Mechanical-to-Electrical Energy Conversion of Piezoelectric Nanofibres and Conducting Polymers

by

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Abstract

Mechanical energy harvesting that converts various sources of mechanical motions, such as body movement, wind, and ocean wave, into electricity, has been attracting enormous research interest over the recent decade. Various mechanical-to-electrical energy harvesters have been developed to harvest small mechanical energy since the first piezoelectric nanogenerator was reported in 2006. However, several critical issues still exist in this area, such as low electrical outputs, poor durability and the requirement on external rectifier to convert alternating current (AC) outputs to useable direct current (DC) electricity. This PhD study offers new and systematic understandings on effectively harvesting mechanical energy using two types of materials: electrospun polyvinylidene fluoride (PVDF) nanofibres and conducting polymers.

Previous work have demonstrated the outstanding mechanical-to-electrical energy conversion property of electrospun PVDF nanofibre mats. Systematic study in this thesis reveals how electrospinning parameters, solution concentration, inter-fibre connection or electron donor/acceptor doping affect energy conversion behaviours. Experimental results have shown that high electric field intensity and intensive fibre stretching in electrospinning process have contributed to the formation of power generating PVDF nanofibre mats with high $\beta$ crystal phase content and oriented electric dipoles. Fibrous mat from non-bead, uniform PVDF nanofibres with smaller diameter showed higher $\beta$ crystal phase content and better mechanical-to-electrical energy conversion property.

Electrospun PVDF fibre mats with interconnected fibre structures have been prepared by a short-distance needle electrospinning process. This novel fibrous
structure has achieved not only high energy conversion efficiency, but also high mechanical strength to maintain the fibrous structure integrity during the compression and decompression process, which make them a promising candidate in developing mechanical energy harvesting devices with long-term stability.

Double-layer PVDF fibre mats that contain electron transfer and hole transfer agents in each layer can be prepared using a two-step electrospinning technique. The presence of tri-\textit{p}-tolylamine (TTA) or 2-(4-tert-Butylphenyl)-5-(4-biphenylyl)-1,3,4-oxadiazole (Butyl-PBD) enhances the electrical outputs of PVDF nanofibre mats and a weak rectification effect can also be observed.

Through the investigation on a conductive polymer coating, polypyrrole (PPy), on PVDF nanofibres, the interesting mechanical energy to electricity conversion behaviour of conducting polymers was discovered. Further experiment of using gold and aluminium as electrodes on each side of a solid plate compressed from conducting polymer powders, a mechanical to electrical energy conversion device with direct current pulse outputs resulted. This finding is different to most of the existing technologies for harvesting mechanical energy, in which the conventional technology can produce only AC outputs, and an external rectification component is needed to convert the output into DC power before use.

This finding triggered a careful investigation into the role of conducting polymer and metal electrodes. It has been found that the formation of a Schottky contact between conducting polymer and metal electrode plays a critical role in the conversion of mechanical energy to DC electricity. A systematic understanding of a simplified device consisting of a free-standing PPy plate, metals gold and aluminium has been established. It’s interesting to find that the generated DC power
had a large output current density, which was sufficient to drive commercial
electronic devices. This novel concept of generating DC electricity is general and
can be applied to the development of various DC devices from different conducting
polymers and metal electrodes as long as it forms a single Schottky contact in the
device.

The fundamental understanding and knowledge generated from this study on
electrospun nanofibres and conducting polymers could be useful for further
development of mechanical energy harvesting devices for various applications
Chapter 1 Introduction

1.1 Significance of research

Recently, generating electricity from small mechanical energies which are associated with body movements, muscle contractions, rotation of vehicle tires, and rainfalls, to name a few, has been agreed as a promising solution to alleviate the overdependence of fossil energy. Harvesting these low-level energies into electricity to charge personal electronics is highly desirable.

Considerable efforts have been devoted to finding effective materials and device structures to achieve this goal. For example, small mechanical energies have been harvested using miniaturized electromagnetic devices and piezoelectric converters. Most of the energy harvesting devices developed so far are mechanically rigid, which can only work at a low strain level and are not suitable for making flexible generator devices. Inorganic materials have been fabricated into nanostructure and incorporated with flexible substrates to achieve device flexibility, however the fabrication processes are rather complex with strict requirements on environment. Electrospinning is a simple and straightforward method to produce electrospun polymer nanofibre mats that can be used to fabricate light-weight and flexible energy harvesters. Although their electrical outputs are relatively lower, they can achieve high energy conversion efficiency. Like many other power generating materials, electrospun nanofibres normally produce AC outputs, rectification is needed to produce direct current (DC) power before use. For developing highly efficient and practically useable nanofibrous energy harvesting devices, it’s of significant importance to fundamentally understand the influence of electrospinning condition, solution parameters and structure stability in the energy
conversion performance. It’s also highly promising to develop self-rectified energy harvesters that can directly produce DC outputs without external rectification.

1.2 Research question and specific aims

My overall research question in this PhD project is:

*How to prepare high performance mechanical-to-electrical power generators?*

Accordingly, this research question can be divided into three specific sub-questions as shown below:

1 *How to prepare high performance mechanical-to-electrical power generators from PVDF nanofibres?*

2 *Can electrospun PVDF nanofibre mats form a self-rectified mechanical-to-electrical energy conversion device?*

3 *Why a multilayer Al/conducting polymer/Au device has a mechanical energy to DC electricity conversion behaviour?*

Previous studies on piezoelectric nanofibres have only demonstrated the possibility of using electrospinning technique to prepare pressure-sensitive nanofibrous materials for mechanical-to-electrical power generation and pressure sensing. Fundamental understandings of PVDF nanofibres and their piezoelectricity are still at their infant stage. Continuous research efforts have to be made to generate essential knowledge in this area, and some of the major knowledge gaps are described below:

*Knowledge gap 1: Nanofibre structure ~ piezoelectric property relationship is unclear.*
It hasn’t been clear that how electrospinning parameters and polymer concentrations influence the energy conversion performance of the PVDF nanofibre. Polymer concentrations and electrospinning conditions, such as applied voltage, spinning distance and electric field intensity, have a direct effect on fibre morphology, diameter and crystal structure, which are all related to piezoelectricity of the nanofibres. A clear nanofibre structure ~ piezoelectric property relationship will help us fully understand the capability of electrospinning in preparing piezoelectric nanofibres.

Knowledge gap 2: No study related to piezoelectric property of short-distance electrospun nanofibre mats.

Two different types of electrospinning approaches have been used to prepare piezoelectric PVDF nanofibres. Single PVDF nanofibres are prepared by near-field electrospinning (spinning distance < 0.5 cm), and PVDF nanofibre mats are obtained from normal electrospinning process (spinning distance > 8 cm). Randomly-orientated fibre mats prepared by a short-distance electrospinning (1 cm ≤ spinning distance ≤ 8 cm) has not been reported so far. It has been known that an interconnected nanofibre mat or even a dense film can be formed when the spinning distance is shorter than normal, however it is still unclear if short-distance electrospun PVDF mats have a piezoelectric feature. According to the law of physics, higher electric field intensity can be formed between two electrodes with a shorter distance, it is reasonable to expect that short-distance electrospun PVDF nanofibres will have better piezoelectric properties. An experimental investigation on these short distances would clarify this.
Knowledge gap 3: power generators often generate only AC outputs.

Mechanical-to-electrical power generators typically generate an AC output. To use this power for driving a microelectronic device, a rectifier has to be used to convert AC outputs to DC power, which reduces the energy efficiency. It would be much more efficient to develop a mechanical-to-electrical power generator that can generate DC outputs without using an external rectifier. More knowledge has to be generated to practically realise this self-rectifying effect in nanofibrous power generators.

Knowledge gap 4: Al/conducting polymer/Au device generate DC outputs.

As an unexpected discovery during the surface coating of PVDF nanofibres using conducting polymer, we have found that a sandwich structure device containing a gold electrode, a free-standing plate compressed from conducting polymer powders and an aluminium electrode (Au/conducting polymer/Al) could generate DC electrical outputs when it was subjected to repeated impact. However, the reason to this unique phenomenon is still unclear.

Accordingly, this PhD project is focused on the following specific aims:

Aim 1: To elucidate the relationship between polymer concentrations, spinning conditions and mechanical-to-electrical performance of the nanofibres prepared by a conventional electrospinning technique.

It has been achieved by the systematic investigation of how electrospinning parameters (applied voltage, spinning distance and electric field intensity), polymer concentrations and fibre mat thickness affect the fibre morphology, crystal structure and mechanical-to-electrical energy conversion performance.
Aim 2: To understand the effect of short-distance electrospinning on nanofibre piezoelectricity.

The morphology structure, crystal structure and mechanical-to-electrical energy conversion performance of fibre mats electrospun at a spinning distance in the range of 1-8 cm have been studied in details.

Aim 3: To explore possible method to achieve a self-rectifying effect in mechanical-to-electrical electrospun PVDF power generators.

It is possible to regulate charge transport in mechanical-to-electrical power generating devices if a p-n junction is formed within the device. A practical approach would be doping the piezoelectric material so that it has a p-type or n-type characteristic and to form a p-n junction. For electrospun nanofibres, doping agents can be easily added into polymer solutions before electrospinning to obtain doped nanofibres. Since the uniform distribution of the doping agents within the solution, they are likely to disperse uniformly in the nanofibres. Electrospun nanofibre mats are formed typically by layered dispersion of nanofibres on a collector. This creates opportunities to control the dopant type and level in different fibre layers within one piece of nanofibre mat. However, little work has been done in this area. Previous work has achieved double layer nanofibre mat with p-n junction formed in between, the aim here will be doping different hole and electron transport materials into PVDF nanofibres to form multilayer power generator devices, and investigating the possible charge transport regulation for self-rectifying.

Aim 4: To explore the possible mechanism of self-rectifying effect of Al/conducting polymer/Au during mechanical-to-electrical conversion.
Schottky contact has the similar fundamental working principles with $p$-$n$ junction that there is an effective barrier potential for separating the charges at interface $^7$. This aim will be achieved by examining various aspects of performance with the Al/PPy/Au device, such as how the electrical outputs response to the strain level, the electrical characteristic, the variation of energy band under compression and so on.

### 1.3 Thesis outline

Apart from this introduction chapter, this thesis includes seven more chapters as described below:

*Chapter 2* is a literature review about background knowledge and recent progress in mechanical energy harvesting, piezoelectric materials, electrospinning technology, piezoelectric nanofibres, conducting polymers and DC electricity generators.

*Chapter 3* introduces the raw materials, experiment processes and characterisation methods used in this project.

*Chapter 4* systematically examines the effects of PVDF concentration and electrospinning parameters on fibre morphology, $\beta$ crystal phase content and mechanical-to-electrical energy conversion properties of electrospun PVDF nanofibre mats.

*Chapter 5* reports that interconnected PVDF fibre mats can be prepared by electrospinning a PVDF solution at a short spinning distance of 1-8 cm. The fibre morphology, $\beta$ crystal phase content and mechanical-to-electrical energy conversion performance of fibre mats electrospun at these spinning distances were studied in detail.
Chapter 6 reports the mechanical-to-electrical conversion performance of electrospun PVDF homojunction nanofibre mat. Although the electrical outputs still show the AC mode, the output values were enhanced compared with those of the single type layer.

Chapter 7 develops a novel concept of using single Schottky contact between a conducting polymer plate and a metal electrode to directly convert mechanical energy into DC electricity. The electric energy generated is sufficient to drive commercial electronic devices, as exemplified by commercial motor and LED diode.

Chapter 8 concludes the main conclusions obtained from this research work. Future work in this area are also proposed.
Chapter 2 Literature Review

Energy shortage is one of the most serious problems we are facing globally. We are using more energies than ever before and most of the electricity is generated from non-renewable fossil resources, which causes considerable environmental issues. At the same time, the rapidly growing number of electronic devices has contributed to the complication of power supply. Finding a renewable and stable energy source for electricity generation and power supply has become an urgent task for us.

For replacing widely used fossil energies, various renewable energy sources have been extensively investigated for electricity generation. Among common renewable energy sources, mechanical energies such as water flow, wind, human body movements, and sound vibration are broadly available in our daily life. If these mechanical energies can be efficiently harvested and converted to electric power, it will not only alleviate our overdependence on fossil energy, but also create opportunities to develop self-powered electronics to harvest energies from the environment to drive themselves. For this purpose, various mechanical-to-electrical power generators have been built with different principles, mainly electromagnetic induction, piezoelectric power generation and triboelectric power generation.

2.1 Mechanical energy harvesting

In the last two centuries, many power stations have been built to convert various large scale mechanical energies, like fall water, wind etc., into electricity through electromagnetic induction effect. The small scale mechanical sources have been ignored for a long time due to their low energy level. However, the boom of personal electronics in recent two decades has dramatically increased the demand
on electric power at low energy level, which directly contributed to the rapidly increasing interests in harvesting small mechanical energies.

2.1.1 Recent progress in piezoelectric nanogenerators

Piezoelectric nanogenerators (NG) are a type of energy harvesting device that converts mechanical energy into electricity based on the energy conversion using nano-structured piezoelectric material. Based on the piezoelectric materials, they can be separated into two groups: inorganic nanogenerators and organic nanogenerators.

2.1.1.1 Inorganic nanogenerators

The first NG was reported in 2006, in which vertically-grown piezoelectric ZnO nanowires were used. When an AFM tip was used to deform a single ZnO nanowire, a voltage output of 9 mV was generated. In order to obtain higher electrical outputs, tens of thousands of nanowires have to be integrated into generator devices \(^9,10\). Many other types of vertically aligned inorganic nanowires (such as InN, GaN, CdS and ZnS) have also been reported to fabricate NGs \(^11-16\). Compared with micro- or even macro- sized piezoelectric generators, NGs show higher energy conversion efficiency because of the size effect and less crystal defects \(^17,18\).

Since the preparation of these single crystalline nanowires requires highly controlled fabrication processes and consumes a large amount of energy, some other techniques have been investigated for preparing piezoelectric nanostructures. For example, piezoelectric PZT nanofibres have been fabricated using a two-step process, which involved electrospinning a PVP/PZT solution into composite nanofibres and calcinating them into pure PZT nanofibres \(^19\). Finally, the PZT
nanofibres were treated within an electric field of 4 V/μm, at a temperature over 140 °C for about 24 hours. The resulted nanofibres had orientated electric dipoles along the electric field and a voltage output as high as 1.6 V was recorded. PZT nanowires prepared by electrospinning have also been reported to fabricate a textile NG for wearable and self-powered devices. PVP and PZT precursor salts including tetrabutyl titanate, zirconium acetylacetonate and lead subacetate were used to prepare the electrospinning solution. The NG fabricated using PZT nanofibres could generate 6 V voltage output and 45 nA current output, which are large enough for powering a liquid crystal display and a UV sensor. Electrospinning process was also used to prepare vertically aligned ultra-long PZT nanowire arrays for an integrated NG device, which generated ultrahigh output voltage of 209 V and current density of 23.5 μA/cm². The electric output can be directly used to stimulate the frog’s sciatic nerve and to induce a contraction of a frog’s gastrocnemius. Highly-efficient piezoelectric PZT thin film NG on a plastic substrate was prepared by a laser lift-off (LLO) process. The device could generate an electric output of 200 V and 150 μA/cm² under periodical bending/unbending motion. The energy harvested from the thin film NG (3.5 cm × 3.5 cm) through human finger motion could directly light up over 100 blue LEDs. However, no organic material has been found to have such a high electric output.

For improving the flexibility of NG, PZT nanofibres were encapsulated by polydimethylsiloxane (PDMS) during device fabrication.

BaTiO₃ (BTO) is another inorganic piezoelectric material that has been used to fabricate NGs. BTO based flexible NGs were prepared through a multistep fabrication. BTO thin films were firstly deposited on a Pt/Ti/SiO₂/(100)Si substrate with a poling treatment within an electric field of 100 kV/cm and then the
metal/BTO/metal structured ribbons were transferred onto a flexible substrate \(^{22}\). By bending, the device could generate a voltage output up to 1.0 V with an output current density of 0.19 \(\mu\text{A/cm}^2\), and the power density reached about 7 mV/cm\(^3\). A nanocomposite generator containing BTO nanoparticles and graphic carbons was reported to generate a voltage output of 3.2 V under a 0.33% strain level \(^{23}\). Recently, a new type of virus-templated BTO NG was reported for driving commercial electrical devices \(^{24}\). The anisotropic BTO nanocrystals were synthesized on an M13 viral template through the genetically programmed self-assembly of metal ion precursors. The outputs of about 300 nA and 6 V were recorded when the device was under periodical mechanical deformations.

2.1.1.2 Polymeric nanogenerators

Inorganic nanogenerators are often fragile and rigid, they normally work at a very low strain level, which limits their practical application in some cases. In this regard, piezoelectric polymers offer better chances to make flexible generators. Traditionally, piezoelectric polymers can be fabricated into piezoelectric dense films through a complicated casting-stretching-poling process. Recent studies have indicated that electrospinning can effectively prepare piezoelectric polymer fibres with high energy conversion efficiency and good flexibility.

PVDF NG was fabricated through direct-writing using a near-field electrospinning process in 2009 \(^{25}\). A voltage output up to 2.5 mV was reported under mechanical stretch of a single PVDF nanofibre (diameter of 700 nm). By directly-writing many aligned PVDF nanofibres, an enhanced voltage output of 76 mV was also reported by the same authors \(^{26}\). Pan et al fabricated PVDF hollow fibre tubes by using near-field electrospinning process with the metallic coaxial needle injector \(^{27}\). The
voltage output generated from the PVDF fibre tubes was about 71.66 mV, which was much higher than that of solid PVDF fibres. At the same time, the output power (856.07 pW) from the fibre tubes was 2.46 times higher than that (347.61 pW) of solid fibres.

Compared with near-field electrospinning, conventional electrospinning is more favourable in producing nanofibres because of its simplicity in setup, broader options of spinning materials and higher fibre productivity. In 2010, Benjemin et al. \(^2^8\) reported the preparation of a NG using aligned PVDF nanofibres electrospun from a conventional electrospinning technique. After an electric poling treatment at 20 kV for 15 min, the device could generate an open circuit voltage of 20 mV and a short circuit current of 0.3 nA at a strain of 0.05%. A similar technique was reported by Luana et al. \(^2^9\) in 2013 to fabricate NGs and pressure sensors using aligned P(VDF-TrFE) nanofibres. Recent investigation has also revealed that among four different kinds of collecting substrates used in electrospinning, glass slide, poly(ethylene terephthalate), poly(ethylene naphthalate) and paper, the PVDF nanofibres collected on the thinnest paper (33 \(\mu\)m thick) substrate resulted in the highest voltage output \(^3^0\).

Other methods were also used for fabricating polymer NGs. Yanchao et al \(^3^1\) developed a novel sponge-like mesoporous piezoelectric PVDF thin film based NG by using a simple casting-etching process. The device (2 cm \(\times\) 1 cm \(\times\) 28 \(\mu\)m) was placed on a flat surface while an aluminium block was placed on the device. An oscillator was located 6 cm away from the NG system and generated surface oscillations with 40 Hz frequency, the device could generate about 11.1 V voltage output and 9.8 \(\mu\)A current output. Nagamalleswara et al \(^3^2\) reported a piezoelectric NG fabricated using a hybrid film containing BaTi\(_{(1-x)}\)ZrxO\(_3\) nanocubes and PVDF
matrix. The flexible NG could generate electrical outputs about 11.9 V and 1.35 μA upon a periodic pushing-releasing 11 N force at a frequency of 21 Hz.

The nanofibre research group at Deakin has a long history of developing electrospinning technology, making functional nanofibres and exploring their advanced applications. Our contribution in this field include a pioneering discovery on highly-efficient mechanical-to-electrical energy conversion based on randomly-oriented PVDF nanofibre mats. Without using any post treatments, randomly-oriented PVDF nanofibre mats can generate a 2.2 V open circuit voltage and a 4.2 μA short circuit current, as shown in Figure 2.1. Our studies have suggested that high electric field intensity in electrospinning process is a key to form PVDF nanofibres with high β phase content and aligned electric dipoles. We have also demonstrated that the generated electricity can be rectified and stored in a capacitor for driving commercial electronic devices such as LEDs.

![Figure 2.1](image)

**Figure 2.1** Piezoelectric (a) voltage and (b) current outputs of an electrospun PVDF nanofibre generator under a 5 Hz repeated compressive impact. (Working area = 2 cm², nanofibre mat thickness = 140 μm.)

We also discovered that needleless electrospinning can be more efficient to produce piezoelectric PVDF nanofibre mats with improved energy conversion performance.
Compared with the single needle spinneret used in normal electrospinning, disc spinning significantly improves fibre productivity. More importantly, the higher applied voltage used in disc electrospinning can lead to higher electric field intensity which results in higher $\beta$ phase content and better molecular orientation. As shown in Figure 2.2, under the same compression condition, the electrical outputs of needleless electrospun nanofibre mats are considerably higher than those of needle electrospun nanofibre mats.

![Figure 2.2](image.png)

**Figure 2.2** Piezoelectric (a) voltage and (b) current outputs of nanofibres power generators prepared by different electrospinning processes. (Peak force of the impact=10 N, working area = 2 cm$^2$, nanofibre mat thickness = 100 $\mu$m.)

To increase the $\beta$ phase content in PVDF nanofibres, different additives (such as salts and carbon nanotubes), have been added into polymer solution for electrospinning. Dipti et al added a nickel chloride hexahydrate (NiCl$_2\cdot$6H$_2$O) into PVDF solution to prepare composite nanofibres. The $\beta$ phase content in the PVDF nanofibres was increased by 30%, and the voltage outputs from the nanofibre mats was three times higher than that of pure PVDF mats. Various amounts of multi-walled carbon nanotubes (MWCNTs) have also been added into PVDF nanofibres to enhance piezoelectricity. It was reported that 5 wt%
MWCNTs was the optimum condition to reach the highest $\beta$ phase content, which increased the voltage output by 200%. A NG based on electrospun PVDF and silver nanowires composite was developed and the device showed better piezoelectricity than the pure PVDF NG 36. Electrospun PVDF-HFP nanofibres doped with silver nanoparticles were prepared 37, and the $\beta$ phase content was increased by the addition of silver nanoparticles. The voltage output of 3 V and a current density of 0.9 $\mu$A/cm$^2$ were achieved from the composite nanofibres.

Another method to improve the piezoelectric outputs is integrating piezoelectric inorganic materials into piezoelectric polymers. PVDF-NaNbO$_3$ nanofibre generator was fabricated to harvest the energy from low-frequency range of human motions 33. Under a compressive pressure of 0.2 MPa, it could generate a voltage of 3.4 V and a current of 4.4 $\mu$A.

### 2.1.2 Recent process of other mechanical-to-electrical nanogenerators

Besides of piezoelectric nanogenerators, other types of nanogenerators have also been investigated with different mechanisms, such as triboelectric effect, electrostatic induction and electromagnetic effect, etc.

#### 2.1.2.1 Triboelectric nanogenerators

Triboelectric effect has been observed for many centuries, however the application of using nanomaterials to harvest triboelectric charges for power generation didn’t exist until a few years ago 38-40. A general TENG is made of two pieces of flexible substrates covered by organic/inorganic films with different triboelectric feature. Due to the different surface electron affinity, the triboelectric charges are generated when the films contact, therefore the mechanical contact/separation process results
in the output of electric power. In this process, electrostatic induction plays an important role for electricity generation. Table 2.1 shows the triboelectric series of different materials, indicating the ability of gain/loss charges. The more positive materials tend to lose electrons while the more negative materials have a tendency of gaining electrons.

**Table 2.1** Triboelectric materials according to the triboelectric polarity.

<table>
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</tr>
</thead>
<tbody>
<tr>
<td>Wood</td>
<td>Hard Rubber</td>
<td>Acetate, Rayon</td>
<td>Polyvinyl alcohol</td>
<td>Polyester (Dacron)</td>
<td>Polyisobutylene</td>
<td>Polyurethane flexible sponge</td>
<td>Polyethylene glycol terephthalate</td>
<td>Polyvinyl butyral</td>
<td>Formo-phenolique</td>
<td>Epoxide resin</td>
<td>Natural Rubber</td>
<td>Polystyrene</td>
<td>Polyethylene</td>
<td>Polypropylene</td>
<td>Polyimide (Kapton)</td>
<td>Polyethylene terephthalate</td>
<td>Polyvinyl Chloride (PVC)</td>
<td>Polyvinylidene fluoride—Silicon</td>
<td>Polytetrafluoroethylene (Teflon) – Fluorinated PEI</td>
</tr>
</tbody>
</table>

Four fundamental modes of TENG have been proposed so far (see figure 2.3) and they are the basics of various prototypes of TENGs.
Figure 2.3 The four fundamental modes of TENGs: (a) vertical contact-separation mode; (b) in-plane contact-sliding mode; (c) single-electrode; and (d) freestanding triboelectric-layer mode.

**Vertical contact-separation mode**

The first invented operation mode of TENGs was vertical contact-separation mode \(^{43,44}\). As shown in Figure 2.3a, two different dielectric films face with each other with the electrodes deposited on the other side. A physical contact of the two films creates oppositely charged surfaces to form a potential difference by applying the external force. Once one of the films is moved away to form a gap between two surfaces, the potential difference drop leads to charge carrier movement in the external circuit in order to balance the electrostatic field. When the gap is eliminated, the triboelectric charge created potential difference disappears and the induced electrons flow back. In this mode, the electricity generation comes from
periodic switching between the contact/separation conditions of the two contact surfaces and AC output is resulted.

**In-plane contact-sliding mode**

In in-plane contact sliding mode (Figure 2.3b), two dielectric films are fully aligned and the electric field is created by the triboelectric charges, but does not cause a potential drop as the positive charges and negative charges are fully balanced. Once a relative sliding in parallel is introduced by an external force, the triboelectric charge balance is interrupted, resulting in the creation of dipole polarization. Thus, a potential difference between two electrodes is generated which drives the electrons to flow in the external circuit. A periodic sliding back and forth generates an AC output \(^{45-47}\).

Compared to the vertical contact-separation mode, the in-plane contact-sliding mode possesses several advantages. Firstly, the generation of triboelectric charges is more effective with an intensive triboelectrification facilitated by sliding friction, which contributes to the enhancement of output power for practical applications \(^ {48}\). Secondly, it is easier to develop a more advanced design for high-performance TENGs. As for vertical charge separation, an air gap is mandatory to be created after the releasing of the external force, which usually requires complicated design of the device structures and results in difficulty for TENG packaging and practical use for some cases.

**Single-electrode mode**

In the two modes discussed above, two electrodes are required to generate and store opposite charges during energy conversion, which considerably limits the TENGs’
applicability for energy harvesting from freely moving object. To solve this problem, a single electrode mode TENG was developed. As shown in Figure 2.3c, this mode contains a moving object and an electrode that connected to the ground.

When the moving object and electrode are fully in contact, the triboelectric charges are generated due to the different surface electron affinity. Once the moving object separates from the electrode, it will cause electron flow from the ground to electrode in order to balance the electric potential. When the moving part moves back and comes into contact with the electrode again, the increasing number of induced positive charges drives the electrons to flow from electrode to the ground until reaching the electrostatic equilibrium.

**Freestanding triboelectric-layer mode**

As shown in Figure 2.3d, a pair of symmetric electrodes are placed underneath a dielectric layer. When the moving object approaches to and/or departs from the electrodes, it creates an asymmetric charge distribution via induction, causing the electron flow between two electrodes to balance the potential distribution. The movement of the electrons between the paired electrodes in response to the forth and back motion of the moving object generates an AC output.

2.1.2.2 Other mechanical-to-electrical nanogenerators

Other approaches have also been used to fabricate mechanical-to-electrical energy harvesters. For electromagnetic induction effect that normally used for harvesting large mechanical energies before has been used for collecting small mechanical energy now, with miniaturized generator size. The ionization of a polymer gel under mechanical deformation can also generate electrical outputs, although only
at a few millivolts \(^57\). And recent study shows that the very small electrical energy can be generated by simply bring two metals with different work functions together \(^58\).

### 2.2 Piezoelectric materials

#### 2.2.1 Piezoelectric crystals and ceramics

The word “piezo” comes from a Greek word “piezein” which means to press and “piezoelectricity” means the electricity generated by pressing. Piezoelectricity was first discovered by Pierre Curie and Jacques Curie in 1880 on quartz. The same piezoelectric phenomenon was later observed on topaz, tourmaline, cane sugar and Rochelle salt (sodium potassium tartrate tetrahydrate). Among these piezoelectric crystals, quartz and Rochelle salt exhibited the highest piezoelectricity. In 1881, a reverse piezoelectric effect was mathematically deduced by Gabriel Lippmann \(^59\) and this opposite piezoelectric effect wasn’t confirmed until an experimental observation by the Curie brothers in 1882. Figure 2.4 shows a schematic of the direct and the converse piezoelectric effect \(^60\). When a voltage is applied to the piezoelectric material, the material will deform in the direction of the poling voltage. On the other hand, mechanical strain on a poled piezoelectric material changes the dipole moment, resulting in a voltage output.
In 1910, Woldemar Voigt published *Lehrbuch der Kristallphysik* (Textbook on Crystal Physics) and described that 20 natural crystal classes among all 32 crystal classes had piezoelectricity. Some natural piezoelectric materials are shown in Figure 2.5.

**Figure 2.4** A schematic of converse and direct effects of piezoelectric materials.
Figure 2.5 Some natural piezoelectric materials.  

The first application of piezoelectric materials was on marine sonar during World War I. Paul Langevin and his co-workers proposed an ultrasonic submarine detector which consisted of a transducer and a hydrophone. The transducer was made of thin quartz crystals and two steel plates to detect the echo of acoustic wave under water. After the WWII, considerable development in piezoelectric materials has been made and they have gained broader applications, such as signal filters, accelerometers, igniters, generators and microphones.

Artificial piezoelectric materials were developed by several research groups in the United States, Japan and the former Soviet Union during the World War II. These researches have led to the discovery of lead zirconate titanate (PZT), the most successful commercial piezoelectric ceramic so far. PZT has the highest piezoelectric coefficient among all piezoelectric ceramics investigated and it has been widely used in many different areas. However, PZT ceramics contain lead and cause health and environment concerns. To avoid the use of lead, a great amount
of research has been conducted to find lead-free piezoelectric ceramics in recent years. Barium titanate (BaTiO$_3$) has a similar perovskite structure to PZT and been identified as a promising candidate to PZT in many applications. Zinc oxide (ZnO) has also shown excellent piezoelectric properties, it has two main crystal forms: hexagonal wurtzite and cubic zinc blende, as shown in Figure 2.6. Recently, other piezoelectric inorganic materials were also reported, including InN, GaN, CdS, ZnS and MoS$_2$ $^{12,16,64}$.

![Figure 2.6](image)

Figure 2.6 (a) hexagonal wurtzite and (b) cubic zincblende crystal structures of ZnO. (Yellow spheres are zinc atoms while grey spheres are oxygen atoms) $^{65}$.

### 2.2.2 Piezoelectric polymers

Another type of piezoelectric material is piezoelectric polymers, and they are fundamentally different to piezoelectric ceramics. Compared with brittle piezoelectric inorganics, piezoelectric polymers are much more flexible which makes them very useful for some applications which requires a high strain level or the adaptability to more complex 3D surfaces $^{66}$. However, piezoelectric polymers usually have lower piezoelectric coefficient than piezoelectric ceramics.
For a polymer to have piezoelectricity, it should meet three basic requirements: (1) large molecular dipoles; (2) well aligned dipole; and (3) recoverable mechanic deformation \(^{66}\).

### 2.2.2.1 Semicrystalline piezoelectric polymers

The first piezoelectric polymer, polyvinylidene fluoride (PVDF), was reported by Kawai in 1969 \(^{67}\) and attracted in a worldwide interest. Since then, more fluoropolymers with piezoelectric properties have been investigated, such as poly(vinylidene fluoride-co-trifluoroethylene) (PVDF-TrFE) and poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP).

Some other semicrystalline polymers with piezoelectricity have also been investigated, for example nylon-11 and polyurea-9. Table 2.2 lists some semicrystalline piezoelectric polymers and their piezoelectric properties \(^{66}\). PVDF has the highest piezoelectric coefficient \((d_{33})\), about 20~28 pC/N. About 50% ~ 60% macromolecular chains in PVDF is crystallized depending on the preparation condition (more details about PVDF are discussed in section 2.2.3 of this thesis).

PVDF-TrFE also exhibits strong piezoelectric property, and its \(d_{33}\) value is about 12 pC/N. Although this value is lower than that of PVDF, piezoelectric PVDF-TrFE has the advantages of higher crystallinity (up to 90%) and higher application temperature. Odd-numbered nylons have a low piezoelectric constant at room temperature. However, their piezoelectric coefficient increases significantly at elevated temperature. So far, the maximum reported \(d_{33}\) value of Nylon-7 and Nylon-11 is 17 pC/N at 200 °C and 14 pC/N at 185 °C, respectively \(^{68}\). However they have not been used in any practical applications, mainly due to their hydrophilic nature that causes performance variation in moisture environment.
Polyureas with odd-number methyl groups also show piezoelectric property, but their piezoelectric coefficients are highly dependent on processing temperature. Hattori et al. synthesized polyurea-9 with piezoelectric property in 1996 and piezoelectric polyurea-5 was successfully prepared after that.

### Table 2.2 Some semicrystalline piezoelectric polymers and their properties

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Structure</th>
<th>$T_m$ (°C)</th>
<th>$T_c$ (°C)</th>
<th>Max Use Temp (°C)</th>
<th>$d_{33}$ (pC/N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF</td>
<td><img src="image" alt="PVDF Structure" /></td>
<td>-35</td>
<td>175</td>
<td>80</td>
<td>20–28</td>
</tr>
<tr>
<td>PTFE</td>
<td><img src="image" alt="PTFE Structure" /></td>
<td>32</td>
<td>150</td>
<td>90–100</td>
<td>12</td>
</tr>
<tr>
<td>Nalon-11</td>
<td><img src="image" alt="Nalon-11 Structure" /></td>
<td>195</td>
<td>195</td>
<td>185</td>
<td>3 at 25°C</td>
</tr>
<tr>
<td>Polyurea-9</td>
<td><img src="image" alt="Polyurea-9 Structure" /></td>
<td>50</td>
<td>180</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

### 2.2.2.2 Amorphous piezoelectric polymers

In addition to semicrystalline piezoelectric polymers, some amorphous polymers also show piezoelectric property. However, study on amorphous piezoelectric polymers has been very limited due to their low piezoelectric coefficient. Table 2.3 lists some common amorphous piezoelectric polymers, include polyvinyl chloride (PVC), polyacrylonitrile (PAN), polyvinyl acetate (PVAc), poly (vinylidene cyanide vinylacetate) (PVDCN/VAc), polyphenylethnitrile (PPEN) and 2,6-bis (3-aminophenoxy) benzonitrile/4,4’ oxydiphthalic anhydride ((β-CN) APB/ODPA).
Table 2. 3 Comparison of piezoelectric properties of some amorphous polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Structure</th>
<th>$T_p$ (°C)</th>
<th>$d_{33}$ (pC/N)</th>
<th>$P_r$ (mC/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC</td>
<td>[CH]_n</td>
<td>80</td>
<td>5</td>
<td>15</td>
</tr>
<tr>
<td>PAN</td>
<td>[CH]_n</td>
<td>90</td>
<td>2</td>
<td>25</td>
</tr>
<tr>
<td>PVAc</td>
<td>[CH–CH]_n</td>
<td>30</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>P(VDCN/VAc)</td>
<td>[CH]_n</td>
<td>170</td>
<td>10</td>
<td>50</td>
</tr>
<tr>
<td>PPEN</td>
<td>[O–O]_n</td>
<td>145</td>
<td></td>
<td>12</td>
</tr>
<tr>
<td>(β-CN) APB/ODPA</td>
<td>[O–O–N]_n</td>
<td>220</td>
<td>5 at 150°C</td>
<td></td>
</tr>
</tbody>
</table>

PVC has a low $d_{33}$ value in the range of 1.5 ~ 5 pC/N, it has still attracted considerable interest because of its stable piezoelectric performance. PAN is one of the most widely used polymers in modern engineering. Theoretical calculation has predicted that PAN could have a very strong piezoelectricity. However, poling treatment of PAN was found to be inefficient, and as a result, the $d_{33}$ value of PAN is very low, only about 2 pC/N.

Strong piezoelectric behaviour was observed in the amorphous copolymer of VDCN and VAc. P(VDCN/VAc) shows the largest piezoelectric coefficient (10 pC/N) among all amorphous polymers which was attributed to its large relaxation strength. Another polymer, (β-CN) APB/ODPA polyimide, synthesized by combining three polar functional groups (pendent nitrile group, main chain dianhydride group and main chain diphenylether group) was reported to have a thermally stable piezoelectric property.
2.2.3 PVDF and its piezoelectricity

PVDF has a simple monomer structure of \(-(\text{C}_2\text{H}_2\text{F}_2)-\), which includes carbon, hydrogen and fluorine atoms. As a member of fluoropolymers, PVDF has a relatively low melting temperature of about 177 °C. Depending on the processing conditions, PVDF can have five different crystalline phases. These crystal phases contain three different chain conformations, all trans (TTT) planar zigzag for \(\beta\) phase, trans-gauche-trans-gauche (TGTG’) for \(\alpha\) and \(\delta\) phases, and trans-trans-trans-gauche-trans-trans-trans-gauche (TTTGTGG’) for \(\gamma\) and \(\varepsilon\) phases (Figure 2.7) \(^74\). The \(\beta\) phase has the highest dipolar moment per unit \((5-8 \times 10^{-30} \text{ C} \cdot \text{m})\) among these crystal phases. The \(\gamma\) and \(\delta\) phases are lower in dipolar moment, while \(\alpha\) and \(\varepsilon\) phases are non-polar.

![Figure 2.7 Chain conformations of \(\alpha\), \(\beta\) and \(\gamma\) PVDF phases \(^74\).](image)

When PVDF is melt, molecular chains don’t show fixed structure and can move freely. By cooling, PVDF solidifies and crystallizes into spherulites-spherical pockets structure growing from the crystal nucleus, mainly forming thermodynamically stable \(\alpha\) and \(\gamma\) phase conformations \(^75\). Figure 2.8 (a) shows a microscope image of PVDF crystallized from polymer melt and both \(\alpha\) and \(\gamma\) phase
spherulites show the radial structure. Figure 2.8 (b) indicates the schematic drawing of PVDF spherulites, which contains crystalline lamellae structure and non-crystalline structure (amorphous). The thin, platelet-like lamellae crystals are separated and surrounded by the amorphous areas. These lamellae are made of crystalline order packed PVDF chains, with the thickness of a few nanometers and lateral dimension of several micrometers. This bi-phase structure can be commonly found in crystallisable polymers. To obtain the \( \beta \) phase PVDF, it normally requires additional manufacturing process like mechanical drawing and electrical poling.

So far, several piezoelectric effect models have been proposed. One can be explained by a simple molecular models shown in Figure 2.9. Without deformation, the positive and negative charges of each molecule are centrally symmetric and the molecular as a whole is in a neutral state. When the molecule is deformed by an external force, an electric dipole is generated (Figure 2.9b). As a result, fixed charges appear on the polymer surface (Figure 2.9c). Figure 2.9 demonstrates the direct piezoelectric effect of PVDF. PVDF also exhibits a reverse
piezoelectric effect, in which a mechanical deformation of PVDF film is resulted upon an electrical field.

**Figure 2.9** A simple molecular model to illustrate piezoelectric: (a) a free molecule with no piezoelectric polarization, (b) polarization under an external force ($F_k$), and (c) piezoelectric charges $^7$.  

In another model shown in Figure 2.10, non-poled piezoelectric materials are in the pristine state that contains randomly oriented molecular dipoles and electrically neutral. After poling treatment, the electric dipoles are aligned along the poling direction which result in the positive dipole charges ($V^+$) and the negative dipole charges ($V^-$) appearing on the two sides of material. To balance the electric charges, they will attract the opposite charges outside to the material surface. When the material is subjected to tensile or compressive strain, this balance is interrupted due to the change of dipole charges ($V^{++}$ or $V^-$), resulting piezoelectric effect $^7$. 
PVDF has been the best piezoelectric polymer so far. Among its five crystal phases, $\alpha$ crystal phase is the most thermodynamically stable phase. However, $\alpha$ phase PVDF doesn’t exhibit piezoelectric property because generated electric charges are neutralized. To obtain $\beta$ phase, the traditional method is doing post-treatments of $\alpha$ phase PVDF. For example, when a melt-cast PVDF film is stretched mechanically to 300% its original length, $\alpha$ phase changes to all-trans $\beta$ phase. Further electrical poling can orient all the electric dipoles into one direction, allowing the formation of a piezoelectric film.

The piezoelectric properties of PVDF are limited in a certain temperature range due to the physical characteristics. When the temperature is below the PVDF glass temperature $T_g$ (about -40 °C), the piezoelectricity will temporarily lose and recover by increasing the temperature above glass temperature. In addition, if the
temperature exceeds the Curie temperature $T_c$ (about 80 °C), the piezoelectricity will vanish permanently because of the change in crystal structure $^{80}$.

Based on the direct and reverse piezoelectric effects, PVDF films have been fabricated into devices for many different applications, including power generators, sensors, transducers and actuators. Piezoelectric sensors can convert physical vibrations into electrical signals, which have been used to test pressure, acceleration, vibration, and orientation. Piezoelectric actuators convert an electrical signal into a displacement to modulate machining tools, mirrors or lenses $^{81}$.

### 2.3 Electrospinning and electrospun nanofibres

#### 2.3.1 Nanofibres

Nanomaterials are defined as the materials with at least one dimension less than 100 nm (1 nm=10$^{-9}$ m) $^{82}$. Their small size, large specific-surface and unique quantum effect enable them to have remarkable mechanical, thermal, electronic, optical and magnetic properties, which have attracted enormous interests in academic and industrial fields over the recent decades. Nanomaterials can be classified into several types: zero dimensional (0D, e.g. nanoparticles), one dimensional (1D, e.g. nanofibres, nanorods and nanotubes), two dimensional (2D, e.g. nanosheets, nanoplates) and three dimensional (3D, e.g. superlattices) nanomaterials.

According to this definition, nanofibres should have a diameter less than 100 nm. However, due to the difficulty in preparing continuous fibres of diameter smaller than 100 nm and requirements (such as on mechanical property and productivity) for many practical applications, the size scope for nanofibres are commonly
expended to a diameter small than 1000 nm and an aspect ratio greater than 100
\cite{83,84}. Benefit from their smaller diameter compared with conventional fibres, nanofibres have much higher specific surface area. Fibrous mats made of nanofibres are highly porous with excellent pore interconnection \cite{85}. These unique characteristics have opened up enormous application potential in various areas such as environment protection, biomedical, energy generation/storage and military purposes \cite{86-90}. Many techniques have been developed to prepare nanofibres, including mechanical drawing, template synthesis, melt-blown, phase separation, self-assembly and electrospinning \cite{91-94}. Mechanical drawing normally produces micro or even thicker fibres. Template synthesis method only produce discontinuous nanofibres of several hundred micrometres in length, and the same limitation applies on phase separation and self-assembly as well. Among these methods, electrospinning is the most promising method to fabricate continuous nanofibres. Electrospun nanofibres are controllable in fibre morphology, diameter and fibrous structure by adjusting the electrospinning parameters and solution conditions.

2.3.2 History of electrospinning

Although the word “electrospinning” appeared recently, such a spinning process actually has a long history. The first relevant observation was recorded in the late 16th century by William Gilbert, who noticed that a spherical water droplet on a dry surface could be deformed to a conical shape when it was approached by a piece of rubbed amber \cite{95}. In 1887, Charles Vernon Boys described a process of fabricating fibres from a simple apparatus containing a small dish which was connected to an electrical machine. The fibres could be prepared from a viscous liquid when it reached the edge of a dish and the liquid could be sealing wax, collodion and
beeswax\textsuperscript{96}. Further development was made by John Zeleny in 1914 when he published his study on electrospraying\textsuperscript{97}. In 1934 and 1944, Anton Formhals published a series of patents about producing continuous polymer fibres using an electrical force, and these patents have been regarded as the origin of modern research on electrospinning\textsuperscript{98,99}. In 1936, the first spinning process using an electric field to prepare fibres from melt solutions was patented by C. L. Norton\textsuperscript{100}. In 1969, Taylor made some important contributions to the fundamental understanding of fluid behaviour under an electric field. He investigated the conical structure formed at the nozzle tip and came to the conclusion that the conical angle could be maintained at around $49.3^\circ$ once the electrostatic force balanced the viscous fluid surface tension\textsuperscript{101}. This conical structure has been referred to as “Taylor cone” afterwards in electrospraying and electrospinning. Taylor also predicted that in a parallel electric field, there exists two critical instabilities including Rayleigh and bending instability in an electrically driven water jet. Rayleigh instability is caused by the surface tension of solution, which tends to minimise solution surface area and break the jet into droplets. And bending instability tends to bend the jet into spiral coil condition.

In 1994, the term “electrospinning” was started to be used to replace “electrostatic spinning” in research publications. Since then, electrospinning has gained increasing attention. This can be clearly seen from the number of scientific publications on electrospinning over the last two decades. As shown in Figure 2.11, almost 20000 scientific papers about electrospinning have been published. Before the year of 2000, there were less than 10 publications per year. However, this number increased dramatically since then, especially in the recent 5 years. Presently, there are over 200 universities and research institutes around the world are doing
research on electrospinning and different applications of electrospun nanofibres.\textsuperscript{102-105}

![Graph showing the number of scientific publications on electrospinning since 1992](image.png)

**Figure 2.11** Numbers of scientific publications on electrospinning since 1992 (Database: Scopus; keyword: electrospinning; search date: 19/05/2016).

### 2.3.3 Electrospinning principle

Figure 2.12 shows the basic setup of electrospinning, which mainly consists of three parts: 1) a high voltage power supply to provide electrostatic charges, 2) a needle nozzle attached to a solution carrier (e.g. syringe) to form jets, and 3) a grounded collector for collecting nanofibres.\textsuperscript{106} Many modifications have been carried out to achieve better control of fibre morphology, orientation, function and fibrous structure.\textsuperscript{107-111} In a solution based electrospinning process, the polymer solution is delivered from the solution carrier to the nozzle tip. If no electric field is applied to the tip, the solution droplets will form and fall off from the nozzle tip due to the gravity. Once a high voltage is applied, the droplet at the nozzle tip will be highly electrified. The high potential difference between the nozzle tip and the grounded
collector leads to droplet deformation into a conical shape (Taylor cone). When the applied voltage is increased, the polymer jet forms from Taylor cone once the electric field force overcomes the surface tension of the solution. Then the charged jet undergoes a bend or whipping process to form a fine filament in the electric field accompanying the evaporation of the solvent. As a result, the dry nanofibres deposit on the collector in a random orientation.

Fibre formation during electrospinning is an incessant process, it can be separated into three stages: jet initiation, jet elongation (bending or whipping instability) and fibre solidification.\textsuperscript{112}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{electrospinning_setup.png}
\caption{A typical electrospinning setup.\textsuperscript{106}}
\end{figure}

**Jet initiation**

Once a high voltage is applied to the solution, the solution is polarized, and driven by the electric field formed between the nozzle and the collector, the solution at the nozzle tip is deformed to form a “Taylor cone”. When the intensity of the electric field reaches a critical value (V_c), the electrostatic force overcomes the surface tension ($\gamma$) of the spinning solution. A solution jet is initiated from the cone. The
Vc is affected by the distance between the nozzle tip and the collector (H), the length of the needle nozzle (L) and its diameter (R), by following the equation below 101:

\[ V_c^2 = 4 \left( \frac{H^2}{l^2} \right) \left( \ln \frac{2L}{R} - 1.5 \right) (0.117\pi R\gamma) \]  

(2-1)

Jet elongation

The jet ejected from the Taylor cone undergoes a thinning process before the newly-formed fibres deposit on the collector. This thinning process happens within a very short period of time, just about several milliseconds. Yarin et al. suggested that while the jet was moving towards the collector, it underwent a chaotic motion or bending instability due to the repulsive force among the injected charges 113. Early observations on jet elongation led to a wrong conclusion that the jet split into many fine fibres during electrospinning, as shown the image in Figure 2.13(a). The jet appears to be split into sub filaments 114. Under high speed camera, a single jet is actually observed, which whips and bends after the initial stable stage (Figure 2.13(b)).

![Figure 2.13 Images of an electrospinning jet taken with a exposure time of (a) 16.7 ms and (b) 1.0 ms](image)

Figure 2.13 Images of an electrospinning jet taken with a exposure time of (a) 16.7 ms and (b) 1.0 ms 114.
Reneker et al. pointed out that the typical path of the jet was a straight segment followed by a coil with the increase of diameter. After whipping for several turns, a new whipping instability formed with a small coil in a turn of the large coil (green part in Figure 2.14). Then even smaller instability coils formed in a turn of the small coils and so forth until the whipping process finished \textsuperscript{115}.

\textbf{Figure 2. 14} A schematic of instantaneous electrospinning jet path containing several levels of electrical bending instabilities \textsuperscript{115}.

\textbf{Fibres solidification}

Fibre solidification is another important stage of electrospinning process. During the course of jet whipping and elongation, solvent evaporation from the jet simultaneously happens to solidify the fibres. The solidification rate is depending on the solvent type, polymer concentration, spinning distance, temperature and humidity \textsuperscript{116}.
2.3.4 Electrospinning parameters

Many parameters can influence electrospinning process and fibre formation. Generally, these parameters can be divided into three categories: polymer solution properties, operating parameters and ambient conditions.\(^\text{117}\)

**Polymer solution**

The solution properties, e.g. polymer molecular weight, solution viscosity, concentration, solution conductivity, dielectric constant, surface tension and solvent, significantly influence electrospinning process and fibre morphology.\(^\text{118,119}\)

Solution viscosity is critical in forming continuous fibrous structure. Normally, electrospray happens if the solution viscosity is too low, and polymer particles are formed from split solution droplets. Uniform polymer fibres can only be formed when solution viscosity reaches a certain level to obtain sufficient macromolecular chain entanglements.\(^\text{120}\) For a given polymer solution system, higher polymer molecular weight and polymer concentration lead to higher solution viscosity. If solution viscosity is just high enough to avoid electrospray, continuous fibres with beaded structure are normally obtained.

The jet is stretched due to repulsion force among the electrostatic charges along the charged jet and interaction between the jet and the electric field during electrospinning. An absolutely non-conductive polymer solution cannot be electrospun due to no electric charges on the droplet surface. Increasing charge density within jet would enhance bending instability, resulting in finer nanofibres.\(^\text{121,122}\) This can be achieved by increasing the solution conductivity or using polar solvents. For instance, poly(acrylic acid) (PAA) solution conductivity was...
significantly increased by adding small amount of NaCl, and finer PAA nanofibres could be collected\textsuperscript{104}. However, extra charges cannot be accumulated on the droplet surface if the solution is highly conductive, which results in difficulty for drawing jet into fine filament due to weak electric stretching force. Coarser fibres are often electrospun from polymer solutions made of a solvent with low dielectric constant\textsuperscript{123}.

The jet initiation in electrospinning requires sufficient electrostatic force to overcome the solution surface tension. In some cases, replacing water with organic solvents in the spinning solution can help to obtain finer fibres. This is because most organic solvents have a lower surface tension than water, which facilitates the electrostatic stretching on the solution jet.

The volatility of solvents also influences the fibre morphology. For some low volatile solvents, wet fibres would be collected if the solvent cannot be evaporated completely before depositing on the collector. In this case, they are easy to merge together to form an interconnected fibrous structure\textsuperscript{124}. For highly volatile solvents, rapid solvent evaporation cools the fibre and induces moisture condensation on the fibre surface, resulting in the formation of porous fibres.

**Process parameters**

In addition to solution properties, operating parameters such as applied voltage, flow rate, needle diameter, spinning distance and collection mode are also critical in electrospinning of nanofibres\textsuperscript{125}.

Applied voltage is the source of electrostatic force, and its intensity directly affects electrospinning behaviour. In electrospinning process, direct-current (DC) voltage
is used in most cases. Although alternating current (AC) voltage can also be used for operating electrospinning process, only a few papers reported on AC power supply due mainly to the safety issue of AC voltage, especially at a high voltage level\textsuperscript{126}.

Electrospinning takes place only when the applied voltage reaches a critical value at which the electrostatic force overcomes solution surface tension to initiate a jet. The influence of the applied voltage on fibre diameter is very complicated and sometimes causes controversy among academics. For examples, Mohammad et al.\textsuperscript{127} reported that the diameter of Nylon 6 nanofibres decreased when the applied voltage was increased from 12 kV to 18 kV. Didem et al.\textsuperscript{128} also reported a similar result on PVA nanofibres. However, Zhang et al.\textsuperscript{129} indicated a slight increase in the average diameter of PVA fibres when increasing the applied voltage from 5 kV to 13 kV. Interestingly, Satoru et al.\textsuperscript{130} reported that an increase in applied voltage from 9.2 kV to 25 kV did not cause a significant change in the average diameter of type I collagen fibres. In general, most studies suggested that finer fibres are formed at a higher applied voltage. But the applied voltage cannot be increased unlimitedly as corona discharge will happen and stop the electrospinning process.

The flow rate of polymer solution can be controlled by a syringe pump. Generally, lower flow rate allows the solution having longer time for polarization. Big solution drop can form and fall off the nozzle tip if the flow rate is too high. The appropriate flow rate is dependent on several factors, such as the solution properties and nozzle diameter\textsuperscript{131}.

The influence of nozzle diameter on fibre diameter was reported by Nuray et al.\textsuperscript{132} who used four types of syringe needles (22G/0.7 mm inner diameter, 20G/0.9 mm,
19G/1.06 mm and 18G/1.25 mm) to electrospin silk fibroin solution. When all other electrospinning parameters were maintained unchanged, the nozzle of larger diameter produced coarser nanofibres. However, Javier et al.’s 133 study on electrospinning of PMMA nanofibres concluded that there was no close correlation between nozzle size and fibre diameter.

Spinning distance in electrospinning is typically referred to as the distance between the nozzle tip and the collector. Since it determines the time for solvent evaporation before the fibres reach the collector, this parameter affects fibre morphology and fibrous structure. Dry nanofibres are often collected at a spinning distance long enough to ensure sufficient solvent evaporation 134. If the distance is too short, the fibres will not have enough time to solidify before reaching the collector, which will result in a network with inter-connected fibres or even a wet dense film.

Different collection modes can also influence the fibre morphology. Metal plate is often used for collecting randomly oriented fibres. For collecting aligned fibres, high speed rotating drum collector or parallel electrodes are often used. Luana et al. 29 reported that aligned PVDF-TrFe nanofibres could be prepared when the drum rotated at the speed of 4000 rpm, corresponding to linear speeds of 16 m/s at the collector surface. Dan et al. 135 found that electrospun fibres could be collected across the gap between the two gold electrodes with high degree of alignment.

**Ambient conditions**

Ambient conditions such as temperature, relative humidity and air flow during electrospinning could influence fibre morphology 136. Vrieze et al. 137 reported that relative humidity could either increase or reduce fibre diameter depending on the polymer type. A similar effect was also observed on the influence of temperature.
Increasing temperature could enhance solvent evaporation, but reduce solution viscosity. The reverse effect results in different trend of fibre diameter change. Electroblowing is a technique combining electrospinning with air flow around the spinneret. Increasing air pressure increases the shear force on a jet and decreases the fibre diameter, as illustrated by Chang Suk Kong et al.\(^{138}\).

### 2.4 Conducting polymers

Conducting polymers refer to a special group of polymeric materials with much higher electrical conductivity than common polymers. The first conducting polymer, polyacetylene, was reported by Alan Heeger, Alan MacDiarmid and Hideki Shirakawa in 1977.\(^{139}\) Because of this important discovery, they were awarded the Nobel Prize for Chemistry in 2000. Since then, many new conducting polymers have been synthesised (Table 2.4)\(^ {140}\). In 1979, Dial et al. used electrochemical polymerisation method to synthesis conductive polypyrrole film\(^ {141}\). In the following a few years, conductive polyaniline film was produced using the same approach, as well as the conducting polythiophene film\(^ {142,143}\). Compared with normal insulating polymers, conducting polymers show significantly higher electrical conductivity and they are sometimes called organic metals.

Unlike metals, polymers do not have free electrons to move around in the lattice. Thus, for conducting polymers, they contain a high degree of $\pi$-bond conjugation with overlapping $\pi$ molecular orbitals. $\pi$-bond conjugation means the remain valence electrons of adjacent carbon atoms overlap and form double bonds\(^ {144}\). When an electron in $\pi$-bond is removed from the carbon backbone, it forms a radical cation (also called polaron) that is delocalised in 3~4 monomer units. When another electron is removed from the backbone, it will form two individual polaron
or one bipolaron. Polaron and bipolarons can be moved and are responsible for electrical conductivity of conducting polymers\textsuperscript{145}.

**Table 2.4** Some conjugated conducting polymers\textsuperscript{140}.

<table>
<thead>
<tr>
<th>Polymer (date conductivity discovered)</th>
<th>Structure</th>
<th>E gap (eV)</th>
<th>Conductivity# (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. Polyacetylene and analogues</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyacetylene (1977)</td>
<td><img src="image" alt="Polyacetylene" /></td>
<td>1.5</td>
<td>$10^3 - 1.7 \times 10^5$</td>
</tr>
<tr>
<td>Polypyrrrole (1979)</td>
<td><img src="image" alt="Polypyrrrole" /></td>
<td>3.1</td>
<td>$10^2 - 7.5 \times 10^3$</td>
</tr>
<tr>
<td>Polythiophene (1981)</td>
<td><img src="image" alt="Polythiophene" /></td>
<td>2.0</td>
<td>$10 - 10^3$</td>
</tr>
<tr>
<td>II. Polyphenylene and analogues</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Poly(paraphenylen) (1979)</td>
<td><img src="image" alt="Poly(paraphenylen)" /></td>
<td>3.0</td>
<td>$10^2 - 10^3$</td>
</tr>
<tr>
<td>Poly(p-phenylene vinylene) (1979)</td>
<td><img src="image" alt="Poly(p-phenylene vinylene)" /></td>
<td>2.5</td>
<td>$3 - 5 \times 10^3$</td>
</tr>
<tr>
<td>Polyaniline (1980)</td>
<td><img src="image" alt="Polyaniline" /></td>
<td>3.2</td>
<td>$30 - 200$</td>
</tr>
</tbody>
</table>

The conjugated polymers are semiconductors or insulators in their pristine, neutral or undoped state. After doping, the electrical conductivity of conjugated polymers can be enhanced significantly, varying from $10^{-12}$ S/cm to about $10^5$ S/cm. Normally, conducting polymer can be $p$-type doped or $n$-type doped upon reaction with an oxidant or a reductant. Figure 2.15 shows the doping process of $p$-type polypyrrole\textsuperscript{144}. Based on their special chemical and physical properties, many applications have been developed around conducting polymers, including electrochromic devices, batteries, artificial muscles and electromechanical actuators etc\textsuperscript{146-149}. 
The oxidation (p-type doping) level in conducting polymers can be controlled at extremely high level, up to 50% \(^{150}\). The doped charges in the polymer are stabilized by counter ions to maintain the material electroneutrality. Chemical dopant selection is limited as the dopant requirements would be dictated by a specific polymer electronic structure. Table 2.5 shows the typical dopants used in conjugated polymer chemical doping and the maximum oxidation levels \(^{151}\).
Table 2.5 Anionic and cationic dopants typically used for chemical doping in conducting polymers 151.

<table>
<thead>
<tr>
<th>Dopant ion</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloride</td>
<td>Cl⁻</td>
</tr>
<tr>
<td>Perchlorate</td>
<td>ClO₄⁻</td>
</tr>
<tr>
<td>Tetrafluoroborate</td>
<td>BF₄⁻</td>
</tr>
<tr>
<td>p-toluene sulfonate</td>
<td>CH₃-C₆H₄-SO₃⁻</td>
</tr>
<tr>
<td>Trifluoromethane sulfonate</td>
<td>CF₃SO₃⁻</td>
</tr>
<tr>
<td>Hexafluorophosphate</td>
<td>PF₆⁻</td>
</tr>
<tr>
<td>Polystyrene sulfonate</td>
<td>(-CH₂CH(C₆H₄SO₃-)ₙ⁻)</td>
</tr>
<tr>
<td>Bromide</td>
<td>Br⁻</td>
</tr>
<tr>
<td>Sulfate</td>
<td>SO₄²⁻</td>
</tr>
<tr>
<td>Iodide</td>
<td>I⁻</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Maximum doping level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(pyrrole)</td>
<td>33% (ClO₄⁻)</td>
</tr>
<tr>
<td>Poly(thiophene)</td>
<td>30% (ClO₄⁻), 6% (PF₆⁻)</td>
</tr>
<tr>
<td>Poly(aniline)</td>
<td>42% (Cl⁻)</td>
</tr>
<tr>
<td>Poly(p-phenylene)</td>
<td>44% (Li⁺)</td>
</tr>
</tbody>
</table>

Chemical doping takes place through redox reaction, which is a straightforward and simple process of adjusting charge carrier concentration. However, there are some drawbacks with this approach, like limited choice of dopants and poor dopant chemical stability. Also another problem comes from the homogeneity of the doped conducting polymers 152, and this problem can be effectively solved by electrochemical doping.

During electrochemical doping process, an electrolyte is used and the doping level in the conducting polymer can be precisely controlled by applied potential. In the case of $p$-type doping, the polymer is oxidised and anions acted as charge balancing ions to diffuse into the polymer film. The electrochemical doping method is widely used in electrochemical transistors, light-emitting electrochemical cells and electrochemical batteries 153-155.

Some other doping methods have also been used, which include charge injection without counter ions involved, photodoping and doping with acid or base 156-158.
In the last two decades, polypyrrole (PPy), polyaniline (PANi) and poly (3,4 ethylenedioxythiophene) (PEDOT) have been extensively studied due to their high electrical conductivity and reasonable environment stability. They can be easily prepared from the monomer by electrochemical or chemical polymerization method \(^{159-165}\). Using pyrrole as an example, pyrrole is heterocyclic aromatic organic compound with a five-membered ring \(^{166}\). Electrochemical polymerization can be carried out by oxidizing pyrrole monomer at anode while chemical polymerization happens by reacting pyrrole monomer in an oxidant environment (typically FeCl\(_3\)). A simple schematic of polymerization process can be found in Figure 2.16. The colour of PPy can be varied from pale yellow at neutral state to black at the fully doped state.

![Pyrrrole](image)

**Figure 2. 16** A schematic of PPy polymerization \(^{167}\).

### 2.5 Charge transport in conducting polymers

Based on the concept of doping, conducting polymers are similar to the traditional inorganic semiconductors according to well-defined electronic bands \(^{168,169}\). However, the conduction mechanisms of conducting polymers and inorganic semiconductors are different. Doping inorganic semiconductors creates free charge carriers by injection or ejection of electrons in the valence or conduction bands, respectively \(^{170}\). For conducting polymers, they have two distinct energy levels: the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular
orbitals (LUMO), which are corresponding to the valence band and conduction band in the inorganic semiconductors. The energy difference between these two bands is band gap. After doping, it creates accessible energy levels between HOMO and LUMO bands.

The microstructure of conducting polymers suggests that the charge carriers move in a discontinuous path while it would be a continuum path in the crystalline inorganic semiconductors. It is supported by the hole/electron hopping mechanism in the conducting polymers, which can be envisioned as a series of redox processes happen within the polymer. Several effects influence the charge transport in conducting polymers.

2.5.1 Effect of morphology on charge transport

A conducting polymer film can be illustrated as a macroscopic assembly of charged polymer chains and ions. Most conducting polymers are amorphous in structure, sometimes with a certain degree of crystallinity. Figure 2.17 shows the typical schematic of conducting polymer structure, including both amorphous and crystalline regions.

![Figure 2.17](image)
Charges in a conducting polymer are generally transported in three ways: intrachain, interchain transport and tunnelling. Intrachain charge transport takes place along the polymer backbone while interchain transport happens involving the charge hoping between the neighbouring chains. Tunnelling charge transport takes place between conducting segments separated by amorphous regions.

Normally, intrachain charge transport contributes more to electrical conductivity than interchain charge transport. Nonetheless, the interchain charge transport can still happen to encourage charge carriers to hop from one chain to another chain instead of being trapped by structure defects or having to move in the opposite direction.

The polymer molecular weight affects chain length, therefore also the charge transport in conducting polymer. Polymer with lower molecular weight always has shorter chain length and more crystallinity than polymer with higher molecular weight, so the charge carrier mobility is always lower.

2.5.2 Effect of charge carrier density on charge transport

Because of the electroneutrality, each positive charge injected into the conducting polymer during the oxidative polymerization will be counter-balanced by an anion. So a conducting polymer with a higher doping level indicates higher concentration of counter ions. Genies et al. observed that the capacitive current of PPy increased with increasing oxidation level.

The mobility of charge carrier is decided by polymer structure, oxidation level and the ionic radii of diffusing species, as illustrated by equation 2-2:

\[ D = \frac{D_e D_f C_T}{D_e C_e + D_f C_f} \]  

(2-2)
Here, $D_e$ and $D_i$ represent electronic and ionic diffusion coefficients, respectively. $C_r$ is the total concentration of redox sites, while $C_e$ and $C_i$ are the concentration of electronic and ionic charges.

According to this equation, it can be believed that a reduced conducting polymer has a lower diffusion rate than that of an oxidized one. At the same time, a smaller diffusion anion travels more quickly \(^{179}\).

### 2.5.3 Effect of insulator-to-metal transition on charge transport

It has been indicated that the charge transport in conducting polymers largely depends on to which side of the metal-insulator (M-I) transition the polymer belongs \(^{180}\). The polaron or bipolaron lattice can be formed progressively filling the energy band gap by doping, which can result in emerging of a distinct band structure. The conductivity of these polymers increases quickly once exceeding the percolation threshold.

### 2.6 Recent progress in DC energy harvesters

Most of the existing technologies for harvesting small mechanical energy can only produce alternating current (AC) outputs. Rectification is needed to produce direct current (DC) power for power supply. This not only reduces the overall energy conversion efficiency but also increases complexity and difficulty in miniaturizing the generator system. Self-rectified energy harvesters that can directly produce DC outputs without extra rectifying are highly desirable.

#### 2.6.1 p-n built-in energy harvesters

For organic solar cells (OSC), their output signals are typically DC power. As shown in Figure 2.18, the basic structure of OSC contains two active layers
(acceptor and donor) between the electrodes (ITO anode and Al cathode). When the solar cell is exposed to light, the electrons jump from HOMO level to LUMO level, leaving positive charged holes in the HOMO level at the interface of donor \((p\)-type\) and acceptor \((n\)-type\) layers. A \(p-n\) junction is formed between the donor and acceptor layers. The electrons and holes move in a specific direction to generate a direct current \(^{181}\). Herein, donor layer is also called hole transport layer or electron blocking layer while acceptor layer is called electron transport layer or hole blocking layer. The materials for these two layers should have differences in electron affinity and ionization energy. Larger the differences are, stronger the electric field among \(p-n\) junction will be formed \(^{182,183}\).

Figure 2.18 A basic bilayer structure of organic solar cells \(^{181}\).

Built-in \(p-n\) junctions have been used in fabricating piezoelectric NGs. The \(p-n\) junction inside could reduce the screening effect that is caused by the present of the free carriers in piezoelectric materials. Keun et al. used poly(3-hexylthiophene) (P3HT) as a \(p\)-type conducting with phenyl-C\(_{61}\)-butyric acid methyl ester (PCBM) on piezoelectric semiconducting ZnO thin film \(^{184}\). The \(p-n\) junction between P3HT and ZnO enhanced electric outputs of the ZnO/P3HT:PCBM power generator. The
voltage output increased by 18 folds and current output by triple folds. Shin et al. deposited an thin layer of CuO on ZnO thin film to form a $p$-$n$ junction\textsuperscript{185}, and they found that the output voltage was enhanced about 7-fold and current density was one order of magnitude higher compared with the ZnO NGs without the CuO layer. Keun et al. also coated P3HT on ZnO nanowires (NWs) directly to fabricate NG\textsuperscript{186}. The coated generator had the 10 times higher of the piezoelectric voltage output and 5 times higher of current output than those of the pristine ZnO NWs generator under the same compression strain. This was because the holes from the $p$-type P3HT polymer reduced the piezoelectric potential screening effect caused by free electrons in ZnO. Recently, Ken et al. reported a ZnO $p$-$n$ homojunction film device for enhancing the mechanical energy harvesting\textsuperscript{187}. The depletion region in the $p$-$n$ homojunction reduced internal screening of strain-induced polarization charges effectively. So far, these studies were all based on ZnO inorganic piezoelectric NGs, and the electrical outputs were actually AC power, sometimes with asymmetric signals, as shown in Figure 2.19\textsuperscript{184}. There are no similar reports on electrospun nanofibres.

\textbf{Figure 2. 19} Electrical outputs from the piezoelectric nanogenerator that contains a $p$-$n$ junction\textsuperscript{184}.
2.6.2 Other mechanism energy harvesters

Piezoelectric DC generators have been reported based on oriented ZnO nanomaterials (e.g. aligned nanowires, nanorods and nanosheets) by forming a Schottky contact between the ZnO nanomaterials and an electrode to regulate the charge transport \(^{188-190}\). However, those devices typically have a low power output (Figure 2.20) and also require precise control of the preparation process \(^{188}\). Besides, DC outputs have also been reported from triboelectric generators with multiple electrification pairs to periodically switch charging directions \(^{47,191}\). A summary of DC power NGs has been listed in Table 2.6.

![Figure 2.20](image)

**Figure 2.20** (a) Reproducible current output of the NG when the ultrasonic wave was turn on and off. (b) Continuous current of NG for an extended period of time \(^{188}\).
Table 2.6 Peak voltage and current outputs of various DC mechanical energy harvesters.

<table>
<thead>
<tr>
<th>Types</th>
<th>Active layer</th>
<th>Peak Voltage (V)</th>
<th>Peak Current Density (µA/cm²)</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Piezoelectric</strong></td>
<td>ZnO nanowire array</td>
<td>0.001</td>
<td>2.5×10⁻⁵</td>
<td>188</td>
</tr>
<tr>
<td></td>
<td>ZnO nanorod array</td>
<td>-</td>
<td>3.7</td>
<td>189</td>
</tr>
<tr>
<td></td>
<td>Tilted ZnO nanorods</td>
<td>-</td>
<td>0.8</td>
<td>192</td>
</tr>
<tr>
<td></td>
<td>ZnO nanowire-nanowall hybrid</td>
<td>0.02</td>
<td>0.5</td>
<td>193</td>
</tr>
<tr>
<td></td>
<td>ZnO nanosheets-anionic layer heterojunction</td>
<td>0.75</td>
<td>16</td>
<td>194</td>
</tr>
<tr>
<td></td>
<td>Vanadium-doped ZnO nanosheets</td>
<td>-</td>
<td>1</td>
<td>195</td>
</tr>
<tr>
<td></td>
<td>ZnO nanosheets with the Zn:Al layered double hydroxide layer</td>
<td>0.38</td>
<td>22.1</td>
<td>190</td>
</tr>
<tr>
<td><strong>Triboelectric</strong></td>
<td>Al-rubber-PTFE rotational motion</td>
<td>3200</td>
<td>20 µA (No area found)</td>
<td>191</td>
</tr>
<tr>
<td></td>
<td>Al-PVC rotating-disk-based</td>
<td>-</td>
<td>0.4</td>
<td>47</td>
</tr>
</tbody>
</table>
Chapter 3 Experimental Details

This chapter provides detailed information of all the materials, experimental details and instruments used in this research work.

3.1 Materials

Poly(vinylidene fluoride) (PVDF) pellets (Mw=275,000), poly(vinyl alcohol) (PVA) (average Mw=130,000) and polyacrylonitrile (PAN) (average Mw=150,000), acetone and N, N-dimethylformamide (DMF) (≥99%), hole transport material tri-p-tolylamine (TTA) (97%), electron transport material 2-(4-tert-Butylphenyl)-5-(4-biphenylyl)-1,3,4-oxadiazole (Butyl-PBD) (≥99%), iron (III) chloride hexahydrate (FeCl₃·6H₂O) (≥98%), pyrrole (≥98%), 3, 4-ethylenedioxythiophene (EDOT) (97%) and aniline (≥99.5%) were all purchased from Sigma-Aldrich and used as received.

3.2 Electrospinning

3.2.1 Preparation of electrospinning polymer solutions

PVDF solution: The electrospinning solutions were prepared by dissolving PVDF pellets into a mixture solvent of DMF/acetone (v/v, 4/6) at 100 °C with magnetic stirring. The PVDF concentration was maintained in the range of 16~26 wt%, and all the electrospinning experiments used freshly prepared solutions.

TTA and Butyl-PBD doped PVDF solutions: After PVDF solutions were prepared, different amounts of TTA or Butyl-PBD were added into the solutions. The doped solution was stirred overnight at 50 °C before electrospinning to make sure they were dispersed homogeneously. The concentrations of TTA and Butyl-PBD to PVDF were among 0.1~10 wt%.
3.2.2 Electrospinning

A needle based electrospinning setup was used to prepare PVDF nanofibres in this work. As shown in Figure 3.1, it contains a needle spinneret, a DC power supply (Gamma High Voltage) and a grounded aluminium rotating drum collector. The electrospinning solution was loaded in a 5 mL plastic syringe capped with a 21G steel needle (inner diameter = 0.8 mm). The solution flow rate was controlled by a syringe pump (KD Scientific) at 1 ml/h. This flow rate was chosen because of the stable electrospinning process regardless the change of other spinning parameters. A high voltage was applied to the needle through a DC power supply. The applied voltage was set in the range of 9~21 kV while the spinning distance was between 9 cm and 21 cm. A rotating drum (length: 10 cm; diameter: 5 cm, rotating speed: 100 rpm) was used to collect the nanofibres. The thickness of fibre mats were controlled by the deposition time during electrospinning. The electrospinning process was conducted at room temperature with normal humidity and all the electrospun nanofibre mats were then dried in an oven at 40 °C for 5 hours to remove the residual solvent.

Figure 3.1 Digital photo of the needle electrospinning setup. (1: needle spinneret; 2: high voltage; 3: drum collector; 4: plastic syringe; 5: syringe pump)
3.3 Conducting polymer preparation

PPy was synthesized using a vapour phase polymerization method. In details, FeCl₃ fine powders were placed in a glass dish in a vacuum chamber, in which pyrrole monomer was placed underneath the glass dish. The pyrrole monomer vapour filled the entire chamber through evaporation under vacuum, and the polymerization of PPy took place on FeCl₃ surface. After 48 hour reaction at room temperature, the brownish FeCl₃ powders turned to black colour, and the black powders were stirred in water for 48 hours to remove unreacted chemicals and any side products. The powders were then washed with distilled water for several times before drying in a vacuum oven at 60 °C. Finally, the as-prepared PPy powders were ground manually into finer powders and then pressed into plates using a steel die (7.5 tonnes for 3 minutes).

PEDOT and PANi plates were produced in a similar process using the monomer of DEOT and aniline, separately.

3.4 Characterizations

3.4.1 Scanning Electron Microscopy (SEM)

Surface morphology of the electrospun nanofibres and conducting polymer powders was observed on scanning electron microscopes (SEM, Jeol Neoscope and Zeiss Supra 55VP). A small piece of nanofibre mat was placed on the SEM stub and a 10 nm thick gold layer was sputter coated onto nanofibre samples (LEICA EM ACE600). The conducting polymer powders were attached on conducting tape on the SEM stub and sputter coated with 5 nm thick gold layer. All SEM images
were taken at an accelerating voltage of 5 kV. The fibre diameter was calculated using an image analysis software (Image J 1.45s) based on the SEM images.

**3.4.2 Energy-Dispersive X-Ray Spectrometry (EDX)**

The element analysis of synthesized conducting polymer powders was carried out on SEM (Zeiss Supra 55VP) equipped for energy-dispersive X-ray spectrometry (EDX, Oxford, UK).

**3.4.3 Fourier Transform Infrared Spectroscopy (FTIR)**

FTIR spectra were obtained on a Bruker Optics spectroscopy in Attenuated Total Reflection (ATR mode). The spectra were recorded under 32 scans at 4 cm\(^{-1}\) resolution using OPUS 5.5 software. All tests were carried out in a controlled environment (20±2 °C). Up to three specimens for each sample were tested.

**3.4.4 X-ray Diffraction (XRD)**

XRD patterns were obtained on a Panalytical X-ray diffractometer with Cu radiation of 1.54 Å. The electrospun fibre samples were scanned in the 2θ range of 5° to 30° with the step size of 0.05°. The conducting polymer samples were scanned in the 2θ range of 10° ~ 80° with the step size of 0.05°.

**3.4.5 Differential Scanning Calorimetry (DSC)**

DSC was performed on TA Q200 machine. A specimen of 5~10 mg was encapsulated in an aluminium pan and measured in a temperature range of 30 °C to 200 °C at the heating rate of 10 °C/min in nitrogen atmosphere.
3.4.6 Fibre Mat Thickness Testing

Thickness of the nanofibre mats was measured under 0.5 kPa pressure using a digital calliper (Mitutoyo Crop. Japan).

3.4.7 Tensile Testing

Tensile property of nanofibre mats was tested on Instron Universal Tensile Tester (5967) with a crosshead speed of 10 mm/min at room temperature. The sample size was 12cm×6cm×0.01cm. Up to three specimens for each sample were tested. The strength of the fibre mats at the axial direction was also performed on Instron using double faced adhesive tape at the different stretching speed (1, 3, 5, 10 and 20 mm/min). The mat size was φ50cm×0.01cm. The preload was controlled at -2.5×10⁻⁴ MPa. All tests were carried out in a controlled environment (20±2 °C and 65±2% relative humidity).

3.4.8 Raman Spectroscopy

Raman spectra of conducting polymers were obtained on a Renishaw InVia Raman microscope equipped with a 514.5 nm laser. A 50× objective lens was used and the laser power was around 5 mW.

3.4.9 X-ray Photoelectron Spectroscopy (XPS)

XPS data were acquired using a Kratos AXIS Ultra (DLD) spectrometer equipped with a monochromated Al Kα X-ray source (energy~1486.6 eV). Survey spectra was recorded at 1 eV/step and a pass energy of 160 eV while high-resolution spectra was performed at 0.1 eV/step and a pass energy of 20 eV. The pressure in the analysis chamber was maintained at about 3×10⁻⁹ Torr. The obtained spectra were analyzed by the CasaXPS software.
3.4.10 Electrospun PVDF Mat Porosity

The electrospun PVDF mat was cut into a 4×4 cm² piece and the mat density was calculated according to:

\[
\text{Mat density} = \frac{W}{16 \times \text{Web thickness}} \quad (g/cm^3) \quad (3-1)
\]

where \( W \) is the weight of the PVDF mat piece. Then the porosity of mat samples was calculated using the following equation \( 196 \):

\[
\text{Mat porosity (\%)} = \frac{1 - \frac{\text{Web density}}{\text{Bulk density}}}{100} \quad (3-2)
\]

in which the bulk density of PVDF is 1.78 g/cm³.

3.4.11 Compression Test

Stress-strain curves were obtained on an Instron Universal Tensile Tester (model 5967), and the equipment was also used to generate desired strain levels on the PPy plates. Rounded structure PPy samples with the diameter of 13 mm were used and the thickness of disks was 1.44±0.10 mm. The compression speed was controlled at 0.08 mm/s while the strain was 10.4%. All the tests were carried out in a controlled environment (20±2 °C and 65±2% relative humidity).

3.4.12 Electrical Property

Mechanical-to-electrical energy conversion property was characterized on an electrochemistry working station (e-Corder 401) and a low-noise current preamplifier (Model SR570, Stanford Research Systems). The electrical resistance of the PPy plate was measured by a Keithley 6514 electrometer. I-V curves and
electrical impedance results were obtained using a CHI 760D electrochemical working station.
Chapter 4 Effect of Electrospinning Parameters and Polymer Concentrations on Mechanical-to-electrical Energy Conversion of Randomly-oriented Electrospun PVDF Nanofibre Mats

In this chapter, the effect of applied voltage, spinning distance, PVDF solution concentration and fibre mat thickness on PVDF $\beta$ crystal phase content in the nanofibres and mechanical-to-electrical energy conversion of randomly-orientated PVDF nanofibre mats was examined. It was interesting to find that finer uniform PVDF fibres showed higher $\beta$ crystal phase content hence the energy harvesting devices having higher electrical output regardless the change of electrospinning parameters and PVDF concentration. The voltage output always changed in the same trend as the change of current output whatever the change trend was caused by operating parameters or polymer concentration. Both voltage and current output changes followed a similar trend to the change of the $\beta$ crystal phase content in nanofibres. Nanofibre mat thickness also played a role in determining the level of electrical outputs.

4.1 Experimental procedure

The electrospinning solutions with different PVDF concentrations were prepared by dissolving PVDF pellets into a mixture solvent of DMF/acetone (v/v 4/6) at 100 °C. A needle based electrospinning setup was employed to prepare PVDF nanofibre mats. During electrospinning, the flow rate was controlled at 1 ml/h. This flow rate condition was chosen because the electrospinning process at this condition maintained stable regardless the variation of other parameters studied. A grounded aluminium rotating drum (diameter: 5 cm; length: 10 cm; rotating speed: 100 rpm) was used as the fibre collector. The thickness of fibre mats were
controlled through the deposition time of the electrospinning process. The electrospinning process was conducted at room temperature and all the electrospun PVDF nanofibre mats were then dried in an oven at 40 °C for 5 hours to remove the residual solvent.

4.2 Results and discussion

PVDF nanofibre mats were prepared using different parameters (e.g. polymer concentration, applied voltage, spinning distance), and the detailed effects of the parameters on nanofibre characteristics and mechanical-to-electrical conversion are described below.

4.2.1 Polymer concentration

Figure 4.1 and 4.2 show the typical SEM images of PVDF fibres prepared from different PVDF solutions. All fibres in the as-spun mats have a randomly-oriented fibrous morphology. As expected, the PVDF concentration affected fibre morphology.
Figure 4.1 (a) ~ (c) SEM images of the PVDF nanofibres electrospun from PVDF solutions of different concentrations (a-16%, b-20%, c-26%), and (d) effect of PVDF concentration on fibre diameter. (Applied voltage: 15 kV; spinning distance: 15 cm; nanofibre mat thickness: 70 μm)

Figure 4.2 SEM images of the PVDF nanofibres prepared at different PVDF concentrations. (Applied voltage: 15 kV; spinning distance: 15 cm; nanofibre mat thickness: 70 μm)
Beaded PVDF fibres resulted when the PVDF concentration was below 20%. The bead morphology and numerical density were also affected by the polymer concentration. When the PVDF concentration increased from 16% to 19%, the bead numerical density decreased and the beads changed from round to oval shape. The average fibre diameter calculated based on the fibre sections increased slightly from 230 nm to 284 nm. When the PVDF concentration was above 20%, non-beaded PVDF fibres were electrospun. With increasing the PVDF concentration from 20% to 26%, the average fibre diameter increased from 284 nm to 810 nm.

The effect of polymer concentration on the morphology and diameter of electrospun nanofibres has been widely examined \(^{127,197}\). With increasing the polymer concentration, electrospun product may show different morphologies, such as beads, beaded fibres, and uniform fibres. This was explained by the entanglement of polymer macromolecular chains in the solution. When the polymer concentration is above the entanglement concentration \((C_e)\), beaded fibres are prepared, and when the solution concentration is 2-2.5 times of \(C_e\), the chain entanglement is sufficient to allow forming uniform fibres \(^{198}\).

The formation of \(\beta\) crystal phase in electrospun PVDF nanofibres has been studied by several groups \(^{199-203}\). It was mainly attributed to the unique formation mechanism of electrospun fibre and molecular structure of PVDF. During electrospinning, the polymer solution jet is highly stretched (stretching ratio up to \(10^5\)), making polymer chain orientate along the fibre length \(^{115,204}\). Such intensive stretching also leads to drawing of polymer chains. On the other hand, the PVDF molecular conformation corresponding to the \(\beta\) crystal phase has the longest chain length among all possible crystal phases, as indicated in Figure 4.3. The dimension data are shown Table 4.1 and Table 4.2. Therefore, intensive stretching facilitates
the conversion of PVDF into $\beta$ crystal phase, and the solvent evaporation contributes to retain the $\beta$ crystal phase in the solidified fibres.

**Figure 4.3** Chain conformations of different PVDF crystal phases and distance between C1 and C10. The geometries were optimized by Molecular Studio 3.0 using DMol³ (GGA/BLYP/DND). The distances marked are in Å.
**Table 4.1** Chain length of a PVDF segment (10 carbon atoms) in different conformations.

<table>
<thead>
<tr>
<th>Crystal phase</th>
<th>Chain length (Å)</th>
<th>DFT method</th>
<th>From cell dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td>α</td>
<td>9.796</td>
<td>11.55</td>
<td></td>
</tr>
<tr>
<td>β</td>
<td>11.395</td>
<td>12.80</td>
<td></td>
</tr>
<tr>
<td>γ</td>
<td>10.417</td>
<td>11.50</td>
<td></td>
</tr>
<tr>
<td>δ</td>
<td>9.895</td>
<td>11.55</td>
<td></td>
</tr>
</tbody>
</table>

The column c in Table 4.2 represents the molecular chain unit length of different crystal phases. It can be used to calculated chain length. Both the calculations indicate that main chain length in β crystal phase is the longest among all the conformations.

**Table 4.2** Unit cell dimension of different PVDF crystal phases.

<table>
<thead>
<tr>
<th>Crystal phase</th>
<th>Unit cell (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a and δ (4 carbon atoms/unit)</td>
<td>a</td>
</tr>
<tr>
<td>β (2 carbon atoms/unit)</td>
<td>0.847</td>
</tr>
<tr>
<td>γ (8 carbon atoms/unit)</td>
<td>0.496</td>
</tr>
</tbody>
</table>

Figure 4.4a shows the XRD curves of PVDF nanofibres electrospun from different PVDF solutions. The XRD peaks at 2θ=17.8° and 26.6° correspond to the (110) and (021) crystal planes of α phase. The peak at 2θ=20.4° is the characteristic of β crystal phase, which is the sum of the diffraction at (110) and (200) planes. The XRD results indicate that PVDF nanofibres mainly contain α and β phases. With increasing the PVDF concentration in the electrospinning solution, the peak
intensity at 20.4° increased gradually until the concentration reached 20%, and the peak decreased with further increasing the concentration.

**Figure 4.4** (a) XRD curves, (b) FTIR spectra of PVDF nanofibres electrospun from different PVDF solutions, (c) calculated β crystal phase contents based on the FTIR spectra, and (d ~ f) electrical outputs of the nanofibre mats. (Applied voltage: 15 kV; spinning distance: 15 cm; nanofibre mat thickness: 70 μm)

Figure 4.4b shows the FTIR spectra of the nanofibres. The α crystal phase shows vibration characteristic bands at 761 cm⁻¹ (CH₂ in-plane bending or rocking), 877 cm⁻¹ (CH₂ out-of-plane bending or rocking) and 976 cm⁻¹ (CH₂ twisting) 208. The
peaks at 840 cm\(^{-1}\) and 1274 cm\(^{-1}\) corresponded respectively to CH\(_2\) rocking/CF\(_2\) asymmetrical stretching and C-F stretching vibrations of \(\beta\) phase \(^{209,210}\). Based on the FTIR spectra, the \(\beta\) phase content, \(F(\beta)\), in the PVDF nanofibres was calculated using the equation (4-1) \(^{210,211}\):  

\[
F(\beta) = \frac{X_{\beta}}{X_{\alpha} + X_{\beta}} = \frac{A_{\beta}}{(K_{\beta}/K_{\alpha})A_{\alpha} + A_{\beta}}  
\]

(4-1)  

Where \(A_{\alpha}\) and \(A_{\beta}\) are the absorbance at 761 cm\(^{-1}\) and 840 cm\(^{-1}\), respectively. \(K_{\alpha}\) and \(K_{\beta}\) are the absorption coefficient at the respective wavenumber, which is \(6.1 \times 10^4\) and \(7.7 \times 10^4\) cm\(^2\)/mol in value \(^{210,211}\).  

Figure 4.4c shows the calculated result of the \(\beta\) crystal phase content. It increased from 78% to 85.9% when the PVDF concentration increased from 16% to 20%. Further increasing the PVDF concentration from 20% to 26% resulted in gradual decrease of the \(\beta\) crystal phase content to 82.5%. The effect of polymer concentration on \(\beta\) crystal phase content can be explained by that solution with higher polymer concentration is harder to be stretched due to the higher viscosity and stronger macromolecular chain entanglement.  

The mechanical-to-electrical energy conversion property of the nanofibre mat was evaluated by repeatedly pressing the energy harvesting devices prepared in a controlled manner. The voltage and current outputs of the PVDF nanofibre mats under 1 Hz compressive impact (stress 25000 Pa) are shown in Figure 4.4d & e. The insets in the figures show the typical outputs from a single compressive impact, which always generate two signals with opposite polarities. The first signal was caused by the compressive deformation of nanofibre mat and the second was related to the recovery deformation \(^3\).
The average positive voltage and current outputs were calculated and presented in Figure 4.4f. Both voltage and current outputs had a similar change trend. The PVDF concentration changed from 16% to 20% during electrospinning led to the change of voltage output from 1.3 V to 2.2 V, and the current output change followed a similar trend, from 1.4 μA to 2.3 μA. The voltage and current increased by 69% and 64%, respectively. However, the β phase content in the nanofibres only increased by 10%.

When the PVDF concentration increased from 20% to 26%, the voltage and current outputs of the resulting nanofibre mat changed to 1.6 V and 1.7 μA, decreasing by 27% and 26%, respectively. However, the corresponding β phase content decreased just by 3.9%. These results indicate a significant effect of β crystal phase content in PVDF nanofibres on the mechanical-to-electrical energy conversion performance. The β crystal phase of PVDF has a net dipole moment and the best piezoelectric coefficient. With the increase of β crystal phase content, the mechanical-to-electrical energy conversion performance enhanced. Since the nanofibre mat prepared from 20% PVDF solution generated the highest electrical outputs, 20% solution was used in the following experiments.

4.2.2 Applied voltage

Electric field is the driving force to jet initiation and fibre thinning during electrospinning. In our study, PVDF solution was electrospun at a constant flow rate (1 ml/h). Uniform nanofibres were prepared when the applied voltage was set in the range of 9 kV ~ 21 kV, as shown in Figure 4.5. Figure 4.6 shows the fibre diameter of the PVDF nanofibres prepared from a 20% PVDF solution at different
applied voltages. All the fibres electrospun were uniform without bead. With increasing the applied voltage from 9 kV to 15 kV, the average fibre diameter decreased from 630 nm to 284 nm, and further increasing the applied voltage to 21 kV led to an increase in diameter to 580 nm.

![SEM images of the PVDF nanofibres prepared at different applied voltages.](image)

**Figure 4.5** SEM images of the PVDF nanofibres prepared at different applied voltages. (Solution concentration: 20%; spinning distance: 15 cm; nanofibre mat thickness: 100 μm)

Increasing the applied voltage results in higher electrostatic force to stretch the jet and filament during electrospinning, therefore decreasing fibre diameter. This is in a good agreement with the trend of fibre diameter change when the applied voltage increased from 9 kV to 15 kV. The increase in fibre diameter when further increasing the applied voltage was attributed to the intensive bending instability, which increased the diameter distribution (see the standard deviation in Figure 4.6).
The formation of coarser fibres when the applied voltage was above 15 kV could be the reason leading to the large diameter distribution.

**Figure 4.6** Effect of applied voltages on PVDF fibre diameters, $\beta$ crystal phase contents and electrical outputs of PVDF nanofibre mats. (PVDF concentration 20%; spinning distance: 15 cm; nanofibre mat thickness: 100 $\mu$m)

The XRD and FTIR results indicated that PVDF nanofibres electrospun at different applied voltages showed similar characteristic peaks, as shown in Figure 4.7 and 4.8. The calculated $\beta$ crystal phase content based on the FTIR spectra is shown in Figure 4.6. With increasing the applied voltage from 9 kV to 15 kV, the $\beta$ phase content increased from 76.7% to 85.9%, and the $\beta$ phase content decreased with
further increasing the applied voltage. For the PVDF nanofibres electrospun at 21 kV, the $\beta$ phase content was 81.6%.

![Figure 4.7 XRD curves of the PVDF nanofibre mats prepared at different applied voltages. (Solution concentration: 20%; spinning distance: 15 cm; nanofibre mat thickness: 100 $\mu$m)](image)

**Figure 4.7** XRD curves of the PVDF nanofibre mats prepared at different applied voltages. (Solution concentration: 20%; spinning distance: 15 cm; nanofibre mat thickness: 100 $\mu$m)

![Figure 4.8 FTIR spectra of the PVDF nanofibre mats prepared at different applied voltages. (Solution concentration: 20%; spinning distance: 15 cm; nanofibre mat thickness: 100 $\mu$m)](image)

**Figure 4.8** FTIR spectra of the PVDF nanofibre mats prepared at different applied voltages. (Solution concentration: 20%; spinning distance: 15 cm; nanofibre mat thickness: 100 $\mu$m)
Figure 4.6 also shows the mechanical-to-electrical energy conversion properties of the nanofibre mats. The voltage and current outputs were shown in Figure 4.9. Both voltage and current outputs showed a similar trend to the $\beta$ phase content, with output maximum of 1.5 V and 1.6 $\mu$A (PVDF nanofibres were electrospun at 15 kV). These results suggest that uniform PVDF nanofibres with higher $\beta$ phase content have higher mechanical-to-electrical conversion ability.

![Figure 4. 9 Voltage and current outputs of the PVDF nanofibre mats prepared at different applied voltages. (Solution concentration: 20%; frequency: 1 Hz; spinning distance: 15 cm; nanofibre mat thickness: 100 $\mu$m)]

4.2.3 Spinning distance

Spinning distance (nozzle tip-to-collector distance) in electrospinning affects fibre stretching and deposition $^{210}$. When electric field force is sufficient to maintain the electrospinning process, increasing spinning distance provides larger space for jet stretching and longer time for solvent evaporation from the fibres. A spinning distance shorter than a critical length often leads to insufficient fibre stretching and solvent evaporation. As a result, wet coarse fibres, and even porous films, result.
To examine the effect from spinning distance, a PVDF solution (20%) was electrospun at a constant applied voltage (15 kV). At the same applied voltage, altering the spinning distance also leads to change in electric field intensity, which affects electrospinning process. To exclude the effect from electric field intensity, we adjusted the applied voltage when different spinning distances were employed, so that the average electric field intensity was maintained at a constant value (1 kV/cm).

4.2.3.1 At constant voltage

When electrospinning was conducted at a constant applied voltage, while the spinning distance changed from 9 cm to 21 cm, the PVDF fibres showed a similar fibrous morphology (see the SEM images in Figure 4.10).

![Figure 4.10 SEM images of the PVDF nanofibres prepared at different spinning distances. (Solution concentration: 20%; applied voltage: 15 kV; nanofibre mat thickness: 100 μm)](image)
Figure 4.11 shows the average diameter of the PVDF fibres prepared at different electrospinning distances. The average fibre diameter decreased when the spinning distance increased from 9 cm to 15 cm. With further increasing the spinning distance, the average diameter increased.

![Graph showing the effect of spinning distances on PVDF fibre diameters, β crystal phase contents and electrical outputs of PVDF nanofibre mats.](image)

**Figure 4.11** Effect of spinning distances on PVDF fibre diameters, β crystal phase contents and electrical outputs of PVDF nanofibre mats. (PVDF concentration 20%; applied voltage: 15 kV; nanofibre mat thickness: 100 μm)

At a constant applied voltage, the electric field intensity reduces with increasing the spinning distance. Increasing the spinning distance initially provides more time
and space for the jets to be stretched. Short spinning distance (<15 cm) in our experiment resulted in coarse fibres with large diameter distribution. When the spinning distance changed from 13 cm to 15 cm, the average fibre diameter decreased significantly from 458 nm to 284 nm. The fibre diameter had a slight increase to 341 nm when the spinning distance was further increased to 21 cm. Again, $\beta$ crystal phase content was calculated based on the FTIR spectra (Figure 4.13). The highest $\beta$ crystal phase content of 85.9% was obtained at the spinning distance 15 cm. The electrical outputs of the PVDF nanofibre mats collected at different spinning distances are shown in Figure 4.11 and 4.14 as well. Both voltage and current followed a similar change trend to the fibre $\beta$ phase content. When the spinning distance increased from 9 cm to 15 cm, the voltage and current outputs reached the maximum level of 1.5 V and 1.6 $\mu$A.

Figure 4.12 XRD curves of the PVDF nanofibre mats prepared at different spinning distances. (Solution concentration: 20%; applied voltage: 15 kV; nanofibre mat thickness: 100 $\mu$m)
4.2.3.2 At constant electric field intensity

Under a constant electric field intensity, all PVDF nanofibres electrospun at different distances had a uniform fibrous morphology, as shown in Figure 4.15.

Figure 4. 13 FTIR spectra of the PVDF nanofibre mats prepared at different spinning distances. (Solution concentration: 20%; applied voltage: 15 kV; nanofibre mat thickness: 100 μm)

Figure 4. 14 Voltage and current outputs of the PVDF nanofibre mats prepared at different spinning distances. (Solution concentration: 20%; frequency: 1 Hz; applied voltage: 15 kV; nanofibre mat thickness: 100 μm)
Figure 4.15 SEM images of the PVDF nanofibres prepared at a constant electric field intensity. (Solution concentration: 20%; nanofibre mat thickness: 100 μm)

Figure 4.16 shows the average fibre diameter calculated based on the SEM images. The average fibre diameter decreased from 392 nm to 284 nm when the spinning distance was increased from 9 cm to 15 cm. A spinning distance of 17 cm could prepare PVDF nanofibres with a similar average diameter (283 nm) to the fibres collected at a 15 cm spinning distance. The fibre diameter had a slight increase when the spinning distance was longer than 17 cm.
Figure 4.16 Effect of electric field intensity on PVDF fibre diameters, $\beta$ crystal phase contents and electrical outputs of PVDF nanofibre mats. (PVDF concentration 20%; nanofibre mat thickness: 100 $\mu$m)

Figure 4.16 also shows the $\beta$ crystal phase content and electrical outputs of the PVDF nanofibres. Figure 4.17 and 4.18 show the XRD and FTIR results. The $\beta$ crystal phase content increased first with increasing the spinning distance until 17 cm ($\beta$ crystal phase content, 86.2%). Similar to the nanofibres produce at a constant applied voltage, further increasing the spinning distance also led to a decrease in the $\beta$ crystal phase content.
Figure 4.17 XRD curves of the PVDF nanofibre mats prepared at a constant electric field intensity. (Solution concentration: 20%; nanofibre mat thickness: 100 μm)

Figure 4.18 FTIR spectra of the PVDF nanofibre mats prepared at a constant electric field intensity. (Solution concentration: 20%; nanofibre mat thickness: 100 μm)
Figure 4.19 shows the electrical output curves of the PVDF nanofibres prepared at different spinning distances with a constant electric field intensity. When the spinning distance increased from 9 cm to 15 cm, the voltage and current outputs increased respectively from 1.1 V to 1.5 V and 1.1 μA to 1.6 μA, respectively. The outputs were almost the same when the spinning distance was in the range of 15 cm – 17 cm. Further increasing the spinning distance decreased both the voltage and current outputs.

![Figure 4.19](image.png)

**Figure 4.19** Voltage and current outputs of the PVDF nanofibre mats prepared at a constant electric field intensity. (Solution concentration: 20%; frequency: 1 Hz; nanofibre mat thickness: 100 μm)

The above results suggest that electric field intensity in electrospinning process plays a dominating role in determining the fibre diameter and β crystal phase content. The finer fibres may result from more effective stretching, hence having higher β crystal phase content. The effect of β crystal phase content on electric outputs of PVDF mats was summarized, as shown in Figure 4.20. It shows the positive trends that the electric outputs go up when the β crystal phase content increases.
4.2.4 Nanofibre mat thickness

PVDF nanofibre mats of different thicknesses were prepared under the same electrospinning condition except for that electrospinning time was varied to control the mat thickness. It was reasonable to anticipate that nanofibres electrospun under the same condition should contain the same level of $\beta$ crystal phase within the fibres. When the fibre mats were prepared into energy harvesting devices, the difference in the device performance should come from the mat thickness.

Figure 4.21 and 4.22 show the effect of PVDF nanofibre mat thickness on the energy conversion performance. When the mat was thinner than 20 $\mu$m, a short circuit occurred occasionally during the compressing process. With increasing the mat thickness from 20 $\mu$m to 70 $\mu$m, both voltage and current outputs increased significantly, to reach 2.2 V and 2.3 $\mu$A, respectively. However, with further increasing the mat thickness, electrical outputs reduced. The increase in the electrical output with increasing the mat thickness can be explained by that increasing mat thickness leads to increase in active material therefore the charge generation. However, increasing the mat thickness also increases the resistance for

Figure 4.20 The effect of $\beta$ crystal phase content on electric outputs.
charge transfer across the mat. Increasing mat thickness could also decrease the strain level of the deformed fibres under the same compressive stress, which reversely affect the power-generating performance of the nanofibre mat.

Figure 4.21 (a) Voltage and (b) current outputs of PVDF nanofibre mats with different mat thicknesses. (Solution concentration 20%; applied voltage 15 kV; spinning distance 15 cm)

Figure 4.22 Voltage and current outputs of the PVDF nanofibre mats with different thicknesses (Solution concentration: 20%; frequency: 1 Hz; applied voltage: 15 kV; spinning distance: 15 cm)

4.3 Conclusion

In this chapter, the effects of PVDF concentration, applied voltage, spinning distance, and nanofibre mat thickness on fibre diameter, PVDF β crystal phase content, and mechanical-to-electrical energy conversion properties of electrospun
PVDF nanofibre mats have been examined systematically. It was interesting to find that finer uniform PVDF fibres show higher $\beta$ crystal phase content hence the energy harvesting having higher electrical outputs regardless the change of electrospinning parameters and PVDF concentration. The voltage output change always follows the same trend as the change of current output whatever the change is caused by operating parameter or polymer concentration. Both electrical outputs follow a similar change trend to the change of $\beta$ crystal phase content in nanofibres. Nanofibre mat thickness affects the mechanical-to-electrical energy conversion. Uniform nanofibres with small diameter and high $\beta$ crystal phase content facilitate to mechanical-to-electrical energy conversion. These novel understanding may benefit to develop piezoelectric nanofibrous devices for various uses in energy field.
Chapter 5 Robust Mechanical-to-electrical Energy Conversion from Short-distance Electrospun PVDF Fibre Mats

In the view of technology, electrospinning is a simple but effective method to produce nanofibres. It involves drawing a viscous solution under a strong electric field to form solid nanofibres. Conventionally, electrospinning is conducted at a nozzle-to-collector distance (i.e. spinning distance) typically greater than 8 cm \(^ {212-214}.\) As a special case, electrospinning is also conducted at a spinning distance shorter than 1 cm (also referred to as “near-field electrospinning”).

The main difference between conventional electrospinning and near-field electrospinning is that the jet in conventional electrospinning typically undergoes a whipping movement. As a result, fine and dry fibres are formed before they deposit on the collector electrode. PVDF nanofibres produced by conventional electrospinning often have a high \(\beta\) crystal phase content, and the chain dipole within the nanofibres turns to align across nanofibre mat thickness \(^ {215}.\) A PVDF nanofibre mat produced by conventional electrospinning can generate an electrical output of several volts when it receives a compressive impact \(^ {3}.\) In contrast, no whipping movement takes place for the jet in near-field electrospinning due to the short spinning distance. The macromolecules in near-field electrospun PVDF fibres were reported to align along fibre length \(^ {216}.\) However, single PVDF nanofibre prepared by near-field electrospinning only shows an electrical output in tens of millivolts under bending \(^ {26}.\)

Despite these studies, little attention has been paid toward electrospinning of PVDF nanofibres at a distance between near-field electrospinning and conventional electrospinning. Previous paper on electrospinning of PVA has indicated that
electrospinning at a spinning distance shorter than 6 cm leads to a macroporous membrane or a dense film attributable to the merging of the highly wet fibres\textsuperscript{217}. Wet PVDF fibres should also result when electrospinning a PVDF at such electrospinning conditions. Since wet casting a PVDF solution often leads to a polymer film with $\alpha$ crystal phase \textsuperscript{3,199}, it is reasonable to expect that electrospun wet PVDF fibres should show low piezoelectricity.

However, our present study has shown that electrospinning at a spinning distance in the range of 1-8 cm (also referred to as “short-distance electrospinning” in this study) still results in a fibrous structure except that fibres are highly interconnected. More interestingly, the interconnected PVDF nanofibres have a comparable $\beta$ crystal phase content and mechanical-to-electrical energy conversion ability to those produced by conventional electrospinning. We have further found that the inter-fibre connection play a role in stabilizing the fibrous structure during repeated compression/decompression. The short-distance electrospun PVDF nanofibre mats have higher delamination resistance and tensile strength than PVDF nanofibre mats produced by conventional electrospinning. Short-distance electrospun PVDF nanofibres could be more robust for making energy harvesters than conventionally-electrospun PVDF nanofibres. In this chapter, the unexpected finding on short-distance electrospun PVDF fibres, and their morphology, crystalline feature, mechanical-to-electrical energy conversion ability and mechanical properties are discussed.
5.1 Experimental procedure

A 20% PVDF solution was used to produce short-distance electrospun fibres, and the flow rate was maintained at 1 ml/h. All the electrospun mats were collected on the rotating drum.

5.2 Results and discussion

5.2.1 Morphology structure of electrospun PVDF mats

Figure 5.1 shows the morphology profile of PVDF electrospun at different parameters. When electrospinning the same PVDF solution using different applied voltages and spinning distances, the resulting PVDF could show different morphologies. The two grey zones in the chart specify the conditions where the solution was un-electrospinnable. In the bottom grey zone, the applied voltage was too low to initiate an electrospinning process, while corona discharge occurred in the top grey zone because the applied voltage was above the breakdown limit. Between the two grey zones, PVDF can be electrospun into three main morphologies: particles (zone I), interconnected fibres (zone III) and separated fibres (zone V). Mixtures of particles with interconnected fibres (zone II) and interconnected fibres with separated fibres (zone IV) were also formed.
Figure 5.1 Morphological profile of PVDF electrospun at different parameters. SEM images of different morphology zones: (I) particles, (II) mixture of particles and interconnected fibres, (III) interconnected fibres, (IV) mixture of interconnected fibres and separated fibres, and (V) separated fibres. (Scale bars: 5 μm)

When the spinning distance was 1 cm, electrospinning resulted in PVDF particles with an average size of 2.9 μm (Figure 5.1I). The formation of particles comes from strong Coulomb repulsion within the jet because of the high electrical field intensity (~8 kV/cm). In this case, the solution jet at the needle tip tended to form highly charged droplets. Due to the short traveling distance, certain amount of solvent remained within the particles, making them bond together on the collector.
By increasing the spinning distance from 1 cm to 2.5 cm, a mixture of particles with interconnected fibres formed when the applied voltage was below 7 kV. The particles had a size around 1.1 μm while the fibres had a slightly larger diameter than the particle size. The fibre formation was attributed to the reduced electrostatic repulsion within the solution jet.

When the applied voltage was higher than 4 kV and the spinning distance was longer than 1.75 cm, particle-free fibres resulted. As highlighted in the yellow zone, the fibres are interconnected with each other with a wide diameter distribution (Figure 5.1III). This can be explained by the insufficient whipping movement and limited solvent evaporation from the jet. Wet fibres deposited on the collector, leading to fibre connection.

![SEM image of separated fibres prepared by a conventional electrospinning. (Spinning distance: 15 cm; applied voltage: 15 kV)](image)

**Figure 5.2** SEM image of separated fibres prepared by a conventional electrospinning. (Spinning distance: 15 cm; applied voltage: 15 kV)

The blue zone in Figure 5.1 represents the conditions leading to separated fibres. The fibres electrospun under such a condition (e.g. applied voltage 12 kV and spinning distance 6 cm) were uniform with a similar morphology to these prepared
under conventional electrospinning condition (e.g. applied voltage 15 kV and spinning distance 15 cm), excepted that the short-distance electrospun fibres were coarser (around 500 nm) than the conventionally electrospun ones (diameter 300 nm) (Figure 5.2). It was noted that the average electric field intensity in the short-distance electrospinning (2 kV/cm) was higher than that of the conventional electrospinning (1 kV/cm), the larger fibre diameter for the short-distance electrospun fibres suggests that jet stretching and solvent evaporation in the short-distance electrospinning are insufficient. In between the separated fibres and the interconnected fibres, there are some spinning conditions which lead to a mixture of the two fibres (e.g. the pink zone in Figure 5.1), and the interconnected fibres always had larger diameter (1.2 µm).

The above results indicate that interconnected PVDF fibres can be prepared by electrospinning a PVDF solution at a short distance (2 cm) under an applied voltage in the range of 5-11 kV. However, maintaining the applied voltage at 7 kV but changing the spinning distance from 1 cm to 8 cm allows electrospinning PVDF into five different morphologies. With those conditions, we further elucidated the effect of applied voltage on the properties of interconnected PVDF fibres, and the effect of PVDF morphology on the properties. These fibres were also compared with those prepared at a conventional electrospinning condition (applied voltage: 15 kV, spinning distance: 15 cm). Our previous research revealed that PVDF nanofibres electrospun at this condition (PVDF concentration 20 w/v%) showed optimal mechanical-to-electrical energy conversion property 5.
5.2.2 Crystallization study

Figure 5.3a shows the XRD patterns of the interconnected PVDF fibres electrospun at different applied voltages (spinning distance 2 cm). Two main peaks occurred at 2θ=18.4 and 20.6, corresponding to the α phase (020) crystal plane and the sum β phase of (110) and (200) planes. The intensity of β crystal phase increased with increasing applied voltage from 5 kV to 7 kV, and the intensity of α phase decreased accordingly. When the applied voltage was further increased from 7 kV to 11 kV, the intensity of β crystal phase decreased. To verify the crystal phase structure, FTIR spectra were also measured. As shown in Figure 5.3b, the characteristic vibration peaks at 840 cm⁻¹ (CH₂ rocking) and 1274 cm⁻¹ (trans band) are assigned to the β phase. Very weak bands at 761 cm⁻¹ and 976 cm⁻¹ attributed to α phase.

It is known that PVDF has five different crystal phases with three different chain conformations: all trans (TTTTT) conformation for α phase, trans-gauche-trans-gauche (TGTG’) for α and δ phases and T3GT3G’ for γ and ε phases. Among them, α and γ phases commonly exist in PVDF; whereas β phase has the highest dipolar moment which plays a significant role in the piezoelectricity.
Figure 5.3 (a) XRD patterns and (b) FTIR spectra of PVDF fibres prepared at different applied voltages (spinning distance: 2 cm); Crystallinity and $\beta$ phase content of PVDF fibres prepared at (c) different applied voltages (spinning distance: 2 cm) and (d) different spinning distances (applied voltage: 7 kV).

The $\beta$ phase content was calculated according to the FTIR result (see the calculation equation 4-1 in Chapter 4). As shown in Figure 5.3c, with increasing applied voltage from 5 kV to 7 kV, the $\beta$ phase content increased from 76.9% to 83.9%. The $\beta$ phase content gradually decreased to 59.9% when the applied voltage was further increased to 11 kV. This trend can be attributed to two effect factors: electric field and whipping movement. When the voltage was 5 kV, low electric field intensity resulted in coarse fibres with low $\beta$ phase content (See the fibre diameter distribution in Figure 5.4). Increasing the applied voltage enhanced the electric field intensity which led to higher electrostatic force to stretch the jet during
electrospinning. With increasing the applied voltage from 5 kV to 7 kV, the average fibre diameter decreased from 1.2 \( \mu \text{m} \) to 0.8 \( \mu \text{m} \). Meanwhile, the \( \beta \) phase content increased. Further increasing the applied voltage to 11 kV caused fibre diameter increase to 2.3 \( \mu \text{m} \) and \( \beta \) phase content decrease. At that time, higher applied voltage resulted in higher fibre deposition speed, causing shorter time for whipping movement. More solvent was remained in the fibres on the collector. They were easy to collapse to form coarse and oval-shaped fibres, and tended to form more \( \alpha \) phase (Figure 5.4).

**Figure 5.4** SEM images of PVDF interconnected fibres obtained from (a) 7 kV and (b) 9 kV. (c) Effect of applied voltage on fibre diameter. (Spinning distance: 2 cm)
DSC analysis was used to estimate the crystallinity of the PVDF fibres, as shown in Figure 5.5. With increasing the applied voltage for electrospinning, the melting endothermic peak of the PVDF shifted to a higher temperature first and then returned to a lower temperature. The fibre crystallinity was calculated and the result was also shown in Figure 5.3c.

The degree of crystallinity ($\Delta X_c$) of each sample was calculated by using the equation $^{221,222}$:

$$
\Delta X_c = \frac{\Delta X_m}{\Delta X_{100}}
$$

(5-1)

Here, $\Delta X_m$ is the melting enthalpy of the sample and $\Delta X_{100}$ represents the melting enthalpy of a 100% crystalline sample. For the samples which contain $\alpha$ and $\beta$ phase PVDF, equation can be written in the following way:

$$
\Delta X_c = \frac{\Delta X_m}{x\Delta X_\alpha + y\Delta X_\beta}
$$

(5-2)

The coefficient of $x$ and $y$ indicate the $\alpha$ and $\beta$ phase content while $\Delta X_\alpha$ and $\Delta X_\beta$ are the melting enthalpy of a 100% crystalline sample in the $\alpha$ and $\beta$ phase. The value of $\Delta X_\alpha$ is 93.07 J/g while $\Delta X_\beta$ is 103.4 J/g, respectively.

The crystallinity in the electrospun PVDF maintained at a constant level when the applied voltage during electrospinning increased from 5 kV to 8 kV. An obvious increase in the crystallinity occurred when the applied voltage increased from 8 kV to 11 kV. It was reported that molecular orientation in electrospun fibres was proportional to the degree of crystallinity $^{223,224}$. The increased crystallinity indicates that molecular orientation degree is enhanced by increasing the applied voltage during electrospinning of PVDF fibres at a short distance.
Figure 5.5 DSC results of PVDF mats prepared from at different applied voltages. (Spinning distance: 2 cm)

In comparison with the PVDF nanofibres electrospun under the conventional electrospinning condition, short-distance electrospun interconnected PVDF fibres had higher crystallinity but lower $\beta$ phase content. Figure 5.6 shows the XRD and FTIR results of conventional electrospun separated fibres. Only the sample prepared at 7 kV had a comparable $\beta$ phase content similar to the conventional electrospun nanofibres. Since the crystallinity represents the sum of $\alpha$ and $\beta$ crystal phase contents in the electrospun fibres, high net $\beta$ phase content in a material should come from the contribution from both crystallinity and $\beta$ phase content.

Figure 5.6 (a) XRD and (b) FTIR results of separated fibres. (Spinning distance: 15 cm; applied voltage: 15 kV)
The effect of PVDF morphology on fibre crystal structure and crystallinity was examined. Figure 5.3d shows the \( \beta \) phase content and crystallinity of PVDF electrospun at 7 kV and spinning distance in the range of 1-8 cm. Figures 5.7–5.9 show the XRD, FTIR and DSC results. The PVDF particles showed higher crystallinity (52%) but lower \( \beta \) phase content (57.2%) than fibrous PVDF. The high electric field intensity at the short spinning distance may contribute to the higher crystallinity in PVDF particles, meanwhile the low \( \beta \) phase content could be resulted from insufficient stretching during particle formation. When the spinning distance was 2 cm, the electrospun product changed completely to fibres with crystallinity and \( \beta \) phase content of 47.7% and 83.9%, respectively. The interconnected fibres showed higher crystallinity than the separated fibres, however, their \( \beta \) phase content was closed to each other. At the constant applied voltage, increasing the spinning distance reduced the electric field intensity. For this reason, jet at longer distance should receive lower electric field force. On the other hand, increasing the spinning distance offers more time and space for jet to undergo whipping movement, facilitating fibre stretching and solvent evaporation. Therefore, the almost unchanged \( \beta \) phase content with the variation of spinning distance in the range of 2-8 cm stems from the effect of fibre drawing and solvent evaporation during electrospinning.
Figure 5.7 XRD pattern of PVDF mats prepared at different spinning distances.  
(Applied voltage: 7 kV)

Figure 5.8 FTIR results of PVDF mats prepared at different spinning distances.  
(Applied voltage: 7 kV)
5.2.3 Mechanical-to-electrical energy conversion property

The mechanical-to-electrical energy conversion property of the electrospun PVDF mats was evaluated by repeatedly compressing and decompressing the PVDF mats. Figure 5.10a shows the electrical outputs of the fibre mats. Under mechanical impact, the mat generated a pulse electrical output, while an electrical output of opposite polarity formed once the mat was decompressed.
Figure 5.10 (a) Voltage and current outputs of PVDF fibre mat electrospun at 7 kV and 2 cm, (b) peak voltage outputs of PVDF fibre mats prepared at different applied voltages (Spinning distance: 2 cm) and (c) different spinning distances (applied voltage: 7 kV). (Mat thickness: 100 μm; working area: 4 cm²)

It should be noted that compressive stress and strain should have effects on the electrical outputs. As shown in Figure 5.11, increasing the compressive stress from 1250 Pa to 37500 Pa led to increase in both voltage and current outputs, and the electrical outputs at low stresses followed a different trend to those at higher ones. At a stress range of 1250-10000 Pa, the voltage and current showed rapid increase with increasing the stress, whereas slight increase in electrical outputs resulted when the stress increased from 10000 to 37500 Pa. This suggests that the fibre mat deforms at a low compression, and the larger stress causes the elastic deformation of the compressed fibres. However, it was difficult to precisely adjust the strain during measurement due to the thin and flexible features of the PVDF nanofibre.
mats. Therefore, in the further study, we kept the compression stress at 25000 Pa (10.0 N) to test all nanofibre mats (working area 4 cm²).

![Figure 5.11](image)

**Figure 5.11** The dependence of (a) voltage and (b) current outputs on the compressive stress. (Mat thickness: 100 μm; working area: 4 cm²)

Figure 5.10b shows the peak voltage outputs of interconnected PVDF fibre mats produced at 2 cm spinning distance and different applied voltages (5-11 kV) (output signals are shown in Figure 5.12). For the fibre mat prepared at 5 kV, the voltage and current output were 1.40 V and 1.35 μA, respectively. Increasing the applied voltage to 7 kV increased both voltage and current outputs to 2.20 V and 2.30 μA. Further increasing the applied voltage resulted in decrease in electrical outputs.

![Figure 5.12](image)

**Figure 5.12** (a) Voltage and (b) current outputs of short-distance electrospun PVDF mats prepared at different applied voltages (spinning distance: 2 cm). (Mat thickness: 100 μm; working area: 4 cm²)
Table 5.1 shows the electrical output of interconnected PVDF fibre mat with different thicknesses. Figure 5.13 indicates the corresponding voltage and current output signals while Figure 5.14 shows the signals obtained from the conventional electrospun fibre mat. For comparison, the electrical outputs of conventionally-electrospun PVDF fibre mat with areal densities of 2.7 mg/cm$^2$ (thickness 100 μm) and 4.4 mg/cm$^2$ (thickness 175 μm) were also included in the Table. Among the short-distance electrospun fibre mats listed, the highest voltage (2.50 V) and current (2.90 μA) were generated from the sample with an areal density of 2.5 mg/cm$^2$ (mat thickness about 54 μm). At the equivalent areal density, the conventionally electrospun PVDF nanofibre mat produced a slightly lower voltage and current outputs.

**Table 5.1** The relationship between areal density, thickness and electrical output of fibre mats.

<table>
<thead>
<tr>
<th>Electrospinning parameters</th>
<th>Areal density (mg/cm$^2$)</th>
<th>Thickness (μm)</th>
<th>Peak voltage (V)</th>
<th>Peak current (μA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>short-distance distance 2 cm voltage 7 kV</td>
<td>1.3</td>
<td>30</td>
<td>1.80</td>
<td>2.00</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>54</td>
<td>2.55</td>
<td>2.90</td>
</tr>
<tr>
<td></td>
<td>3.6</td>
<td>78</td>
<td>2.45</td>
<td>2.65</td>
</tr>
<tr>
<td></td>
<td>4.4</td>
<td>100</td>
<td>2.20</td>
<td>2.30</td>
</tr>
<tr>
<td></td>
<td>6.2</td>
<td>130</td>
<td>1.90</td>
<td>1.90</td>
</tr>
<tr>
<td></td>
<td>13.4</td>
<td>270</td>
<td>0.75</td>
<td>0.85</td>
</tr>
<tr>
<td>conventional distance 15 cm voltage 15 kV</td>
<td>4.4</td>
<td>175</td>
<td>1.55</td>
<td>1.55</td>
</tr>
<tr>
<td></td>
<td>2.7</td>
<td>100</td>
<td>2.25</td>
<td>2.35</td>
</tr>
</tbody>
</table>
Figure 5.13 (a) Voltage and (b) current outputs of PVDF mats with different areal densities, (c) voltage and (d) current output signals with different areal densities. (Working area: 4 cm²)

Figure 5.14 (a) Voltage and (b) current output of PVDF nanofibre mat prepared from conventional electrospinning. (Applied voltage: 15 kV; spinning distance: 15 cm; mat thickness: 100 μm; working area: 4 cm²)
It was also noticed that at the similar areal density level, the short-distance electrospun fibre mat was only around half thickness of the conventionally electrospun one due to the larger bulk density. At the same thickness (e.g. 100 μm), the conventionally electrospun PVDF nanofibre mat showed a similar electrical output to the short-distance electrospun PVDF fibre mats.

The excellent mechanical-to-electrical energy conversion properties of the short-distance electrospun interconnected PVDF fibre mat can be explained by two reasons: 1) The dense fibrous structure facilitates charge transfer across the mat and hence decreasing the internal resistance; 2) The fibre-fibre interconnection assists in charge transfer because it eliminates the boundary. These allow the interconnected fibre mats more efficient in the energy conversion than separated fibre ones.

![Figure 5.15](image)

**Figure 5.15** (a) Voltage and (b) current outputs of short distance electrospun PVDF mats prepared at different spinning distances. (Applied voltage: 7 kV; mat thickness: 100 μm; working area: 4 cm²)

Figure 5.10c shows the peak voltage outputs of PVDF with different morphologies (output signals are shown in Figure 5.15). The lowest electrical outputs were recorded on the PVDF particle film (0.75 V and 0.70 μA). The fibrous PVDF (from...
zone III-V) showed considerably higher electrical output than PVDF particle film. The voltage output showed a similar trend to $\beta$ phase content. This indicates that $\beta$ phase in the electrospun product played a critical role in deciding the electrical output, which was in accordance to the results in Chapter 4.

### 5.2.4 Mechanical property

Another advantage of fibre-interconnection is the ability to maintain structure integration. Figure 5.16 shows a series of photos taken during fast compression and decompression of a PVDF fibre mat. For the mat made of separated fibres which are prepared by conventional electrospinning, fibres adhered the top load if the edge was not fixed. It took about 274 seconds to completely detach the mat from the top load. This substantial expansion of fibrous structure caused damage of fibre mat and faulty of the fibrous device. For the interconnected fibre mat produced by short distance electrospinning, however, it firmly attached one side without expansion, indicating the excellent structure cohesiveness.

![Figure 5.16](image-url)  
**Figure 5. 16** Digital photos of interconnected and separated fibre mats during the decompression.
Figure 5.17a shows the delamination resistance of the PVDF fibre mats (the measurement setup is illustrated in the inset). The two sides of the PVDF fibre mat were mounted on the sample holders with double-side stick tape. Figure 5.18a shows the delamination strength increased with the increase of cross-head speed. For the interconnected fibre mat, it required 280 Pa to delaminate the mat when the cross-head speed was 20 mm/min, which was as strong as the sticking force between two layers of stick tapes (Figure 5.18b). However, for the fibre mat prepared by conventional electrospinning, the delamination strength was very small, only about 40 Pa.

**Figure 5.17** (a) Delamination resistance of the PVDF mats, (b) stress-strain curves of PVDF fibre mats, effect of applied voltages on (c) tensile properties and (d) mat porosity.
Figure 5.18 Delamination resistance of (a) the PVDF interconnected mats and (b) two layer double-side stick tapes and direct contact between top and bottom load without any tape or PVDF mat in between.

We also measured the tensile property of the PVDF fibre mats, as seen in Figure 5.17b (also see Figure 5.19 and 5.20). Before fracture, the fibre mats experienced two typical deformation stages: nonlinear deformation and linear elastic deformation \(^{225,226}\). The nonlinear elastic stage at the low stress comes from the guided alignment of randomly oriented fibres in the mat. At the second stage, the curves showed a linear elasticity as the intrinsic property of aligned PVDF fibres.

Figure 5.19 Stress-strain curves of short-distance electrospun PVDF mats prepared at different applied voltages. (Spinning distance: 2 cm)
Figure 5.20 (a) Stress-strain curves of short-distance electrospun PVDF mats prepared at different spinning distances and (b) effect of spinning distance on tensile properties. (Applied voltage: 7 kV)

Figure 5.17c shows tensile properties of interconnected fibre mats prepared by short-distance electrospinning at the spinning distance of 2 cm. The mat obtained at 5 kV had tensile strength and elongation at break of 13.82 MPa and 229.5%, respectively. When the applied voltage was increased to 6 kV, the tensile strength and elongation at break both decreased to 13.01 MPa and 201.22%. Increasing the voltage to 8 kV, the elongation at break decreased to 178.75% while the tensile strength increased to 22.75 MPa. When the applied voltage increased from 8 kV to 11 kV, both tensile strength and elongation at break decreased. Also the mats looked like a transparent film that were very brittle and a plateau stage in the stress-strain curves appeared (see Figure 5.19). The stress-strain curve of PVDF nanofibre mat prepared by conventional electrospinning is also shown in Figure 5.17b and c. The higher tensile strength was attributed to denser fibrous structure. As shown in Figure 5.17d, the interconnected fibre mats had lower porosity than conventional PVDF nanofibre mat.
The effect of spinning distances on tensile properties was also studied. It was indicated that interconnected fibre mats always had a higher tensile strength than separated fibre mat (see Figure 5.20).

For piezoelectric materials, they often undergo mechanical deformation during energy conversion. The active layer may receive forces from various directions, e.g. longitudinal or horizontal. The result that interconnected fibre mats obtained from short-distance electrospinning show evidently higher mechanical strength suggests that the interconnected fibre mat should be more durable than that of the separated fibre mat.

### 5.3 Conclusion

In this chapter, we have proven that interconnected PVDF fibre mats can be prepared by electrospinning a PVDF solution at a spinning distance of 2-8 cm. Most of the interconnected fibres have higher crystallinity than those prepared by conventional electrospinning, and the highest $\beta$ phase content is comparable to that of the conventionally-electrospun PVDF nanofibres. At the optimized condition, the interconnected PVDF fibre mat shows comparable mechanical-to-electrical conversion performance than the conventionally electrospun PVDF nanofibre mat. However, interconnected fibre mats have higher delamination resistance and tensile strength. The higher mechanical strength allows the interconnected fibre mat more robust to maintain structure integrity during compression and decompression. This makes interconnected PVDF fibre mats very promising for in development of mechanical energy harvesters.
Chapter 6 Mechanical-to-electrical Energy Conversion of PVDF Nanofibre Mat Containing Electron-hole Transfer Agents

Except for the limited electric outputs, there are some other concerns of electrospun PVDF fibre energy harvesting. Firstly, the crystallinity of PVDF and $\beta$ crystal phase content of electrospun PVDF nanofibre mats are low, which lead to small outputs. We previously studied the effects of electrospinning parameters (e.g. applied voltage and spinning distance) and polymer concentration on fibre morphology and $\beta$ crystal phase contents systematically and found that the fibre mats obtained from 20% PVDF concentration, 15 kV applied voltage and 15 cm spinning distance had the highest $\beta$ crystal phase contents (around 84%) $^5$. Other researches also reported that adding additives (e.g. MWCNTs, modified montmorillonite) into electrospinning solution could enhance the $\beta$ crystal phase content of PVDF nanofibres $^{34,227}$. Secondly, high electrical resistance of electrospun PVDF mats also leads to low outputs. Thus, conductive additives can increase the surface charge density of PVDF nanofibre mats to enhance the output power $^{34}$. Thirdly, the piezoelectric potential screening effect that caused by the present of the free carriers in piezoelectric PVDF is one of the most important issues that prevents the large power output performance $^{186,228}$. To improve the piezoelectric output, $p$-$n$ junctions have been formed within energy harvesters to reduce the screening effect. So far, the efforts have all been made on ZnO inorganic piezoelectric NGs, there are no related reports on electrospun PVDF mats yet.

When nanofibres are prepared by electrospinning, doping agents can be easily added into nanofibres through blending dopants into polymer solutions. Since the uniform dispersion of the doping agents within the solution, their uniform distribution within nanofibres can be achieved. In addition, layered fibre deposition
also creates opportunities to control the dopant type and level in different fibre layers within a nanofibre mat.

In this chapter, we studied the effect of small molecular doping on nanofibre properties and their mechanical-to-electrical performance. It was interesting to find that the mechanical-to-electrical outputs of fibre mats were enhanced after doping. In the charge transfer agents containing PVDF fibre mats, we have observed more than two-fold higher output voltages and currents by comparison to the pure PVDF fibre mats.

### 6.1 Experimental procedure

Based on the results in Chapter 4, optimized electrospinning parameters (20% solution concentration, 15 kV applied voltage and 15 cm spinning distance) were used in this chapter.

After preparing 20% PVDF solutions using mixture solvents of DMF/acetone, different amounts of TTA (0.3%, 0.5%, 0.7%, 1%, 5% and 10 wt% relative to PVDF) or Butyl-PBD (0.1%, 0.5%, 1%, 1.5%, 5% and 10%) were added into the solutions separately and mixed uniformly. During the electrospinning, the flow rate was maintained at 1 mL/h. For preparing the charge transfer agents containing PVDF fibre mats, TTA (hole) doped fibre layer was spun on the collector first and followed by depositing another layer of Butyl-PBD (electron) doped fibres. All electrospinning experiments were carried out at room temperature.
6.2 Results and discussion

6.2.1 Morphology structure of PVDF mats

TTA and Butyl-PBD were commonly used as hole transport material (p-type) and electron transport material (n-type) in organic light-emitting diodes \(^{229,230}\). As the name suggests, hole transport material can be in favour of transporting hole carriers and blocking the electron transport. Electron transport materials have exactly opposite function. Figure 6.1a and b show SEM images of the PVDF nanofibres doped with 0.5% TTA and 1% Butyl-PBD. Both nanofibres were uniform with a rough surface structure. The average diameter of 0.5% TTA doped nanofibres was around 290 nm while 1% Butyl-PBD doped nanofibres was slightly finer with an average diameter of 275 nm.

![Figure 6.1 SEM images of (a) 0.5% TTA and (b) 1% PBD doped PVDF nanofibres. Insert: high magnification SEM images (Scale bar: 200 nm). Average diameter distribution of nanofibres with various (c) TTA and (d) Butyl-PBD doping contents.](image)

**Figure 6.1** SEM images of (a) 0.5% TTA and (b) 1% PBD doped PVDF nanofibres. Insert: high magnification SEM images (Scale bar: 200 nm). Average diameter distribution of nanofibres with various (c) TTA and (d) Butyl-PBD doping contents.
Figures 6.2 and 6.3 show the SEM images of the PVDF nanofibres with different TTA and Butyl-PBD contents and their diameter distribution was shown in Figure 6.1c and d. It can be seen that the fibre diameter did not change much after the TTA concentration was increased from 0.3% to 10%, neither was the fibre surface morphology. By doping 0.1% Butyl-PBD, the fibres became thinner. However, no obvious diameter change was observed by increasing the Butyl-PBD doping content to 10%.

Figure 6.2 SEM images of PVDF nanofibres with various TTA doping contents: (a) 0%, (b) 0.3%, (c) 0.7%, (d) 1%, (e) 5% and (f) 10%. (Scale bar: 1 μm). Insert: high magnification SEM images (Scale bar: 200 nm).
Chapter 6

Figure 6.3 SEM images of PVDF nanofibres with various Butyl-PBD doping contents: (a) 0.1%, (b) 0.5%, (c) 1.5%, (d) 5% and (e) 10%. (Scale bar: 1 \textmu m).

Insert: high magnification SEM images (Scale bar: 200 nm).

As we know, the fibre diameter is influenced by the electrical conductivity of electrospinning solution \textsuperscript{199,231,232}. The increase in conductivity improves the jet whipping instability and thus thinner fibres are normally resulted. The effect of TTA and Butyl-PBD dopants on electrical conductivity of electrospinning solution was studied, as shown in Figure 6.4. It can be found that TTA had little effect on PVDF solution conductivity. As a consequence, the nanofibre diameters were kept almost constant. Meanwhile, an obvious increase in solution conductivity from 4 \textmu s/cm to around 10 \textmu s/cm was resulted when 0.1 % Butyl-PBD was added into the solution and the value was kept stable when the doping content was increased from 0.1\% to 10\%. The change in solution conductivity had a good agreement with the average fibre diameter.
6.2.2 Crystallization study

The crystal phase structure of nanofibres was studied by XRD and FTIR. Figure 6.5a shows the XRD patterns of the PVDF mats with different TTA contents. A peak at $2\theta=20.6^\circ$ is observed which is assigned to the characteristic peak of $\beta$ crystal phase. It is the sum of total reflection of (110) and (200) planes. A small peak at $18.4^\circ$ corresponds to the diffraction of (020) plane of $\beta$ phase. The intensity of $\beta$ crystal phase was increased dramatically when the doping concentration was increased from 0% to 0.5%. When the doping content was further increased from 0.5% to 10%, the intensity decreased which indicated that the amount of $\beta$ crystal phase went down. FTIR results could indicate valuable information about PVDF crystalline structure. Besides of crystalline structure bands, some other bands associated with the amorphous phase are also revealed. As FTIR spectra shown in Figure 6.5b, the characteristic peaks at 840 cm$^{-1}$ and 1274 cm$^{-1}$ were assigned to the absorption bands of $\beta$ crystal phase. Weak bands at 761 cm$^{-1}$, 795 cm$^{-1}$ and 976 cm$^{-1}$ corresponded to $\alpha$ crystal phase. The $\beta$ crystal phase content in the
nanofibres was estimated according to the FTIR results by using the equation of 4-1 in Chapter 4.5.

Figure 6.5c shows the calculation result. The $\beta$ crystal phase went up from 86.1% to 90.2% when the doping content increased from 0% to 0.5%. Further increasing the doping content from 0.5% to 10% results in gradual decrease of the $\beta$ crystal phase content to 86.8%. During the electrospinning process, the electric stretching and poling happened simultaneously promote the formation of polar $\beta$ crystal phase. Addition of little amount of dopants can enhance $\beta$ crystal phase formation due to ionic interactions of the polymer with polar solvent and dopants.35 However, when the concentration of dopants increased to higher than 0.5%, large amount of $\beta$ phase spherulites formed and tended to reunite together. Meanwhile, $\alpha$ crystal phase is easily to form in the inter-region between spherulites.36,233 Thus, the content of $\beta$ crystal phase went down.

**Figure 6. 5** (a) XRD patterns and (b) FTIR spectra of PVDF nanofibres with various TTA doping contents. (c) Corresponding calculated $\beta$ crystal phase content. (d) DSC results and (e) corresponding calculated crystallinity with various TTA doping contents. (f) DSC result of TTA.
DSC was performed to study the crystallinity of different PVDF fibre mats. Figure 6.5d shows the DSC results of the mats with different TTA doped contents. With the increase of TTA dopants, a small peak at around 110 °C was observed, which was contributed to the melting of dopant (Figure 6.5f). The peak at around 167 °C was assigned to the melting of $\alpha$ and $\beta$ crystal phase PVDF. The $\beta$ crystal phase presents a similar melting temperature to $\alpha$ crystal phase. Therefore, DSC results cannot be used for distinguish this two crystal phases, but enable to calculate the crystalline percentage of the mats. The crystallinity $\Delta X_c$ was calculated (see the calculation equation 5-1 and 5-2 in Chapter 5).

The crystallinity with different doping contents was plotted, as shown in Figure 6.5e. It remained at a stable value, around 47%. In the electrospinning process, PVDF solution was induced by the high electric field. When the jet underwent from the need tip to the collector, the crystallization of PVDF happened. It can be concluded that the presence of TTA dopant does not have significant effect on the degree of crystallinity.
Figure 6.6 (a) XRD patterns and (b) FTIR spectra of PVDF nanofibres with various Butyl-PBD doping contents. (c) Corresponding calculated β crystal phase content. (d) DSC results and (e) corresponding calculated crystallinity with various Butyl-PBD doping contents. (f) DSC result of Butyl-PBD.

The effect of Butyl-PBD doping on PVDF fibre crystal structure and crystallinity was also investigated (Figure 6.6). Figure 6.6c indicates the β crystalline phase content of PVDF nanofibres with different Butyl-PBD doping contents.

The β phase content increased gradually and reached the maximum value of 91.6% when the doping content was 1%. Further increasing the doping content, the β phase content decreased. A small peak at around 139 °C in DSC result was assigned to melting of Butyl-PBD. The crystallinity was not considerably changed, keeping at around 48%. This value was a little higher than that of TTA doping nanofibre mats.

The Butyl-PBD doped electrospinning solutions had higher electric conductivities which resulted in better stretching and poling during whipping process.
6.2.3 Mechanical-to-electrical energy conversion property

The mechanical-to-electrical energy conversion property of the PVDF fibre mats was evaluated by subjecting to a repeated compressive impact (peak stress 25000 Pa, frequency 1Hz). The circuit voltage and circuit current were recorded and shown in Figure 6.7 and 6.8.

![Figure 6.7](image1.png)  
**Figure 6.7** (a) Voltage and (b) current outputs of electrospun PVDF nanofibres with different TTA doping contents. (Mat thickness: 100 μm; working area: 4 cm²)

![Figure 6.8](image2.png)  
**Figure 6.8** (a) Voltage and (b) current outputs of electrospun PVDF nanofibres with different Butyl-PBD doping contents. (Mat thickness: 100 μm; working area: 4 cm²)
Figure 6.9 Peak voltage (a) and current outputs (b) of PVDF nanofibres with various TTA doping contents. (Inserts: voltage and current output signals of PVDF nanofibres with 0.5% TTA doping content). Peak voltage (c) and current outputs (d) of PVDF nanofibres with various Butyl-PBD doping contents. (Mat thickness: 100 μm; working area: 4 cm²)

Figure 6.9a and 6.9b indicate that the voltage and current output went up from 1.5 V and 1.55 μA to 2.55 V and 2.65 μA when the TTA dopant content was increased from 0% to 0.5%. The mechanical-to-electrical property was enhanced 1.70 time in voltage and 1.71 time in current. Continuing to increase the doping content led to decrease in both outputs. A slight difference in peak value of front and back output was observed which was possibly caused by the different speed in the deformation and recovery of the active PVDF fibre mats. It can be concluded that the mat with higher β phase content always have a better mechanical-to-electrical property. This enhancement in the electrical output was also due to the increase in
the piezoelectric potential via blocking the free electron carrier movement existing in the PVDF mat.

Similar phenomenon was also observed in the Butyl-PBD doping system. The sample with 1% PBD doping content had the maximum outputs, around 2.65 V and 2.7 µA (Figure 6.9c and 6.9d). These values are 1.77 time in voltage and 1.74 time in current higher than these of pure PVDF fibre mat. At that case, free hole carrier movement blocking plays significantly role to increase the electrical output besides of high β phase content.

![Figure 6.10](image)

**Figure 6.10** (a) voltage and (b) current outputs of electron-hole transfer double layer PVDF nanofibre mat with different thickness ratios of hole transfer layer and electron transfer layer.

To further enhance the electrical outputs, PVDF electron-hole transfer double layer fibre mats were prepared by electrospinning TTA doped and Butyl-PBD doped solutions through a two-step fibre deposition. When the double-layer mat was subjected to a compressive strain, positive and negative piezoelectric charges were induced. Due to hole and electron transport movement blocking property in the respective layers, the free electrons and holes were attracted at the interface of double layer mat. In that case, the screening effect for the generated piezoelectric
potential was reduced, leading to an improvement in the piezoelectric output voltage and current \(^{184,185,187}\).

Also it can be understood using capacitor theory that when three capacitors are connected in series, the overall capacitance is less than that of either \(^{184}\). PVDF electron-hole transfer double layer fibre mat acts as a capacitor containing three individual capacitors connected in series: hole transfer PVDF layer, electron transfer PVDF layer and interface of that double layers. Thus, the overall capacitance is less than that of either one. The reduced capacitance of the energy harvester improves the electrical outputs.

Figure 6.10a and b show the circuit voltage and circuit current of the double layer mats with different thickness ratios of hole transfer layer and electron transfer layer. All the fibre mats were controlled at the thickness of 100 nm. Five different thickness ratios of hole transfer layer and electron transfer layer were prepared: 3:1, 2:1, 1:1, 1:2 and 1:3, respectively. A stable output voltage and current were observed around 3.2 V and 3.4 \(\mu\)A, no matter how the thickness ratios changed. These values were much higher than these of the original ones, approximately 2.1 times of voltage and 2.2 times of current. Also they were higher than TTA doped or Butyl-PBD doped homogeneous layer. A thin layer of depletion region was formed at the interface of hole transfer layer and electron transfer layer, regardless of thickness ratio. The depletion region plays an important role in increasing the piezoelectric potential via neutralization of the free electrons existing in the active layer.
6.3 Conclusion

In summary, we have demonstrated that the electrospun PVDF electron-hole transfer double nanofibre layer structure to enhance mechanical-to-electrical property for the first time. By systematically studying on the doping content, the optimal contents were found. The high piezoelectric performance was achieved by blocking holes or/and electrons existing in the PVDF under mechanical strain. The output voltage and current of double PVDF layer were observed as high as 3.2 V and 3.4 $\mu$A, respectively. These values were approximately 2.1 times in voltage and 2.2 times in current higher than these of the undoped PVDF nanofibres. The ratio thickness of hole transfer layer and electron transfer layer has little effect on the mechanical-to-electrical property. As different type of dopants can be added in the electrospinning solution, we expect the further piezoelectric performance enhancement by optimizing the dopant types.
Chapter 7 Polymer-Metal Schottky Contact with Direct-Current Outputs

Conducting polymers, such as polypyrrole (PPy), have demonstrated property of mechanical-to-electrical energy conversion. Previous reports on mechanical energy harvesting involving PPy are often based on interaction with an electrolyte solution. The minute voltage output (e.g. 0.28 mV) and use of electrolyte solution make these devices unsuitable to be integrated into solid-state devices (e.g., wearable electronics). As far as we are aware, electric generation from mechanical deformation of a dry, freestanding PPy without electrolyte has not been reported to date.

In this chapter, PPy was pressed into the form of a plate and its mechanical-to-electrical energy conversion properties were carefully investigated. It has been found that with one side to form a Schottky contact and the other side an Ohmic contact with two different metal electrodes, a freestanding PPy plate can generate DC voltage with an output current density as high as 218.6 μA/cm² upon mechanical deformation. We have further demonstrated that the electric energy thus generated can be directly stored into a capacitor without rectification to power electronic devices, as exemplified by lighting up a commercial LED.

7.1 Experimental procedure

The preparation of PPy, PANi and PEDOT powders were introduced in Chapter 3 in details. In a typical experiment, PPy was synthesized using FeCl₃ as oxidant, and PPy plates (diameter: 13 mm; thickness: 1.44 ± 0.10 mm) were fabricated by mechanically pressing the PPy powders in the same manner as FTIR KBr plates were made.
To measure the mechanical-to-electrical conversion of the PPy plate, we used an aluminium foil and a gold sheet as electrodes and devised the electrical circuit, as shown in Figure 7.1. The gold sheet was supported by a dense polyethylene terephthalate (PET) film of the same size. During the test, the PPy plate was mounted on the Al electrode, whereas the Au electrode was laminated to a non-conductive PET film and fixed to a movable load. The circuit is connected just during compressive impact of the PPy plate by the PET/Au-load. By moving up-and-down the gold electrode with the load, the PPy plate was compressed and decompressed to generate electric signals.

![Figure 7.1 Circuit (forward connection) for measurement of electrical outputs under strain.](image)

### 7.2 Results and discussions

#### 7.2.1 Early finding in laboratory

As discussed before, the low conductivity of PVDF may have contributed to the limited electrical outputs of PVDF nanofibre mats. For enhancing the electrical conductivity, PVDF nanofibres were coated with PPy particles by vaper phase polymerization and the experiment process is reported in Appendix part.
Figure A.1 shows the PVDF mats coated with PPy particles while the corresponding SEM images are shown in Figure A.2. When the molar concentration of FeCl$_3$·6H$_2$O/ethanol solution was below 0.1 mol/L, separated PPy particles were observed on the surface of PVDF nanofibres. A uniform PPy particle layer could only be achieved on PVDF nanofibres surface when solution molar concentration reached 0.25 mol/L.

The mechanical-to-electrical performance of these samples were tested under the load of 10 N at 1 Hz. As shown in Figure A.3, AC electrical outputs were recorded when PVDF mats treated with 0.05 and 0.1 mol/L of FeCl$_3$·6H$_2$O/ethanol solutions. Interestingly, DC electrical outputs were observed when the PVDF fibres were completely covered by PPy particles. With increasing the molar concentration of solution from 0.25 mol/L to 1 mol/L, the DC output voltage and current increased significantly from 0.06 V and 250 nA to 0.38 V and 1600 nA. Furthermore, similar DC signals were also observed on other electrospun nanofibre mats (PVA and PAN) coated with PPy, suggesting the interesting energy conversion behaviour of PPy. Thus, the mechanical-to-electrical energy conversion performance of PPy plates will be carefully studied in this chapter.

7.2.2 Morphology and structure of PPy

Figure 7.2 shows the chemical structure of PPy and digital image of the as-prepared PPy plate. The SEM image in Figure 7.3 shows a typical globular morphology for PPy$^{236}$. It also indicates that the PPy particles contain the elements of C, N, O and Cl.
7.2.3 Mechanical-to-electrical energy conversion property of Al/PPy plate/Au devices

Figures 7.4a and b show the voltage and current outputs, respectively, when the device was compressed to a strain up to 10.4% at a speed of 0.08 mm/s and then decompressed at the same speed. As can be seen, the peak current reaches up to 290 μA (current density 218.6 μA/cm², Figure 7.4b) at a peak voltage of 0.7 V (Figure 7.4a). The voltage and current outputs can be generated repeatedly over more than thousands of compression-decompression cycles as the 10.4% strain is within the elastic deformation of the PPy plate (Figure 7.5).
Figure 7.4 Typical (a) voltage and (b) current outputs from a PPy plate under repeated compressive deformation. (Strain level: 10.4%; compression speed: 0.08 mm/s; frequency: 0.27 Hz; PPy plate thickness: 1.44 ± 0.10 mm)

Figure 7.5 Stress-strain curves of the PPy plate at different maximum strain levels.

Compared to various reported energy harvesting devices as shown in Tables 2.6 and 7.1, our PPy-based energy harvesting unit shows a much higher current density, though voltage output is relatively low (0.7 V).
Table 7.1 Peak voltage and current outputs of various mechanical energy harvesters.

<table>
<thead>
<tr>
<th>Types</th>
<th>Active layer</th>
<th>Peak Voltage (V)</th>
<th>Peak Current Density (μA/cm²)</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Piezoelectric</strong></td>
<td>ZnO nanowires</td>
<td>1.26</td>
<td>0.0089</td>
<td>239</td>
</tr>
<tr>
<td></td>
<td>PVDF-TrFE sandwiched graphene electrodes</td>
<td>4</td>
<td>0.4</td>
<td>78</td>
</tr>
<tr>
<td></td>
<td>BaTiO₃</td>
<td>6</td>
<td>0.048</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>Insulating ZnO-based</td>
<td>1.25</td>
<td>3.1</td>
<td>186</td>
</tr>
<tr>
<td></td>
<td>Sponge-like PVDF film</td>
<td>11</td>
<td>4.9</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>PZT</td>
<td>200</td>
<td>150</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>Single-atomic-layer MoS₂</td>
<td>0.018</td>
<td>54</td>
<td>64</td>
</tr>
<tr>
<td><strong>Triboelectric</strong></td>
<td>Cu-FEP radial-arrayed rotary</td>
<td>850</td>
<td>38.2</td>
<td>240</td>
</tr>
<tr>
<td></td>
<td>Au-PTFE film Flutter-driven</td>
<td>250</td>
<td>1.9</td>
<td>52</td>
</tr>
<tr>
<td></td>
<td>Al-FEP freestanding</td>
<td>135</td>
<td>0.9</td>
<td>241</td>
</tr>
<tr>
<td></td>
<td>Al-PVC multi-layered sliding</td>
<td>800</td>
<td>0.6</td>
<td>242</td>
</tr>
<tr>
<td></td>
<td>PVDF-Nylon nanowire-based</td>
<td>1163</td>
<td>11.5</td>
<td>243</td>
</tr>
<tr>
<td></td>
<td>PTFE-Al network</td>
<td>569.9</td>
<td>6.5</td>
<td>244</td>
</tr>
<tr>
<td><strong>Ionization induced</strong></td>
<td>Poly (acrylic acid) gels</td>
<td>0.0012</td>
<td>-</td>
<td>57</td>
</tr>
<tr>
<td></td>
<td>Polymethacrylic acid hydrogels</td>
<td>0.017</td>
<td>-</td>
<td>245</td>
</tr>
<tr>
<td></td>
<td>Nafton film</td>
<td>-</td>
<td>0.76</td>
<td>246</td>
</tr>
<tr>
<td><strong>Work function</strong></td>
<td>Al-Cu</td>
<td>0.32</td>
<td>-</td>
<td>58</td>
</tr>
<tr>
<td><strong>Our generator</strong></td>
<td>PPy</td>
<td>~0.7</td>
<td>~218.6 (Initial)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>~62.4 (stable)</td>
<td></td>
</tr>
</tbody>
</table>

The power ($P$) outputs at different external resistances were calculated by the equation: $P = I^2 \cdot R$, where $I$ is the peak current at the corresponding external resistance ($R$). Figure 7.6a shows the output power as a function of external load resistance from 1 Ω to 0.1 MΩ (see Figure 7.6b for the $I \sim R$ and $V \sim R$). The output power initially increased with increasing the external resistance to reach a maximum value of 0.15 W m⁻² at 8.2 kΩ, and then decreased with further increase in the $R$ value. It is known that an energy device shows a maximum $P$ value when it works at an external resistance equivalent to the internal resistance 247.
Figure 7.6 (a) Relationship between the output power and the external load resistance; (b) Effect of external load resistance on the electrical outputs of PPy plate. (Strain level: 10.4%; compression speed: 0.08 mm/s; frequency: 0.27 Hz; PPy plate thickness: 1.44 ± 0.10 mm)

Figure 7.7 (a) Electrical outputs of PPy plate as a function of strain change; (b) electrical outputs of PPy plate at a given compassion condition (Pressing time t1= 300s, t2= 300s; external load: 8.2 kΩ); (c) & (d) effect of plate size and thickness on electrical outputs (Strain = 10.4%).
To gain further insights of the mechanical energy-electricity conversion by the PPy plate, we employed different strain-time functions. Figure 7.7a shows the response of electrical outputs to a triangle compression-decompression strain cycles. As can be seen, the device voltage and current outputs show a synchronous response to the compression under a periodic compression at a crosshead speed of 0.08 mm/s to the maximum strain of 10.4%; both voltage and current increase with increasing the strain value. However, the electrical outputs responded to the strain in a nonlinear manner. The rates of voltage and current increases for the strain change from 0% to 5% were much lower than those for the strain change from 5% to 10%. Once the strain was removed, the outputs dropped to zero spontaneously. Figure 7.8 indicates that the compression speed has little effect on the electrical outputs while the electrical outputs increase with increasing the compression strain.

![Figure 7.8](image_url)

**Figure 7.8** Electrical output change with (a) compression speed and (b) strain level. (External load: 8.2 kΩ)

When the PPy plate was pressed and held for certain period of time and then decompressed to the natural state, the electrical output profile changed with the duration ($t_1$) of holding the plate at certain strain. As shown in Figure 7.7b, both
voltage and current decay slowly over several minutes even if the strain is kept at 10.4%. Once the strain is released from the PPy plate, however, both the outputs drop to zero immediately (Figure 7.7b). The observed unique mechanical-to-electrical conversion responses were repeatable for many cycles. The $t_1$ and $t_2$ represent the pressing time and the releasing period between two compressions. The $t_1$ did not affect the voltage and current peak outputs. However when $t_2$ is decreased from 300 s to 25 s, both peak voltage and peak current outputs decreased, as shown in Figure 7.9.

**Figure 7.9** Effect of compression conditions on electrical outputs: (a) $t_1 = 100$ s, $t_2 = 300$ s; (b) $t_1 = 25$ s, $t_2 = 300$ s; (c) $t_1 = 300$ s, $t_2 = 100$ s; (d) $t_1 = 300$ s, $t_2 = 25$ s.
We further investigated the effects of the PPy plate geometrical dimensions on the electrical outputs. As seen in Figure 7.7c, the current output increases from 7 μA to 83 μA (current density from 38.9 μA/cm² to 62.4 μA/cm²) when the PPy plate area increases from 0.18 cm² to 1.33 cm² while keeping the plate thickness unchanged. However, the voltage output remained almost the same (Figure 7.7c). Similarly, changing the plate thickness while keeping the PPy plate diameter the same only changed the current output to a certain extent but had little effect on the voltage output. This is presumably due to the effect of internal resistance on the current output. Increasing the plate thickness or decreasing the area leads to increase in the internal resistance, hence reducing the current output.

![Figure 7.10](image)

**Figure 7.10** (a) Schematic of output recording; (b) voltage and (c) current outputs of the PPy plate. The test was performed by using Al electrode as the travelling electrode.

We also noted that the impact side had little influence on the electrical outputs. As shown in Figure 7.10, no matter which electrode was connected to the travelling load for compression, the PPy device generated the same level of electrical signals.
under the same strain. In addition, the electrical outputs were not affected by the electrode-PPy connection modes. When both electrodes are connected constantly to the PPy plate (Figure 7.11a), the device shows similar electrical outputs to those from the device with one of the electrodes discontinuously connected the PPy plate, as shown in Figure 7.4. When the connection reversed, the output DC voltages reversed the polarity (Figure 7.12).

Figure 7.11 (a) Schematic of output recording; (b) voltage and (c) current outputs of the PPy plate when the two electrodes were closely connected with PPy all the way as a whole during compressive impact. (Pre-load: 0.2 N)

Figure 7.12 (a) Schematic of output recording and (b) electrical outputs of the PPy plate at the reversed electrical connection.
Figure 7.13 I-V characteristics of the (a) Au/PPy/Al, Al/PPy/Al and (b) Au/PPy/Au devices at gentle contact (Strain: 1%) and compressed (Strain: 10.4%) states; (c) voltage response of Al/PPy/Al and Au/PPy/Au devices under compressive strain (Strain level: 10.4%; compression speed: 0.08 mm/s); (d) proposed energy band diagram of the Al/PPy/Au device at freestanding state and under compressive strain.

To investigate the mechanism for the novel mechanical-to-electrical energy conversion, we measured the $I-V$ curve and electrical impedance spectrum (EIS) of the Au/PPy/Al device. As shown in Figure 7.13a, a nonlinear $I-V$ curve with a Schottky diode feature is observed on the device in both gentle contact (1% strain level, to ensure the electric connection) and compressed states with a stronger rectifying effect for the device under a compressive strain. From the Nyquist plots (Figure 7.14), we estimated the internal electrical resistance of the device after the compression test to be approximately 8.3 kΩ, which is very close to that established from Figure 7.6a (8.2 kΩ).
Figure 7.14 (a) I-V characteristics of the Au/PPy/Al device at different strain levels and (b) Nyquist plots of the Au/PPy/Al device before and after the compression test; (c) I-V characteristics and (d) Nyquist results of the devices with reverse circuit connection. W: working electrode.

The rectifying effect indicates that a Schottky contact should exist within the device. To find out the Schottky contact, we examined devices with the same type of metal electrodes on both sides of PPy the plate (i.e. Au/PPy/Au and Al/PPy/Al). As shown in Figure 7.13b, a linear I-V characteristic is observed on the Au/PPy/Au device, indicating an Ohmic contact between the Au and PPy plate with an electrical resistance as low as 80 Ω (Figure 7.13b). For the Al/PPy/Al device, a non-linear I-V relationship was observed with an electrical resistance as high as 12 kΩ, calculated based on the linear segment (Figures 7.13a and 7.15). This suggests that Schottky contact should form between PPy and Al. Schottky contact between PPy
and Al \textsuperscript{144,248} and Ohmic contact between PPy and Au \textsuperscript{249} have been reported previously. Our study was in good accordance with these reports.

![Figure 7.15](image)

**Figure 7.15** (a) Schematic of AC impedance testing; (b) Nyquist plot of the Al/PPy/Al device at 10.4% compressive strain.

To understand this energy generation phenomena under compression, we tested the mechanical-to-electrical conversion response of the Au/PPy/Au and Al/PPy/Al devices. As shown in Figure 7.13c, no electrical generation is observed on the Au/PPy/Au device under compression, but uneven positive and negative outputs with weak voltage output peaks of average around 0.1 V were generated on the Al/PPy/Al device under compressive impact (also see current output in Figure 7.16). However, the output voltage from the Al/PPy/Al device is not only significantly lower than that of the Al/PPy/Au counterpart but also in an AC mode. These results suggest that single Schottky contact in the Al/PPy/Au device plays a critical role in conversion of mechanical energy into DC power. And there is no electrical outputs observed in the Al/Au/PPy device under compressive impact, as shown in Figure 7.17.
Figure 7.16 Current response of (a) Au/PPy/Au and (b) Al/PPy/Al devices under compressive strain. (Strain level: 10.4%; compression speed: 0.08 mm/s)

Figure 7.17 (a) Current and (b) voltage outputs of Al/Au/PPy under compressive strain. (Strain level = 10.4%; compression speed = 0.08 mm/s)

PPy is a $p$-type semiconductor with a LUMO and HOMO energy level of -2.7 and -5.6 eV, respectively. Metals Al and Au have a work function of 4.06–4.26 eV and 5.1–5.47 eV, respectively. Figure 7.13d illustrates the energy band diagram for the Al/PPy/Au device. The Al-PPy Schottky contact leads to electron flow to the metal side. The saturation current density of the Al/PPy/Au device can be estimated by equations:

$$ J = J_0 \exp \frac{eV}{kT} $$

(7-1)
Chapter 7

\[ J_0 = A^*T^2 \exp\left(-\frac{\varphi}{kT}\right) \]  

(7-2)

where \( A^* \) is the effective Richardson’s constant, \( \varphi \) is the effective barrier potential, \( T \) is the absolute temperature, \( k \) is the Boltzmann constant, and \( V \) is the applied voltage. The barrier potential under compressive strain can be thus estimated based on equation (7-1) as:

\[ \varphi_{\text{strain}} = \varphi_{\text{non-strain}} - kT \ln\left(\frac{J_{\text{strain}}}{J_{\text{non-strain}}}\right) \]  

(7-3)

Here \( J_{\text{strain}} \) and \( J_{\text{non-strain}} \) are the current density at the same voltage in the linear part of the I-V curve. Since \( J_{\text{strain}} > J_{\text{non-strain}} \), the barrier potential under strain (\( \varphi_{\text{strain}} \)) is smaller than that at nature state (\( \varphi_{\text{non-strain}} \)). Such a reduction in the barrier potential would facilitate the movement of electrons from PPy to Al \(^{64,144,252,253}\).

The physical compression also increases charge density in the PPy plate because of the decreased volume. If the metal electrodes are not deformed under such a compressive impact, the increased charge density in the PPy together with the reduced interfacial barrier potential would allow more electrons move to the Al side. As a result, the potential difference increases. The Schottky diode plays a role in directional transfer of electrons, resulting in a DC output.

We also measured the effect of compression on the through-thickness resistance of the PPy plate. The resistance was found to decrease with increasing the strain value. Once the strain was removed, the electrical resistance went back to the initial level (Figure 7.18 and 7.19). The observed resistance changes can be attributed to the reversible effect of compression on the PPy chain packing. Under compression, the PPy packing density increased with the intermolecular chain distance decreased, leading to an enhanced conductivity.
Figure 7.18 (a) Schematic of output recording; (b) electrical resistance change under a compressive impact up to 10.4% strain and (c) electrical resistance change under different maximum strains.

Figure 7.19 Al/PPy/Au device resistance change under different compression strain and the corresponding stress-strain curve.

It is known that frequent contact between two different materials could cause triboelectric charging. Energy devices based on triboelectric effect can be as high as 1163 V \(^{243}\). In our case, the compressive impact between PPy plate and metal
electrode during mechanical energy-to-electricity conversion might involve a triboelectric contribution. To examine the role of triboelectric effect, we prepared a device using two PPy plates from the same batch of PPy. By closely connecting Au and Al electrodes separately with the two PPy plates, and making the two PPy plates contact each other during compression, the triboelectric contribution can be eliminated. We noted that this Au/PPy/PPy/Al device can generate a similar voltage output but slightly reduced current output value (Figure 7.20), when compared with the device with single PPy plate (i.e. Au/PPy/Al) and PPy-Au contact/dis-contact during compression (Figure 7.21).

**Figure 7.20** (a) Schematic of output recording; Voltage and current outputs when PPy plate compressed another PPy plate at the different thickness combinations: (b) no PPy upside and 2.8 mm PPy plate downside; (c) 1.78 mm upside and 1.02 mm downside PPy plates; (d) 1.40 mm upside and 1.40 mm downside PPy plates; (e) 1.02 mm upside and 1.78 mm downside PPy plates. (Strain level = 10.4%; compression speed = 0.08 mm/s)
Figure 7.21 Voltage and (b) current outputs of the PPy plate under continuous pressing-and-release impacts (Strain level: 10.4%; compression speed: 0.08 mm/s; frequency: 0.27 Hz) for 2.5 hours.

Triboelectric contribution can be eliminated using closely packed Au/PPy/Al device structure (see the result in Figure 7.11). These results indicate that the mechanical energy-to-electricity conversion of our Au/PPy/Al is not based on triboelectric effect, though triboelectricity could contribute electrical output at certain condition.

XRD, FTIR, Raman and XPS were tested for PPy plate before and after compressive impact, as shown in Figure 7.22 and 7.23. The XRD shows a broad peak at around 26.2°, corresponding to the amorphous structure of PPy. After compression for 8 hours, almost no change is shown in the XRD curve, indicating no notable change in stolid characteristic after the compression. Peaks in FTIR and Raman spectra are assigned in the Table 7.2 below. The FTIR results showed that a broad peak appeared at 3330 cm\(^{-1}\). The Raman spectra showed new peaks appeared at 933, 978 and 1047 cm\(^{-1}\) after compression. These changes suggest that the PPy plates slightly degrade during the compression cycles.
Figure 7.22 (a) XRD patterns, (b) FTIR, (c) Raman spectra of the PPy plate before and after compressive impact. (Strain level: 10.4%; compression speed: 0.08 mm/s)
Table 7.2 Assignment of FTIR and Raman peaks

<table>
<thead>
<tr>
<th>Vibration modes</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without compression</td>
<td></td>
</tr>
<tr>
<td>N-H stretching vibration in pyrrole ring</td>
<td>255</td>
</tr>
<tr>
<td>C-H stretching</td>
<td>256</td>
</tr>
<tr>
<td>C-N stretching</td>
<td></td>
</tr>
<tr>
<td>C=C bond and/or C=N bond which represent the oxidizing state of PPy</td>
<td>257</td>
</tr>
<tr>
<td>In-plane deformation vibration of N-H \textsubscript{2} for doped PPy</td>
<td></td>
</tr>
<tr>
<td>C-C stretching</td>
<td></td>
</tr>
<tr>
<td>C-H bending</td>
<td></td>
</tr>
<tr>
<td>C-C out-of-plane deformation</td>
<td></td>
</tr>
<tr>
<td>C-H out-of-plane deformation</td>
<td></td>
</tr>
<tr>
<td>C-C out-of-plane ring deformation or C-H rocking</td>
<td></td>
</tr>
<tr>
<td>C=C backbone stretching</td>
<td></td>
</tr>
<tr>
<td>C-N stretching</td>
<td>261</td>
</tr>
<tr>
<td>Ring stretching mode</td>
<td>262</td>
</tr>
<tr>
<td>C-H in-plane bending vibration</td>
<td></td>
</tr>
<tr>
<td>Ring deformation associated with polaron</td>
<td></td>
</tr>
<tr>
<td>Ring deformation associated with bipolaron</td>
<td></td>
</tr>
</tbody>
</table>

XPS results are shown in Figure 7.23 and Table 7.3. After compression, the PPy plate shows higher content of oxidation states both in C 1s and N 1s high-resolutions. In C 1s the oxidation states increase from around 39.31% to 41.6% while they go up from 49.37% to 56.96% in N 1s high-resolution. These results
indicate that the conjugated planes were deformed after repeated compression which is matched with FTIR and Raman results.

Figure 7.23 (a) XPS survey spectrum of the PPy plate before and after compressive impact; (b) high-resolution C 1s and (c) High-resolution N 1s of the PPy plate before and after compressive impact. (Strain level: 10.4%; compression speed: 0.08 mm/s; experiment time: 8 hours)
Within the elastic region, the compression-induced change in the through-thickness resistance is reversible. However, after many cycles of compression and decompression, slight degradation in PPy chain occurred.

**Table 7.3** Assignment of XPS peaks

<table>
<thead>
<tr>
<th>XPS</th>
<th>Without compression</th>
<th>After compression</th>
<th>Assignment of peaks</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1s</td>
<td>283.9 eV</td>
<td>283.9 eV</td>
<td>(\beta)-carbon of the pyrrole rings</td>
<td></td>
</tr>
<tr>
<td></td>
<td>284.8 eV</td>
<td>284.8 eV</td>
<td>(\alpha)-carbon of the pyrrole rings</td>
<td></td>
</tr>
<tr>
<td></td>
<td>285.9 eV</td>
<td>285.9 eV</td>
<td>C=(N), C-OH and (=C-NH^+) (polaron) bonds</td>
<td>(264)</td>
</tr>
<tr>
<td></td>
<td>287.6 eV</td>
<td>287.6 eV</td>
<td>C=O and (-C=NH^+) (bipolaron) bonds</td>
<td>(266)</td>
</tr>
<tr>
<td>N1s</td>
<td>399.7 eV</td>
<td>399.7 eV</td>
<td>Neutral amine nitrogen (-NH-)</td>
<td>(267)</td>
</tr>
<tr>
<td></td>
<td>400.4 eV</td>
<td>400.4 eV</td>
<td>-NH(^+-) (polaron)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>402.5 eV</td>
<td>402.5 eV</td>
<td>=NH(^+-) (bipolaron)</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 7.24** The change of Au/PPy/Au bulk resistance after compression for different periods of time. (Strain level: 10.4%)
electrodes. After repeated compressing for half an hour, Al foil was replaced by another Au sheet and then the bulk electrical resistance was tested at the strain level of 10.4%. This loop was repeated for 7 times and all the resistance values were plotted as shown in Figure 7.24. The electrical resistance showed a linear increase over compression time.

The energy generation from our novel structure fabricated should come from a switching process, however a solid mechanism has yet been developed at this stage. It is believed that the DC nature of the electrical outputs of PPy/metal device under strain comes possibly from the following three important aspects: 1) built-in Schottky contact with the metal, 2) strain-induced decrease in barrier potential of the Schottky contact allowing extra electron transfer to the metal side, and 3) increased electron density and reduced resistance in PPy under compression.

<table>
<thead>
<tr>
<th>Device Configuration</th>
<th>Schottky Contact</th>
<th>Voltage Outputs (V)</th>
<th>Current Outputs (μA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au-press/PPy/Al</td>
<td>PPy-Al</td>
<td>0.7</td>
<td>91</td>
</tr>
<tr>
<td>Au-press/PPy/Al alloy</td>
<td>PPy-Al alloy</td>
<td>0.75</td>
<td>77</td>
</tr>
<tr>
<td>Au-press/PPy/304 stainless steel</td>
<td>PPy-304 stainless steel</td>
<td>0.30</td>
<td>20</td>
</tr>
<tr>
<td>ITO-press/PPy/Al</td>
<td>PPy-Al</td>
<td>0.64</td>
<td>45</td>
</tr>
<tr>
<td>Cu-press/PPy/Al</td>
<td>PPy-Al</td>
<td>0.61</td>
<td>34</td>
</tr>
</tbody>
</table>

*Strain level = 10.4%, compression speed = 0.08 mm/s

To verify this phenomena, we used other metals (e.g., stainless steel, Al alloy and Cu) and ITO to replace Al and Au. We found that the device was able to generate
DC output under compressive impact as long as a Schottky contact formed on one side of PPy plate, and an Ohmic contact formed on the other (see Table 7.4). In addition, a similar DC piezoelectric energy generation feature was achieved for other types of conducting polymers, including polyaniline and polythiophene (Figure 7.25 and 7.26). Therefore, the built-in Schottky barrier distinguishes our devices from the conventional piezoelectric energy harvesters, and the methodology developed in this study can be considered as a general platform technology for producing DC power from various metal/conducting polymer Schottky diodes under strain.

Figure 7.25 (a) Stress-strain curve, (b) current and (c) voltage outputs of the polyaniline plate. (Thickness: 0.53mm; strain level = 7.5%; compression speed: 0.08 mm/s)
Figure 7.26 (a) Stress-strain curve, (b) current and (c) voltage outputs of the PEDOT plate. (Thickness: 0.53mm; strain level = 10.4%; compression speed: 0.08 mm/s)

7.2.4 Applications

To demonstrate the potential applications for the energy generated from the Al/PPy/Au device, we used a capacitor to directly collect the electrical output without using external rectifier. Figure 7.27 shows the voltage change of the capacitor charged by the working device. It took less than 20 seconds to charge a 220 μF capacitor to 0.7 V, while charging 1.0 mF and 2.2 mF capacitors to the same voltage took 2.5 minutes and 7 minutes, respectively.
Figure 7.27 (a) Voltage ~ time during charging of capacitors with an Au/PPy/Al device; Insert: the charge circuit.

By connecting 10 charged 2.2 mF capacitors in parallel, the stored electric energy was able to drive miniature electric motor and power commercial LED (Figure 7.28 and 7.29).

Figure 7.28 Electric circuit for storing the electricity in capacitors that used for driving (a) miniature electric motor and (b) commercial LED device.
Figure 7.29 Pictures taken from video to show the rotation of a motor powered by a PPy plate and lighting of a commercial LED.

To further facilitate the practical use, we also prepared a coin-type mechanical energy-electricity conversion device based on the Al/PPy/Au plate by using the accessories for making coin batteries. Figure 7.30 shows a photo of the coin energy generator, along with the device structure. By finger taping the device, electric signals generated.

Figure 7.30 A photo of coin generator and corresponding device structure.
7.3 Conclusion

In this chapter, we have developed a novel concept of using single Schottky contact between a conducting polymer plate and a metal electrode to directly convert mechanical energy into DC electricity. The built-in Schottky barrier plays a key role in the self-rectification. The generated peak current reaches up to 290 μA (current density 218.6 μA/cm²) at a peak voltage of 0.7 V. The electrical energy thus generated is sufficient to drive commercial electronic devices, as exemplified by commercial motor and LED diode. This novel DC electricity may open up new avenues for further fundamental research and experimental development of DC energy harvesting systems of practical significance.
Chapter 8 Conclusions and Future work

8.1 Main conclusions of the thesis

This PhD research has focused on obtaining fundamental knowledge of how to prepare high performance mechanical energy harvester from electrospun nanofibres and conducting polymers. Several key results are summarised below:

(1) The effect of applied voltage, spinning distance, PVDF concentration and fibre mat thickness on PVDF $\beta$ crystal phase content in the electrospun nanofibres and mechanical-to-electrical energy conversion of randomly-orientated PVDF nanofibre mats were examined systematically.

When the PVDF concentration was below 20%, beaded PVDF fibres were prepared. With increasing the PVDF concentration from 20% to 26%, the average fibre diameter went up from 284 nm to 810 nm. XRD and FTIR results show that the fibre obtained from 20% PVDF solution had the highest $\beta$ crystal phase content of 85.9%. At the same time, it exhibited the best mechanical-to-electrical energy conversion property. Under a compressive impact of 25000 Pa stress at 1Hz, it could generate 2.2 V output voltage and 2.3 $\mu$A output current.

Uniform nanofibres without beads were prepared when the applied voltage was set in the range of 9 kV ~ 21 kV. With increasing applied voltage from 9 kV to 15 kV, the fibre diameter decreased and reached the finest. Further increasing the applied voltage to 21 kV led to increasing the diameter. The fibre mat obtained from 15 kV applied voltage showed the highest $\beta$ crystal phase content and highest electrical outputs. These results suggest that uniform PVDF nanofibres with higher $\beta$ phase content have higher mechanical-to-electrical conversion ability.
The spinning distance in the range of 9 ~ 21 cm with constant applied voltage (15 kV) and constant electrical field intensity (1 kV/cm) was studied, respectively. The fibre mat obtained from 15 kV and 15 cm were finest and had the highest $\beta$ crystal phase content and the best mechanical-to-electrical energy conversion property. Mat thickness also influences the electrical outputs. When the mat was thinner than 20 $\mu$m, a short circuit occurred occasionally during the compressing process. With increasing the mat thickness from 20 $\mu$m to 70 $\mu$m, both voltage and current outputs increased significantly to reach 2.2 V and 2.3 $\mu$A, respectively. However, with further increasing the mat thickness, electrical outputs decreased.

(2) The effect of short-distance electrospinning on fibre mat mechanical-to-electrical property was examined. Electrospinning at a spinning distance in the range of 1~8 cm still results in a fibrous structure except that fibres are highly interconnected.

When 20% PVDF solution was electrospun at different applied voltages and spinning distances, the resulting PVDF showed five different morphologies: particles, mixture of particles and interconnected fibres, interconnected fibres, mixture of interconnected fibre and separated fibres, and separated fibres. The interconnected PVDF fibres can be prepared by electrospinning a PVDF solution at a distance of 2 cm under applied voltage in the range of 5-11 kV. In addition, maintaining the applied voltage at 7 kV but changing the spinning distance from 1 cm to 8 cm could lead to the formation of five different morphologies.

By increasing the applied voltage from 5 kV to 7 kV, the $\beta$ crystal phase content of interconnected fibres went up from 76.9% to 83.9%. The $\beta$ crystal phase content
gradually decreased to 59.9% when the applied voltage was further increased to 11 kV.

The interconnected PVDF fibre mat obtained at 2 cm spinning distance and 7 kV applied voltage had the highest voltage and current outputs about 2.2 V and 2.3 μA under a 25000 Pa impact stress at 5 Hz. At the equivalent areal density, the interconnected fibre mat produced much higher voltage and current outputs than the conventionally electrospun PVDF nanofibre mat.

In addition, the interconnected fibre mat showed much better mechanical property than the separated fibre mat. Not only the tensile strength was much larger, but also the interconnected fibre mat also showed much higher delamination resistance.

(3) The doping effect of PVDF nanofibre mats on the fibre morphology and mechanical-to-electrical energy conversion property was examined. The fibre mats with TTA doping range of 0~10% or Butyl-PBD doping range of 0~10% showed no obvious change either on fibre surface morphology or fibre diameter.

It has been shown that the fibre mat doped with 0.5% TTA had the highest β crystal phase content among all the TTA concentrations, as well as the mat doped with 1% Butyl-PBD among all the Butyl-PBD concentrations. These two doping concentrations also led to the best mechanical-to-electrical energy conversion property. The sample with 0.5% TTA doping had the voltage and current outputs around 2.55 V and 2.65 μA, respectively. The voltage and current values were 1.70 times and 1.71 times higher than these of un-doped PVDF fibre mat. For the 1% Butyl-PBD doped sample, it generated voltage and current signals of 2.65 V and 2.7 μA, which were 1.77 times and 1.74 times current higher than these of un-doped PVDF fibre mat.
PVDF electron-hole transfer double layer fibre mats were prepared using TTA doped and Butyl-PBD doped solutions through two-step electrospinning. It has been observed that no matter how the thickness ratio was, the electrical outputs were enhanced to around 3.2 V and 3.4 μA.

(4) We have, for the first time, proven that a freestanding conducting polymer plate with one side to form a Schottky contact and the other side an Ohmic contact with two different metal electrodes can generate DC voltage with a large output current density upon mechanical deformation. The single built-in Schottky barrier plays a key role in the self-rectification effect. The barrier potential under strain is much smaller than that at nature state. Such a reduction in the barrier potential would facilitate the movement of electrons. In addition, the PPy packing density increased with the intermolecular chain distance decreased, leading to an enhanced conductivity. Increased electron density and reduced resistance in PPy under compression contribute to the large DC output current density.

The device voltage and current showed a synchronous response to the compression strain. Both voltage and current outputs increased with the increasing strain level. When the strain was kept for a period of time, the voltage and current decayed slowly. Once the strain was removed, the outputs dropped to zero spontaneously.

Under a compression strain of 10.4%, PPy plate can generate a DC power with a current density as high as 62.4 μA/cm² and voltage of 0.7 V. The electrical energy can be stored into a capacitor directly without using a rectifier and used for powering the electronic devices.

The mechanical-to-electrical conversion response of devices with two Schottky contacts or two Ohmic contacts was also studied. It is interesting to find that no
electrical generation is observed on the device with two Ohmic contacts under the same compression conditions, but uneven positive and negative outputs with weak voltage output were generated on the two Schottky contact device.

8.2 Future work

To continue the study in this thesis, the following directions are suggested to be followed:

1) To find out the appropriate doping agent combination that can achieve the self-rectification in the PVDF nanofibre mats. As we know, the matching of energy band is very important to electron-hole transport for forming DC electricity. Thus, it is very worthwhile to explore.

2) PPy particles will be incorporated onto or inside of electrospun PVDF nanofibres to prepared fibrous DC power generator. The mechanical-to-electrical property study of one-dimensional composite materials should be significantly important and could help to understand more fundamentals of DC electricity generation.

3) Similar to Schottky contact that plays a critical role in Al/PPy/Au device for DC electrical energy harvesting, $p$-$n$ junction can be designed into the generator devices to replace the Schottky contact, for instance, Al/SnO$_2$/PPy/Au device, Al/ZnO/PPy/Au device, Al/Al$_2$O$_3$/PPy/Au device etc (Figure A.4~A.6). The development in this direction will enrich the research of mechanical energy conversion and provide invaluable opportunities in fabricating novel structured harvester devices.
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Appendix: PPy Coating on Electrospun PVDF Nanofibres and P-N Junction Based DC Power Generator

**Figure A. 1** The digital photo of PVDF samples coated with PPy particles by immersing in FeCl$_3$·6H$_2$O ethanol solutions with different molar concentrations.................................................................181

**Figure A. 2** SEM images of PPy coated PVDF mats with different FeCl$_3$·6H$_2$O/ethanol molar concentrations. ..........................................................182

**Figure A. 3** Voltage and current outputs of PPy coated PVDF nanofibre mats with different FeCl$_3$·6H$_2$O/ethanol molar concentrations. .........................183

**Figure A. 4** (a), (c) Open-circuit voltage and (b), (d) short-circuit current outputs of Au/PPy/SnO$_2$/Al device under continuous pressing-releasing impacts (PPy thickness: 1.064 mm; SnO$_2$ thickness: 0.932 mm; Strain level: 3.8%; Compression speed: 0.02 mm/s). ....................................................183

**Figure A. 5** (a) Voltage and (b) current outputs of the Au/PPy/Al$_2$O$_3$/Al device (PPy plate thickness: 1.064 mm; Al$_2$O$_3$ plate thickness: 0.936 mm; Strain level: 3.8%; Compression speed: 0.02 mm/s). ........................................184

**Figure A. 6** (a) Voltage and (b) current outputs of the Au/PPy/ZnO/Al device (PPy plate thickness: 1.064 mm; ZnO plate thickness: 0.938 mm; Strain level: 3.8%; Compression speed: 0.02 mm/s). ..............................................184
**Experimental**: Pure PVDF nanofibre mats were firstly produced by conventional needle electrospinning from a 20% PVDF concentration, at 15 kV applied voltage and 15 cm spinning distance. PVDF mats were immersed into FeCl₃·6H₂O/ethanol solutions with different molar concentrations (0.05, 0.1, 0.25, 0.5, 0.75, 1, 1.5 and 5 mol/L) for about 12 hours, respectively. Then the mats were taken out of the solution and placed in an oven at 60 °C for about 4 minutes. Subsequently, the FeCl₃ coated mats were transferred into a small chamber filled with pyrrole vapour to carry out the polymerization reaction at the room temperature for about 24 hours. The PPy coated PVDF mats were dipped into distilled water and HCl solution for 24 hours each to remove the unreacted pyrrole monomers and Fe ions. Finally, the mats were rinsed by the distilled water for several times and dry in oven at 60 °C.

*Figure A. 1* The digital photo of PVDF samples coated with PPy particles by immersing in FeCl₃·6H₂O ethanol solutions with different molar concentrations.
Figure A. 2 SEM images of PPy coated PVDF mats with different FeCl₃·6H₂O/ethanol molar concentrations.
Figure A. 3 Voltage and current outputs of PPy coated PVDF nanofibre mats with different FeCl₃·6H₂O/ethanol molar concentrations.

Figure A. 4 (a), (c) Open-circuit voltage and (b), (d) short-circuit current outputs of Au/PPy/SnO₂/Al device under continuous pressing-releasing impacts (PPy thickness: 1.064 mm; SnO₂ thickness: 0.932 mm; Strain level: 3.8%; Compression speed: 0.02 mm/s).
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