open-circuit output voltage of a double-fibre nanogenerator measured by applying an external pulling force at a motor speed of 80 r.p.m.  

Liao et al. ¹⁵⁵ reported a fibre-based piezoelectric device with the help of foldable ZnO paper. (Figure 2.13) External force moved the Au-coated ZnO layer towards back and down direction, resulting in the formation of piezoelectric field. Flexible paper substrates could be folded at any angle and provide steady physical contact along with enlarged effective working area. The device showed an output voltage of 17 mV and current density of 0.09 μA cm⁻². These figures can be further
improved through device integration. A LED was lit up by the power generated from a combination of 600 fibres.

Figure 2.13  (a) Schematic of ZnO paper-based piezoelectric device; (b) output voltage and (c) current of multi-fibre based piezoelectric generator subjected to repeated cycles of FP and FR under forward-connected mode. ¹⁵⁵

Hybrid PVDF/ZnO device was prepared by incorporating both ZnO nanowires and PVDF polymer onto a fibre substrate. ZnO was considered as the main piezoelectric generator and served as semiconducting electrodes which also improved piezoelectric coefficient of PVDF. PVDF was coated for multiple purposes. It served as a protective layer, piezoelectric generator and surface contact enhancer. Hybrid feature endowed the device with better contact between two piezoelectric materials along with the improvement of output signal and stability. It has been further demonstrated that electrical outputs could be generated by the releasing and folding processes of human elbow after attaching the fibre generator to a human arm. A 2 cm long fibre device was able to generate a voltage output of 0.1 V, current density of 10 nA cm⁻² and power density of 16 μW cm⁻³. ¹⁵⁶
2.4.4 Energy storage

2.4.4.1 Supercapacitors

Fibre-shaped supercapacitors are more portable and ready to be woven into textiles when compared with their planar counterparts. A typical fibre-shaped supercapacitor consists of two electrodes and electrolyte which acts as a separator and an ion transport domain. Recent studies on fibre-shaped supercapacitors are summarized in Table 2.4.

Table 2.4 Recent progress on fibre-shaped supercapacitors.

<table>
<thead>
<tr>
<th>Year</th>
<th>Structure</th>
<th>Electrode</th>
<th>Performance</th>
<th>Features</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2013</td>
<td>TFD</td>
<td>CNT/PANI</td>
<td>Specific capacitance of 274 $\text{F g}^{-1}$</td>
<td>Stable under bending</td>
<td>68</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Good weavability</td>
<td></td>
</tr>
<tr>
<td>2013</td>
<td>SCSFD</td>
<td>Ti/P3HT:PCBM/PEDOT:PS/CNT</td>
<td>Energy density of $1.61 \times 10^{-7} \text{Wh cm}^{-2}$</td>
<td>Integration of solar cell and supercapacitor</td>
<td>69</td>
</tr>
<tr>
<td>2014</td>
<td>FEWFD</td>
<td>CNT/PANI</td>
<td>Energy density of $12.75 \text{ Wh kg}^{-1}$ and power density of $1494 \text{ W kg}^{-1}$</td>
<td>Colour indication</td>
<td>48</td>
</tr>
<tr>
<td>2014</td>
<td>SCSFD</td>
<td>CNT/PANI</td>
<td>Specific capacitance of $79.4 \text{ F g}^{-1}$ after stretching at a strain of 300% and $100.8 \text{ F g}^{-1}$ after bending</td>
<td>High stretchability over 400%</td>
<td>74</td>
</tr>
<tr>
<td>Year</td>
<td>Type</td>
<td>Composition</td>
<td>Specific Capacitance</td>
<td>Feature</td>
<td></td>
</tr>
<tr>
<td>------</td>
<td>----------</td>
<td>--------------------------------------</td>
<td>----------------------</td>
<td>--------------------</td>
<td></td>
</tr>
<tr>
<td>2015</td>
<td>FEWFD</td>
<td>CNT/PEDOT:PSS</td>
<td>30.7 F g⁻¹ at 0.5 A g⁻¹</td>
<td>Working at up to 350% strain</td>
<td></td>
</tr>
<tr>
<td>2016</td>
<td>SCSFD</td>
<td>MWCNT/PANI</td>
<td>11 F g⁻¹</td>
<td>High output voltages up to 1000 V</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>In-Series feature</td>
<td></td>
</tr>
<tr>
<td>2016</td>
<td>SCSFD</td>
<td>Thermoplastic polyurethane/CNT</td>
<td>24 F g⁻¹</td>
<td>Shape-memory features</td>
<td></td>
</tr>
<tr>
<td>2016</td>
<td>PCFD</td>
<td>GO/PEDOT:PSS/Vitamin C</td>
<td>Energy density of 27.1 µW h cm⁻² and power density of 66.5 µW cm⁻²</td>
<td>Hollow fibre electrodes</td>
<td></td>
</tr>
<tr>
<td>2016</td>
<td>Hybrid</td>
<td>Rubber/CNT</td>
<td>Specific capacitance of 2.38 mF cm⁻¹</td>
<td>Against deformation</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Twistable sandwich structure</td>
<td></td>
</tr>
<tr>
<td>2016</td>
<td>TFD</td>
<td>Microporous carbon/CNT</td>
<td>Energy density of 11.3 mWh cm⁻³ and power density of 2.1 W cm⁻³</td>
<td>High performance</td>
<td></td>
</tr>
</tbody>
</table>

Single fibre-shaped supercapacitor was reported by Bae et al. ⁷⁷ in 2011. They prepared a SCSFD that could convert energy and store it simultaneously. ZnO nanowires and graphene were deposited on the central plastic wire and copper mesh.
as two electrodes, followed by the infiltration of PVA/H₃PO₄ gel electrolyte. The calculated specific capacitance reached to 0.4 mF cm⁻² and 0.025 mF cm⁻¹. Since then, giant leaps have been made towards two directions: improvement of capacitance and enhancement of mechanical properties. Electrode optimization is the most commonly used method to improve specific capacitance. CNTs and their combination with metal, conducting polymer, or other carbon-based materials have been reported to improve the capacitance of the devices. For example, graphene and CNT hybrid electrode has shown promising properties in making wire-shaped electronic devices, where graphene sheets served as conducting bridges and decreased contact resistance.¹⁵⁹ CNT sheets were drawn out from CVD synthesized CNT arrays and stacked together with the addition of graphene oxide solution. The resulting CNTs exhibited multi-walled feature with a diameter of 10 microns. After reduction, strong interconnection between CNTs and graphene was established owing to π-π bonds. As-prepared energy device exhibited specific capacitance of 31.50 F g⁻¹, which was superior to bare CNT electrode.

Conducting polymers, such as PANI and PEDOT, can provide extra specific surface area, effective pathway for charge transport and pseudocapacitance when introduced into CNTs, leading to a significant increase in specific capacitance. Cai et al.⁶⁸ reported a PANI/CNT fibre supercapacitor with specific capacitance of 274 F g⁻¹. Figure 2.14 shows the influence of PANI on electrochemical properties. Two redox peaks were observed in the potential range between 0.3 to 0.4 V, indicating pseudocapacitance feature. Symmetrical galvanostatic charge–discharge curves and stability test proved that the device exhibited improved stability. This significant improvement was attributed to the synergy of CNTs and PANI, where CNTs provided physical stability and effective contact and PANI offered charge
transfer pathway and high specific surface area. The weight percentage of PANI plays a crucial role in specific capacitance. Specific capacitance was increased with the increase of PANI weigh until a turning point was reached. The reverse trend after the turning point can be explained as excess PANI covered the surface of aligned CNTs and deteriorated electrical properties of CNTs. Meanwhile, stable mechanical properties of CNTs ensured the device could be operated under bending conditions.

Figure 2.14 Electrochemical properties of supercapacitor wires; (a) Cyclic voltammogram of a supercapacitor with 24% PANI weight; (b) Galvanostatic charge–discharge curves of a supercapacitor with 24% PANI weight; (c) Dependence of specific capacitance and Coulomb efficiency on cycle number of a
supercapacitor with 34% PANI weight; (d) Dependence of specific capacitance on the PANI weight percentage; (e) Schematic of the unbending and bending morphologies; (f) Dependence of the specific capacitance of a supercapacitor with 34% PANI weight on bending cycle number. 68

Apart from specific capacitance, supercapacitors also require robust mechanical properties which ensure devices can withstand various physical deformation. To date, most fibre-shaped supercapacitors have achieved the ability to work under bending states with little performance loss. However, other features such as stretchability is still highly desired. Yang et al. 160 have prepared SCSFD structured supercapacitor with high stretchability based on an elastic fibre. (Figure 2.15(a)) As-prepared device managed to achieve 18 F g⁻¹ specific capacitance after being stretched by 75% for 100 cycles. Other features, such as self-healing and long lifetime fibrous devices have been investigated as well.161 As shown in Figure 2.15(b), a self-healing polymer was used as the substrate, which was wrapped by CNTs and Ag nanowires. As-prepared device showed excellent performance (specific capacitance of 140.0 F g⁻¹) and could recover up to 92% of its original specific capacitance after repeated breaking-healing cycles.
2.4.4.2 Fibre-shaped Li-ion battery

The development of fibrous Li-ion battery follows similar directions with fibre supercapacitors. Current fibre-shaped Li-ion batteries are originated from a prototype reported by Kwom et al.\textsuperscript{162} in 2012. A cable-shaped Li-ion battery was produced by employing a hollow Ni-Sn anode with multi helix structure and LiCoO$_2$ cathode. Hollow structure reduced cell resistance and enlarged specific surface area, resulting better electrolyte permeability and electrical conductivity. A comparison between non-hollow and hollow structured devices is depicted in Figure 2.16. Device with hollow electrode can be charged and discharged repeatedly with less capacity loss.
Figure 2.16 Electrochemical properties of the cable battery with hollow anode compared with a device with a dense anode; (a) Images of the cable batteries with dense and hollow anode system; (b) First charge and discharge profiles of cable batteries; (c) Capacity retention of cable batteries; (d) AC impedance spectra of cable battery after one cycle in the frequency range from 100 kHz to 1 Hz. 162

Ren et al. 163 fabricated a wire-shaped battery with FEWFD structure that achieved a specific capacitance of 13.31 F g\(^{-1}\), where lithium wire and MWCNTs were adopted as the electrodes. Later, they made a further improvement by coating silicon onto the exterior of MWCNTs as a composite anode. 164 When the weight percentage of Si increased from 0 to 38.1%, the specific capacities increased from 82 to 1670 mAh g\(^{-1}\) owing to remarkable specific capacity of Si. 165 The power
density was further improved to 10217.74 W kg\(^{-1}\) by employing LiMn\(_2\)O\(_4\) (LMO)/CNT and polyimide (PI)/CNT hybrid fibres as cathode and anode respectively, which was the highest reported value in this area and was comparable to planar thin-film lithium ion batteries (Figure 2.17).\(^7^9\)

![Figure 2.17 Schematic and electrochemical performance](image)

A typical method to improve the mechanical properties of fibre batteries is to use a core-sheath structure with a stable substrate. For example, self-healing
devices have been produced by applying self-healing polymers to reconstruct their morphology after deformation.\textsuperscript{166-168} Zhao et al.\textsuperscript{166} produced a self-healing Li-ion battery with an energy density of 32.04 Wh kg\textsuperscript{-1}. The discharge voltage only decreased from 1.58 to 1.45V after three times cutting and self-healing processes. Specific capacity decreased from 28.2 to 17.2 mAh g\textsuperscript{-1} after the fifth self-healing process. Aside from self-healing features, lithium ion batteries with high stretchability have also been fabricated. A conventional solution to enhance stretchability is to introduce elastomeric polymers into the device as substrate.\textsuperscript{160, 169-170} However, the addition of elastic substrates increases both size and weight of devices. A new solution to this issue is to use spring-like CNT fibres with coiled loops as electrodes instead of elastic polymers, as shown in Figure 2.18.\textsuperscript{171} By twisting CNT fibres into springs, an elongation of 305\% and tensile stress of 82.7 MPa were attained. The volume and weight of this device can be reduced by 400\% and 300\% respectively, when compared with devices contain traditional PDMS or rubber. At a 100\% strain level, the capacity of devices maintained 85\% of its original capacity.
Figure 2.18 (a–c) Scanning electron microscopy (SEM) images of a spring-like fibre at different magnifications; (d–f) SEM images of a fibre at different strains (d) 0 %, (e) 50 % and (f) 100 %; (g) Evolution of resistances of the fibre during a stretching and releasing process with a strain of 100 %; (h) Tensile stress–strain curve of a fibre. 171

2.4.5 Transistors

Transistors are semiconductor components that amplify or switch electronic signals. Fibre-shaped field organic effect transistors (OFET) and organic electrochemical transistor (OECT) have become the mainstream of research interest among various types of transistors. Figure 2.19 presents a comparison between OFET and OECT. 172 For an OFET, the conductivity of polymer is subjected to the
potential applied on gate electrode. More charges are accumulated within the polymer channel with increased conductivity when the device is under “ON” mode. When it is switched to “OFF” mode, the number of accumulated charges reduces, leading to a decline in conductivity. In an OECT, the control of gate electrode results in conductivity change via the injection/extraction of ions from electrolyte.

Figure 2.19 Working schematic of (a) OFET and (b) OECT with respect to their “ON” and “OFF” states. 172
Advantages of OECT include high current in channel and low cost. Additionally, an OECT does not require smooth substrate surface, making it more practical to be applied in wearable applications. However, restricted by the working mechanism which is originated from the doping/de-doping features of conducting polymers, this type of transistor can only be operated in depletion mode. Meanwhile, the response time of OECT is longer than OFET since ion transport processes in ionic liquid are slower. Hamedi et al. combined OECT and OFET by adopting poly(3-hexylthiophene) (P3HT) and imidazolium ionic liquid as electroactive materials. Conducting channel was established by the field-effect current at the interface of P3HT/electrolyte, followed by a significant response made by doping/de-doping process of P3HT. It possessed advantages of both FET and OECT and could be operated at a low potential with large current density.

2.4.6 Electroluminescent device

Electroluminescent materials can emit light in response to the potential applied or current passed through. Fibre-shaped electroluminescent device can be woven into fabrics for better information conveying functions. For example, Zhang et al. prepared a fibre-shaped polymer light emitting device by constructing a CNT/electroluminescent polymer (EP)/CNT core-sheath fibre. When the potential applied reached to a threshold, the EP switched to n-doped and p-doped states at cathode and anode respectively, exhibiting a uniform electroluminescent effect. (Figure 2.20)
Figure 2.20 (a) The dependence of luminance on the observation angle for a “luminescent fibre”. Here $L_0$ and $L$ correspond to the luminance measured at 0 and at other observation angles; (b–d) Images of woven “luminescent fibres” being selectively lightened. 173

The minimum working potential of resulting light emitting device was 8.8 V and the maximum light intensity reached at 505 cd m$^{-2}$ respectively. As-prepared device also exhibited remarkable performance under bending states where 91.2% of brightness was retained after 100 bending cycles.
3 Materials and Characterization Approaches

In this chapter, materials, experimental details, characterization instruments and modelling approaches used in the PhD project are introduced.

3.1 Materials

3.1.1 Chemicals

3,4-ethylenedioxythiophene (EDOT), 3-methylthiophene (3MT), tungsten powder, poly(methyl methacrylate) (PMMA), Poly(vinyl alcohol) (PVA), lithium perchlorate (LiClO₄), 30% hydrogen peroxide solution (H₂O₂), polycarbonate, Sulfuric acid (H₂SO₄), ethanol (AR), acetone (AR) were purchased from Sigma-Aldrich. All chemicals were used as received.

The chemical structures of PEDOT and P3MT are shown in Figure 3.1.

![Chemical structures of PEDOT and P3MT](image)

Figure 3.1 Chemical structures of (a) poly(3,4-ethylenedioxythiophene)(PEDOT) and (b) poly(3-methylthiophene) (P3MT).
3.1.2 Other materials

PVC wires of 2 mm diameter were purchased from local electronics store (Jaycar electronics). PET films and fishing lines with different diameters were purchased from a local store (Spotlight Geelong).

3.2 Experimental details

3.2.1 Preparation of fibre with PCFD structured electrode

A template method was used to form two parallel coil electrodes on a single fibre. The procedure for producing the fibre based device is illustrated in Figure 3.2 (a). In brief, four strips of adhesive tapes were closely wrapped onto the fibre substrate, followed by removing two of the strips from the fibre. A thin layer of gold was then sputter-coated onto the exposed fibre surface. To ensure deposition of gold on all the exposed surface, the sputter-coating process was performed for a few times with the fibre rotated by a certain angle each time. After resting two adhesive tapes were removed off, the fibre with two parallel coil-shaped gold electrodes was ready for making a fibre device. This approach is universal and can be easily applied to a variety of fibrous substrates regardless of their size. For example, Figure 3.2(b) and (c) show the digital photos of parallel coil electrodes integrated onto a fishing line and PVC wire respectively.
Gold electrodes were sputter coated onto the pre-patterned fibrous substrate where the coating conditions were set at 40 mA current and 100 nm thickness. Given the difficulty in characterizing the thickness of Au layer coated on curved surface, a flat film was used as substrate for simplicity in AFM characterization while all else was kept constant. Figure 3.3 illustrates the surface features of Au layer deposited on flat film substrate, where black area refers to uncoated substrate and yellow area is Au coated surface.
3.2.2 Preparation of gel electrolyte

Gel electrolyte LiClO$_4$/PMMA was prepared by dissolving LiClO$_4$ in a mixture of PC and PMMA with the addition of acetone. In details, 2.1 g LiClO$_4$ was dissolved in 8 mL PC solvent, followed by the addition of 12 mL acetone. PMMA (20 wt. %) was added later and the entire solution was stirred for 24 hours prior to use. Similarly, H$_2$SO$_4$/PVA-based electrolyte is prepared by mixing 1 g H$_2$SO$_4$ and 1 g PVA in 10 mL deionized water and stirred until a clear gel electrolyte solution was formed.

3.2.3 COMSOL Finite element method (FEM) analysis

Finite element analysis solves engineering and mathematical problems by using numerical methods to simulate actual physical systems. FEM has been widely applied in structural analysis, electrochemistry, mass transport, heat transfer, etc. In general, FEM divides the actual problem into simpler and smaller parts which are
called finite elements. The solution to actual problem can be solved approximately by solving finite elements and assembling them altogether.

In this thesis, COMSOL Multiphysics 5.2 was chosen as a FEM software that simulated the actual physical and chemical conditions of devices with parallel coil electrodes.

3.2.3.1 MultiPhysics® calculation for chapter 4:
Model: Electric current (EC) physical interface of AC/DC model was used for potential distribution of as-prepared device under stationary study mode.

Dimensions (W × D × H): Gold coated counter electrode: 1 × 10 × 0.1 mm
PEDOT coated working electrode: 15 × 10 × 0.1 mm
Gap between two electrodes: 1 × 10 × 0.1 mm
Gel electrolyte: 17 ×10 × 5 mm (Model I); 19 × 10 × 5 mm (Model II)

Materials:
Electrical conductivity (S/m): 45.6 x 10^{-6} (Gold); 0.05 (PEDOT); 0.2 (Electrolyte)
Relative permittivity: -1300 (Gold); 250 (PEDOT); 64.6 (Electrolyte)
Potential applied: 0.6 V (Gold counter electrode (s)); 0 V (PEDOT coated working electrode (s))

3.2.3.2 COMSOL MultiPhysics® calculation for chapter 5
Module: Secondary current distribution and diluted species transport
Dimensions: Each of the 3D coil electrode with a screw pitch of 10 mm and 10 revolutions was finalized in Solidworks® 2015 version. The thickness and width of electrode was set to 1 mm and 3 mm respectively.

Mesh: Physical controlled mesh with finer free tetrahedrons

Electrical conductivity of electrolyte: $2 \times 10^{-4}$ S m$^{-1}$

Electrical conductivity of electrode: 3.8 S m$^{-1}$

Upper limit of lithium concentration: 7068 mol m$^{-3}$

Anode and cathode empirical constant: 0.5

Diffusivity of lithium ion: $3.9 \times 10^{-8}$ m$^2$ s$^{-1}$

Potential applied on electrode surface: -1.5 V

Open circuit potential of WO$_3$ device: 2.5 V

Initial value of concentration of lithium ion: 1000 mol m$^{-3}$

3.3 Experimental instruments

3.3.1 Surface and cross-section morphology

Scanning electron microscopy (ZEISS Supra 55 VP) was used to characterize surface and cross-section morphology of gold and PEDOT coated substrates. Cross-sectional samples were obtained by truncating fibrous devices with a surgical knife blade. As-prepared cross-sectional samples were further stucked onto sample holders before being entered into the SEM chamber. A very
thin layer (5 nm thickness) of gold was sputter coated on the surface of PEDOT to avoid charging, along with a relatively low working voltage (5 kV).

Figure 3.4 Scanning electron microscopy (Supra 55 VP).

3.3.2 Gold electrode preparation

Gold electrodes prepared in this thesis were achieved via a Leica EM ACE 600 Sputter Coater. Typically, the sample was kept in the chamber until a vacuum condition (i.e., $2 \times 10^5$ mbar) was achieved. To ensure deposition of gold on all the exposed surface, the sputter-coating was performed for a few times with the fibre rotated by a certain angle each time with a pre-set coating thickness of 100 nm.
3.3.3 Electrochromic performance characterization

As can be seen in Figure 3.6, electrochromic performances presented in Chapter 4 and 5 were characterized by a set of instruments including a light source (Ocean Optics DH-2000-BAL, Light Source for the UV-Vis-NIR spectrum), a detector (Ocean Optics USB4000) and a fibrous probe. The fibrous probe was mounted vertically a certain distance above the characterization area.

Figure 3.5 Leica EM ACE600.

Figure 3.6 Experimental setup for optical properties characterization.
3.3.4 Electrochemical properties characterization

A CHI760D (manufactured by Shanghai Chenhua Instrument Co.,Ltd.) electrochemical workstation was used to prepare and characterize the electrochemical properties of fibrous electronic devices. (Figure 3.7) In Chapters 4 and 5, cyclic voltammetry (CV) technique and chronopotentiometry were used to obtain CV curves and charge/discharge curves of as-prepared devices, along with amperometric I-t Curve technique that was employed to electrodeposit conducting polymer PEDOT and P3MT from their monomer solutions. The influence of potential on electrochromic performance was investigated by multi-potential steps technique. Linear sweep voltammetry method was adopted to investigate the contact types between PEDOT and metal electrodes in Chapter 6.

Figure 3.7 CHI 760D electrochemical workstation.

3.3.5 Raman Spectrum

Raman spectrum was obtained via a Renishaw InVia Raman spectrometer with a 633 nm laser. All tests were carried out in a controlled environment (20 ± 2°C and 65 ± 2% relative humidity).
3.3.6 Controllable movement of aluminium tip

NLS4 Series Precision Linear Stage (Newmark Systems) is used in the characterization part of Chapter 6. To control the movement of an aluminium tip, the tip was mounted into the sliding component of linear stage by a self-made holder. The linear stage was controlled by a programmable software in order to drive the tip at a precisely controlled constant speed.
3.3.7 Electrical signal recording

In Chapter 6, PEDOT generated electrical signals were collected and monitored by e-corder (top) and Stanford Research System (SR570) (bottom) as shown below.

Figure 3.10 Experimental setup for piezoelectric signal collecting and monitoring.
4 Electrochromic/Supercapacitive Dual Functional Fibres

In this chapter, a single fibre, which has two electronic functions electrochromism and supercapacitor, with a parallel coil electrode structure and its facile preparation are proved. The device was prepared using a template method to generate two coil electrodes on the fibre surface, followed by electrochemical deposition of poly(3,4-ethylenedioxythiophene) on the electrode surface. An overlay of gel electrolyte was applied on the whole fibre. The fibre device showed a reversible electrochromic effect with fast response time (<5 s) at a potential of 0.6 V. It had a specific capacitance of 20.3 F g\(^{-1}\). The two functions happened simultaneously without interference with each other. Such an electronic fibre may find applications in wearable displays, personal power supplies and protective garments.

4.1 Experimental

4.1.1 Electrodeposition of PEDOT in electrochromic fibre

PEDOT was coated on the gold electrodes through electrical polymerization in a three-electrode cell. The electropolymerization was conducted in a 20 mL PC solution containing 0.2 g LiClO\(_4\) and 0.1 g EDOT monomer, with the coil structured gold electrode as working electrode, platinum plate (2 cm x 2 cm) as counter electrode and Ag/AgCl standard electrode as reference electrode. A potential of 1.3 V was potentiostatically applied to generate a light blue polymer layer on gold electrode. After 20 s of electropolymerization, the fibre was rinsed with deionized
water and ethanol three times to remove residues, and dried in a 50 °C vacuum oven for 12 hours.

According to Faraday’s law, the total mass of PEDOT deposited onto fibre substrate can be calculated as follows.\(^{174}\)

\[
m = \frac{QM}{zF} \quad (4-1)
\]

where \(Q\) is the charge (C) passed through within the system during electrodeposition process, \(M\) is the molar mass of material (140.13 for PEDOT), \(z\) is referred to as the amount of electron transferred each unit material (2.3 for PEDOT) and \(F\) is Faraday’s constant (96485 C/mol).

The schematic of as-prepared device is illustrated in Figure 4.1.

---

Figure 4.1 Schematic of preparation routine of electrochromic/supercapacitive dual functional fibre.
4.2 Results and Discussion

4.2.1 Surface morphology

Figure 4.2(a) shows the surface morphology of the PEDOT-coated gold electrode and the uncoated gap between two gold electrodes. The enlarged SEM view in Figure 4.2(b) shows that the PEDOT layer has a rough surface and was composed of some micro-particles on the surface.

Figure 4.2 SEM images of dual functional fibre: (a) Surface morphology of PEDOT coated area and uncoated area; (b) Magnified view of PEDOT coated area.

4.2.2 Energy dispersive X-ray analysis

Figure 4.3 shows the energy dispersive X-ray (EDX) spectra taken from the PEDOT-coated gold electrode and the gap between two electrodes. Element S appeared on the PEDOT coated Au electrode surface but not in the gap area, confirming that PEDOT was only coated on Au.
4.2.3 FTIR and Raman Spectrum

The PEDOT layer was also verified by FTIR and Raman measurement as shown in Figure 4.4. The peaks around 830 and 930 cm\(^{-1}\) can be assigned to the vibrations of C-S bonds in PEDOT structure. The peaks at 1100 and 1160 cm\(^{-1}\) are considered as the stretching of the C-O-C bonds in ethylene dioxy groups. The peaks appeared near 1300, 1400 and 1500 cm\(^{-1}\) can be attributed to the stretching of the thiophene ring. The Raman spectrum of PEDOT electrode agrees well with the results presented elsewhere.\(^{175}\)
4.2.4 Electrochromic properties

Figure 4.5 shows the colour change of the fibre device when the PEDOT-coated electrodes are connected to an external power supply. At 0 V, the electrodes showed natural gold colour. When the potential switched from 0 V to 0.6 V, the PEDOT coated on cathode turned dark blue, while the anode showed no change in colour. When the bias potential was switched to a reverse direction, the cathode electrode in dark blue restored the naturel gold colour, while the other electrode in natural gold changed to dark blue. All these colour changes were reversible and can take place for many cycles. These results clearly indicate that the single fibre device has an electrochromic feature. It is noticed that the above electrochromic transitions happened even if the fibre device was bent. Figure 4.5(b) illustrates the electrochromic transition when the device was in a “U” shape, suggesting that the fibre device works flexibly in different shapes.
Figure 4.5 (a) Digital photos to show the single fibre device at colourized and decolourized states; (b) Electrochromic transition when the device at a bending state.

Figure 4.6 shows the optical absorbance spectra of the fibre device at the colouration and decolouration conditions. There appeared an absorption peak at 610 nm during colouration, which corresponds to the dark blue colour of the PEDOT layer.\textsuperscript{176}

Figure 4.6 Optical absorbance spectra of the single fibre device at the electrochromic colouration and decolouration states.

The chromaticity diagram (CIE 1931) based on the standard D65 illuminant was employed to measure the digital colours. As shown in Figure 4.7, the PEDOT coated gold electrode at normal state showed a natural gold appearance, and the
coordination (x, y) was (0.28, 0.25) with a colour purity of 0.26. When the electrode was at colouration state, which is dark blue, the coordination and colour purity were (0.46, 0.44) and 0.71, respectively.

Figure 4.7 Coordination of colour at decolourized (0.46, 0.44) and coloured (0.28, 0.25) states (obtained through CIE1931 chromaticity diagram).

The electrochromic switching behaviour of the fibre device is depicted in Figure 4.8. When a square wave potential (± 0.6 V) was applied at 5 seconds interval, the relative reflectance difference at wavelength of 610 nm ($\Delta \rho$) reduced to approximately 25% of the decolour state. The current - time curve in Figure 4.8 shows a decrease in current at the inception. This was caused by the depletion of electroactive species, indicating the occurrence of redox reaction. The redox reaction reached an equilibrium when the current dropped to a constant level. The overall $\Delta \rho$ also reduced gradually with increasing the scan numbers.
Figure 4.8 Monitored variation of reflectance and corresponding current of fibre-based device at applied potential switching between -0.6 V and +0.6 V.

The time required for the electrochromic device to achieve 90% of $\Delta \rho$ after switching from normal non-colour state to full colourized state, which is also referred to as “colouration time” can be calculated based on Figure 4.8 as 3.6s ($T_{\text{colouring (90%)}}$). Similarly, the time required for restoring 90% of $\Delta \rho$ from the colourized to the non-colour state, also referred to as “bleaching time”, was calculated as 4.2s ($T_{\text{bleaching (90%)}}$). The specific colouration efficiency ($\eta$, cm2/C) was calculated according to the equation: \(^{177}\)

$$\eta = \frac{\Delta \text{OD}}{Q/A} = \frac{A}{Q} \log \left( \frac{R_b}{R_c} \right)$$

(4-1)
where $\Delta OD$ is the optical density difference, $R_b$ and $R_c$ are the reflectance at decolouration and colouration states, respectively. $Q$ is the charge consumed during electrochromic transition, and $A$ is the colouration area.

The surface area of electrode can be calculated by subtracting the area of gaps (i.e., the area of strips removed from substrate) from the surface area of fibre substrate. The latter was calculated by the following equation where the substrate is considered as a cylinder:

$$A = 2\pi rh$$  \hspace{1cm} (4-2)

where $r$ is the radius of fibre substrate and $H$ is the length of the substrate.

At 0.6 V, the $\eta$ at 610 nm was calculated as 360 cm$^2$/C, which is comparable to those PEDOT-based electrochromic devices with two-dimensional layered structures. \(^{178-179}\)

The stability of electrochromic property is important for practical applications. Figure 4.9 shows the optical reflectance change of the electrochromic device during repeated colourization-decolouration transition ($\pm$ 0.6 V square wave, 5 s for each direction). The overall reflectance reduced with increasing the numbers of electrochromic transition. After 250 cycles of the electrochromic transition, the overall reflectance difference dropped from 16 to 11.2\%.
Figure 4.9 Variation of reflectance of the device during repeated colouration and
decolouration for 250 cycles.

Figure 4.10 further shows the drop of Δρ after 1000 cycles of colouration
and decolouration, being approximately 30%, indicating the reasonable stability of
our device. The performance loss can be attributed to the repeating doping/de-
doping process of the PEDOT layer, which causes degradation of PEDOT.\textsuperscript{180-181}
The degradation of active layer also resulted in slight decrease in the current as well.
Herein, the degradation refers to the occurrence of cracks, delamination and
detachment of PEDOT layer. It is widely believed that above mentioned physical
damages are highly related to the mechanical properties (e.g., adhesion strength) of
PEDOT. For example, Wei et al. reported that the PEDOT layer has relatively poor
adhesion to inorganic metallic and semiconducting substrates.\textsuperscript{182} Ouyang et al. found
that PEDOT films tend to crack or delaminate from solid substrates during long-
term application.\textsuperscript{183} Hence, mechanical properties play a crucial role in determining
the stability of PEDOT device and this parameter should be evaluated in the future
work.
When conducting polymers undertake multicycles of redox reaction, two major changes could take place: (1) entrapping of dopant within polymer matrix, which blocks further redox reaction\textsuperscript{184}; (2) dimensional contrast between the doped and de-doped stated, which results in detachment from the metal substrate.\textsuperscript{185-187} To find out the performance loss in our fibre devices, it was observed that the morphology and element profile of the PEDOT layer before and after 1000 cycles of cyclic voltammetry scans. Indeed, some PEDOTs detached from PEDOT layer after the repeated scans. (See Figure 4.11)

Figure 4.10 Loss of $\Delta \rho$ value during the repeated colouration/decolouration cycles.
On the other hand, the SEM-EDX also indicated that the element Cl, which was absent in de-doped PEDOT sample prior to the cycle test, appeared in the de-doped PEDOT sample after 1000 cycles. (See Figure 4.12)
These results suggest that the performance decay comes from both physical damage and entrapping of dopant within the PEDOT structure. Additionally, the volatilization of acetone used as a solvent in gel electrolyte also limits the ions transfer and increases the electric resistance as time goes on. The applied potential showed an effect on the reflectance property. Here, the reflectance difference before and after colouration ($\Delta \rho$) at the same wavelength was used to measure the colour change. With increasing the applied potential, the working current and the $\Delta \rho$ both increased. (Figure 4.13) This can be explained as higher current facilitates the redox reactions.
4.2.5 Supercapacitive properties

During the electrochromic transition, the fibre device also showed supercapacitance feature. Figure 4.14(a) shows the cyclic voltammetry (CV) curves of the fibre-based device at scan rates in the range of 0.1 - 0.5 V/s. The redox peaks were found at approximately -2.1 V and 2.2 V. It is noticeable that the potential window here is relatively wider when comparing with other PEDOT-based electrochromic devices and this might be caused by the lower ion mobility (10^{-2} S cm^{-1}) of the gel electrolyte than that (10^{-3} S cm^{-1}) of its liquid counterparts.\textsuperscript{188}

Based on the CV curves, the specific capacitance ($C_s$, F g$^{-1}$) of the device can be calculated by the equation:\textsuperscript{189}

$$C_s = \frac{\int I \, dV}{2mv\Delta V} \quad (4-2)$$

where $\int I \, dV$ refers to the integration area of the positive and negative sweeps in a CV curve, $v$ is the potential scan rate (V s$^{-1}$), $m$ is the total mass of electroactive
materials over two electrodes, and $\Delta V$ is the potential difference. The corresponding specific capacitance at various scan rates is shown in Figure 4.14(b). The specific capacitance decreased with increasing the scan rate, from 0.1 V s$^{-1}$ to 0.5 V s$^{-1}$.

Figure 4.14 (a) Cyclic voltammetry curves of the fibre-based device at different potential scan rates; (b) Relationship between specific capacitance and scan rate.

Figure 4.15(a) shows the galvanostatic charge-discharge profile of the fibre-shaped device. The device was charged and discharged within a potential range from 0 to 1.0 V under five different current levels (i.e., 0.02, 0.05, 0.1, 0.2 and 0.3 mA). The specific capacitance (mF mg$^{-1}$) of the device was calculated as follows:

$$ C_s = \frac{I \Delta t}{m \Delta V} \quad (4-3) $$

where $I$ is the constant charge–discharge current (mA), $m$ refers to the total mass of electroactive materials, $\Delta V$ represents the charge-discharge potential and $\Delta t$ is the discharge time (s). The specific capacitance based on the charge-discharge profile is calculated in Figure 4.15(b) for comparison. With increasing the current, the specific capacitance decreased. In the meanwhile, increasing current led to a significant shorter discharge time and less capacitance. This is because PEDOT
pseudocapacitor works based on the doping/de-doping of counter ions. At a high discharge rate, the doping/de-doping is hindered significantly.

Figure 4.15 (a) Galvanostatic charge-discharge profile at various currents; (b) Relationship between specific capacitance and current.

The supercapacitor stability was examined by repeating the charge-discharge scan for 1,000 cycles. The corresponding capacitance loss is plotted in Figure 4.16(a), where a 30% capacitance loss after 1,000 cycle times resulted, which is in agreement with the \( \Delta \rho \) loss and this should be originated from the over-oxidation of the PEDOT layer during redox reaction. Despite the device capacitance loss after repeated scans, the redox peaks in the CV curve were still observable at -2.1 V and 2.2 V after 1,000 cycles of charging and discharging (Figure 4.16(b)).
Figure 4.16 (a) Specific capacitance loss after 1000 charging and discharging cycles; (b) CV curves of the first and 1000th cycle at a scan rate of 0.1 V/s.

During charging-discharging process, the device simultaneously showed colour change. The stability of this electrochromic property during charging-discharging process was studied by recording the reflectance difference loss. Similar to the above-mentioned result, over 80% $\Delta \rho$ was maintained after 1,000 cycles of charging-discharging at 0.1 mA. (See Figure 4.17)

Figure 4.17 Loss of reflectance difference of fibre-based dual functional devices under galvanostic charge-discharge test.
The bending test has been conducted to demonstrate the flexibility of the fibrous device. As shown in Figure 4.18(a), the CV curves of device are depicted when it was bent into various angles ranging from 0° to 180°. It can be clearly seen that the bending angle had little effect on its capacitance performance. The stability test result of the device is shown in Figure 4.18, which reveals that 73% of the capacitance could be maintained after 1000 bending cycles at a bending angle of 90°.

Figure 4.18 (a) CV curves of the device under various bending angles at 0.1V/s; (b) Stability of capacitance after 1000 bending cycles at 90° bending angle.

4.2.6 FEM analysis

It is believed that the capacitance loss was predominately attributed to the physical deformation of electrode materials caused by repeated bending. Electrochromic effect occurs only if the electric potential is above a critical value. Electrode geometry should affect the electric potential profile in the device. To calculate the electric potential distribution (i.e., 0.6 V), we used a finite element
method (COMSOL Multiphysics) to analyse two models, model I and model II, as indicated in Figure 4.19.

![Figure 4.19 (a) Electric potential distribution of single counter electrode model (Model I) obtained by COMSOL Multiphysics; (b) Simulated potential distribution along x-axis (Model I).](image)

In model I, a pair of metal strips were used as electrodes and the wider electrode was coated with PEDOT. An electrolyte gel layer was covered on the entire top of the electrodes and gap. The width of gap between the two electrodes, gold electrode and PEDOT coated electrode was set as 0.1 cm, 0.1 cm, or 1.5 cm, respectively. Figure 4.19(a) shows the electric potential distribution profile over the PEDOT coated Au electrodes. Under an external voltage, the electric potential at the edge of the electrodes was significantly higher than that in the gap area and the middle part of the electrode. Figure 4.19(b) also shows the potential distribution along the x axis (from x=0 to x=1.7 cm) when the potential applied on Au electrode varies from 0.1 V to 1.5 V. The inset shows an enlarged view of the PEDOT coated...
electrode from x=0.2 to x=1.6. Higher potential applied on the Au electrode results in larger area on PEDOT coated electrode that can reach a certain potential threshold.

In model II, a double counter electrodes structure was used to analyse the potential distribution. (Figure 4.20(a)) Such an electrode structure is similar to the one that was used for making single fibre device. Figure 4.20(b) shows the potential distribution along x-axis when a potential (0.1-1.5 V) is simultaneously applied on the two Au electrodes. It is worthy to note that potential overlap occurs on the PEDOT coated Au electrode, leading to higher potential when compared with model I.

![Figure 4.20 (a) Electric potential distribution of double counter electrode model (Model II); (b) Simulated potential distribution along x-axis (Model II).](image)

We also conducted an experiment using models with dimensions which are identical to those of the model I and model II. The colouration width of the PEDOT coated Au electrode was recorded when applied potential (0.1-1.5 V) on Au electrode (Figure 4.21(a)). According to our experiment, a potential threshold at 0.5 V was observed where electrochromism will occur when the potential applied on
Au electrode is above that threshold, otherwise the device will remain unchanged. Assuming the threshold is still valid in our simulated models, a straight line that simulates the relationship between applied potential and colouration width can be plotted. Accordingly, any value of potential on PEDOT coated electrode above that threshold is able to drive the PEDOT to undergo a colouration transition. The x-axis values of intersection of potential curve and threshold can be regarded as the width of colouration area under different potentials. For instance, in Figure 4.21(b), the potential curve of 0.7 V intersects threshold at the point \((x=0.37, y=0.1)\) suggesting that the colouring width of PEDOT coated electrode is 0.17 cm (after subtracting 0.1 cm Au electrode and 0.1 cm gap width). Based on above assumptions, the calculated colouring width in model I and II is plotted in Figure 4.21(b) respectively. These results agreed well with the experimental results in Figure 4.20(a). Both the simulated and experimental data curves are positively sloped and they show a similar trend. This relationship between potential and colouring width implies that we can maximize the colouration electrode and minimize the counter electrode simultaneously and therefore improve the visual effect of device.
Figure 4.21 (a) Experimental data of the relationship between applied potential and colouration width (x-axis value), (b) Simulated data of the relationship between applied potential and colouration width (x-axis value).

4.3 Conclusion

A single fibre device with electrochromic and energy storage functions was prepared. The two concurrent functions are both based on the redox of PEDOT, but they do not interfere with each other. The fibre device shows colouring/bleaching time less than 5 s useful for making electrochromic fabrics or flexible electrochromic devices. It has a specific capacitance of 20.3 F g⁻¹. When used as supercapacitors, the electrochromic function indicates the capacitive working performance.
5 Multicolour Electrochromic Fibre with Helix-patterned Electrode

In this chapter, a systematic understanding of multicolour electrochromic fibres has been established by depositing poly(3-methylthiophene) (P3MT) and WO₃ separately on the two electrodes with PCFD structure. Consequently, WO₃|electrolyte|WO₃, P3MT|electrolyte|P3MT and WO₃|electrolyte|P3MT fibres have been obtained and characterized. The hybrid WO₃|electrolyte|P3MT shows three electrochromic colours, i.e. dark red, green and gold, depending on the voltage applied, with good colouration efficiency and fast response. A finite element method (FEM) was used to analyse the distribution of electric potential and electrolyte on the fibre device.

5.1 Experimental

5.1.1 Overview of multi-coloured electrochromic fibres preparation

Figure 5.1 presents a general overview of the preparation processes and working states of three electrochromic fibres (i.e., WO₃|electrolyte|WO₃, P3MT|electrolyte|P3MT and WO₃|electrolyte|P3MT) included in this chapter.
Figure 5.1 Schematic of preparation process of (a) PCFD electrodes; (b) WO₃|electrolyte|WO₃; (c) P3MT|electrolyte|P3MT; (d) WO₃|electrolyte|P3MT electrochromic fibres and their working states.

5.1.2 Electrodeposition of WO₃ in electrochromic fibre

Tungsten powders (1.8 g) were dissolved in 60 mL 30% H₂O₂ solution. The reaction was performed in an ice bath and stirred intensively for 12 hours. Yellowish solution was obtained after stirring and the electrodeposition of WO₃ was carried out at -0.45 V for 200 seconds. Afterwards, the residues were washed by ethanol and deionized water for three times. The WO₃ deposited substrate was kept in a vacuum drier at 60°C for future use.

5.1.3 Electrodeposition of P3MT in electrochromic fibre

0.4 g 3-methylthiophene was dissolved in 20 mL propylene carbonate (PC) which contains 0.2 g lithium perchlorate. Electro-polymerization of 3MT was conducted in a three-electrode system as mentioned above at a potential of 1.5 V
for 30 seconds. The resulting fibre with P3MT deposition layer was washed by deionized water and vacuum dried at 60 °C for 12 hours.

5.2 Results and Discussion

5.2.1 Cyclic voltammetry curves of WO₃ coating

Figure 5.2 exhibits CV curves of an electrodeposited WO₃ film in the presence of 0.1 M lithium perchlorate electrolyte solution at various scan rate from 0.02 to 0.3 V s⁻¹. Those CV curves are in line with typical CV curves which were reported elsewhere, indicating that WO₃ has been successfully deposited onto the parallel coil electrodes.

![Cyclic voltammetry curves of electrodeposited WO₃ film in three-electrode system of 0.1 M lithium perchlorate electrolyte solution.](image)

Figure 5.2 Cyclic voltammetry curves of electrodeposited WO₃ film in three-electrode system of 0.1 M lithium perchlorate electrolyte solution.
As shown in Figure 5.3(a), symmetric characteristic peaks are observed in CV curves of the assembled device, which possesses a symmetrical WO₃|electrolyte|WO₃ configuration. A stability test was taken on as-assembled device where the sample was scanned from -2 to +2 V with 0.1 V s⁻¹ scan rate. According to Figure 5.3(b), the CV curve after 1000 scanning times exhibited expected decay. More detailed stability test in terms of electrochromic function will be presented later in this chapter.

Figure 5.3 Cyclic voltammetry curves of the as-prepared device (a) at a various scan speeds; (b) at 0.1 V s⁻¹ before and after 1000 times cycles.

5.2.2 Energy dispersive X-ray analysis of WO₃ coating

EDX-SEM spectra of WO₃ coated area indicating the component elements can be found in Figure 5.4, where strong peaks of element tungsten can be observed at around 1.7 and 1.9 keV. Those peaks further confirmed that WO₃ coating has been achieved on coil-shaped electrodes.
5.2.3 Surface morphology of WO₃ coating

The influence on deposition potential has been investigated as shown in Figure 5.5. Increasing working potential would lead to less deposition time for same amount of WO₃ coatings. However, it will also increase the possibility of WO₃ coatings to get cracked or agglomerated if working potential was set too high. Figure 5.5(a) to (c) illustrate the resulting coating morphology under various magnification levels when working potential was set at -0.5 V, where small agglomerated WO₃ particles and only few cracks can be observed. Once the potential was increased to -1 V, more cracks appeared and some coating layer started to detach from substrate (Figure 5.5(d) to (f)). Large agglomeration and significant exfoliation have been noticed when WO₃ was deposited under a bias of -2 V. (Figure 5.5(g) to (i)) Further increase of working potential led to more significant cracks which could be observed by naked eyes.
Figure 5.5 SEM images of WO₃ coating layer deposited at various potentials: (a) to (c) WO₃ deposited under -0.5 V with high, medium, and low magnifications respectively; (d) to (f) WO₃ deposited under -1 V with high, medium, and low magnifications respectively; (g) to (i) WO₃ deposited under -2 V with high, medium, and low magnifications respectively.

The formation of cracks and other physical failures can be attributed to the thickness of electrochromic materials. For example, Cui et al. reported that the thickness of electrodeposited PEDOT has direct influence on the mechanical failure observed. Minor cracks were observed on thinner coatings while delamination were found on coatings with higher thickness. Besides, coating thickness is determined by the electrode area and the mass of electrodeposited materials and the later can be expressed by the following equation:\(^{174}\)

\[ m = \frac{QM}{zF} \]
Where $Q$ is the charge passed during the deposition process, $M$ is the molar mass of the material, $z$ is the number of electrons transferred per unit material and $F$ is Faraday's constant.

Accordingly, both deposition time and bias can affect the mass of materials deposited. For instance, longer deposition time and higher bias will result in more charge ($Q$) pass through during the electrodeposition process, which leads to more materials deposited ($m$) within given surface area and further results in higher coating thickness. Therefore, one can optimize the coating thickness by adjusting the deposition time and bias. Based on the deposition results mentioned above, it was figured out that a bias below -0.5 V would be suitable for the growth of WO$_3$ over electrode surface. Hence, the working potential for WO$_3$ electrodeposition was optimized at -0.45 V in order to get optimal surface morphology. The resulting surface morphology of WO$_3$ coating has been characterized by SEM as shown in Figure 5.6. After 200 s electrodeposition at a bias of -0.45 V, WO$_3$ distributed over the electrode surface smoothly in the form of small particles and a clear gap between two helix-shaped electrodes can be observed.

![Figure 5.6](image)

Figure 5.6 (a) SEM image of WO$_3$ coated Au interdigital electrodes and the uncoated gap; (b) Magnified SEM view of WO$_3$ covered surface.
5.2.4 Electrochromic performance of WO₃|electrolyte|WO₃ fibre

Digital photos in Figure 5.7 show reversible electrochromism of WO₃ under both straight and bending status, suggesting flexibility of as-prepared device. At normal state, the device looked to have a golden colour because of the helix Au electrodes. The colour of cathode switched to dark green immediately when a +1.5 V bias was applied, while the anode remained unchanged. When a reverse bias, i.e. -1.5 V, was applied, the colours of two electrodes exchanged. The anode became dark green whereas the dark green on the cathode disappeared. This colour changing phenomenon was reversible. Here, it should be pointed out that the WO₃ layer when undertaking an electrochromic reaction changed colour from colourless to blue because of the redox reaction below:\(^{(5-1)}\):

\[
\text{WO}_3 + x\text{e}^- + xM^+ \rightleftharpoons_{\text{Nearly uncolored}}^{\text{Dark blue}} M_x\text{W}_{(1-x)}\text{O}_3 \quad (5-1)
\]

The appearance colour of dark green was originated from a colour combination between the doped WO₃ and the gold electrode.

Figure 5.7 Digital photos to show the colouration and decolouration of WO₃|electrolyte|WO₃ electrochromic fibre.
Figure 5.8 shows the optical reflectance of the fibre device before and after applying -1.5 V voltage. The reflectance of the WO$_3$ layer (marked in red line) without voltage was quite low, and the current stimuli significantly increased the reflectance (green line).

![Reflectance spectrum variation of WO$_3$|electrolyte|WO$_3$ fibre under bleaching and colouring status.](image)

Figure 5.8 Reflectance spectrum variation of WO$_3$|electrolyte|WO$_3$ fibre under bleaching and colouring status.

The colour switching speed of the device was further investigated. To do this, an optical fibre UV-VIS spectrometer was placed right above the electrode surface. The reflectance of the area detected was initially around 40%, and it increased to above 80% within first a few seconds. (Figure 5.9) This tendency indicates that the reactions completed mainly within the first few seconds and reaction speed was slowed down significantly afterward. The upward trend became smooth during the rest of time. Similarly, the reflectance dropped quickly at the beginning of bleaching process and experienced a slower decrease afterward. Here, we define the time required for the electrochromic device to achieve 90% of
reflectance change (Δρ) after switching from golden to the dark green colour as “colouration time” and the time required for restoring 90% of the Δρ from dark green to the original golden colour as “bleaching time”. Based on the data in Figure 5.9, the average colouration time and bleaching time of the fibre device was calculated, being 3.8 s and 7.5 s, respectively.

Figure 5.9 Monitored variation of reflectance at applied potential switching between +1.5 and -1.5 V.

Figure 5.10 exhibits the colour changing effect of WO₃ at various bias ranging from 0 to 1.5 V through the colour visualization made by Wolfram Mathematica®. Colours appeared at different potential levels were decomposed and mapped into a three-dimensional RGB colour space where three coordinate axis was used to refer to as green, blue and red colour respectively. When potential applied was lower than 0.6 V, colour dots mainly distributed within yellow area, suggesting that gold colour remains dominated in WO₃|electrolyte|WO₃ fibre. As the potential increased, a shift of colour dots was observed from yellow to green.
The scattered distribution of colours indicates a transitional stage of the device from yellow to green. Owing to the mixture of gold and blue fully doped-WO₃, the device appeared a dark green colour at 1.5 V.

Figure 5.10 3D mapped colour space of colours appeared of WO₃|electrolyte|WO₃ electrochromic fibre.

The colouration efficiency (CE) was used to evaluate the performance of an electrochromic device, where higher CE leads to larger optical modulation with less charges during doping and de-doping processes. CE (η, cm² C⁻¹) was calculated based on the equation (5-2): ¹⁴

\[ \eta = \frac{\Delta \text{OD}}{\Delta Q/A} \]  

(5-2)

where \( \Delta \text{OD} \) is the optical density difference, \( \Delta Q \) is the charge consumed during electrochromic transition, and \( A \) is the colouration area. At +1.5 V, the CE for the WO₃ device at 610 nm was 77.82 cm² C⁻¹. The CE values are comparable to those reported in the literatures¹⁹¹-¹⁹², suggesting this novel parallel coil electrodes would not impair the performance of electrochromic materials loaded. The electrochromic feature of the fibre device is summarized in Table 5.1.

Table 5.1 Electrochromic properties of the three fibre devices.

| Potential applied | Properties | WO₃|□|WO₃ | P3MT|□|P3MT | P3MT|□|WO₃ |
|------------------|------------|-----------|--------|--------|--------|--------|--------|
| +1.5 V           | Colour     | ![Yellow] | ![Green] | ![Red] | ![Yellow] | ![Green] | ![Red] |
5.2.5 Electrochromic performance of P3MT|electrolyte|P3MT fibre

In a similar way, we prepared a P3MT|electrolyte|P3MT device by depositing P3MT onto the dual helix electrodes. Figure 5.11 illustrates the colour changes on the P3MT|electrolyte|P3MT device. At normal state, the device looked to have a dark green colour because of the colour of the doped P3MT.

At the bias of +1.5 V, the cathode turned red, while the anode remained unchanged in colour. When the bias was switched to -1.5 V, the colour of the two electrodes exchanged. The electrochromism behind the P3MT device can be described by the equation (5-3):
Figure 5.12 depicts the reflectance spectrum of P3MT between doped status (purple line) and de-doped (red) status before and after applying -1.5 V voltage.

Figure 5.13 illustrates the switching behaviour of P3MT|electrolyte|P3MT fibre at 650 nm wavelength. The average colouration and bleaching times of the devices were calculated at 4.1 s and 6.6 s respectively.
The trends of the P3MT colouration at different bias is shown in Figure 5.14. Initially the device exhibited dark green colour, and the colour started to disappear when a potential was applied. This making the device looked as a mixture of green and gold at low bias. With increasing the potential, the device colour gradually shifted from green towards dark red.

Figure 5.14 3D mapped colour space of colours appeared of P3MT|electrolyte|P3MT electrochromic fibre.
5.2.6 Electrochromic performance of WO₃|electrolyte|P3MT fibre

By depositing WO₃ and P3MT separately to the different helix electrodes in the same fibres device, a hybrid WO₃|electrolyte|P3MT electrochromic fibre was prepared. When a -1.5 V bias was applied to the fibre device, i.e. the WO₃ and P3MT electrodes connecting to the positive and the negative electrodes of the external power supply respectively, both electrodes showed deep green, and single colour was observed on the entire fibre device. (Figure 5.15)

![Figure 5.15 Digital photos of reversible colouration of WO₃|electrolyte|P3MT fibre under +1.5 and -1.5 V bias.]

The underlying mechanism of as-observed electrochromic colours can be described as follows:

\[
\text{WO}_3 \text{ (bleached)} + x \text{ e}^- + \text{Li}^+ \rightarrow \text{Li}_x\text{WO}_3 \text{ (blue)} \quad (5-4)
\]

\[
P3MT \text{ (light red)} + x \text{ ClO}_4^- \rightarrow [P3MT+\text{ClO}_4^-]_x \text{ (deep blue)} + x \text{ e}^- \quad (5-5)
\]
In this case, the WO$_3$ was doped into Li$_x$WO$_3$ which appeared dark green colour, while the P3MT remained at the ClO$_4^-$ doped state. When a bias of +1.5 V was applied to the device, the P3MT turned red, while the WO$_3$ layer became transparent leaving gold colour. WO$_3$ and P3MT deposited in this hybrid possessed similar electrochromic properties (i.e., reflectance spectrum, response time) with results presented before, suggesting that integrating the two electrochromic materials into the same fibre device does not interfere with their original electrochromic properties. The electrochromic behaviours are summarized in Table 5.1.

The colours exhibited on the WO$_3$|electrolyte|P3MT fibre were analysed by Wolfram Mathematica® as well. Figure 5.16 shows a 3D chromaticity diagram. All the four colours were allocated into a three-dimensional chromaticity coordinate system, where each coordinate (x, y, z) represents a specific colour. The colour of de-doped P3MT was red and the colour coordinates of the dark green for the coloured WO$_3$ was similar to that of the doped P3MT.

Figure 5.16 3D chromaticity of colours originated from the corresponding two status of WO$_3$ and P3MT respectively.
Figure 5.17 shows the stability of the P3MT|electrolyte|WO₃ device. Initially, the reflectance difference of the electrodes was recorded and calculated as $\Delta \rho_0$. The reflectance differences $\Delta \rho$ after multicycle bias sweeps (between 1.5 V and -1.5 V with a time interval of 10 s) were calculated, and the ratio $\Delta \rho/\Delta \rho_0$ was used to indicate the working stability. The stability of WO₃ was superior to that of P3MT, which can be attributed to the intrinsic stability of inorganic materials. Both of WO₃ and P3MT retained more than 70% of their original $\Delta \rho_0$ after 200 cycles of sweeps.

![Figure 5.17 Stability test of electrochromic performance of WO₃ and P3MT electrodes.](image)

5.2.7 FEM analysis

To gain a comprehensive understanding of the fibre device, a finite element analysis of the potential distribution and concentration profile of Li⁺ was conducted. The analysis was generalized as following steps: physics selection $\rightarrow$ model establishment $\rightarrow$ data input $\rightarrow$ meshing $\rightarrow$ computing $\rightarrow$ outcome analysis. Electrochromic reactions involve the transfer of lithium ions between WO₃ layers.
in different helix electrodes. The lithium ion insertion caused the WO₃ switching from transparent to blue colour.

Two physical modules, secondary current distribution and transport of diluted species modules, were selected for the analysis. Secondary current distribution module was used to describe potential distributions within the device and transport of diluted specie module was employed to investigate the concentration of Li⁺ within the device. Since the intercalation and extraction of Li⁺ occurred at the interface between electrolyte and electrode, the remaining concentration of Li⁺ in electrolyte was considered as an effective estimator to measure the extent of the redox reactions involved and the electrochromic behaviour of the device.

A 3D model was established in COMSOL Multiphysic® software as illustrated in Figure 5.18. Inset is a digital photo of as-prepared device used as reference. The thickness of sputter coated Au layer was negligible, tungsten oxide layers were electrodeposited onto two helix electrodes and gel electrolyte covered the entire device.

Figure 5.18 Device geometry (inset: digital photo of actual device).
Three governing equations that describe physical and chemical phenomenon occurred have been selected out as follows: Ohm’s law, Bulter-Volmer equation, and mass transport equation:

Ohm’s law was applied to all domains of the device. Accordingly, the electron current and ionic current passed through within the device can be expressed as:

\[ j_i = -\sigma_i \nabla \phi_i \quad (5-6) \]

where \( j_i \) is electron/ionic current density and \( \sigma_i \) is electrical conductivity of layer \( i \) and \( \phi_i \) is electrical potential.

Bulter-Volmer equations, which described the intercalation and extraction of \( \text{Li}^+ \) at the interface between electrolyte and electrode surface, were applied to the interface between electrode surfaces and electrolyte and can be written as:

\[ j_{\text{loc}} = i_0(\exp(\frac{\alpha_a F \eta}{RT}) - \exp(\frac{-\alpha_c F \eta}{RT})) \quad (5-7) \]

\[ i_0 = (c_i^{\text{max}} - c_i)^{\alpha_a}(c_i)^{\alpha_c}FK \quad (5-8) \]

\[ \eta = \phi_s - \phi_l - U_i \quad (5-9) \]

where \( j_{\text{loc}} \) and \( i_0 \) are referred to local current density and exchange current density respectively, \( \alpha_a \) and \( \alpha_c \) are empirical constants at anode and cathode respectively, \( c_i^{\text{max}} \) and \( c_i \) are the maximum and actual concentration of \( \text{Li}^+ \) at interface respectively, \( \eta \) is the overpotential, \( F \) is the Faraday constant, \( T \) is the temperature and \( K \) is the reaction rate constant, \( \phi_s \) is referred to as the potential at electrode surface, \( \phi_l \) is referred to as the potential in electrolyte, \( \eta \) is over-potential and \( U_i \) is open circuit potential respectively.
Equations that described mass transport can be viewed as:

\[ R_i = \frac{\partial c_i}{\partial t} + \nabla(-D_i \nabla c_i) \]  (5-10)

\[ R = \frac{v_{loc}}{nF} \]  (5-11)

where \( c_i \) represents Li\(^+\) concentration at certain location \( i \), \( R \) is referred to as the homogeneous chemical reaction term at electrode surface, \( D_i \) is diffusivity of Li\(^+\) at certain location \( i \), \( F \) is the Faraday constant, \( n \) is the electron participated in reaction and \( v \) is the stoichiometric number. It is noteworthy here that above-mentioned mass transport equation is abbreviated since migration and convection are not taken into considerations for simplicity.

Important parameters (e.g., conductivity, concentration, ion diffusivity) set for this analysis were obtained from literature\(^{193-194}\) and listed in Chapter 3, therefore the analysis was considered as a qualitative one from the content view point.

Figure 5.19 shows the meshing features of device model established. To reduce possible error in meshing, free tetrahedrons with extra fine size were applied at the interface between electrode and electrolyte. Normal sized tetrahedrons were applied for the rest of device. This would help us to better focus on the interface area as well.
In order to simulate the experimental conditions where 1.5 V potential was applied on the fibre, 3.2 V cathode potential and 1.7 V anode potential were set as boundary conditions at the most left end and the most right end of each coil electrode respectively. Those initial potential values made the driving voltage (i.e., cell voltage) equalled to 1.5 V. The relationship between cell voltage and cathode voltage can be expressed as the following equation:

\[ V_{\text{Cell}} = V_{\text{Cathode}} - V_{\text{Anode}} \]  

(5-12)

Where \( V_{\text{Cell}} \) is referred to as the cell potential applied on this device, \( V_{\text{Cathode}} \) and \( V_{\text{Anode}} \) is the potential at cathode and anode respectively.

Figure 5.20 shows the calculated electric potential on electrodes surface over the entire fibre, which exhibiting an uneven distribution. The red area on the left end of one coil electrode (ca. 3.2 V) and blue area on the right end of the other coil electrode (ca. 1.7 V) represent areas where pre-set cathode and anode voltage was applied respectively.
Figure 5.20 Electric potential distribution within the entire fibre.

Figure 5.21 depicts the cathode and anode potential variation along X-axis. The cathode potential decreased from 3.2 V to 2.3 V and anode potential increased from 2.6 V to 1.7 V respectively along the X-axis direction. This observed potential variation was attributed to the effect of Ohmic drop, which was resulted from the spread resistance of two coil electrodes over the distance.\textsuperscript{193} This investigation would be important since it can be used to design and optimize the dimension of as-prepared device with little Ohmic drop on voltage. In addition, it is observed that the potential difference between each neighbouring cathode and anode was higher in two ends of fibre than that of central part of fibre.
Figure 5.21 Electric potential at the interface between electrode and electrolyte along X-axis direction.

Figure 5.22 exhibits the distribution of Li$^+$ concentration ($c_{Li^+}$) in electrolyte over the entire fibre. The initial value of $c_{Li^+}$ in electrolyte was set at 1.0 mol L$^{-1}$ prior to the beginning of electrochromic reactions. Uneven $c_{Li^+}$ distribution was observed mainly near cathode and anode electrodes while $c_{Li^+}$ in the rest area of electrolyte remained unchanged. The blue colour near cathode coil electrode showed the surrounding $c_{Li^+}$ was lower than initial value and red colour surrounded the anode coil can be viewed as the $c_{Li^+}$ was higher than initial value. These changes were attributed to the doping and de-doping processes occurred at cathode and anode respectively, which resulted in corresponding decrease and increase in $c_{Li^+}$. 
Figure 5.22 Concentration distribution within the entire fibre.

Figure 5.23 provides an overview of $c_{Li^+}$ along X-axis within the first 6 seconds after the beginning of reactions. Driven by above-mentioned uneven potential distribution, it was observed that the $c_{Li^+}$ variation was more significant in fibre ends than the central of fibre, indicating electrochromic reactions occurred more intensively at two ends. This can be mainly originated from the Ohmic drop within the device structure. According to Ohm’s law, the voltage drop can be calculated to be equal to the product of the current ($i$) and the resistance ($R_\Omega$):^{195}

$$\Delta E_{ohmic} = iR_\Omega \quad (5-13)$$

where $\Delta E_{ohmic}$ is the ohmic drop or iR drop, and $R_\Omega$ is the Ohmic resistance, or uncompensated resistance, and $i$ is the current passed through.

Assuming that the passage of current does not affect the potential of the reference electrode, the actual potential of the working electrode is given by the equation:^{195}
\[ E_{\text{actual}} = E_{\text{applied}} - \Delta E_{\text{actual}} = E_{\text{applied}} - iR_D \]  

(5-14)

In addition, the Ohmic drop is affected by the current and potential distribution which in turn are highly related to the geometry of the device. For instance, various shape and size of electrode will lead to corresponding changes of equipotential lines. Therefore, the unevenly occurred reactions can be finally attributed to the difference in geometry feature of the ending areas and the central areas. Besides, the concentration change occurred more intensively at inception and then slowed down after 4 s.

Figure 5.23 Li\(^+\) concentration at the interface between electrode and electrolyte along X-axis direction.

Figure 5.24 presents the time-dependent \(c_{Li^+}\) variation within the first 6 seconds at two points at the edge and middle of (denoted as point A and point B) anode coil electrode respectively, which showed \(c_{Li^+}\) distribution feature on a single
coil. Although the decrease in $c_{Li^+}$ variation rate was observed at both point A and B, the $c_{Li^+}$ variation was higher in the very edge of each single coil than that of the middle part of the coil, suggesting that the uneven distribution of $c_{Li^+}$ not only occurred on the entire fibre but also on each individual coil as well.

Figure 5.24 Time-dependent Li$^+$ concentration in electrolyte within marginal area (point A) and central area (point B) of one coil electrode.

Above exhibited computations provided theoretical guidance in device design and fabrication in terms of further optimization of wearable applications. For example, it was implied that the width of each electrode coil should not be designed too large. An increasing in electrode width would lead to a decrease in concentration at central area. Lower concentration would resulted that the central area would not be fully coloured if the concentration could not reach an electrochromic threshold. A balance between electrochromic area and colouration level should be sought by figuring out the optimized gap/electrode ratio.
5.3 Conclusion

In this chapter, helical electrode-based electrochromic fibre with multiple colours have been prepared. Electrochromic materials WO$_3$ and P3MT were used to demonstrate as-prepared device works compatibly for both inorganic and organic systems. Reversible multicolour electrochromic phenomenon was observed with fast time response and reasonable stability. A finite element analysis was performed via COMSOL Multiphysics$^\text{®}$ to predict trends of potential distribution and the concentration of lithium ion of device with helix-patterned electrodes under various assumed conditions.
6 Motion Sensors from Conducting Polymer–Metal Schottky Contact

In this chapter, sensors based on the poly(3,4-ethylenedioxythiophene) (PEDOT)-Al Schottky contact were prepared. The resulting sensor would sensitively response to touch and sliding with different speed and load by generating different DC signals. Output potential generated was found to be subjected to surface morphology and was positively correlated with sliding velocity and load. Moreover, the unusual DC output signal ensures the potential possibility of making rectifier-free self-powered electronics.

6.1 Experimental

6.1.1 Electrodeposition of PEDOT in sensor

PEDOT layer was electrodeposited onto an aluminium substrate by EDOT monomer within a three-electrode system. The electropolymerization was conducted in a PC solution containing 0.2 g LiClO₄ and 1 g EDOT monomer, where platinum plate (2 cm × 2 cm) and Ag/AgCl standard electrode were used as the counter and reference electrode, respectively. The electrodeposition of PEDOT was carried out at 1.3 V for 120 seconds using a CHI760D electrochemical workstation.
6.1.2 Experimental setup

In a typical experiment, a 100 nm thickness layer of Au was sputter-coated onto the PET film, followed by electrodeposition of a layer of PEDOT. Figure 6.1 shows the FTIR spectrum of as-deposited PEDOT layer. Peaks located at 1540 and 1401 cm\(^{-1}\) are attributed to the C=C and C-C stretching in the thiophene ring. Peaks around 1111, 984 cm\(^{-1}\) represent the vibration mode of C-S bond in the thiophene ring. The peak at 668 cm\(^{-1}\) is ascribed to the stretching of C-S-C bond in the thiophene ring.\(^{196-197}\)

![FTIR spectrum of PEDOT layer.](image)

Experimental setup was established as illustrated in Figure 6.2. An aluminum rod with 5 mm diameter was set vertically and used as metal probe, which was mounted onto a programmable positioning system. When the Al rod attached to the PEDOT surface, a Schottky contact formed between Al and PEDOT. The Al-
PEDOT contact and deformation of the PEDOT layer led to generation of electrical signals.

Figure 6.2 (a) Schematic of experimental setup; (b) specification of aluminium rod.

6.2 Results and Discussion

6.2.1 Surface morphology of PEDOT sensor

The PEDOT film looked smooth on surface. Using SEM, we examined the microscopic structure of the PEDOT surface, which was very rough as can be seen in Figure 6.3. The conglomeration of PEDOT particles was observed over the surface. The PEDOT had a thickness of 114 μm from the cross-sectional image with a surface resistance of 0.9 Ω/sq.
Figure 6.3 SEM imaging of (a) surface morphology of PEDOT sensor; (b) magnified view of PEDOT coated surface; (c) cross-sectional view of PEDOT coated device.

Using AFM, one can measure the surface roughness. The surface profiles of PEDOT coating deposited at various time were compared. Figures 6.4(a), (b) and (c) illustrate a $15 \times 15 \, \mu m^2$ area which was selected from PEDOT samples with 30 s, 60 s and 120 s deposition time respectively.

Figure 6.4 AFM imaging of PEDOT samples deposited at different times: (a) 30 s; (b) 60 s and (c) 120 s.

Resulting AFM images revealed that longer deposition time would lead to large PEDOT particles agglomerated over the surface and higher surface roughness values. Accordingly, the root mean square (RMS) roughness of samples deposited
at 30 s, 60 s and 120 s were calculated at 118 nm, 166 nm and 316 nm respectively. Although longer deposition time increased the surface roughness of PEDOT layer, it was favorable since the sufficient Al-PEDOT contact can be ensured and potential short circuit can be avoided by increasing the amount of PEDOT being deposited.

6.2.2 Mechanical to electrical energy conversion from touching

Before testing the sensing property, the energy conversion performance of the Al-PEDOT contact was characterized. Starting with disconnection, the device gave no electric signal (i.e. \( V = 0 \)). Once Al rod attached to the PEDOT surface, a voltage output appeared. Figure 6.5 illustrates the output value generated by attaching the Al rod at three different locations, namely location A, B and C. At 1 N pressure, slightly different output values resulted when this happened at different locations on the PEDOT film. This can be attributed to the effect of internal resistance. When the connection at different locations, the device has different system resistance values.
Figure 6.5 Output curve of Al rod repeatedly attaching and detaching at three different locations of the PEDOT film.

Figure 6.6 depicts the typical outputs generated by a short time connection of Al and PEDOT at different pressures. At the same location, the Al-PEDOT connection led to a rapid increase of voltage. In less than 5 seconds, the output value reached a plateau. When the rod detached from the PEDOT surface, the output tuned zero sharply. The pressure applied to the PEDOT surface through the Al tip affected the output value. Higher output value generated from higher attachment pressure.
Figure 6.6 Output curve when Al rod attaching and detaching PEDOT surface at different pressures at the same location.

Such a trend can be explained by the fact that higher pressure resulted in larger deformation on PEDOT, leading to larger strain. It should be pointed out that the device output during the attaching and detaching process was in single polarity, showing a DC voltage characteristic. Such as DC output feature is similar to the layered film Al|PEDOT|Au device reported in our previous paper. To verify the Schottky contact, the I-V curve of the Al|PEDOT|Au setup was measured. The existence of Schottky effect can be proven by the I-V curves shown in Figure 6.7, where the curves of the Au|PEDOT|Al device exhibited non-linear relationship, suggesting the presence of Schottky contact. On the contrary, linear relationship was observed in curves of Au|PEDOT|Au device, indicating the contact type was Ohmic contact and therefore no electric potential could be generated.
Figure 6.7 I–V plots for (a) Au/PEDOT/Al and (b) Au/PEDOT/Au devices with 100 and 200 grams load.

Figure 6.8 shows the influence of pressure on output value when the Al rod was kept attaching to the PEDOT film. Initially, when the Al tip was gently attached to the PEDOT surface at a pressure of 0.05 N. The output was maintained at 200 mV with a slight decay in value. When larger pressure, e.g. 0.5 N, was loaded on the Al tip, the voltage increased rapidly to 400 mV, and then stabilized at 400 mV. Further increasing the pressure from 0.5 to 1.0 N led to a smaller increase in output value. However, when the pressure was above 1.0 N, the output increase became smaller. This is presumably due to the deformation level of underlying PEDOT film reached its limit. This trend is different to that in attaching/detaching mode. Since the attachment of Al on PEDOT involves an impact at certain speed, extra kinetic energy caused a larger impact deformation at the initial stage.
Figure 6.8 Voltage change when pressing the PEDOT film at different pressures.

Figure 6.9 shows the output profile when the Al rod was kept attaching to the PEDOT surface for a long time. In 16 hours of constant connection, the output voltage decayed from initial 600 mV to 100 mV. The inset chart in Figure 6.9 shows an enlarged view of output signal in the first 600 seconds. A stable output was observed before 200 seconds followed by a slump in output value. For practical detection, 200 seconds of stable output is adequate for signal collection.
Figure 6.9 Long time output profile when Al rod constantly connecting to PEDOT. (at the same location)

6.2.3 The detection of movement

To prove the ability to sense a moving object, we moved the Al rod on the PEDOT surface. In one of the experiments, the Al tip initially disconnected with PEDOT film, and it then attached to the film at a constant speed. Once the tip touched the PEDOT, a voltage signal was detected. In this case, the output signal fluctuated with time. Figure 6.10 depicts the typical output profile for the sliding tests at the same area but different sliding speeds. Sliding at higher speed resulted in higher output value. The fluctuation of the output signals suggests variable pressure on the PEDOT layer which leads to dynamic change in the strain. The increase of output voltage could also come from the temporarily increased contact area between Al and PEDOT surface.
Figure 6.10 Typical signals generated by sliding movement.

Figure 6.11 shows the output signals generated when the Al rod moved back and forth within the same location at a certain speed which ranged from 0.18 to 0.88 cm s\(^{-1}\) (the negative speed indicated the movement was in opposite direction). The accelerating and decelerating time can be neglected since the accelerated and decelerated times were very short (less than 0.01 second). The output signals generated quasi-linearly increased with the increase in speed. Apart from the correlation between speed and output signals, the shapes of two output signals generated within the same location and speed but opposite directions were almost symmetric. Given identical pressure and movement speed, this similarity in output signals generated during two sliding processes can be explained by the similar PEDOT deformation level and strain.
Figure 6.11 Electric output generated at different movement speeds.

Figure 6.12 shows the output signals generated by movement at different acceleration models. During the test, the Al rod moved at different accelerated speeds (i.e., 0.02, 0.18, 0.53 cm s\(^{-2}\) for top, middle and bottom plot respectively) in the same distance. The maximum speed was controlled at 0.18 cm s\(^{-1}\). When the Al tip moved at an accelerated speed 0.02 cm s\(^{-2}\) and then decelerated at opposite accelerated speed, i.e. -0.02 cm s\(^{-2}\), the output voltage increased with the increase in the speed and then reduced correspondingly. However, the maximum output occurred just after the maximum speed value. This voltage hysteresis was caused by the variation of the strain. The acceleration phase gradually increased the strain and deformation force, while the deceleration phase reduced force. As a result, a combined effect on the voltage output resulted. In the constant speed period, the output signals kept fluctuating during movement presumably because of the variance in PEDOT deformation level and strain. In this circumstance, the
movement of Al rod was considered as same as that presented in Figure 6.10, where high accelerated and decelerated speeds applied. When the accelerated speed was increased to 0.53 cm s$^{-2}$, a similar trend resulted.

Figure 6.12 Electric output generated with different acceleration modes.
Figure 6.13 shows the effect of pressure on the output profile when the Al tip moved along the PEDOT surface at 0.18 cm s\(^{-1}\). With increasing the tip pressure higher output value resulted, whereas the output profile had a very small change. Therefore, this Schottky device is responsive to not only touching but also sliding at different pressures and movement profiles.

![Figure 6.13 Electric output generated at different pressure levels (sliding speed at 0.18 cm s\(^{-1}\)).](image)

Figure 6.14 shows a comparison of three waves, in which the waves A & B were generated from repeated sliding in the same location while the wave C was generated at a different location of the same PEDOT film. Here, Pearson’s correlation coefficient between two input data series was employed to characterize the output waves. The Pearson correlation coefficient was calculated by the equation (6-1):

\[
 r = \frac{\sum_{i=1}^{n}(x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^{n}(x_i - \bar{x})^2} \sqrt{\sum_{i=1}^{n}(y_i - \bar{y})^2}}
\]  
(6-1)
where \( n \) is the number of total data points collected, \( x \) and \( y \) are the output value of input value, \( \bar{x} \) and \( \bar{y} \) are the means of potential of two input waves. For the output waves A and B, the \( r \) value was calculated as 0.93. The \( r \) value being close to +1 suggests the two waves having high similarity.\(^{198}\) Therefore, sliding in the same location leads to similar outputs. The \( r \) value between the waves A and C was calculated as 0.35, indicating that high similarity of output signals can be generated by sliding at the same location with identical pressure and speed. The \( r \) value between waves B and C was 0.19. This location-dependent output was attributed to the variance in surface morphology of the PEDOT layer, which is originated from the sample fabrication process.

![Figure 6.14 Repeatability of output signals generated at same location and different locations.](image)

To verify this, we compared the surface morphology of the two typical 15 \( \mu \text{m} \times 15 \mu \text{m} \) areas selected from two different locations (denoted as location A and B) of PEDOT film deposited at 120 s as shown in Figure 6.15. According to the 2D and 3D AFM images, the surface morphology selected from the same sample differed significantly in terms of the size and distribution of PEDOT particles. In addition, for each selected area, the surface roughness was both high (i.e., RMS
roughness of 369 nm and 316 nm for Figures 6.15 (a) and (c) respectively) and maximum height difference within each area was both above 2 µm. This variance in surface morphology caused variation in contact area between PEDOT and Al tip and deformation level of the local PEDOT, which subsequently affected output signals. Uniform PEDOT film with a smooth surface would allow the output has higher similarity when sliding at different locations of the same film.

Figure 6.15 AFM imaging of PEDOT film deposited at 120 s: (a) 2D and (b) corresponding 3D profile of surface profile from location A; (c) 2D and (d) corresponding 3D profile of surface profile from location B.

6.2.4 Speed and load weight sensing

Apart from Al rod, other objects were used as tip for detection of movement. To do this, the tip was covered with an aluminum sheet. Figure 6.16 illustrates the
experimental setup of using pencil as tip which covered with a thin layer of Aluminum.

Figure 6.16 Experiment setup of using Al coved pencil as tip.

Figure 6.17(a) shows the effect of movement speed on the output feature generated by the devices using Al-covered pencil as probe. At the same weight load, two pencils with different harnesses (6H and 6B) were used. Both pencils were driven to slide on the PEDOT surface at a speed in the range of 0.18 to 1.8 cm s⁻¹. A quasi linear relationship between speed and resulting maximum output value was observed for both pencil involved devices, regardless of the pencil hardness. The output voltage increased with increasing the tip traveling speed. The 6H pencil showed slightly larger output values when compared with that for the 6B pencil, indicating that the tip hardness had an influence on the output. The influence of tip pressure on output values is shown in Figure 6.17(b). Higher output resulted from larger pressure on the PEDOT layer.
6.2.5 Speed sensing with patterned PEDOT film

Apart from using a continuous PEDOT film, a patterned PEDOT film was used to precisely sense the speed of the object movement. It was found that the patterned PEDOT film enabled the possibility to measure the sliding speed with high sensitivity. Figure 6.18 shows an example of the PEDOT film which has a periodically arranged gaps. When the Al tip moved to the edge of the PEDOT layer, the output value started to reduce because of the decreased contact area. The output dropped to zero once the tip entirely disconnected with PEDOT in the gap zone.
Figure 6.18 Schematic of patterned PEDOT film.

Figure 6.19 shows the influence of gap width on output signals when the tip was set right above the device surface. The ratio of tip diameter (D) to gap width (W) was calculated to indicate the contact area between Al tip and PEDOT.

Figure 6.19 Influence of gap width on output signals when the tip was right above the device surface.
Based on this feature, the speed of underlying object can be detected by measuring the time when the tip moved into and out of a gap. Here, the time \( t \) required for the tip to travel through the gap can be described as:

\[
t = \frac{d}{v \cos \theta} \quad (6-2)
\]

where \( v \) is the incident speed of tip, \( d \) is the distance of gap and \( \theta \) is the incident angle of tip.

Accordingly, \( v \) can be estimated. Figures 6.20(a) - (c) show the output profiles generated when the tip moved at three different speeds (i.e., 14.00, 5.25 and 1.75 mm s\(^{-1}\)) across the same gap. Based on the time for traveling through the gap, the travel speeds were measured as 14.20, 5.30 and 1.90 mm s\(^{-1}\) respectively, which were very similar to the preset values. The gap width must be wide enough to ensure that the detected object can completely detach from PEDOT film during movement.

Figure 6.20 Voltage profiles generated by pencil at (a) 0.18 cm s\(^{-1}\) (b) 0.53 cm s\(^{-1}\) and (c) 1.4 cm s\(^{-1}\) speed at same location.
6.2.6 Transformation from film into fibre with coil electrode structure

After above investigation of structure-performance relationship, we have further transformed the film-shaped PEDOT sensor into a fibre-shaped one which has a coil electrode structure. The fibre with coil electrode structure was prepared via template method mentioned in Chapter 4. The significance of transformation is to enhance its availability for potential application in wearable electronics. To our delight, the performance remained consistent after the transformation. Figures 6.21(a) and (b) demonstrate the corresponding output signals generated by identical speed and pressure from sliding on two fibre-shaped devices without and with gaps. The corresponding shapes indicated that the fibrous substrate did not impair the functionality of PEDOT sensor. This is attributed to the fact that the diameter of Al-tip was much smaller than that of the underlying fibrous substrate, making the sliding movement on fibre as same as that on film in terms of micro-topography. Moreover, the coil-shaped electrodes resulted in the natural formation of blank gaps along fibre axial direction as well, enabling the regulation of output signals and potential applications in speed indicator.
6.3 Conclusion

In this chapter, a Schottky contact consisting of a metal tip and a conducting polymer film was used for sensing touching and sliding movements. The output shows DC voltage feature, and the output value is determined by the force applied to the conducting polymer layer, the travel speed of the metal tip and profile of the conducting film. When a patterned conducting polymer film is employed, the movement speed of the metal tip can be directly estimated. This principle is also working when the device is formed using a single fibre as substrate. The ability to detect touching and sliding movements at different speeds and pressures together with the DC output makes the conducting polymer-metals Schottky contact very promising for development of novel movement sensors.
7 Conclusions and future work

7.1 Summary

The results generated during this PhD candidature period can be summarized as below:

In this PhD study, a comprehensive literature review on prevalent fibre-shaped electronic devices was conducted. Single fibre-based electronic devices with PCFDs structure were developed. As-developed structure exhibited unique features over other existing counterparts in terms of compact size, electric field distribution, physical structure stability, elimination of colour overlaps for electrochromic application etc. A purpose-developed template method was employed to integrate above-mentioned electrode structure into various fibrous substrates including PVC wires and fishing lines with various diameters.

Conducting polymer PEDOT was mainly used as a functional material in devices with PCFDs structure. In chapter 4, PEDOT served as both electrochromic and supercapacitive material to demonstrate the availability of above-mentioned electrode structure. The resulting fibrous electronic device showed good electrochromic and supercapacitive performance along with reasonable stability. Meanwhile, the compact and stable structure ensured that this device can be operated under repeated bending deformation.

Aside from PEDOT, an improvement on electrochromic performance was made in Chapter 5 by making inorganic/organic (i.e., WO₃ and P3MT) hybrid electrochromic device. With the presence of P3MT, as-prepared device could appear either multiple colours or uniform colours along axial direction. A 3D model
was established using finite element analysis, where an in-depth structure-function relationship was investigated. This theoretical model also revealed the potential and concentration distribution of doping ions over the device surface, providing guidance for further optimization.

In Chapter 6, single fibre motion sensor with PEDOT deposited coil electrode was prepared. The motion sensor was initially prepared on a flexible film to demonstrate the feasibility of polymer-metal Schottky contact and was transformed to a fibrous substrate with coil electrode for wearable applications. It is responsive to sliding and touching by generating corresponding DC output signals. The underlying mechanism is the Schottky contact between PEDOT and aluminium. Gaps formed by coil electrode were arranged along the axial direction of fibrous substrate, making it suitable for potential application in speed sensing and biometric authentication fields.

In conclusion, a comprehensive understanding of single fibre-based electronic device with have been established, including its preparation, characterization and modelling. As-prepared fibrous device showed versatility in many emerging fields including but not limited to electrochromic colouration, supercapacitor and motion sensing, etc. It is expected that this versatile structure will open a new direction of the development of wearable electronics.
7.2 Future work

7.2.1 Improvement on stability and durability of electronic devices with PCFDs structure

Although the fabrication of electronic devices with PCFDs structure has been achieved in Chapter 4, 5 and 6, the stability and durability of existing PCFDs are still lower than those of planar counterparts for practical uses. For example, the electrochromic performance of PEDOT electrochromic fibre dropped to 70% of its original level after 200 cycles. Hence, there is still considerable room for the improvement of cycle number of fibre-based electrochromic devices. In addition, the PEDOT-based motion sensor failed to withstand repeated sliding with pressure owing to the low adherence between PEDOT and Au layer. The improvement can be originated from both fabrication process and device design. For instance, a flexible packaging layer can be wrapped outside the gel electrolyte of PEDOT electrochromic fibre. This would prevent the solvent in electrolyte from evaporating and enhance its long-term durability.

7.2.2 Combination of electrochromic fibre and PEDOT-based DC generator

As described in Chapter 6, the PEDOT-based motion sensor generates novel DC output signals, which is highly desirable in terms of making self-powered devices. However, existing output signals generated from movement and pressure are still too small (i.e., ~1 V and 1 μA) to power electronic devices. The development of self-powered electronic devices with DC output remains premature.
Future work is supposed to focus on increasing the output current and potential by material and structural optimization.

### 7.2.3 Motion sensors with mapping functions

Since the sensor prepared in chapter 6 showed great potential in detecting speed and other external stimulus such as surface morphology, this fibrous electronic device should be further developed in conjunction with other components. For example, one promising direction is to develop this device into a probe for surface mapping. Ununiformed surface roughness will cause variations in contact area between detecting probe and the point of interest during scanning process of probe. These variations will cause corresponding changes in output potential which will be monitored simultaneously. Hopefully, the surface morphology will be revealed by the difference in output potential signals while other factors are kept constant.

### 7.2.4 Comprehensive study on finite element method (FEM) analysis of fibre with PCFD structure

Both the electrochromic and sensing fibres prepared in this PhD project utilized PCFD structures, which exhibiting considerable advantages over its conventional counterparts. Therefore, a more comprehensive theoretical understanding of as-prepared structure should be established, rather than being limited in electric and electrochemical FEM study. In addition, FEM presented in this thesis still subjected to several assumptions and the models used are simplified as well, resulting the calculated data still fail to provide more realistic guidance and prediction in terms
of device design and structural optimization. Hence, future work on the FEM model should broaden the application fields and optimize input data for a better understanding of as-prepared device with PCFD structure.

### 7.2.5 Investigation on the influence of mechanical properties on the stability of electrochromic devices

The stability of electrochromic performance of fibre-shaped devices reported in this thesis remains to be improved. As mentioned before, mechanical properties such as adhesion strength play important roles in determining the long-term stability of electrochromic devices. Hence, the adhesion strength should be taken into consideration when evaluating the performance of fibre-shaped electronics. In details, electrodeposition of materials will be carried on several substrates which are either chemically treated or have different mechanical properties. The corresponding adhesion strength can be evaluated by surface morphology characterization such as the comparison of digital photos and SEM images of as-prepared devices before and after sonication. Finally, the long-term stability will be tested and compared for a better awareness of how mechanical properties affect stability.

### 7.2.6 Investigation on the energy conversion ability of Au|PEDOT|Al devices with different substrates

Mechanical properties of PEDOT film is important for energy conversion since it can affect the level of PEDOT deformation. In order to optimize the device
performance, the substrate should be elastic as high elasticity will lead to more significant deformation of PEDOT film. The underlying mechanism is similar with that of triboelectric nanogenerators (TENG) where an elastic component (e.g., a spring or restorative polymer substrate) can be favourable for the better contact-separation process of a TENG. In details, future work will include the selection of proper substrates from a few candidates (e.g., PTFE, PET, nylon) and the energy conversion ability on various substrates will be tested in order to optimize the device performance.
8 References


