Electrospun nanostructures for solar energy harvesting and motion sensing

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**NANYANG
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UNIVERSITY**

SINGAPORE

**ELECTROSPUN NANOSTRUCTURES
FOR SOLAR ENERGY HARVESTING
AND MOTION SENSING**

MA SHAOYANG

SCHOOL OF ELECTRICAL & ELECTRONIC ENGINEERING

2019

**Electrospun Nanostructures
for Solar Energy Harvesting
and Motion Sensing**

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School of Electrical & Electronic Engineering

A thesis submitted to the Nanyang Technological University
in partial fulfillment of the requirement for the degree of
Doctor of Philosophy

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

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..10 Jan 2019

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Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

10 Jan 2019

Wei Lei

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Date

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Authorship Attribution Statement

This thesis contains material from 3 papers published in the following peer-reviewed journals where I was the first and/or corresponding author.

Chapter 3 is published as T. Ye, S. Ma (equal contributor), X. Jiang, M. Petrovic, V. Chellappan, S. Ramakrishna, and L. Wei, Electrospayed TiO₂ nanoporous hemispheres for enhanced electron transport and device performance of formamidinium based perovskite solar cell, *Nanoscale* 9, 412-420 (2017). DOI: 10.1039/c6nr07369g

The contributions of the co-authors are as follows:

- The initial project direction was raised by A/Prof. L. Wei, Dr. V. Chellappan and Prof. S. Ramakrishna.
- I prepared the manuscript drafts. The manuscript was revised by Dr. T. Ye, Dr. V. Chellappan, Prof. S. Ramakrishna and A/Prof. L. Wei.
- I co-designed the study with Dr. T. Ye and A/Prof. L. Wei
- I performed part of the laboratory work at the School of Electrical & Electronic Engineering of NTU, School of Materials Science and Engineering of NTU, Department of Chemical and Biomolecular Engineering of NUS and Dr. T. Ye performed other laboratory work at Institute of Materials Research and Engineering(IMRE) of A*STAR.
- I prepared the TiO₂ nanoporous hemispherical structures, did the FDTD simulations, conducted the characterization of SEM and XRD, and conducted data evaluation.
- Dr. T. Ye synthesized the perovskite material, fabricated the PSC devices, and measured the photovoltaic parameters, and helped in the data analysis.
- Dr. X. Jiang assisted in the characterization of TEM.
- Dr. M. Petrovic helped in the TPV data evaluation.

Chapter 4 is published as S. Ma, T. Ye, T. Wu, Z. Wang, Z. Wang, S. Ramakrishna, V. Chellappan, and L. Wei, Hollow rice grain-shaped TiO₂ nanostructures for high-

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- I co-designed the study with Dr. T. Ye and A/Prof. L. Wei
- I performed part of the laboratory work at the School of Electrical & Electronic Engineering of NTU, School of Materials Science and Engineering of NTU, and Dr. T. Ye performed other laboratory work at Institute of Materials Research and Engineering(IMRE) of A*STAR.
- I prepared the hollow rice grain-shaped TiO₂ nanostructures structures, did the FDTD simulations, conducted the characterization of SEM, TEM, XRD and analyzed the results.
- Dr. T. Ye fabricated the PSC devices and measured the photovoltaic parameters.
- Ms. T. Wu assisted in FDTD model building.
- Mr. Zhe Wang and Mr. Zhixun Wang participated in the modification of TiO₂ nanostructures.

Chapter 5 is published as S. Ma, T. Ye, T. Zhang, Z. Wang, K. Li, M. Chen, J. Zhang, Z. Wang, S. Ramakrishna, and L. Wei, Highly oriented electrospun P(VDF-TrFE) fibers via mechanical stretching for wearable motion sensing, *Advanced Materials Technologies* 3, 1800033 (2018). DOI: 10.1002/admt.201800033

The contributions of the co-authors are as follows:

- The initial project direction was raised by A/Prof. L. Wei.
- I prepared the manuscript drafts. The manuscript was revised by Prof. S. Ramakrishna and A/Prof. L. Wei.
- I co-designed the study with and A/Prof. L. Wei and performed all the laboratory work at the School of Electrical & Electronic Engineering of NTU and School of Materials Science and Engineering of NTU.

- I prepared the P(VDF-TrFE) nanofiber, did the COMSOL simulations, conducted the characterization of SEM and XRD, measured the mechanical and electrical properties and analyzed the results.
- Dr. T. Ye participated in the discussion on electrospinning parameters setting.
- Dr. T. Zhang, Dr. K. Li, and Mr. Zhe Wang assisted in the building of the testing platform.
- Dr. M. Chen helped in optical observation using fluorescence.
- Mrs. J. Zhang and Mr. Zhixun Wang assisted in the test of fiber bundle integrated into cloth.

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The moment I am writing these words is the New Year's Eve of 2019. A few hours later, we will greet a brand new year with great enthusiasm and hope. Four years ago, when I landed at Singapore on Christmas Eve of 2014, I can hardly imagine that one day I will reach so far on the road of pursuing a Ph.D. degree. I am so grateful that I have this precious chance to gain more experience, to see the wider world, to meet more

people and to know more beautiful things. During these four years, so many things happened around the world, and so many lives faded away. I was so touched and so taught that the world is too vast and life is too fleeting, and we shall cherish each coming day as a gift, spend it with the greatest respect, live the life and do something meaningful.

一千四百八十日，不过人生二十分。

终年长夏无寒暑，四季遥看羨秋春。

友朋殷殷常相携，师长谆谆尽苦心。

回首再忆南洋时，繁花似锦木森森。

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Abstract

With the rapid development of human technology, we are continuously facing new problems and challenges. On one hand is the limited natural resources, and on the other hand is the increasing demands for convenient lifestyle. It is not a good idea to sacrifice one aspect to satisfy the other, but we should seek a balance between sustainable development and the comfortable living concept. Thus it becomes a very crucial task to explore the low cost, large scale and environmental friendly fabrication methods for wide applications.

Electrospinning is a top-down method in which polymeric or melt components are drawn out from a solution system onto a collector by electrostatic force. In comparison with other methods, including drawing, template synthesis, chemical vapor deposition and so on, electrospinning offers some attractive features. One of the most important advantages is its industrial scalability, which makes it possible to directly transfer the results from lab research to the industry. In general, the unique advantages of electrospun nanostructures including high spatial interconnectivity, high porosity, and large surface-to-volume ratio, make it a promising fabrication method in energy harvesting applications. The objective of this work is to develop nanostructures used for solar energy harvesting and motion sensing through electrospinning techniques.

First, titanium dioxide (TiO_2) nanoporous hemispheres (NHSs) with a radius of ~ 200 nm are fabricated for the construction of mesoporous TiO_2 layer of perovskite solar cells (PSCs) by electrospraying. The resulting TiO_2 NHSs are highly porous, which are beneficial to the infiltration of perovskites and provide a larger contact area, as building blocks for PSCs. By varying the TiO_2 NHSs collecting period (15 s, 30 s, 60 s and 90 s) during the electrospraying process, the performance of PSCs changes with different TiO_2 NHSs distribution densities. The optimized PSC employing TiO_2 NHSs (60 s) exhibits a PCE as high as 19.3% with a short circuit current density (J_{SC}) of 23.8 mA cm^{-2} , an open circuit voltage (V_{OC}) of 1.14 V and a fill factor (FF) of 0.71. Furthermore, the PSC possesses a reproducible PCE value with little hysteresis in its current density-voltage (J - V) curves.

Second, hollow rice grain-shaped TiO_2 nanostructures (NSs) with the radius of 200-300 nm are fabricated by electrospinning titanium isopropoxide solution and further

calcination. The resulting hollow rice grain-shaped TiO_2 NSs are applied as the building blocks to construct the mesoporous TiO_2 layer for the large-area PSCs. By varying the spin coating speed (2000 rpm, 4000 rpm, and 8000 rpm, respectively), the performance of PSCs changes with different TiO_2 NSs distribution densities. The optimized PSC employing the 4000 rpm spin coating speed exhibits a PCE of 14.2% with the J_{SC} of 21.6 mA cm^{-2} , V_{OC} of 1.07 V and fill FF of 0.61, which is superior to both the plain structure based control group with the PCE of 9.6% and conventional meso- TiO_2 based group with the PCE of 12.1%. Furthermore, the PSC possesses a reproducible PCE value with weak hysteresis in its J - V curves. Moreover, photoluminescence (PL) measurements and finite-difference time-domain (FDTD) optical simulations reveal the enhanced fast charge carrier extraction/transport and light absorption in the proposed system, which makes electrospun hollow rice grain-shaped TiO_2 NSs a promising electron transportation material for high-efficiency and large-area photovoltaic devices.

Last, electrospinning is a widely applied technique to produce an extended length of fiber-shaped piezoelectric devices. A stretching-induced alignment method is demonstrated to achieve highly oriented electrospun poly[(vinylidene fluoride-co-trifluoroethylene) P(VDF-TrFE) fibers on a large scale. These globally aligned electrospun P(VDF-TrFE) fibers exhibit an enhanced piezoelectric property and high mechanical endurance. Using this simple stretching method, a high average output voltage of 80% aligned electrospun P(VDF-TrFE) fibers is 84.96 mV, about 266% of their original randomly distributed counterpart. Furthermore, when woven into an outfit, the aligned electrospun P(VDF-TrFE) fiber bundle can work both individually and combined to monitor body gestures including angles of elbow bending and directions of a swinging arm, which may lead to the further development of motion-tracking technology in wearable smart devices.

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List of Abbreviations

AM	air mass
CB	conduction band
CNF	carbon nanofiber
CNT	carbon nanotube
C-TiO ₂	Compact-TiO ₂
DI water	deionized water
DMAC	N,N-dimethyl acetamide
DMSO	dimethyl sulfoxide
DSSC	dye-sensitized solar cell
ETL	electron transport layer
FA	NH=CHNH ₃ ⁺ , formamidine cation
FDTD	Finite-difference time-domain
<i>FF</i>	fill factor
FTO	fluorine-doped tin oxide
HTL	hole transport layer
HTM	hole transport material
IPCE	incident photon-to-electron conversion efficiency
<i>I-V</i>	current-voltage
<i>J_{sc}</i>	short circuit current density
<i>J-V</i>	current density-voltage
MA	CH ₃ NH ₃ ⁺ , methylammonium cation
meso-TiO ₂	mesoporous TiO ₂
NF	nanofiber
NHS	nanoporous hemisphere
NP	nanoparticle
NS	nanostructure
P(VDF-TrFE)	poly[(vinylidene fluoride-co trifluoroethylene)]
PCE	power conversion efficiency
PET	polyethylene terephthalate
PL	photoluminescence
PSC	perovskite solar cell

PVAc	polyvinyl acetate
PVDF	Polyvinylidene difluoride
PVP	polyvinylpyrrolidone
SAED	selected area electron diffraction
SEM	scanning electron microscopy
SP	spherical structure
Spiro-OMeTAD	2,2',7,7'-tetrakis(N,N-dip-methoxyphenylamine)-9,9'- spirobifluorene
TEM	transmission electron microscope
TPV	transient photovoltage
TTIP	titanium isopropoxide
UV-vis	UV-visible Spectroscopy
V_{oc}	open circuit voltage
XRD	X-ray diffraction

Chapter 1: Introduction

1.1 Background

With the rapid development of human technology, we are continuously facing new problems and challenges. On one hand is the limited natural resources, and on the other hand is the increasing demands for convenient lifestyle. It is not a good idea to sacrifice one aspect to satisfy the other, but we should seek a balance between sustainable development and the comfortable living concept. Thus it becomes a very crucial task to explore the low cost, large scale and environmental friendly fabrication methods for wide applications. In the following sections, we will detailedly introduce the severe background of the challenges we are facing.

For the past of decays, the unprecedented high-speed development of human society has consumed tremendous energy resources and the demanding for energy will surely keep growing extremely fast. In 1990, the total energy production all over the planet was calculated as 1.02×10^5 TW, but this number has increased by around 50% over the next twenty years, reaching 1.49×10^5 TW in 2010. And this figure is expected to exceed 2.11×10^5 TW in 2030 and 2.25×10^5 TW in 2035, much faster than linearly growth¹. And this kind of increase is not affordable for conventional fossil energy resources like fuel, natural gas, and coal, because the formation of such resources is on the geologic scale, much slower than the consumption speed. With the depleting of conventional energy resources, along with the pollution and greenhouse gas problems brought by the consumption of traditional energy, it becomes an enormous challenge to explore and develop new sustainable energy resources as replacement of conventional fossil energy. the great nature can provide human a wide choice of renewable energy sources, including solar energy (both thermal and photovoltaics), ocean energy, wind, geo- and solar thermal electricity etc. as Figure 1.1 shows. The solar energy shows great potential for addressing this problem. The solar energy power arriving at earth surface

per day is even more than the global power consumption of a whole year^{1,2}. But the key to the matter is how to harvest and utilize the power efficiently.

Figure 1.1 Energy resources of the world².

Solar cells are devices that can convert solar energy into electricity. With the efforts devoted to the efficient conversion from solar energy into electricity, solar cells are developed into three generations so far. The first generation which is also the most commonly used solar panels nowadays are silicon based solar cells, but the problem of silicon solar cells is the high cost because high quality crystalline silicon material is necessary whose production process is very costly at present. So the second generation of solar cells emerged as thin film solar cells. This type of solar cells reduces the cost by utilizing common materials such as copper indium gallium selenide (CIGS)/copper zinc tin sulfide (CZTS), and low cost fabrication process. After that, the third-generation solar cell of mesoscopic solar cells was raised and widely explored for the past thirty years. The first efficient mesoscopic solar cells were dye-sensitized solar cells (DSSCs) fabricated in 1991³.

In a typical mesoscopic solar cell, there is a mesoscopic layer consists of metal oxide (TiO_2 , SnO_2 and so on) nanostructures. When the dye molecules absorb the incident light and generate free carriers, the photogenerated free carriers will be injected and transport through the nanostructures in the mesoscopic layer before reach the electrodes. In a conventional solar cell, the photogenerated free carriers need to transport through the whole bulk semiconducting layer which will cause a large number of annihilation and recombination^{3,4}. But in a mesoscopic solar cell, the photogenerated

free carriers only need to transport a short path before they inject the mesoscopic layer, and this will bring less annihilation and recombination, thus benefit the energy conversion efficiency of the device. Later, with the exploration and adoption of perovskite materials into mesoscopic solar cells, the crucial problem of limited power conversion efficiency has been improved greatly.

Figure 1.2 (a) Crystal structure of the ABX₃ perovskite. (b) The atomic structure of the three A site cations explored, and (c) corresponding UV-Vis spectra for the APbI₃ perovskites formed⁵.

The term perovskite usually refers to a group of materials sharing the same crystal structure of calcium titanium oxide mineral species (CaTiO₃). The general formula of perovskite family can be expressed as ABX₃ as Figure 1.2 a shows, and for perovskite materials which are commonly used for solar cells, A refers to Cs⁺ (cesium), MA (CH₃NH₃⁺, methylammonium cation), or FA (NH=CHNH₃⁺, formamidinium cation) as Figure 1.2 b shows; B refers to Sn²⁺ or Pb²⁺, and X refers to Cl⁻, Br⁻ or I⁻. Since 2009,

the organic-inorganic lead halide perovskites have become an emerging light absorbing materials for various photovoltaic applications due to their unique optoelectronic properties, including tunable bandgap as Figure 1.2 c shows, high absorption coefficients, and micrometer-scale carrier diffusion length⁵⁻⁸. And up to nowadays, the highest certificated power conversion efficiency (PCE) of organic-inorganic metal halide perovskite based solar cell has reached 23.7%⁹. One main challenge of photovoltaic devices is how to reduce the manufacturing cost for large-scale fabrication while maintaining the perfect performance.

Another continuously increasing demand for human is the pursuit of high quality lifestyle, which makes people put lots of effort to stay in health. Thus a new class of devices become essential, which is wearable smart electronics with various functions, including sensing, displaying and the ability of self-powering and capable of working under different conditions as Figure 1.3 shows. These wearable smart devices have been emerging to serve as perfect platforms for health management due to its advantages of flexibility, portability, light in weight and low energy consumption.

Figure 1.3 illustration of wearable smart devices with health monitoring system¹⁰.

A wearable smart device must possess multiple functions simultaneously, and to monitor a person's health status, various of parameters should be collected including but not limited to blood pressure, blood oxygen saturation, respiratory rate, heart rate, and muscle activities. These parameters can reflect the person's health status and help to diagnose in emergency cases. Only a few years ago, most of these parameters can only be available in hospital and clinics, measured by professional apparatus, which means the timeliness and monitoring frequency is very poor. So the wearable smart

devices that can monitor these parameters continuously and in real time are of tremendous significance. And with the rapid development in wearable technology, it becomes possible to realize this kind of accurate, real-time, continuous measurements.

One essential requirement of wearable smart devices is flexibility, that can be worn directly on the human body and keep fit in movement. To address this issue, fiber and textile based flexible wearable electronic systems hold great potentials. Fiber and textile based clothing system have been developed for thousands of years due to the excellent properties like breathability, softness, deformability, ductility, and reusability. And with the fast development of nanotechnologies, the miniaturization of electronics has been accelerated, which makes it possible to integrate large-scale circuit and multiple functions within a single wearable device.

Recently, fibers and textiles with multi-materials add-on or built-in multi-functional units have become a hot research area for researchers. Fiber and textile based flexible electronics have shown great possibilities in numerous applications including flexible circuits^{11–13}, skin-like pressure sensors¹⁴, transistors^{15–17}, memory devices^{18,19} as well as displays^{20–22}. Similar like solar cells, wearable smart devices also face the same problem which is how to guarantee low-cost and production scale simultaneously.

Electrospinning is an excellent solution to address these problems. Compared to other material processing methods, electrospinning is more suitable for large-scale commercial applications to produce long-lasting continuous polymer micro- and nanofibers²³, due to all the merits including easy accessibility, simple synthesis, well-controlled parameters, and low cost.

First raised in early 20th century²⁴, electrospinning has been utilized to process materials for over a hundred years, but not until recent decades, has it been widely applied to various researching fields. With the well-developed techniques and versatile functionalities, electrospinning method is widely adopted in various applications, including energy conversion and storage, wearable smart devices, environment-related applications as well as biomedical applications.

1.2 Objectives

In this thesis, we aim to apply the electrospinning technique, the low-cost large-scale material processing method, into the fields of solar energy harvesting and motion sensing of wearable smart devices fabrication. The main objectives of our works are:

1. To establish a fabrication method which yields TiO_2 nanoporous hemispheres (NHSs) by electrospraying hydrothermal synthesized TiO_2 nanoparticles (NPs) suspension solution in a controllable and scalable manner. The resulting TiO_2 NHSs are used as the mesoscopic layer of perovskite solar cells (PSCs). The numerous pores can help to improve the infiltration of the perovskite, and the large surface area increases the contact area between perovskite and TiO_2 NHSs, leading to efficient electron injection. All these properties are expected to enhance the photovoltaic properties of PSCs.
2. To develop hollow rice grain-shaped TiO_2 nanostructures (NSs) with large surface area and abundant nanopores by simple and versatile electrospinning followed with calcination. The synthesized TiO_2 NSs are then applied to construct the meso- TiO_2 layer of large area PSCs. The optimized distribution condition of rice grain-shaped TiO_2 NSs is explored and analyzed by various methods including absorption and photoluminescence (PL). Finite-difference time-domain (FDTD) optical simulations are to be carried out to study the optical power distribution and transmittance in different TiO_2 /perovskite models.
3. To demonstrate a simple dynamical mechanical stretching process that enables the formation of large-scale highly oriented electrospun P(VDF-TrFE) fibers obtained under low rotation speed of drum collector. And these globally parallel fibers which exhibit enhanced mechanical and piezoelectric properties are further twisted into fiber bundles and woven into a daily outfit for body motion sensing. The performance of these functional fibers bundles is recorded and analyzed.

1.3 Major Contributions

The novelty of the studies and my contributions to this thesis include:

1. Develop TiO_2 NHSs for electron transport layer of PSCs by versatile electrospray technique. In this study, TiO_2 NHSs are fabricated by electrospray method and act as the electron transporting media in PSCs. The electrsprayed TiO_2 NHSs are highly porous with ultra large surface area which benefits the photovoltaic properties of the $\text{FA}_{0.81}\text{MA}_{0.15}\text{Pb}(\text{I}_{0.836}\text{Br}_{0.15})_3$ based PSC with a high photovoltaic conversion efficiency of 19.3%. By analyzing the photovoltaic properties in details, the distribution density effect of TiO_2 NHSs is discussed and the optimized distribution density is investigated. And longer free carrier lifetime is found within TiO_2 NHSs based PSC than that in TiO_2 NPs based PSC by utilizing small perturbation transient photovoltage (TPV) method.
2. Demonstrate hollow rice grain-shaped highly-porous TiO_2 NSs for large area PSCs fabricated by electrospinning method followed by calcination. In this study, uniformly-sized and highly-porous hollow rice grain-shaped TiO_2 NSs are produced by a simple and versatile electrospinning technique and further applied to large-area PSCs (the active area is 1 cm^2) as the mesoporous layer. The photovoltaic properties of the TiO_2 NSs based PSC are significantly enhanced with a PCE of 14.2%, increased by about 47.9% compared to its plain counterpart. The distribution density effect of TiO_2 NSs on the photovoltaic performance of PSCs are also explored by discussing the enhancement of carrier injection/transportation from the perovskite layer to the carrier transporting layer. FDTD simulation is also adopted to study the local optical field enhancement on meso- TiO_2 /perovskite interface.
3. Develop a simple and versatile fabrication method to achieve highly oriented ultra-long P(VDF-TrFE) fibers on a large scale. In this study, highly oriented ultra-long P(VDF-TrFE) fibers are obtained on a large scale by mechanical stretching. The resulted aligned fiber proportion of $\sim 91.4\%$ is achieved globally, while the originally aligned fiber proportion is only $\sim 10.3\%$. The highly oriented P(VDF-TrFE) fibers possess better

piezoelectric properties and mechanical endurance. The output voltage of 80% aligned P(VDF-TrFE) fibers is about 266% of their original randomly distributed counterpart. The resulting highly oriented electrospun P(VDF-TrFE) fibers are further twisted into fiber bundles and then woven into a daily outfit. The functional fiber bundles can be used both individually and combinedly to monitor body gestures including angles of elbow bending and directions of the swing arm.

1.4 Organization of Thesis

This thesis consists of 6 chapters:

Chapter 1 gives a brief introduction on the general background of the energy resources environment and demands of wearable smart devices, and the challenges we are facing, as well as emphasizes on the objectives and scope of the research study. The motivation and organization are illustrated in this section.

Chapter 2 explains the basic mechanisms of electrospinning technology, working principles of solar cells and the fundamentals of piezoelectric polymers. And it also reviews the development and applications of electrospinning technique, mesoscopic solar cells and piezoelectric polymers in recent years.

Chapter 3 demonstrates the fabrication of TiO₂ NHSs by versatile electrospray technique which is applied to act as the electron transport layer of PSCs. The photovoltaic properties are analyzed and discussed in details and the distribution density effect are investigated.

Chapter 4 describes the synthesis of uniformly-sized and highly-porous hollow rice grain-shaped highly-porous TiO₂ NSs fabricated by electrospinning method followed by calcination and further used for large area PSCs as the mesoporous layer. The photovoltaic properties and distribution density effect are also investigated and analyzed. Furthermore, FDTD simulation is adopted to study the local optical field enhancement on meso-TiO₂/perovskite interface.

Chapter 5 introduced the mechanical stretching induced highly oriented ultra-long P(VDF-TrFE) fibers. Both the mechanical properties and electrical properties are

carefully investigated. The resulting highly oriented electrospun P(VDF-TrFE) fibers are further twisted into fiber bundles and used both individually and combinedly to monitor body gestures including angles of elbow bending and directions of the swing arm.

Chapter 6 draws the conclusions and puts forward future research plans.

Chapter 2: Literature Review

In this chapter, a comprehensive literature review in terms of the mechanism, development and various applications of electrospinning/electrospray techniques, mesoscopic solar cells as well as piezoelectric polymers are presented.

More precisely, Section 2.1 will introduce electrospinning/electrospray techniques and applications; Section 2.2 will present the fundamental information and development history of mesoscopic solar cells and the electrospun nanostructures in mesoscopic solar cells. Section 2.3 will introduce the basic information and working principles of piezoelectric polymers and the applications of electrospun piezoelectric polymer.

2.1 Electrospinning/Electrospray Techniques and Applications

Ultrathin one-dimension structures like micro- and nanofibers, compare to three-dimension bulk and two-dimension film structures, possess numerous advantages, such as large surface area-to-volume ratio, tensile strength, good flexibility, etc. And these amazing characteristics make fibers a competitive candidate for large quantity of applications, including energy harvesting, multifunctional sensing, bio-tissue growing, and many other fields.

There are many ways to fabricate one-dimension structures, including fiber drawing^{25,26}, template growing^{27,28}, vapor growing^{29,30}, self-assembly^{31,32} as well as electrospinning. Compared to other synthesis methods, electrospinning is more suitable for large-scale commercial applications to produce long-lasting continuous polymer micro- and nanofibers²³, due to all the merits including easy accessibility, simple synthesis, well-controlled parameters, and low cost.

2.1.1 Electrospinning Method and Apparatus

2.1.1.1 The development history of electrospinning

The concept of electrospinning could retrospect to very early of the last century²⁴ and was developing slowly during the following decades³³. It was not until the mid-1990s,

that electrospinning started to regain the attention of an increasing number of researchers as a promising method to fabricate continuous micro- and nanofibers³⁴, and developed rapidly since the entry of this century as shown by Figure 2.1.

Figure 2.1 Annually number of publications related to electrospinning and the location distribution²³.

For the past two decades, this versatile synthesis technique has been applied to a wide range of researching fields, including energy conversion and storage, environment-related applications, biomedical application etc. and we will discuss the applications in detail later in Section 2.1.3.

2.1.1.2 Mechanism and parameters

Electrospinning is a process in which polymer solutions or melts are drawn into fiber structure by electric force.

The apparatus for electrospinning is showed by Figure 2.2. There are several necessary parts for a standard electrospinning setup, including a spinneret (usually a needle with a syringe), a pump which can maintain the feeding, a high-voltage power source (usually several tens of kilovolts) and a conductive collector to gather the resultant.

Figure 2.2 Horizontal electrospinning (left side) and vertical electrospinning (right side) apparatus³⁵.

After high electric potential difference is applied between the spinneret and the collector, the droplet at the needle tip will be charged and stretched under the combined forces of static electric force and liquid surface tension. With the increase of the electric potential difference, the static electric force will overcome the surface tension and the solution will form a Taylor cone (shown as Figure 2.3) and a stream of liquid will erupt from the surface. The liquid jet will stay in a single stream status if molecular cohesion overcomes electrostatic repulsion or break up into multiple streams otherwise. And with the evaporation of the solution solvent, the jet dries in flight and is then elongated with small bending due to the electrostatic repulsion, and finally reaches the collector to form micro- and nanoscale uniform fibers³⁶.

Figure 2.3 Photograph of a Taylor cone in the process of electrospinning³⁷.

There are several crucial parameters that can affect the electrospinning process and the morphology and diameter of the resultant electrospun fiber, including solution viscosity and molecular weight, applied voltage difference, distance between spinneret to the collector, the feed rate of solution and humidity.

Proper solution viscosity and solvent molecular weight is the prerequisite to conducting the electrospinning process. If the solution is too dilute, the product of the electrospinning process will be particles instead of fibers while too thick solution will increase the difficulty to maintain a steady feed rate and cause instability of the process³⁸. High voltage difference (usually several tens of kilovolts) is also a vital element in the electrospinning process. For most cases, higher voltage will result in a larger stretching force on the solution jet and decrease the diameter of electrospun fiber resultant. But the distance between spinneret and collector also need to be taken into consideration together with the voltage, since these two factors together decide the electric field³⁹. Feed rate is another important process parameter to adjust the morphology of electrospun fibers as it can affect the transfer rate of materials. A lower feed rate is often preferable since it can ensure enough time for solvent evaporation⁴⁰. Besides, high humidity will restrain the evaporation of aqueous solvent as well as enhance the pores within the electrospun fibers⁴¹. So it is important to design the solution and processing parameters properly as well as control the ambient parameters before the electrospinning process is carried out.

2.1.2 Special Electrospinning Techniques

Besides the conventional electrospinning method introduced above, there are many special electrospinning techniques which can serve to fabricate specialty fibers. This greatly enriches the production of electrospun fibers and promotes the range of electrospun fiber application.

2.1.2.1 Highly aligned electrospun fibers and single electrospun fibers

First is the continuous electrospinning of aligned nanofibers. The approaches to gain highly aligned electrospun nanofibers are mainly by customizing collectors as Figure 2.4 shows. One most commonly adopted way is to use high speed rotating drum as the collector, and the rotating speed range is from 2000 rpm to 4000 rpm⁴²⁻⁴⁴. Another approach is to replace the highly rotating drum with a rotating disk with an extremely sharp edge⁴⁵⁻⁴⁷. Furthermore, the interdigital electrode is also an ideal substitute as the collector. By varying the configurations of the interdigital electrode, researchers can get parallel electrospun nanofibers with different length^{48,49}. Besides the frequently used methods above, the collector can also be replaced by evenly distributed metal wire⁵⁰, parallel auxiliary electrodes⁵¹, or U-shape collector⁵². The various electrospun aligned nanofibers are shown in Figure 2.5. Similar methods of modifying collector are also used to get single electrospun fibers, including using cardboard frame^{53,54}, a substrate with micro-channels⁵⁵ and parallel electrodes⁵⁶.

Figure 2.4 Different approaches to acquire aligned electrospun nanofibers by (a) highly speed rotating drum⁴², (b) sharp-edged rotating disk⁴⁶, and (c and d) parallel distributed electrodes^{49,50}.

Figure 2.5 Images of electrospun aligned nanofibers using different methods. (a) sharp-edged rotating disc collector⁴⁷, (b) interdigital electrode⁴⁸, (c) parallel auxiliary electrodes⁵¹, and (d) U-shape collector⁵².

2.1.2.2 Wet-electrospinning

Sometimes, the electrospun fibers are preferable with 3-dimensional structure, so the wet-electrospinning system is established. If the collector of electrospinning process is immersed into solvent, or replaced by solvent container directly as Figure 2.6 shows, this process is called wet-electrospinning.

Figure 2.6 Schematic drawing of the wet-electrospinning setup⁵⁷.

In a previous study, pullulan nanofiber was fabricated by wet-electrospinning to explore how the solvent concentration can affect the fiber diameter. In this study, ethanol coagulation bath was used to collect the electrospun pullulan nanofibers⁵⁷. Another work has reported a spongiform 3-dimensional fabric made by the wet-electrospinning system, which possesses a lower fiber density than the counterpart made by conventional electrospinning system⁵⁸, as Figure 2.7 shows. Furthermore, a PEI nanofiber mat was synthesized by novel wet-electrospinning method and used as affinity membrane for filtering heavy ions⁵⁹.

Figure 2.7 Images of PGA mat fabricated using (a) traditional electrospinning and (b) wet-electrospinning system⁵⁸.

2.1.2.3 Core-shell electrospinning

Except customizing the collector, the spinneret is another component that can be remolded to expand the morphology and functions of electrospinning products. For example, by using a special spinneret as Figure 2.8 shows, core-shell electrospun nanofiber is obtainable⁶⁰. The special spinneret is made of two coaxial capillaries, through which two different, usually incompatible liquids are ejected to form a continuous, coaxial jet simultaneously.

Figure 2.8 Schematic illustration of the setup for core-shell electrospinning⁶⁰.

This core-shell electrospinning method is often used to process precursors of inorganic material. By calcining the electrospun core-shell nanofiber under high temperature condition, the as-spun nanofiber will convert into desired inorganic

components^{60–62}. And by adding functional particles into core liquid which will be removed later, hollow nanofibers with decorated surfaces are obtained^{63,64}.

Figure 2.9 TEM images of coaxial nanofibers when (a) as-spun and (b) calcined at 450 ° and (c) corresponding SEM image⁶¹.

2.1.2.4 Melt electrospinning

In some special cases like biomedical applications, the residual solvent is unwanted due to the potential toxicity to cells and tissues, or the residual repulsive charge may compromise the consistent density and thickness of electrospun fabrics. Then melt electrospinning is a way to address these problems.

Figure 2.10 Schematic of melt electrospinning onto a static collector⁶⁵.

Nowadays, melt electrospinning has been widely used in industry for many applications including filtration, reverse osmosis membranes, fuel cell catalyst

technologies textiles, separator, and biomedical uses^{66,67}. Melt electrospinning can be further combined with core-shell electrospinning technology to explore its joint application⁶⁸.

2.1.2.5 Electrospray technique

Electrospray, sharing the same mechanism and apparatus with electrospinning, also works on the principle of applied electric fields. Compared to electrospinning, the solution for electrospray is with less viscosity or smaller molecular weight, so that when applied with a high voltage difference, the electrostatic repulsion overcome the molecular cohesion and continuous liquid jet will break up into highly charged liquid droplets and radially disperses. By regulating the feed rate and applied voltage, the size of the electrosprayed droplets can be controlled precisely⁶⁹, from micro to nano level.

Figure 2.11 Schematic illustration of how the concentration, flow rate, and voltage effect the electrosprayed/electrospun resultant⁷⁰.

Due to its versatility and feasibility, electrospray has been involved in many nanoscience and nanotechnology area, especially in micro/nanoparticles fabrication for biomedical applications such as bone tissue engineering and drug delivery^{70–73}.

Figure 2.12 Schematic setup of the coaxial electrospraying process⁷⁴.

The core-shell electrospinning technique is also practical with electrospray as Figure 2.12 shows. The morphology of electrosprayed nanoparticles can also be modified by regulating the molecular weight of the solvent, the kind and composition ratio of the solvents and other critical parameters mentioned previously.

Figure 2.13 Electrosprayed particles from (a) 5% w/v HMw PLGA and (b) 6% w/v LMw PLGA in pure DCM (5% w/v of BSA served as the core at a shell:core flow rate of 1.0:0.1 ml/h)⁷⁴.

2.1.3 Materials and Applications

With the well-developed techniques and versatile functionalities, electrospinning method is widely adopted in various applications, including energy conversion and storage, environment-related applications as well as biomedical applications.

2.1.3.1 Energy conversion and storage

Electrospun semiconducting nanostructures are frequently used in many low cost devices related to energy conversion and storage.

Dye-sensitized solar cells (DSSCs), as a promising alternative to silicon solar cells, became the mainstream of third generation solar cells³. In a typical structure of DSSC as shown by Figure 2.14, various of metal oxides with wide band gap like TiO_2 , In_2O_3 , ZnO and SnO_2 etc. are used to construct the mesoporous layer. But among all the metal oxides, TiO_2 is the most commonly adopted materials for DSSCs so far, since the numerous advantages including absorption of the light absorber, porosity to provide large contact area, and good charge transportability. Electrospinning is one attractive method to synthesize multiple kinds of TiO_2 polymorphs.

Figure 2.14 Schematic drawing of working principle of a DSSC⁷⁵.

The first reported use of electrospun TiO_2 in DSSC can be dated back to early of this century⁷⁶. Titanium(IV) isopropoxide and poly(vinyl acetate) (PVAc) solution were electrospun onto a conductive glass substrate, followed by solidification process, constructed the TiO_2 electrode and found to be penetrated. In the following years, electrospinning techniques started to be rapidly applied in the DSSC device fabrication

with the TiO_2 electrode as nanofibrous membranes with complicated 3D structures which benefited the dye loading⁷⁷, nest-shaped structure as a light scattering layer which enhanced the photocurrent of DSSCs⁷⁸, 1D assembly nanoparticles which improved the PCE by enhancing light absorption *via* improved light scattering and longer electron lifetime⁷⁹, and nanowires with rough surface which improved the surface area and short-circuit current density⁸⁰. Electrospinning was also used to modified metal oxides electrode by incorporating other functional materials like nitrogen and graphene oxide (GO) doped TiO_2 which can help in the light absorption and electron transport thus leading to improvement of DSSC performance⁸¹, or dysprosium, holmium and erbium ions doped In_2O_3 , which improved the DSSC performance by the modulating of band gap, and enhancing recombination resistance and extending the electron lifetime⁸². Besides the fabrication of TiO_2 layer, the electrospinning method was also adopted in DSSC fabrication for graphene-embedded carbon nanofiber as a new counter electrode⁸³.

Another solar energy conversion device that often adopts electrospinning technique is perovskite solar cells (PSCs). In a typical device of PSC, the perovskite light absorbing material (MAPbX or FAPbX) is sandwiched between the electron transport layer (ETL) and hole transport layer (HTL), as shown by Figure 2.15 in which the meso- TiO_2 plays the role of ETL and Spiro-OMeTAD is HTL. When perovskite absorbs light and generates electron-hole pairs, the photogenerated carriers will reach the external circuit through ETL and HTL to generate electricity. Similar like DSSCs, electrospun TiO_2 structures are also commonly used as ETL material for electrons transport.

Figure 2.15 Cross-section SEM image of a typical PSC device⁸⁴.

TiO₂ nanofibers (NFs) doped with lead are fabricated by electrospinning technique and further used in PSC preparation as perovskite-sensitized photoanode⁸⁵. The direct rapid path provided by TiO₂ NFs for transmission and collection of the photogenerated electrons and better contacting between perovskite material and photoanode brought higher PCE. In another reported work, TiO₂ nanofibers are directly electrospun on top of the compact TiO₂ layer to act as the photoanode for efficient PSCs⁸⁶ and yield an enhanced PCE. And electrospun TiO₂ nanofibers can be further modified by the hydrothermal process to get hyperbranched meso-structured nanofiber–nanorod arrays for meso-TiO₂ layer. The performance of hyperbranched-based PSCs is greatly improved compared to single layer based PSCs⁸⁷. Electrospinning technique can also be used to integrate other functional materials into the metal oxides. Gold nanoparticles were embedded into TiO₂ nanofibers while electrospinning process and generate plasmon-enhancement in PSCs⁸⁸. Other metal oxides except for TiO₂ can also be modified by the electrospinning method. Zn₂SnO₄ nanofiber scaffolds modified with reduced graphene oxide (rGO) played the role as ternary metal oxides (TMOs) based ETL for mixed halide PSCs, and reduced the slow decay lifetime, leading to more efficiently electron injection⁸⁹.

Furthermore, different from solar cells that can transfer solar energy into electricity, fuel cell is another promising energy conversion device that utilize the chemical energy of fuels. Electrospun one-dimensional materials like carbon nanofibers (CNFs) and carbon nanotubes (CNTs) are used in fuel cells recently^{90–92}.

Besides used in energy conversion area, electrospinning technique is also widely applied to energy storage devices including Lithium-ion (Li-ion) batteries and supercapacitors.

The Li-ion batteries were firstly commercially available from the early 1990s and one-dimensional nanostructures can benefit for the improvement on rate capability, cycle stability and capacity of Li-ion batteries⁹³. In 2012, electrospun one-dimensional TiO₂–graphene (TiO₂–G) composite nanofibers were synthesized and characterized for further use as Li-ion batteries' anodes. The reported TiO₂–G nanofibers showed a 25% enhancement on reversible capacity after 300 cycles, compared to native TiO₂ fibers⁹⁴. In the following year, electrospun one-dimensional TiO₂N_x nanofibers for lithium rechargeable batteries were fabricated and tested. The results showed that nitrogen-doped one-dimensional morphology facilitates the charge/discharge process of Li⁺⁹⁵. And nitrogen-doped one-dimensional TiO₂ nanofibers were then decorated by mesoporous carbon, and they showed a high capacity after 100 cycles⁹⁶. Hierarchical vanadium oxide nanowires fabricated by electrospinning method provides a higher discharge capacity and improved the cycling stability, thus facilitating the performance of Li-ion batteries⁹⁷. And electrospun porous carbon nanofiber optimized by cobalt and cobalt oxide nanoparticles also delivered excellent cyclic stability and high rate capability⁹⁸.

Supercapacitors are another promising energy storage devices. Electrospinning technique was adopted to synthesize the amorphous NiO nanofibers coated by carbon, porous carbon nanofibers, hollow carbon nanofibers doped by nitrogen, amorphous TiO₂/carbon nanofibers composite and maleic anhydride embedded carbon nanofibers for supercapacitors^{99–103}.

2.1.3.2 Environment related applications

In recent years, many countries around the world have been suffering from lack of clean water resources due to the pollutions, climate change while the demand is increasing. One of the solutions to address this problem is to re-utilize wastewater, and semiconducting metal-oxide based photocatalysis is a good choice for water treatment. And electrospinning technique, with the series advantages including low-cost, easy processing and feasibility, proves to be a good way to fabricate the catalysts/sensitizers nanostructures for photocatalysis process.

Anatase TiO_2 is a commonly used material for light-induced redox process of photocatalysis, various of TiO_2 nanostructure is synthesized through electrospinning method. Electrospun Ag- TiO_2 nanofibers decorated with polypyrrole showed improved photocatalytic activity for the visible incident wavelength¹⁰⁴. Highly porous TiO_2 nanotubes membranes fabricated by an electrospinning method, which exhibit large specific surface areas, is also applied to catalysis and have excellent catalytic activities¹⁰⁵. Superhydrophilic TiO_2 can also be coated on the glass by utilizing electrospinning technique which showed a self-cleaning property and further used for photocatalysis¹⁰⁶. Rutile nanorods TiO_2 nanorods were combined onto the electrospun anatase TiO_2 nanofibers with high density, making a three-dimensional structure which showed superior photocatalytic activity to pure anatase nanofiber¹⁰⁷. Another interesting TiO_2 nanostructure called tube-in-tube fibers as shown by Figure 2.16 were also made by electrospinning. And the ability to degrade 2-chlorophenol and 2,4-dichlorophenol under UV to visible incident wavelength range is explored and showed a satisfied performance¹⁰⁸.

Figure 2.16 TEM images of a) low magnification, b) high magnification, and c) individual tube-in-tube TiO_2 synthesized by using a pinhead with a 0.6 mm pinhole and calcination at 500°C for 4 h. d) HRTEM image of TTIT shown in Figure c (the investigated part is marked with the white frame)¹⁰⁸.

2.1.3.3 Biomedical related applications

Another main applied field of electrospinning is biomedical related applications such as wound dressing, drug delivery, and tissue engineering.

Electrospun biodegradable polymer nanofibers are often utilized to address wound or burns of the skin. Since the polymer materials can keep the wound from drying up and its antibacterial properties can prevent the wound from infection while absorbing the exudates and providing a comfortable environment for healing¹⁰⁹. There are many well-designed wound dressing systems using various of electrospun polymer nanofibers such as polyurethane nanofibers encapsulated with Ag nanoparticles, chitosan-coated PVA nanofibers, and antimicrobial PLGA ultrafine fibers^{110–113}.

Electrospinning technique is also used in the drug delivery field since it can fabricate nanofibers with a high surface area which can act as the drug carrier and incorporate drug during the synthesis process¹¹⁴. The electrospun nanofibers can deliver a rather wide range of drugs including gene, protein as well as enzymes^{114–116}.

And when talking about electrospun nanofibers and fiber meshes applied in tissue engineering, there are several factors that need to be taken into consideration, including the kind of materials, surface modification, fiber orientation, and porosity¹¹⁷. The main goal of tissue engineering is to use the combination of cells, bioactive agents and biomaterials to restore injured tissue¹¹⁸.

2.2 Electrospun Nanostructures in Mesoscopic Solar Cells

A solar cell is a device that can directly convert solar energy into electricity by photovoltaic effect. This process will not generate any toxic by-product nor greenhouse gases which is commonly appeared in traditional fuel energy systems. To convert light energy into electricity, there are three procedures happening within a solar cell. First, the light absorbing material absorbs the light and become excited to generate electron-hole pairs or excitons. Then the photogenerated electron-hole pairs will be separated under the effect of electric field. At last the separated electrons and holes will be

extracted at opposite electrodes respectively and generate electricity to an external circuit.

2.2.1 Fundamentals of Solar Cells

Figure 2.17 Illustration of the basic structure of a solar cell.

Figure 2.17 is the fundamental structure of a semiconductor p-n junction solar cell. When light casts onto the cell surface, penetrates the transparent electrode and reaches the light absorbing layer, the light absorbing semiconductor layer will be activated by incident photons with energy higher than the bandgap of the semiconductor material. Then electrons in the low level of valence band will be excited onto the high level of the conduction band, thus generating electron-hole pairs or excitons, which will be further separated by the built-in potential of the p-n junction of the cell, and finally transport to their corresponding positive and negative electrodes, respectively. But during the whole process, there are some photogenerated carriers that will recombine due to different reasons including auger recombination, radiative recombination, and Shockley-Read-Hall recombination¹¹⁹.

There are several most commonly used parameters that can be used to measure the performance of a solar cell, as follows:

The solar cell devices meant for terrestrial applications are usually illuminated with a simulated air mass 1.5 spectrum (AM 1.5). This represents the global average irradiance at the surface of the earth (i.e. at the rate of 100 Mw/cm²).

Figure 2.18 A typical I - V curves of a solar cell under dark and illuminated conditions, respectively¹²⁰.

The current-voltage (I - V) curve of a solar cell is an important data that can reveal many properties of the solar cell. Figure 2.18 is typical I - V curves of a solar cell under dark and illuminated conditions, respectively. A photovoltaic device can be regarded as a current source which can provide different constant currents at different illumination levels. When exposed to illumination by a light source, a photovoltaic device will develop a photovoltage between 0 V and V_{oc} (open-circuit voltage), and then derives a current I corresponding to the device resistance (as defined by the Ohm's law). In this thesis, the current I is expressed in a more suitable term as current density J (mA/cm²).

A J - V measurement setup shown in Figure 2.19 is customized to measure the photocurrent-photovoltage (I - V) curve for further PCE calculation. For each I - V curve, the crucial parameters can be extracted from the data as follows:

- open-circuit voltage (V_{oc}): the maximum voltage a device can achieve when the current is zero, the unit is V;
- short circuit current density (J_{sc}): the current to area value when the device is short-circuited, the unit is mA/cm²;

- fill factor (FF): the ratio of the area with the largest rectangle which fits in the I - V curve to the whole area of the rectangle defined by V_{oc} and J_{sc} , as illustrated in Figure 2.18, defined as:

$$FF = \frac{I_{mp} \times V_{mp}}{I_{sc} \times V_{oc}}$$

Figure 2.19 Standard spectrum of AM 1.5G and spectra from two simulators, and the schematic of the photovoltaic parameters measurement setup

Then the power conversion efficiency (PCE) of a solar cell can be calculated as:

$$PCE = FF \times I_{sc} \times V_{oc} / P_{in}$$

Another important parameter is incident photon-to-electron conversion efficiency (IPCE) which is also known as quantum efficiency, which can show the ratio of the photogenerated carriers to the incident photons into the device. IPCE is a wavelength related photovoltaic conversion efficiency defined as:

$$IPCE = \frac{hc}{e} \times \frac{J_{sc}}{\lambda G}$$

where h is Boltzmann constant, e and c are constants of elementary charge and light speed, λ is the light wavelength, G is the illumination power, respectively. Figure 2.20 gives an example of a typical IPCE curve of a perovskite solar cell.

Figure 2.20 A typical IPCE spectrum of a PSC device (blue) and the integrated photocurrent density of the IPCE spectrum with the AM 1.5G photon flux is also shown (red line)¹²¹.

The IPCE spectra in this thesis were measured using a homemade setup. The light source is from a Newport-Oriel Xenon lamp; spectra are resolved using an Oriel Cornerstone 130 monochromator. Electrical signals are measured using a Keithley 2400 source meter. The light density of the setup is calibrated with a silicon photodiode. And measurements are conducted in a glovebox filled with N₂. More details will be discussed in the Experiment Sections of the following chapters.

2.2.2 Development and Architecture of Mesoscopic Solar Cells

Mesoscopic solar cells are a category of solar cells which make use of the advantages of mesoscopic structural features which can offer extra-large contact surface area between the light absorber and electrode, thus benefit the photogenerated carriers in transporting and collecting. In this section, we are mainly discussing dye-sensitized solar cells (DSSCs) and perovskite solar cells (PSCs).

The concept of the mesoscopic solar cell was first proposed in 1991 when O'Regan and Grätzel developed a DSSC using mesoscopic TiO₂ film which was

sensitized by dye molecules³. The mesoscopic TiO_2 film offered a smooth pathway for photogenerated free electrons and an impressive PCE ~7% was obtained.

DSSCs, as representatives of low cost solar cell, are mainly based on cheap materials to pursue a satisfied performance. While researches put lots of efforts in synthesizing light absorbers of dye^{122,123}, exploring various mesoporous metal oxide film as semiconductor electrodes^{87,124–127}, improving the liquid electrolyte^{128–130} and optimizing the electrodes¹³¹, the PCE of DSSCs did not show remarkable improvement and remained around 13% in laboratory and 10% in prototype modules, respectively.

Figure 2.21 Device structure and working principles of a typical liquid electrolyte mesoscopic DSSC¹³².

Figure 2.21 is the structure of a typical liquid electrolyte mesoscopic DSSC. A typical device consists of a transparent conductive photoanode, a mesoporous TiO_2 layer which acts as ETL and can let dye molecules adhere to its surface, liquid electrolyte and a counter electrode. When light enters the DSSC and reaches the light absorber layer, the dye molecules will be excited by the photon and one electron will jump from highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) of each dye molecule, and then transport to the electrode through the conduction band of the mesoporous TiO_2 layer. At the same time, the generated oxidized dye molecule will be reduced by the electrons from the external circuit, at the counter electrode.

But serious problems such as instability, the corrosive nature of the electrolyte and current leakage, have limited the commercialization of the DSSCs¹³³. To address these crucial obstacles, researchers turned their attention to all-solid-state devices where solid hole transport materials (HTM) were used to take the place of liquid electrolyte. By using an organic HTM: 2,2',7,7'-tetrakis(N,N-dip-methoxyphenylamine)-9,9'-spirobifluorene (spiro-OMeTAD), the first solid-state DSSC was fabricated by Bach et al. in 1998, exhibiting a PCE of 0.74%¹³⁴. Then after continuous efforts to optimize DSSCs by interface engineering on modifying electron transport layer and exploring dopants for hole transport material, and varying many kinds of dyes, Grätzel group successfully increased the PCE of DSSCs to 7.2% in 2011¹³⁵. And from the following year, organic-inorganic lead halide perovskite started to take the place of dyes to become the light absorbing material in solid-state DSSCs and gained a wide investigation from then on^{136,137}.

Figure 2.22 (a) SEM image of the cross-section of a MAPbI₃ perovskite sensitized device; (b) enlarged local image of the active layer-compact layer-FTO interface; (c) diffuse reflectance spectrum of the MAPbI₃-sensitized TiO₂ film; (d) schematic energy level diagram of TiO₂, MAPbI₃ and the organic HTM¹³⁸.

Methylammonium lead iodide (MAPbI₃) perovskite, as a semiconductor material with a direct bandgap of ~1.55 eV, is a promising candidate to act as the light absorber of a solar cell^{139,140}. As the liquid electrolyte can dissolve the perovskite material and

cause instability of the device, perovskite based solar cells are more likely to adopt solid state HTM. Figure 2.22 is a perovskite based solar cell with all-solid-state configuration using organic molecule HTM (spiro-OMeTAD), and that device yielded a PCE of 9.7% which was highest at that time. And from then on, PSCs are all fabricated following this kind of solid-state configurations.

Figure 2.23 (left) BX_6 octahedral and (right) AX_{12} cuboctahedral geometry of perovskite materials with an ABX_3 formula¹⁴¹.

The term perovskite usually refers to a group of materials sharing the same crystal structure of calcium titanium oxide mineral species ($CaTiO_3$) as Figure 2.23 shows. The general formula of perovskite family can be expressed as ABX_3 , and for perovskite material which is commonly used for solar cells, A refers to Cs (cesium), MA ($CH_3NH_3^+$, methylammonium cation), or FA ($NH=CHNH_3^+$, formamidinium cation); B refers to Sn and Pb, and X refers to Cl^- , Br^- and I^- . Since 2009, the organic-inorganic lead halide perovskites have become an emerging light absorbing materials for various photovoltaic applications due to their unique optoelectronic properties, including large optical tunability, high absorption coefficients, and micrometer-scale carrier diffusion length⁶⁻⁸.

Since 2012 when Kim et al. reported the first efficiency solid-state mesoscopic PSC¹³⁸, researchers have been devoted in exploring PSCs to enhance the device performance, reduce the cost, ensure the device stability as well as commercialize the fabrication process. To be specific, they have made effort on testing different perovskite materials, from pure perovskites to mixed perovskites^{5,142-150}; and exploring different processing method, including one-step deposition¹⁵¹⁻¹⁶⁴ and two-step deposition techniques^{158,165-168}; and evolving the device architectures, including mesoscopic

structure^{65,152–164} and planar structure^{182–187}, etc. So far, the highest certificated PCE of PSC has reached 23.7% in single-junction architectures⁹.

2.2.3 Electrospun TiO₂ Nanostructures in Mesoscopic Solar Cells

In a typical mesoscopic solar cell, the functional layers working for charge carrier generation, extraction and transport are deposited by each other, thus resulting interfaces in the device. These interfaces are very important that they can directly affect the charge behaviors and the device performance because recombination often occurs at interfacial areas where defects exist. So to optimize a device's performance to the most, besides choosing the appropriate materials for each functional layers, adopting best device structure and controlling the morphology, it is also important to engineering the interfacial areas.

With the help of various time-resolved spectroscopy techniques developed in recent years, the working mechanism of mesoscopic solar cells is investigated. The photogenerated electrons and holes appear at ETL/perovskite and perovskite/HTM junctions at the same time, dissociate into free carriers rapidly (~ 2 ps)⁶, and then inject into corresponding carrier selective layer ultrafast with similar timescale. The lifetimes of the free carriers have been observed to be microsecond scale. But due to the imbalance carrier mobilities, electrons accumulation happens at the ETL/perovskite interface. Thus researchers have been trying to optimizing the mesoporous layer and the ETL/perovskite interface to balance the charge carrier mobilities.

TiO₂ nanostructures have been most commonly utilized in both DSSC and PSC as an active scaffold to enable the electron transportation from light-absorbing material to electrode through its conduction band. Therefore, researchers have cast lots of effort to improve the mesoporous TiO₂ layer of mesoscopic solar cells. The mesoporous TiO₂ layer is required to be: (1) unconsolidated to accept the light absorber, (2) nanoporous to enlarge the contact area with perovskite to obtain highly efficient charge injection, and (3) defect-free to minimize grain boundaries for the purpose of suppressing charge recombination and trapping. For this reason, mesoporous TiO₂ nanostructures synthesized by different methods have been applied in DSSCs^{188–195} and PSCs^{196,197}. As we have previously discussed in 2.1.3, electrospinning technique is a very facile and feasible method to fabricate many kinds of nanostructures used for DSSCs and PSCs.

Table 2.1 is a summary of DSSCs based on different electrospun TiO₂ nanostructures and their corresponding performances and Figure 2.24 are the SEM images of different morphologies of electrospun TiO₂ structures. S. Ramakrishna group reported a rice grain-shaped TiO₂ nanostructure synthesized by electrospinning technique and used as ETL in DSSCs¹⁹⁸. They found different from the bulk material, the band gap of rice grain-shaped TiO₂ nanostructure is slightly less as 3.17eV, which may be attributed to unique morphology and a mixed crystal structure that benefits the electron dissociation. And the DSSC based on this structure showed a relatively high V_{OC} with 0.96 V. The large surface area and porous structure avails the infiltration of dye molecules and the excellent inter-grain contact is good for electron transport.

Table 2.1 Device performances of DSSCs based on different electrospun TiO₂ nanostructures.

Morphology	J_{SC} (mA/cm ²)	V_{OC} (V)	FF	PCE (%)
TiO ₂ rice grain ¹⁹⁸	8.2	0.96	0.62	5.1
TiO ₂ nanorod ¹⁹⁹	11.16	0.808	0.67	7.11
TiO ₂ nanowire ²⁰⁰	5.71	0.782	0.642	2.87
TiO ₂ nanotube ²⁰¹	7.15	0.78	0.682	3.8
TiO ₂ hollow nanotube ⁶¹	8.99	0.738	0.64	4.25
Multiwall carbon nanotube ²⁰²	18.53	0.75	0.734	10.24
Microspheres ²⁰³	6.13	0.46		1.16
Yellow-bristle grass ²⁰⁴	10.78	0.761	0.74	8.02

Figure 2.24 SEM images of different electrospun TiO₂ nanostructures used in DSSCs. (a) Nanorice¹⁹⁸. (b) Nanowire²⁰⁰. (c) Nanorods¹⁹⁹. (d) Microspheres²⁰³. (e) Hollow-nanotube⁶¹. (f) Multiwall carbon nanotube²⁰². (g) Nanotube²⁰¹. (h) Yellow-bristle grass²⁰⁴.

Besides zero-dimensional TiO₂ nanostructures like nano rice grains and spheres, researchers also fabricated one-dimensional TiO₂ nanostructure as nanowires and

nanotubes. Hierarchical porous TiO_2 nanorods were prepared by microemulsion electrospinning method for DSSCs¹⁹⁹. The one-dimensional nanorods showed strong light scattering effect, longer electron lifetime and yield a high PCE of 7.11%. TiO_2 nanorods with further modification, for example, decorated with 0.1% multiwall carbon-nanotubes, enhanced the PCE to 10.24% due to the largely improved fill factor²⁰². The enhancement was derived from the improvement on charge transport and suppression on recombination. Another interesting one-dimensional TiO_2 nanostructure is yellow-bristle grass like TiO_2 - SiO_2 composite nanofibers, which exhibited fibrous morphology but were highly porous at the surface²⁰⁴.

Figure 2.25 (a) Sketch for fabricating PSCs. (b) SEM image of electrospun TiO_2 nanofibers. (c) Cross-sectional SEM images of TiO_2 ETL²⁰⁵.

Electrospun TiO_2 nanostructures were also widely applied to PSCs in recent years. We have introduced some previous works in Section 2.1.3^{85–88}, in which researchers utilized various of electrospun TiO_2 nanofibers as ETL of PSC and got enhanced performance of the devices. In the passing year, the electrospun TiO_2 nanostructures have not gone out of fashion. Xiong group used thick and high-porosity one-dimensional electrospun TiO_2 nanofibers as the mesoporous ETL and fabricated PSC as Figure 2.25 shows, and the device exhibited a huge improvement in J_{SC} , thus enhancing the PCE from 7.5% to 11.6% compared to zero-dimensional TiO_2 nanostructures based devices²⁰⁵. This is due to the better loading condition for perovskite material and protection the ETL offered against moisture. Another complicated but fantastic structure

was developed by Uddin group, who synthesized SnO₂-TiO₂ composite nano-flower using electrospinning technique as Figure 2.26 shows²⁰⁶. This branch-structured system can better benefit the dispersion of accumulated electrons at the ETL/perovskite interface, which we have mentioned as a main obstacle for PSC performance improvement, thus yielding PCE of 17.25% (21% higher compared to control device).

Figure 2.26 SEM images of electrospun SnO₂-TiO₂ composite nano-flower at different magnification²⁰⁶.

2.3 Electrospun Piezoelectric Polymer and Applications

Polyvinylidene difluoride (PVDF) as a very attractive functional polymer on electroactivity including ferroelectricity, piezoelectricity, and pyroelectricity, together with its copolymers, have become very attractive materials in numerous applications due to their excellent properties like lightweight, processability, flexibility and electrochemical stability.

2.3.1 Conformations of Piezoelectric Polymer and How to Enhance the Piezoelectric Property

The formula of PVDF is $-(CH_2-CF_2)_n$ and the structure lies between polyethylene (PE) $-(CH_2-CH_2)_n$ and polytetrafluoroethylene (PTFE) $-(CF_2-CF_2)_n$, which makes PVDF possess the flexibility of PE and the stereochemical constraints of PTFE, leading to four distinct polymorphs of PVDF^{207,208}. In all four polymorphs, the dipoles of the α phase are subtractive and show no net dipole at all while β , γ and δ phases whose dipoles are additive and lead to a net dipole. Of all the polar polymorphs, the β form is greatest in spontaneous polarization per unit cell, thus exhibiting the highest piezoelectric and

ferroelectric properties. To make the greatest use of the advantages of β form PVDF, researchers have been exploring numerous ways. And all the attempts can be classified into four categories, i.e. to modify the chemical structures, to apply stretching forces, to introduce additives and treat the material with high temperature and pressure.

Figure 2.27 Schematic drawing of the polar and non-polar phase of PVDF. Carbon atoms are grey, hydrogen atoms are white and fluorine atoms are striped²⁰⁹.

2.3.1.1 Modification of the chemical structures

PVDF material can transfer between the four phases by applied different conditions. For example, by applying an electrical field, the α phase can be converted to the δ phase, while γ phase is obtainable under high temperature crystallization²¹⁰. Since β phase is the only phase out of the three polar phases, that all dipoles are parallel and experiences no cancellation of anti-parallel dipoles which will diminish the net dipole within the crystal. Therefore, β phase PVDF exhibits stronger electroactivity when given stimulated. So here we mainly focus on how to promote the PVDF material into the β phase.

β phase can be obtained in several ways. First is the mechanical drawing of α phase films, and the efficiency is positively correlated to the draw ratio, but the process must be conducted under a low temperature. Higher temperature will reduce the transformation proportion of α phase into the β phase. When the temperature is too high,

the transformation will not happen at all²¹¹. Another way to convert PVDF powder from the α phase into the β phase is by cryogenic mechanical milling. The proportion of β phase is increasing with the milling time, but exceeding limit time will cause reduced crystallinity of the PVDF material till amorphous state²¹². By introducing a small amount of long multi-walled carbon nanotube during melting PVDF can also help to increase the β phase presence since the carbon nanotube plays a role of nuclei when PVDF crystallizing and charges accumulate at its surface, but the amount of carbon nanotube should be optimum for that extra carbon nanotube will reduce β phase formation due to its conductivity²¹³. High pressure is another way to conduct the crystal transformation of PVDF²¹⁴, but the most frequently adopted method to form β phase PVDF is by applying high electric field²¹⁵⁻²¹⁷. So electrospinning technique is often utilized to process piezoelectric polymer since it can polarize the material simultaneously while processing the material.

2.3.1.2 Copolymerization

Even we have discussed so many ways to improve the proportion of β phase in PVDF materials, it is still very difficult to obtain full β phase PVDF. So researchers turned to the copolymers of PVDF with TrFE (-CHF-CF₂-), TeFE (-CF₂-CF₂-) and HFP (-CF₂-CF(CF₃)-), etc. Each of these monomers possesses some unique advantages, though the introduction of these monomers as defects and can decrease the melting point and ferroelectric transition temperatures of the polymer.

TrFE and TeFE monomers, when copolymerized at significant concentration together with PVDF, may result in a direct all-*trans* conformation without further processes, which is similar to the β phase of PVDF. Sterical hindrance derived from the different size between a fluorine atom and hydrogen atom occurs when the monomer inserted into PVDF chain, and result in the superiority of *trans* conformation over the *gauche* conformation. The replacement of some hydrogen atoms by the fluorine atoms reduces the availability of the dipole moment forming between hydrogen and fluorine, which will make the unit cell of copolymer a little larger than pure PVDF and the dipole moment is averagely weaker. For the same reason, the order of copolymers electroactivity are as follows: PVDF-TrFE > PVDF-TeFE > PVDF-HFP.

On the other hand, when the concentrations of monomers are low in the copolymerization with PVDF, the insertion of monomers will not change the

crystallization behavior but will still act as defects which lead to a decrease of crystallinity which will make the process of copolymer easier. Although this change decreases the electroactivity of the copolymers of PVDF, this kind of copolymer still provides distinct advantages which pure PVDF does not possess.

2.3.1.3 Additives to enhance piezoelectric property

Another commonly used method to promote the piezoelectric property of polymers is to introduce additives.

Hydrated salts are one of the additives that can be introduced to control the water content when casting PVDF solution and help to form high β phase PVDF films, reported by Gregory group²¹⁸. The reproducible enhancement may be due to the hydrogen bonding between polar C-F within the polymer chain and water molecular^{219,220}. Organo-modified clay is also used for the enhancement of β phase derived from the interaction between PVDF chain and charged clay surface, and the intercalated clay can prevent PVDF molecular chains from relaxation, but the confinement effect generated when clay intercalated will cost the crystallinity^{221–223}. Carbon nanotubes can also cause enhancement of the β -phase in PVDF^{224–226} whose formation cause is similar to the organo-modified clay which is the interaction between surface and chains.

But all the additives caused enhancement on β -phase dipoles of PVDF are randomly distributed, so post poling process is necessary to drive the dipoles to the oriented direction and make the electroactive properties of PVDF to the maximum. That is the reason why electrospinning technique is a perfectly suitable method for processing PVDF and its copolymers since it can make the dipoles well aligned while the formation of the material.

2.3.2 Applications of Electrospun PVDF and Its Copolymers

As we have discussed in the previous section, electrospinning technique has a great advantage in processing PVDF and its copolymers as it can both benefits the material in conversion to β phase and help to orient the dipoles in the same direction, which will lead to the enhanced piezoelectric performance of the material. So in this section, we will introduce several main applications of electrospun PVDF and its copolymers utilizing the piezoelectric property.

2.3.2.1 Energy harvesting

With the rapid consumption of non-renewable energy resources, it becomes an urgent task to explore clean and sustainable energy resources in the ambient environment, among which mechanical energy is a very widely distributed and commonly available resource including vibration, sounds, human motions etc. And with the development of wearable smart devices, the demanding of light, flexible energy resource is also increasing for self-powered devices. Therefore, piezoelectric harvesting of mechanical energy keeps receiving lots of attention in recent years. Electrospun piezoelectric polymers have been proved to be a good mechanical energy generator due to its various advantages.

Figure 2.28 Testing the device based on electrospun PVDF nanofiber²²⁷.

In 2013, J. Nunes-Pereira et al. developed a voltage generator based on electrospun PVDF nanofibers as Figure 2.28 shows, and the highest efficiency generated by this device is $0.02\mu\text{W}$ and $25\mu\text{W}$ at low and high mechanical deformation, respectively²²⁷. But due to the mechanical stiffness, the output power will finally decrease. C. Lee et al. fabricated highly-aligned PVDF nanofiber doped with BaTiO_3 nanoparticles which can enhance the piezoelectric property²²⁸. And the uniaxially-aligned electrospun PVDF nanofiber can be further used for power applications in

biomedical devices. Besides piezoelectric ceramics, other additions can also be introduced to improve the performance of electrospun PVDF nanofiber devices, such as carbon nanotubes. H. Yu et al. prepared piezoelectric nanogenerators based on electrospun PVDF nanofiber without post-poling treatment and enhanced the fiber surface conductivity by doping multiwall carbon nanotubes (MWCNTs), which benefits the output power. The output generated by 5wt% MWCNTs PVDF generator is 6V and 81.8nW, increased by 200% and 44.8% compared to pure PVDF nanofiber generator without MWCNTs²²⁹. Besides piezoelectric property, electrospun PVDF fibers also possess another interesting property called triboelectric which can produce high outputs. And to combine the piezoelectric and triboelectric property in one power generator may be a very promising method to fabricate high power resource for wearable devices²³⁰.

Copolymers of PVDF are also used to fabricate energy harvesting devices. For example, Gerardo Ico et al. synthesized P(VDF-TrFE) nanofiber by electrospinning for energy harvesting. They explored the relationship between the maximum output power and the fiber diameter. And the results illustrated a negative correlation between these two factors. The maximum power generated by electrospun P(VDF-TrFE) nanofiber with an average diameter of 90 nm is about 27 nW, nearly 4 times of the fiber with an average diameter of 960 nm²³¹. Similar to the electrospun PVDF nanofibers, P(VDF-TrFE) nanofiber can also be used for hybrid piezoelectric and triboelectric nanogenerators, and the output power of this hybrid nanogenerator can be as high as 441 μ W and is able to light up LEDs²³².

2.3.2.2 Sensing

Sensing is another main application of electrospun PVDF and its copolymers, especially for demanding of portable and flexible devices. Force and pressure sensors based on electrospun piezoelectric polymer fibers have attracted increasing attention from researchers and been widely investigated.

Figure 2.29 Setup for characterizing PVDF force sensors²³³.

Y. H. Wang et al. developed a flexible force sensor based on electrospun PVDF fabrics without mechanical further poling treatment and characterized the sensor using the setup as Figure 2.29 shows. The best sensitivity of the sensor is 42 mV/N with the highest β -phase proportion²³³. Y. Xin et al. improved the device performance by doping nanoclay^{221–223} to enhance the β -phase conversion as we have discussed in the previous section and using modified “near distance-wheeling” electrospinning (NWS) method. The enhancement of the piezoelectric response is acquired²³⁴. By replacing the PVDF by P(VDF-TrFE), the force sensor based on aligned electrospun nanofiber synthesized by L. T. Beringer et al. showed a greatly enhanced sensitivity of 0.4 V/8 mN (50 V/N). The improved property makes it possible to test very small mechanical forces in extreme conditions such as cellular mechanics²³⁵. Aligned electrospun P(VDF-TrFE) were also formed into flexible and free-standing sheets and used as a pressure sensor which exhibited excellent responses to small pressure inputs (0.1 Pa)²³⁶.

Acoustic sensors are another type of pressure sensor since it will respond to the tiny pressure generated by a sound wave. As Figure 2.30 shows, C. Lang et al. fabricated an electrospun PVDF nanofiber based acoustic sensor. In order to let the PVDF nanofiber receive the acoustic wave directly, a through hole was cut on the PET substrate. The results showed that thinner nanofibers without beads will respond better to the acoustic inputs, and the sensor was more sensitive to lower frequency sound wave²³⁷. Another self-polarized electrospun PVDF sensor was developed by E. Ghafari and N.

Lu recently, which exhibited promising potential for both active and passive system for health monitoring²³⁸.

Figure 2.30 (a) Sketch of the acoustic sensor based on electrospun PVDF, (B) SEM images of as-spun PVDF nanofibers, (c) testing setup²³⁷.

Chapter 3: Electrosprayed TiO₂ Nanoporous Hemispheres for Enhanced Electron Transport and Device Performance of Perovskite Solar Cells

In this chapter, titanium dioxide (TiO₂) nanoporous hemispheres (NHSs) with a radius of ~200 nm are fabricated by electrospraying a hydrothermally synthesized TiO₂ nanoparticle (NP) suspension solution. The resulting TiO₂ NHSs are highly porous, which are beneficial to the infiltration of perovskites and provide a larger contact area, as building blocks to construct a mesoporous TiO₂ layer for FA_{0.81}MA_{0.15}Pb(I_{0.836}Br_{0.15})₃ based perovskite solar cells (PSCs). By analyzing the photovoltaic properties in details, the distribution density effect of TiO₂ NHSs is discussed and the optimized distribution density is investigated. And small perturbation transient photovoltage (TPV) method are adopted to explore the free carrier lifetime within TiO₂ NHSs based PSCs and its TiO₂ NPs based control group.

3.1 Introduction

Metal halide perovskites with a formula of APbB₃ [A = Cs⁺, MA (CH₃NH₃⁺, methylammonium cation), or FA (NH=CHNH₃⁺, formamidinium cation); B = Cl⁻, Br⁻ and I⁻], as emerging light absorbing materials, offer a promising path to construct highly efficient photovoltaic devices, owing to their unique optoelectronic properties, including large optical tunability, high absorption coefficients and micrometer-scale carrier diffusion length. The efficiency of perovskite solar cell (PSC) has kept growing in recent years and the certificated highest efficiency is 23.7% up to now^{9,138,158,159,239–245}. Among the recently proposed PSC architectures, mesoporous TiO₂ layer functions as an “active” scaffold to enable the electron transportation from perovskite light-absorber to the fluorine doped tin oxide (FTO) layer through its conduction band (CB)^{117,141, 142,171,180,223–230}. Therefore, the mesoporous TiO₂ layer is required to be: (1) unconsolidated to accept perovskite, (2) nanoporous to enlarge the contact area with perovskite to obtain highly efficient charge injection, and (3) defect-free to minimize grain boundaries for the purpose of suppressing charge recombination and trapping¹⁹⁶.

As the thickness of the TiO₂ layer strongly affects the efficiency of mesoscopic PSCs, a submicron thick (200-300 nm) mesoporous TiO₂ layer made from TiO₂ nanoparticles (NPs) with sizes of 20-50 nm is commonly adopted to enhance the electron transportation and minimize the loss of electrons caused by the charge recombination when fabricating PSCs^{141,147,247-249}. While tiny TiO₂ NPs with large surface area possess small pores that will block the effective infiltration of the perovskite, large TiO₂ NPs with better infiltration ability of perovskite normally generate small surface area¹⁹⁶. For this reason, nanoporous TiO₂ spherical structures (SPs) synthesized by different methods^{172-179, 234-237}, which have been applied in dye-sensitized solar cells¹⁸⁸⁻¹⁹⁵ and quantum dots solar cells,^{251,254-257} are introduced to replace TiO₂ NPs in PSCs^{191,196} and reveal superiorities over TiO₂ NPs on both providing large surface area for the deposition of perovskite and generating efficient porous structure for electrolyte diffusion. For example, a notable photovoltaic conversion efficiency (PCE) improvement has been achieved from 14.73% of a 30 nm TiO₂ NPs based PSC to 18.41% of a 100 nm TiO₂ SPs based device.¹⁹⁶ However, the large TiO₂ SPs diameter significantly reduces the contact area between nanoporous TiO₂ SPs and the substrate, which further holds back the electron injection from TiO₂ SPs CB into the substrate. To solve this, mechanical compression treatment, which can increase the inter-particles connection as well as the contact area with the substrate, has been used in dye-sensitized solar cells,^{188,189} but this will cause counteracting of the enlarged pores brought by SPs and potential risk to mechanically damage the compact TiO₂ layer or FTO substrate.

Here, we establish a fabrication method which yields TiO₂ nanoporous hemispheres (NHSs) by electrospraying hydrothermal synthesized TiO₂ NPs suspension solution in a controllable and scalable manner. The “soft” touch of electrosprayed TiO₂ on “hard” FTO/compact TiO₂ substrate automatically forms hemispherical structures. The resulting TiO₂ NHSs are monodispersed with ultra large surface areas and a considerable number of pores to improve the infiltration of the perovskite, and the large surface area increases the contact area between perovskite and TiO₂ NHSs, leading to efficient electron injection. All these properties make them preferable to replace the conventional mesoporous TiO₂ NPs based mesoporous layer. Moreover, TiCl₄ treatment is applied to provide strong interconnectivity among the TiO₂ NPs within the TiO₂ NHS, making the charge transportation through TiO₂ layer more efficient. We demonstrate

that the fabricated TiO₂ layer formed by electrosprayed TiO₂ NHSs greatly enhances the photovoltaic properties of PSCs.

3.2 Fabrication and Characterization

3.2.1 Synthesis of MABr

MABr was synthesized by slowly dropping hydrobromic acid (48 wt% in water, Sigma-Aldrich) into a solution of CH₃NH₂ (33 wt% solution in absolute ethanol, Sigma-Aldrich) at 0 °C.¹¹ The solution was magnetically stirred for 4 hours at room temperature, and followed by rotary evaporation at 50 °C until no obvious liquid remained. The crude solid was then dissolved in small amount of ethanol (Sigma-Aldrich), and reprecipitated by diethyl ether (Sigma-Aldrich) three times. The resulting white solid was collected and dried at room temperature under vacuum for 2 days before using.

3.2.2 Synthesis of TiO₂ Nanoparticles

Titanium isopropoxide (Sigma-Aldrich) was used as the TiO₂ precursor. Acetic acid (Sigma-Aldrich) and nitric acid (Sigma-Aldrich) was used to control the pH (around 1 with roughly 0.1 M H⁺) of the solution, and the solution was transferred to Teflon cups in an autoclave for the following hydrothermal process (240 °C for 15 hours).³⁸ The TiO₂ paste was made by adding 0.65 g TiO₂ nanoparticles and 0.5 g ethyl cellulose (Sigma-Aldrich) into 3.22 mL α -terpineol (Sigma-Aldrich) and 3.22 mL methoxyethanol (Sigma-Aldrich). The paste was then sonicated for 2 hours until a homogenous suspension solution without aggregation was obtained. Next, the TiO₂ paste was diluted by ethanol in a weight ratio of 1:10. The diluted solution was loaded into a plastic syringe which was connected to a high voltage power supply and then electrosprayed directly onto the compact TiO₂ layer.

3.2.3 Fabrication of PSCs

The patterned FTO-coated glass (NSG) was sequentially cleaned using detergent, DI water, acetone (Sigma-Aldrich), isopropanol (Sigma-Aldrich) and finally treated under UV ozone treatment for 10 minutes at 100 °C. A thin compact TiO₂ (C-TiO₂) layer was deposited on top of the cleaned FTO substrate by spin-coating the TiO₂ flat film precursor solution at 6000 rpm for 30 s and dried at 120 °C for 5 minutes in a nitrogen

(N₂) glovebox. Then, it was gradually heated up to 450 °C for 30 minutes in the air. To prepare the TiO₂ flat film precursor solution, titanium isopropoxide (1 mL, Sigma-Aldrich) and 12 M HCl solution (10 µL, Sigma-Aldrich) were diluted in ethanol (10 mL). Then the substrate was treated with a 50 mM TiCl₄ (Sigma-Aldrich) aqueous solution at 80 °C for 20 minutes and followed with annealing at 450 °C for 20 minutes. To prepare the TiO₂ NHSs with a radius of about 200 nm, the electrospraying process was carried out with a commercial electrospinning setup (ET-2535, Ucalery). The electric field of 15 kV was applied between the metal needle and the conducting collector, and the solution feeding rate was controlled by a syringe pump at 0.3 mL/h. The electrospraying process generates droplets and simultaneously applies a charge by means of an electric field. During the electrospraying process, particle stacking proceeds under the forces of the electric field and liquid surface tension. The final shape of the TiO₂ NHSs was controlled by adjusting parameters of electrospraying process, including voltage (15 KV), collecting distance (10 cm), humidity (50%-70%) and feeding rate (0.3 mL/h), to ensure when the droplets reached the collector, the solvent was not evaporated completely. The shape of TiO₂ NHS is therefore deformable, which further leads to a flat contact area with the substrate. The collecting periods are 15 s, 30 s, 60 s and 90 s, respectively. After the electrospraying process, the as-prepared TiO₂ meso-layer was placed on a hot plate and sintered at 500 °C for 20 minutes in the air. Then, the substrate was treated with a 50 mM TiCl₄ (Sigma-Aldrich) aqueous solution at 80 °C for 20 minutes and followed with annealing at 500 °C for 15 minutes. For the fabrication of TiO₂ NPs PSC, a ~180 nm thick TiO₂ NPs layer was deposited on top of the substrate by spin-coating the prepared TiO₂ paste (the other procedures are same with the TiO₂ NHSs PSC). Next, perovskite film was deposited on the substrate by a spin-coating process in glovebox: first, 2000 rpm for 10 s; second, 6000 rpm for 30 s, then chlorobenzene (110 mL, Sigma-Aldrich) was dropped in 8-10 s during the second spin-coating process. The substrate was then heated at 100 °C, 60 minutes. The recipe of the precursor solution was the same with a recent study:¹¹ The precursor solution was prepared by dissolving 0.265 g PbI₂ (TCI), 0.037 g PbBr₂ (TCI), 0.011 g MABr and 0.094 g FAI (Dyesol) in 0.4 mL anhydrous N, N-dimethylformamide (Sigma-Aldrich) and 0.1 mL anhydrous dimethylsulfoxide (Sigma-Aldrich). Spiro-OMeTAD (Merck) was further deposited by spin-coating at 3000 rpm for 30 s. The spiro-OMeTAD solution was prepared by dissolving 74 mg spiro-OMeTAD, 28.5 µL 4-tert-butylpyridine (Sigma-Aldrich), 17.5 µL of a stock solution of 520 mg/mL lithium bis

(trifluoromethylsulfonyl) imide (Sigma-Aldrich) in acetonitrile (Sigma-Aldrich) and 29 μL of a stock solution of 100 mg/mL tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)-cobalt(III) tris(bis(trifluoromethylsulfonyl) imide) (Sigma-Aldrich) in acetonitrile in 1 mL anhydrous chlorobenzene. Finally, 80 nm of gold was deposited as an electrode by thermal evaporation at an average deposition rate of 0.3 $\text{\AA}/\text{s}$. Epoxy was used to protect the fabricated devices from contact with moisture and the encapsulated devices were collected in a dessicator for the stability study.²³⁹

3.2.4 Characterization

J-V characterization was performed in an inert environment (MBraun glovebox, N_2 atmosphere) with a solar simulator (SAN-EI Electric XES-301S 300W Xe Lamp JIS Class AAA) and a Keithley 2400 source meter. The solar cells were masked with metal apertures to define the active areas which were typically 0.09 or 0.08 cm^2 . Incident photon-to-current efficiency (IPCE) as a function of light wavelength was measured in the same glovebox with a customer-made setup consisting of an Oriel 300-W Xe lamp in combination with an Oriel Cornerstone 130 monochromator and an SRS 810 lock-in amplifier (Stanford Research Systems). A calibrated Si diode was used as the reference to calculate the number of photons incident on the device for each wavelength. The IPCE photocurrent was recorded by a Keithley 2400 source meter. The surface and cross-section morphologies of perovskite films and the entire PSC were investigated by using a scanning electron microscope (SEM, JEOL 6340F) at 5 kV. The morphologies of prepared TiO_2 NPs and NHSs were studied by using a transmission electron microscope (TEM, JEOL 2100F) at 200 kV. X-ray diffraction (XRD) experiments were conducted by Shimadzu XRD-6000 X-ray diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). The simulations of optical power distribution within the functional layers were conducted by means of finite-difference time-domain methods (Lumerical FDTD Solutions). The absorption spectra were measured on a PerkinElmer Lambda 950UV/VIS/NIR spectrometer.

3.3 Results and Discussion

3.3.1 Fabrication and Morphology Analysis

In order to study the photovoltaic properties of electrospayed TiO_2 NHSs based PSCs, TiO_2 NPs are firstly synthesized using a hydrothermal method, and then TiO_2 NHSs are fabricated by electrospaying this TiO_2 NPs suspension solution. Figure 3.1 schematically illustrates the fabrication process of both TiO_2 NHSs based PSC and its control group based on conventional TiO_2 NPs.

Figure 3.1 Fabrication process of PSCs.

The TiO_2 NPs are fabricated by a hydrothermal method with titanium isopropoxide as the precursor in an acidic condition ($\text{pH} \sim 1$). The concentration of H^+ in the solution is a critical factor to determine the synthesis product when preparing TiO_2 by hydrothermal reaction. To be specific, when under extreme acidic conditions ($\text{pH} < 0$), rutile TiO_2 is usually formed, while anatase TiO_2 is obtainable under significantly less acid condition ($\text{pH} > 1$).^{246,258–260} So both acetic acid and nitric acid are used in our process to adjust the pH value of the aqueous solution. SEM image (Figure 3.2 a) and

TEM images of different magnifications (Figure 3.2 b and c) present the mesoscopic and morphological structure of the synthesized TiO_2 NPs. Fig. 2b shows a group of TiO_2 NPs with an average size of 30 nm which are well controlled and uniformly distributed. High resolution TEM (Figure 3.2 c) illustrates the crystal structure of the synthesized TiO_2 NPs, which is oriented along [101] direction, similar to some previously reported results.^{259,260} To reveal the structure of the TiO_2 NPs in this study, XRD pattern (Figure 3.2 d) is measured, and the well-resolved diffraction peaks are indexed to (101), (004), (200), (205), (211), (204) and (215), indicating the anatase nature of the synthesized TiO_2 NPs^{196,246,258–260}.

Figure 3.2 a) SEM; b) Low-magnification TEM; c) High-resolution TEM images, and d) XRD pattern of the hydrothermal synthesized TiO_2 NPs. The SEM image a) and XRD spectrum d) were documented from a sample fabricated by spin-coating TiO_2 NPs on top of FTO/C- TiO_2 substrate; to obtain the TEM images, the TiO_2 NPs were deposited on the copper mesh TEM grids for the measurement.

TiO_2 NHSs are fabricated by electrospraying the suspension solution of TiO_2 NPs and then form dense structure due to the evaporation of the solvent. SEM and TEM images of electrosprayed TiO_2 NHSs are shown in Figure 3.3. Compared to TiO_2 spherical structures formed with fully and ultrafast evaporation of solvent during electrospraying,^{188,189} we control both the size and shape of TiO_2 NHSs by adjusting various parameters during the electrospraying process. More precisely, by employing relatively shorter collecting distance, larger feeding rate, and higher humidity, there will

be a small amount of solvent remains within the suspension droplets when they reach the substrate. With the high momentum provided by the electric field, the droplets deform into hemispherical structures with flat surfaces contacting with the substrate.

Figure 3.3 Side view SEM images of a) a single TiO_2 NHS and b) a 60 s collecting time sample on FTO/compact TiO_2 substrate. Plan view SEM images of TiO_2 NHSs c) before and d) after TiCl_4 treatment; TEM images of TiO_2 NHSs e) before and f) after TiCl_4 treatment.

Figure 3.3 a and b clearly show the hemispherical structure of a single TiO_2 NHS and a group of TiO_2 NHSs on top of an FTO/compact TiO_2 substrate. TiO_2 NHSs are highly porous structures, as shown in Figure 3.3 c, which will improve the infiltration of perovskite light-absorber into the mesoporous TiO_2 layer. However, the interconnectivity among the TiO_2 NPs within the electrosprayed TiO_2 NHS is weak, which may suppress the electron transport within the TiO_2 NHSs. So, we utilize dilute TiCl_4 aqueous solution to treat the as-electrosprayed TiO_2 NHSs for the purpose of

improving the interconnectivity of the TiO_2 NPs.^{188,189} Figure 3.3 c and e show the TiO_2 NHSs before TiCl_4 treatment, and Figure 3.3 d and f are the images of TiO_2 NHSs after the treatment. TiO_2 NPs within TiO_2 NHSs after treated with TiCl_4 are connected more strongly than the case before the treatment, which provides a fast transporting channel for photogenerated electrons to transport inside the TiO_2 NHSs.

Figure 3.4 Surface SEM image of $\text{FA}_{0.81}\text{MA}_{0.15}\text{Pb}(\text{I}_{0.836}\text{Br}_{0.15})_3$ film based on a) TiO_2 NHSs and b) TiO_2 NPs layer for the control group. Scale bar is 200 nm. c) Grain size distribution of perovskite film.

The prepared TiO_2 NHSs are then employed to fabricate mesoporous TiO_2 layer. For comparison, the same TiO_2 NPs synthesized by hydrothermal reaction are also applied using the spin-coating method as a control group. Then the $\text{FA}_{0.81}\text{MA}_{0.15}\text{Pb}(\text{I}_{0.836}\text{Br}_{0.15})_3$ layer is deposited on the mesoporous TiO_2 layers by two-steps spin-coating process²³⁹. Figure 3.4 a shows the surface morphology of the prepared $\text{FA}_{0.81}\text{MA}_{0.15}\text{Pb}(\text{I}_{0.836}\text{Br}_{0.15})_3$ layer. Compared to the control group (Figure 3.4 b), the crystal size of $\text{FA}_{0.81}\text{MA}_{0.15}\text{Pb}(\text{I}_{0.836}\text{Br}_{0.15})_3$ film is more uniform on electrosprayed TiO_2 NHSs layer than that on TiO_2 NPs layer. In addition, the average ~ 400 nm $\text{FA}_{0.81}\text{MA}_{0.15}\text{Pb}(\text{I}_{0.836}\text{Br}_{0.15})_3$ crystal size is observed in the TiO_2 NHSs sample, while the average crystal size in TiO_2 NPs sample is ~ 250 nm as Figure 3.4 c shows. The large average crystal size and even size distribution of the deposited $\text{FA}_{0.81}\text{MA}_{0.15}\text{Pb}(\text{I}_{0.836}\text{Br}_{0.15})_3$ on top of the TiO_2 NHSs layer lead to less grain boundaries within the perovskite film, which reduces the recombination and trapping probability in the injection and transportation processes of photogenerated free electrons¹⁹⁶.

XRD spectra (Figure 3.5) shows that the intensities and bandwidths of $\text{FA}_{0.81}\text{MA}_{0.15}\text{Pb}(\text{I}_{0.836}\text{Br}_{0.15})_3$ peaks are not varied due to the change of mesoporous TiO_2 layer, and the characteristic XRD peak positions of the prepared $\text{FA}_{0.81}\text{MA}_{0.15}\text{Pb}(\text{I}_{0.836}\text{Br}_{0.15})_3$ samples are identical with the previous results.²³⁹

Figure 3.5 XRD results of the fabricated $\text{FA}_{0.81}\text{MA}_{0.15}\text{Pb}(\text{I}_{0.836}\text{Br}_{0.15})_3$ films on top of TiO_2 NHSs and NPs layers, respectively.

Next, $\text{FA}_{0.81}\text{MA}_{0.15}\text{Pb}(\text{I}_{0.836}\text{Br}_{0.15})_3$ based PSCs are fabricated as described in Figure 3.1. Figure 3.6 gives the cross-sectional SEM image of the fabricated PSC employing electrosprayed TiO_2 NHSs with the collecting period of 30 s and corresponding device based on conventional meso- TiO_2 layer. The image gives the thicknesses and morphology of each functional layers of the TiO_2 NHSs based device. As demonstrated, the functional layers within the PSC from bottom to top are FTO, compact TiO_2 layer (~ 40 nm), mesoporous TiO_2 layer with $\text{FA}_{0.81}\text{MA}_{0.15}\text{Pb}(\text{I}_{0.836}\text{Br}_{0.15})_3$ (~ 600 nm), HTM (~ 150 nm) and Au electrode (~ 80 nm), respectively. Each layer connects tightly to its adjacent layers, which enables the unimpeded interlayer transport of photogenerated free carriers. From the image, a few TiO_2 NHSs locates above the TiO_2 compact layer and the $\text{FA}_{0.81}\text{MA}_{0.15}\text{Pb}(\text{I}_{0.836}\text{Br}_{0.15})_3$ film shows high crystallinity.

Figure 3.6 Cross-section SEM image of TiO₂ NHSs based PSC and control group.

3.3.2 Devices Performance and Discussion

PSCs with different collecting period of TiO₂ NHSs are fabricated. Figure 3.7 a presents the typical current density-voltage (J - V) curves for these resulting devices.

Figure 3.7 a) J - V curves, and b) IPCE of PSCs with different collecting time of TiO₂ NHSs.

Generally, both the short circuit current density (J_{sc}) and open circuit voltage (V_{oc}) remain at a similar level for PSCs with the TiO₂ NHSs collecting period of 15 s, 30 s and 60 s, but drop remarkably when collecting period reaches 90 s. In addition, the PSC based on 60 s collecting of TiO₂ NHSs (PSC-60 s) offers the best fill factor (FF) of 0.63, while the FF of PSC-90 s is as low as 0.34. Overall, the 60 s TiO₂ NHSs collecting time yields the best PSC with a typical PCE of 16.01%. This is in good agreement with the IPCE measurement (Figure 3.7 b), which also indicates that PSC-60 s can convert photons into electricity more effectively.

To clearly compare the photovoltaic performance of PSC with different collecting period of TiO₂ NHSs, the main photovoltaic parameters (including J_{sc} , V_{oc} , FF , and

PCE) for these devices are plotted in Figure 3.8. It is obvious that the FF of PSC-60 s is superior to other resulting devices in this study, and the PCE indicates that 60 s is the optimum collecting time of efficient PSC based on the proposed electrosprayed TiO_2 NHSs.

Figure 3.8 Main photovoltaic parameters. a) J_{sc} , b) V_{oc} , c) FF and d) PCE for PSCs based on different collecting period of TiO_2 NHSs (15 s, 30 s, 60 s and 90 s). 20 devices are made and tested for each collecting period

This is attributed to the different electron transporting mechanisms within TiO_2 /perovskite heterojunctions, under different TiO_2 NHSs distribution density conditions, as demonstrated in Figure 3.9 (the NHS structure can be clearly seen in Figure 3.10 a). To be more specific, for collecting period of 15 s, 30 s and 60 s, the population of TiO_2 NHSs is small in relative terms of the substrate area, so most of the TiO_2 NHSs are evenly distributed and in a monodisperse state as plotted in Figure 3.9 a-c (the SEM image of 30 s and 60 s collected TiO_2 NHSs is shown in Figure 3.10 b and c, the density of TiO_2 NHSs is <0.1 , $0.1\sim0.5$ and $0.5\sim2$ per square micrometer for 15 s, 30 s and 60 s of collecting time, respectively).

Figure 3.9 Schematic drawing of the TiO₂ NHS dispersion with different collecting time. NHSs distribution status with collecting time of a) 15 s, b) 30 s, c) 60 s, and d) 90 s, respectively, and cross-section schematics for collecting time of e) 60 s and f) 90 s.

In this case, photoinduced electrons generated in perovskite tend to inject into the CB of the nearest TiO₂ NHS, as illustrated in Figure 3.9 e. Electrons transport/inject more efficiently into the TiO₂ CB with more TiO₂ NHSs. Also, the hysteresis effect is significantly minimized within more mesoporous TiO₂ nano structures^{196,239,246}. Thus enhanced J_{SC} and FF can be obtained in the PSC-60 s. But when the TiO₂ NHSs accumulate after a longer time (90 s in this case) when the density becomes relatively large, as illustrated in Figure 3.9 d and f (the SEM image of 90 s collected TiO₂ NHSs

is shown in Figure 3.10 d, the density of TiO_2 NHSs is >2 per square micrometer), TiO_2 NHSs pile up which lead to some non-direct contacts between TiO_2 NHSs and FTO/ TiO_2 compact layer substrate. In this case, some photogenerated electrons have to pass through the interface between upper and lower TiO_2 NHSs before they can finally reach the FTO. As a consequence, the distance, in which electrons need to transport to the substrate, is extended and more free electrons may be annihilated during this period^{196,246,261}, which lead to a reduction in the number of electrons that finally reach FTO. Therefore, the performance of the PSC-90 s is worse than that of the PSC-60 s. And for the same reason, the IPCE curves of the PSCs shown in Figure 3.7 b stay at a similar level when the collecting time is below 60 s, and drop evidently when the collecting time increases to 90 s.

Figure 3.10 SEM images of the prepared TiO_2 NHSs. a) shows the nanoporous structure of the prepared NHS; b) shows the TiO_2 NHSs layer with 30 s collecting time, c) shows the TiO_2 NHSs layer with 60 s collecting time and d) shows the TiO_2 NHSs layer with 90 s collecting time. TiO_2 NHSs pile up with the 90 s collecting time.

As a comparison, anatase TiO_2 NPs prepared by the same hydrothermal method are used in the PSCs with identical device configuration and fabrication process to the TiO_2 NHSs ones, as shown in Figure 3.10. Figure 3.11 a plots the J - V curves for corresponding champion devices based on both TiO_2 NHSs and TiO_2 NPs. It is apparent that most of the photovoltaic parameters of the TiO_2 NHSs based device, including V_{OC} (1.14 V), J_{SC} (23.8 mA/cm^2) and FF (0.71), are superior to the corresponding data (V_{OC}

of 1.12 V, J_{SC} of 22.2 mA/cm² and FF of 0.68) of the TiO₂ NPs counterpart. Thus, the TiO₂ NHSs based device generates a PCE of 19.3%, which is better than the 17.0% efficiency provided by the TiO₂ NPs based device. For the IPCE curves, as shown in Figure 3.11 b, there is an obvious enhanced response in the wavelength range from 500 nm to 760 nm.

Figure 3.11 a) J - V curves and b) IPCE spectra of champion devices fabricated based on TiO₂ NHSs and the control group based on TiO₂ NPs.

Figure 3.12 The simulated optical power distribution at TiO₂/perovskite interface of a) FTO/C-TiO₂/Meso-TiO₂ NPs/perovskite and b) FTO/C-TiO₂/TiO₂ NHS-60 s/perovskite samples; c) the absorption spectra of the FTO/C-TiO₂/Meso-TiO₂/perovskite samples based on TiO₂ NPs and TiO₂ NHSs with different collecting times (30 s, 60 s and 90 s). The FDTD model for a) was set as follows: radius of TiO₂ NHS was 200 nm, distance between two adjacent TiO₂ NHSs centers was 600 nm, and thickness of TiO₂ NHS-60 s/perovskite layer was 600 nm; and for b): thickness of meso-TiO₂ NPs layer was 200 nm and thickness of the perovskite layer was 600 nm, and both input light wavelengths were 700 nm.

This enhancement may be related with optical interference effect caused by TiO₂ NHSs arrays. For $\lambda > 500$ nm the cavity of PSC operates in the low-finesse thin-film interference regime,²⁶² so the TiO₂ NHSs arrays with the dimension of sub-wavelength may cause the interference of input light and generate optical field enhancement within the perovskite layer, which will lead to more efficient light absorption. The FDTD²⁶³

simulations show the difference of optical power distribution at the TiO₂/perovskite interface between NPs based model and NHSs (60 s) based model (Fig. Figure 3.12 a and b), which indicates the effect of optical interference. Optical absorption spectra also show the enhanced light absorption in the FTO/C-TiO₂/TiO₂ NHSs 60 s/perovskite sample (Figure 3.12 c).

Furthermore, little hysteresis^{196,239,246} is found in the $J-V$ curve of the champion device of PSC-60 s (Figure 3.13). A preliminary stability investigation of these PSCs has been operated for 60 days, which shows that the devices stored in the dark at room temperature are relatively stable, with just a 0.7% PCE drop in the entire testing period (Table 3.1).

Figure 3.13 $J-V$ characteristics of the PSC based on TiO₂ NHSs measured under simulated 1 sun condition with forward and backward scans. As for the reverse scan: J_{sc} : 23.8 mA/cm²; V_{oc} : 1.14 V; FF : 0.72 and PCE of 19.6%. Little hysteresis can be seen in this kind of device.

Table 3.1 Photovoltaic parameters for the stability of perovskite solar cell measured under simulated 1 sun (solar cell was encapsulated and stored in a dessicator).

	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	PCE (%)
Initially	1.14	23.8	0.71	19.3
10 days	1.15	23.9	0.71	19.6
20 days	1.14	23.7	0.70	19.1
60 days	1.13	23.6	0.69	18.6

3.3.3 Carrier Behavior Discussion

To study the photogenerated free carrier behavior in the PSC based on 60 s collected TiO₂ NHSs, small perturbation TPV is utilized to observe the fast decay component occurrence within the system with time relaxation constant in the nanosecond (ns) scale.^{264–266} Thus, we operate complementary small perturbation TPVs by using a white light source to vary the back illumination level and a ns-pulsed 532 nm Nd/YAG laser to induce the small voltage perturbations and the results are shown in Figure 3.14.

Figure 3.14 Normalized small perturbation TPVs of the PSC.

The TPVs show one component of the photovoltage decays, lifetime that span from 102 to 174 μ s in a wide back illumination level from 0.8 V to 0.2 V (as summarized in Table 3.2), which is much longer than its mesoporous TiO₂ NPs counterpart (only 4

μs in the back level of 1 V, shown in Figure 3.15). This is ascribed to the increase of the contact area between $\text{FA}_{0.81}\text{MA}_{0.15}\text{Pb}(\text{I}_{0.836}\text{Br}_{0.15})_3$ and TiO_2 . Also, the use of TiO_2 NHSs can further optimize the device structure to obtain the optimal combination of the series resistance and shunt resistance. Thus, the free carriers can transport a longer distance in this TiO_2 NHSs/ $\text{FA}_{0.81}\text{MA}_{0.15}\text{Pb}(\text{I}_{0.836}\text{Br}_{0.15})_3$ heterojunction and this TiO_2 NHSs layer is indeed a good replacement to its predecessor-mesoporous TiO_2 NPs layer in the application of efficient PSCs. Moreover, the obtained lifetime is much longer than that in the typical TiO_2 NPs based $\text{CH}_3\text{NH}_3\text{PbI}_3$ solar cell (3 to 92 μs with the back illumination level 0.7 V to 0.1 V).²⁶⁶ As a result, the free carriers are able to transport a longer distance in this $\text{FA}_{0.81}\text{MA}_{0.15}\text{Pb}(\text{I}_{0.836}\text{Br}_{0.15})_3$ light absorbing layer, compared to the MAPbI_3 layer.

Table 3.2 The lifetime versus voltage parameters extracted from TPV experiment with an error range of $\pm 2\%$.

Back (mV)	200	400	500	800
Lifetime (μs)	174	164	115	102

Figure 3.15 TPV result of the control group device (based on TiO_2 NPs). The TPV lifetime is just 4 μs when the back level is 1 V.

3.4 Conclusion

In summary, we have exploited an electrospray method using hydrothermal synthesized TiO_2 NPs suspension solution to fabricate TiO_2 NHSs with an average radius of ~ 200 nm. The TiO_2 NHSs have been further employed as a mesoporous layer of $\text{FA}_{0.81}\text{MA}_{0.15}\text{Pb}(\text{I}_{0.836}\text{Br}_{0.15})_3$ based PSCs. The detailed electron transporting mechanisms are discussed based on the difference of TiO_2 NHSs distribution densities with various electrospraying collecting time. The PSC with the collecting period of 60 s demonstrates an optimized 19.3% PCE with J_{SC} of 23.8 mA/cm^2 , V_{OC} of 1.14 mV and FF of 0.71, which is superior to the TiO_2 NPs based control group with the champion PCE of 17.0%. TPV measurement indicates that PSC-60 s, compared to the control group adopting 30 nm TiO_2 NPs, exhibits notably efficient carrier injection/transport from $\text{FA}_{0.81}\text{MA}_{0.15}\text{Pb}(\text{I}_{0.836}\text{Br}_{0.15})_3$ to both TiO_2 NHS and HTM layers. This is due to the increase of the contact area between $\text{FA}_{0.81}\text{MA}_{0.15}\text{Pb}(\text{I}_{0.836}\text{Br}_{0.15})_3$ and TiO_2 caused by this unique TiO_2 NHS network and optimized overall device structure.

Chapter 4: Electrospun Hollow Rice Grain-Shaped TiO₂ Nanostructures for High-Efficiency and Large-Area Perovskite Solar Cells

In this chapter, hollow rice grain-shaped highly-porous TiO₂ nanostructures (NSs) with radius of 200–300 nm are fabricated by electrospinning method followed by calcination, and further used for large area PSCs (the active area is 1 cm²) as the mesoporous layer. By varying the spin coating speed (2000 rpm, 4000 rpm and 8000 rpm, respectively), the distribution effect of TiO₂ NSs on performance of PSCs are investigated. Moreover, photoluminescence (PL) measurements and finite-difference time-domain (FDTD) optical simulations are utilized to reveal the enhanced fast charge carrier extraction/transport and light absorption in the proposed system.

4.1 Introduction

Metal halide perovskites, as the emerging light absorbing materials due to their excellent optoelectronic properties, have been applied to various photovoltaic devices in recent years^{130,155,116,171,224,225,229,256–259}. The photovoltaic conversion efficiency (PCE) of perovskite solar cell (PSC) has kept growing and the highest certificated efficiency of single-junction PSC has reached 23.7 %⁹. But the active area of the PSC with the highest PCE is typically less than 0.1 cm², which may cause some potential problems such as measurement contacts, film uniformity, and peripheral effects^{271–274}. Especially, when the active area increases substantially based on the same fabrication technique, the PCE usually drops significantly^{275,276}. So, it is critical to explore new techniques and materials that are suitable for achieving large-area PSCs with high PCE²⁷⁷.

Among the functional layers of a PSC, the mesoporous titanium dioxide (meso-TiO₂) layer plays an important role as an active scaffold for electron transportation from perovskite light-absorber to the outer circuit through its conduction band (CB)^{196,240,241,268}. As an electron transporting path, the mesoporous TiO₂ layer has to meet some requirements, such as providing nanoporous for better infiltration of

perovskite, enlarging the contact area of TiO₂/perovskite, and enabling defects-free to reduce the loss of charge carriers. To meet these requirements, the meso-TiO₂ layer is commonly fabricated using TiO₂ nanoparticles (NPs) with the sizes of around 30 nm for small-area PSCs and the total thickness of an optimized meso-TiO₂ layer is around 200 nm^{84,141,147,247–249,278,279}.

However, the traditional meso-TiO₂ layer constructed by small radius nanoparticles may not be suitable for fabricating large-area PSC, since the surface states generated from a large number of grain boundaries can trap the photogenerated free electrons, resulting in the degraded device performance^{158,159,244,274–277}. Thus, the isolating distributed nanostructures with relatively big TiO₂ nanoparticles can be a potential solution to address this issue to efficiently transport most of the photogenerated free electrons with reduced charge carrier recombination center. Meanwhile, such structure can benefit the adjusting optical power distribution within the system²⁴⁹. Furthermore, electrospinning/electrospray technology has been applied to fabricate meso-TiO₂ layer, as the resulting isolating distributed TiO₂ nanostructures (NSs) offer much reduced grain boundaries, the larger contact area between TiO₂ NSs and the light absorber, and specific electron transport direction^{198,280–283}.

Here, we demonstrate hollow rice grain-shaped TiO₂ NSs with large surface area and abundant nanopores by simple and versatile electrospinning followed with calcination. Then, they are applied to construct the meso-TiO₂ layer of PSCs. The optimized distribution condition of rice grain-shaped TiO₂ NSs is explored and analyzed by various methods including absorption and photoluminescence (PL). To study the optical power distribution and transmittance in different TiO₂/perovskite models, we carried out the finite-difference time-domain (FDTD) optical simulations. And we have observed enhanced light absorption of perovskite film in the rice grain-shaped TiO₂ NSs based sample. The champion PCE of 14.2% is obtained for large area PSC with an active area of 1 cm², increased by about 47.9% compared to 9.6% of its plain counterpart. This improvement is attributed to a combination of multiple reasons, including the reduced grain boundaries (surface states), the large contact area between TiO₂/perovskite and direct transportation introduced by rice grain-shaped TiO₂ NSs. And the minimized nonradiative recombination and trapping of photogenerated carriers and optical adjustment also contribute to the promotion of the performance.

4.2 Fabrication and Characterization

4.2.1 Materials

Unless otherwise specified, all materials were purchased from Sigma-Aldrich. Spiro-OMeTAD was purchased from Merck KGaA. Methylammonium iodide (MAI) was purchased from Dyesol. PbI_2 was purchased from Tokyo Chemical Industry Co., Ltd. (TCI).

4.2.2 Synthesis of Rice Grain-Shaped TiO_2 NSs

To prepare the electrospinning solution, 1.5 g polyvinyl acetate (PVAc, $M_w = 500000$) was dissolved in 10 mL N, N-dimethyl acetamide (DMAc). After magnetic stirred at 60 °C for 6 h, 1 mL titanium isopropoxide (TTIP) and 1.5 mL acetic acid were added into the solution and further stirred for 1 h to acquire a homogeneous solution. Electrospinning process was then carried out with a commercial electrospinning setup (ET-2535, Ucalery). The applied electric field was 20 kV, the distance between needle and collector was 10 cm and the feed rate was 1 mL/h. The as-spun freestanding fiber membrane was carefully peeled off the aluminum substrate, first solidified at 280 °C in the air for 1 h and finally sintered at 500 °C in the air atmosphere for 2 h. Heating rate for both processes was 2 °C/min. Unique rice grain morphology arises from the result of poor solubility of TiO_2 in the PVAc matrix which leads to their micro-phase separation during the solvent evaporation at the initial stages of the solidification process. The resulting hollow rice grain-shaped TiO_2 NSs were manually grinded for better dispensability in ethanol, and polyvinylpyrrolidone (PVP) was used to adjust the viscosity of the TiO_2 paste.

4.2.3 Perovskite Solar Cell Fabrication

FTO glass [Nippon Sheet Glass Co., Ltd.(NSG)] was cleaned with detergent (2% Hellmanex III solution), DI water, acetone, isopropanol (IPA), and dried with clean pure N_2 . The substrate underwent a UV ozone treatment for 10 min at 100 °C prior to deposition of compact TiO_2 layer. A thin (~40 nm) TiO_2 layer was deposited on top of the FTO by spin-coating TiO_2 precursor solution at 5000 rpm for 30 s. Then, it was heated at 450 °C for 30 min in air. The TiO_2 precursor solution was prepared by diluting TTIP (1 mL) and 12 M HCl solution (10 μL) in ethanol (10 mL). Then meso- TiO_2 layer

was deposited by a spin-coating method using the TiO₂ paste prepared above under the speed of 8000, 4000 and 2000 rpm, respectively. The substrate was then annealed at 500 °C for 20 min. Next, perovskite film was deposited on the substrate by a spin-coating process in a glovebox. A mixture of 461 mg of PbI₂, 159 mg of CH₃NH₃I, 78 mg of DMSO (molar ratio 1:1:1) and 600 mg of DMF was prepared at room temperature and stirred for 1 h. The completely dissolved precursor solution was spin-coated on the prepared FTO substrate at 2500 rpm for 35 s when 0.5 mL of diethyl ether was slowly dripped on the rotating substrate in 8 s. The obtained transparent film was then heated at 50 °C for 3 min and 100 °C for 12 min to form a dense CH₃NH₃PbI₃ film. A $\approx$ 150 nm Spiro-OMeTAD (Merck KGaA) layer as the hole transporting material (HTM) was deposited by spin coating at 3000 rpm, 30 s. The spiro-OMeTAD solution was prepared by dissolving 74 mg spiro-OMeTAD, 28.5 μ L 4-tert-butylpyridine, 17.5 μ L of a stock solution of 520 mg mL⁻¹ lithium bis (trifluoromethylsulphonyl) imide in acetonitrile, and 29 μ L of a stock solution of 100 mg mL⁻¹ tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)-cobalt(III) tri s(bis(trifluoromethylsulfonyl) imide) in acetonitrile in 1 mL chlorobenzene. Finally, 80 nm of gold was deposited as an electrode by thermal evaporation with an average deposition rate of 0.3 Å s⁻¹.

4.2.4 Characterization

J-*V* characteristics were measured in the glovebox with a solar simulator (SAN-EI Electric XES-301S 300W Xe Lamp JIS Class AAA) and a Keithley 2400 source meter. The solar cells were masked with metal apertures to define the active areas which were typically 1 cm². IPCE was recorded with a Keithley 2400 source meter combined with an Oriel 300-W Xe lamp, an Oriel Cornerstone 130 monochromator, and an SRS 810 lock-in amplifier (Stanford Research Systems). A calibrated Si diode was used as the reference. The surface and cross-section morphologies of the samples were investigated by a scanning electron microscope (JEOL FESEM 6340F) at 5 kV. The morphologies of the samples were studied using a transmission electron microscope (TEM, JEOL 2010). X-ray diffraction (XRD) experiments were conducted by Shimadzu XRD-6000 X-ray diffractometer with Cu K α radiation (λ = 1.54 Å). The optical absorption spectra were measured on a PerkinElmer Lambda 950UV/VIS/NIR spectrometer and the samples for this study were prepared with the same procedures of device fabrication. PL spectra were recorded by using FluoroMax-4 (HORIBAs industry) and the emission for the number of the absorbed photons at the excitation wavelength has been corrected.

The perovskite samples for PL measurements were fabricated with the same method as solar cell fabrication.

4.2.5 FDTD Simulations

The simulations of optical power distribution and transmittance within the compact-TiO₂/perovskite functional layers with and without rice grain-shaped TiO₂ NSs were conducted by means of FDTD methods (Lumerical FDTD Solutions). The FDTD model was set as follows (the FTO glass substrate, spiro-OMeTAD layer, and gold electrode were not involved in the model for the purpose of reducing the complexity of the system): thickness of compact- TiO₂ was set to 40 nm, thickness of the perovskite layer was 600 nm, and the thickness of the grain-shaped TiO₂ layer was 200 nm. The morphology of the grain-shaped TiO₂ layer was derived from the SEM image. The monitor was placed 200 nm above of the compact TiO₂ layer.

4.3 Results and Discussion

4.3.1 Fabrication and Morphology Analysis

Figure 4.1 schematically illustrates the fabrication process of PSCs using rice grain-shaped TiO₂ NSs as the meso-TiO₂ layer via electrospinning. Firstly, the polyvinyl acetate (PVAc)/ titanium isopropoxide (TTIP) solution was prepared and adjusted to proper viscosity for electrospinning, and acetic acid is added to prevent the TTIP from fast hydrolyzation (more details can be found in Section 4.2.2 Synthesis of rice grain-shaped TiO₂ NSs). The SEM image of the as-spun fibers in Figure4.1 shows the continuity and uniformity with the diameter ranging from 150 nm to 350 nm. The as-spun fibers were solidified at 280 °C and then calcined at 500 °C for an hour to remove all the polymer components. The hollow rice grain-shaped TiO₂ NSs were manually grinded and dispersed into the polymer solution to form a uniform suspension solution which was applied to construct the meso-TiO₂ layer by spin-coating onto the TiO₂ compact layer. Next, the perovskite light absorber (CH₃NH₃PbI₃) and HTM layers were deposited successively, and the gold electrode was finally attached by thermal evaporation.

Figure 4.1 Fabrication of PSC using rice grain-shaped TiO_2 NSs as the meso- TiO_2 layer via electrospinning.

Figure 4.2 is the morphology characterization of the hollow rice grain-shaped TiO_2 NSs. Figure 4.2 a and b are SEM images of the resulting fibers solidified at 280 °C and sintered at 500 °C, respectively. When the as-spun fibers were solidified at 280 °C for 1 h, the rice grain-shaped structures started to form, but the polymer components still remained. After further sintered at 500 °C for 1 h, the polymers were totally removed and only the inorganic rice grain-shaped TiO_2 NSs were kept. As shown in Figure 4.2 b, the resulting hollow NSs can benefit the infiltration of perovskite solution.

Figure 4.2 SEM images of the hollow rice grain-shaped TiO_2 NSs (a) solidified at 280 °C and (b) sintered at 500 °C, low resolution TEM of TiO_2 NSs (c) solidified at 280 °C and (d) sintered at 500 °C, and high resolution TEM of TiO_2 NSs (e) solidified at 280 °C and (f) sintered at 500 °C. Insets are selected area electron diffraction (SAED) patterns.

Figure 4.2 c and d are the corresponding TEM images of TiO_2 NSs obtained under two temperatures, which show that the size of rice grain-shaped TiO_2 NSs is around 500 nm in length and 200~300 nm in diameter. Also, the hollow structure is revealed with a shell thickness around 50 nm. As shown in Figure 4.2 d, the resulting rice grain-shaped TiO_2 NS consists of abundant small TiO_2 crystal grains which makes the structure porous and provides a large contact surface with the perovskite material^{198,282,283},

indicating that this NS is very befitting to fabricate the meso-TiO₂ layer of PSCs. To find out the crystal nature of the NS, Figure 4.2 e and f are the high resolution TEM images of the TiO₂ NSs treated at 280 °C and 500 °C, respectively. In Figure 4.2 e, there are no obvious crystal structures, which means the TiO₂ NSs are in the transformation from an amorphous state to crystalline phase²⁸⁴, while the lattice structure in Figure 4.2 f indicates that the TiO₂ NSs after calcined at 500 °C are in the crystalline anatase state. The selected area electron diffraction (SAED) pattern in the inset also supports this result.

Figure 4.3 SEM images of the distribution of the hollow rice grain-shaped TiO₂ NSs at the spin-coating speed of (a) 8000 rpm, (b) 4000 rpm, and (c) 2000 rpm, respectively. (d) XRD pattern of the spin-coated meso-TiO₂ layer.

Secondly, meso-TiO₂ layer was formed by spin coating hollow rice grain-shaped TiO₂ NSs suspension solution. As illustrated in Figure 4.3, the expected isolating distributed TiO₂ NSs are obtained. To explore the best condition to form this meso-TiO₂ layer, different spin coating speed (8000, 4000, and 2000 rpm, respectively) was adopted to vary the TiO₂ NSs density, as shown in Figure 4.3 a-c. When using higher spin-coating speed, the distribution of rice grain-shaped TiO₂ NSs became more dispersed, while lower spin-coating speed resulted in the denser distribution of the TiO₂ NSs. Figure 4.3 d is the XRD patterns of TiO₂ NS powder and the meso-TiO₂ layer fabricated by different spin coating speeds. The well-resolved diffraction peaks are indexed to

(101), (004), (200), (105) and (211), indicating the anatase nature of the TiO_2 NSs^{196,246,280}, and there is no obvious peak shift when these TiO_2 NSs spin-coated into meso- TiO_2 layer.

Figure 4.4 SEM images of the perovskite layer on top of the meso- TiO_2 layer fabricated at the spin-coating speed of (a) 8000 rpm, (b) 4000 rpm, and (c) 2000 rpm, respectively. (d) XRD pattern of the perovskite layer.

Then, the perovskite layer was deposited on the meso- TiO_2 layer (more details can be found in Section 4.2.3 Perovskite solar cell fabrication). Figure 4.4 shows how the density of rice grain-shaped TiO_2 NSs affects the morphology of the perovskite layer surface. For the perovskite layer based on lower distribution density of rice grain-shaped TiO_2 NSs, the size of perovskite crystal is more uniform, and the surface is smoother. But with the increase of the distribution density, some surface areas start to show smaller perovskite crystal sizes, and even protuberances (indicated with the dotted circles) appear on the perovskite surface. We believe these are caused by the fluctuant underlying surface due to the piled up TiO_2 NSs. In Figure 4.4 d, the XRD patterns of perovskite layers with and without meso- TiO_2 layer are identical¹⁷², except one peak is derived from TiO_2 .

Figure 4.5 Cross-section SEM images of the PSC device structure based on TiO_2 NSs at the spin-coating speed of (a) 8000 rpm, (b) 4000 rpm, (c) 2000 rpm and (d) plain structure.

Next, HTM and gold electrode were attached successively by spin-coating and thermal evaporation, respectively. Figure 4.5 shows the cross-section SEM images of the completed PSC devices based on different distribution densities of the hollow rice grain-shaped TiO_2 NSs. As shown in Figure 4.5 a and b, for low TiO_2 NSs density, the functional layers of a PSC contact seamlessly with each other, which are beneficial for the smooth transportation of photogenerated carriers from the perovskite light absorber to the outer circuit. Furthermore, each layer of the PSC is well controlled in thickness. But the superfluous accumulated TiO_2 NSs shown in Figure 4.5 c brought by the very low spin-coating speed can cause local destruction of the device perfection (compared to the plain device in Figure 4.5 d), which is corresponding to the protuberances in Figure 4.4 c. These micrometer scale local protuberances produce barriers preventing the uniform disperse of the perovskite layer and further the attachment of HTM and gold electrode, which will cause a negative impact on the PSC performance.

4.3.2 Device Performance and Discussion

Figure 4.6 describes the photovoltaic performance of all 4 groups of PSCs based on different distribution densities of the hollow rice grain-shaped TiO_2 NSs. Different spin-coating speeds are used to differ the experimental groups, for example, PSC-2000 rpm represents the PSC based on the meso- TiO_2 layer fabricated using the 2000 rpm spin-coating speed, and PSC-Control is the plain PSC without the meso- TiO_2 layer.

Figure 4.6 (a) J - V curves, (b) average PCE of the control and hollow rice grain-shaped TiO_2 NSs based samples.

Figure 4.6 a presents the typical current density-voltage (J - V) curves of these devices. Despite the short-circuit current density (J_{SC}) of the plain PSC is higher than most PSCs with meso- TiO_2 layer, the highest J_{SC} value is yielded by the PSC-4000 rpm group. While the open circuit voltage (V_{OC}) mainly increases with the distribution density of the hollow rice grain-shaped TiO_2 NSs, only drops when there are too many accumulated TiO_2 NSs. Both the J_{SC} and V_{OC} of the PSC-4000 rpm are superior to other groups. The average PCE shown in Figure 4.6 b also shows the same trend that the PCE keeps increasing with the distribution density of the hollow rice grain-shaped TiO_2 NSs and then drops at the speed of 2000 rpm. The highest average PCE of 12.7% is obtained by the PSC-4000 rpm group.

Figure 4.7 shows the PCE distribution of the best-performed group PSC-4000 rpm. In addition,

Table 4.1 summarizes the photovoltaic parameters of the champion devices from each group. The PSC-4000 rpm yields the highest PCE of 14.2% with the J_{SC} of 21.6 mA, V_{OC} of 1.07 V and fill factor (FF) is 0.61, which is comparable to some previously reported results^{274,277}.

Figure 4.7 PSC-4000 rpm group PCE distribution.

Table 4.1 Photovoltaic parameters of the champion devices of all PSC groups.

	J_{SC} (mA/cm ²)	V_{OC} (V)	FF	PCE (%)
PSC-Control	21.2	0.97	0.47	9.6
PSC-8000 rpm	21.4	0.99	0.55	11.8
PSC-4000 rpm	21.6	1.07	0.61	14.2
PSC-2000 rpm	19.5	1.04	0.61	12.4

Figure 4.8 (a) $J-V$ curves of the champion device based on plain structure, commercial meso-TiO₂, and hollow rice grain-shaped TiO₂ NSs, respectively. (b) XRD pattern of TiO₂ NSs based electron transport layer and the conventional meso-TiO₂ layer, respectively.

Figure 4.8 a provides the $J-V$ curve of the PSC based on meso-TiO₂ layer using conventional TiO₂ NPs with an average size of 30 nm, and the corresponding

photovoltaic parameters are shown in Table 4.2 (XRD spectra are shown in Figure 4.8 b). The performance of TiO₂ NPs based PSC is inferior to the TiO₂ NSs based device for all parameters including J_{SC} , V_{OC} , FF , and PCE, but superior to the plain structure device only except for J_{SC} . This result supports our assumption that compared to uniform meso-TiO₂ layer, isolating distributed TiO₂ NSs with reduced grain boundaries are more suitable for large area PSCs^{285,286}.

Table 4.2 Photovoltaic parameters of champion devices based on plain structure, commercial meso-TiO₂, and hollow rice grain-shaped TiO₂ NSs, respectively

			J_{SC} (mA/cm ²)	V_{OC} (V)	FF	PCE (%)
Hollow rice grain-shaped NS based group			21.6	1.07	0.61	14.2
Conventional meso-TiO ₂ group			20.3	1.00	0.60	12.1
Plain structure control group			21.2	0.97	0.47	9.6

Furthermore, the J - V curves under dark condition is measured and shown in Figure 4.9. The dark current primarily results from the recombination and electron leakage current at the interfaces of the heterojunctions. Larger dark current density suggests that more recombination events occur. So the defect densities within the PSC-4000 rpm device are lower than that of the control device²⁸⁷, which means the rice grain-shaped TiO₂ NSs can help to reduce the recombination centers of the PSC and prevent the recombination of photogenerated carriers.

Figure 4.9. Dark J - V characteristic of the control group and the hollow rice grain-shaped TiO_2 NSs samples, respectively.

The IPCE curves shown in Figure 4.10 a are in good agreement with this trend and the integrated photocurrent that is expected to be generated under AM 1.5G irradiation is shown in Figure 4.10 b. To be specific, the conversion of photons into electricity of PSCs with the meso- TiO_2 layer is more effective at the shorter wavelength region, and the PSC-4000 rpm behaves the best. Also, the hysteresis effect is found insignificant within the PSC-4000 rpm, as shown in Figure 4.11. A preliminary stability investigation of these PSCs has been operated for 60 days, which shows that the device stored in the glovebox at room temperature behaves relatively stable, with just a 1.0% PCE drop in the entire testing period (as Table 4.3 shows).

Figure 4.10 (a) IPCE, of the control and hollow rice grain-shaped TiO_2 NSs based samples. (b) IPCE of PSC-4000 rpm and the integrated photocurrent that is expected to be generated under AM 1.5G irradiation.

Figure 4.11 Hysteresis effect of PSC-4000 rpm device.

Table 4.3 Photovoltaic parameters for the stability of PSC measured under simulated 1 sun (the solar cell was encapsulated and stored in a glovebox).

	J_{SC} (mA/cm ²)	V_{OC} (V)	FF	PCE (%)
Initially	21.6	1.07	0.61	14.2
10 days	21.6	1.07	0.62	14.5
20 days	21.4	1.06	0.60	13.7
40 days	21.2	1.05	0.60	13.5
60 days	19.1	1.05	0.59	13.2

To explore the reasons behind this phenomenon, the absorption spectra were measured, as shown in Figure 4.12, indicating that the PSC based on TiO₂ NSs layer can absorb light more efficiently, which means that more photons are converted into electron-hole pairs and contribute to the generated electricity.

Figure 4.12 Absorption spectra of the control and hollow rice grain-shaped TiO_2 NSs based samples

Furthermore, the PL was tested to analyze the behaviour of the carrier within the TiO_2 /perovskite system⁸⁴. As shown in Figure 4.13 a, the PL intensity of the plain structure based control group is far larger than the meso- TiO_2 layer based samples. This means that the extraction/transport of the photogenerated electron in the TiO_2 compact/perovskite sample is relatively slow, but after the introduction of the grain-shaped TiO_2 NSs layer, the photogenerated electrons can be extracted/transported more easily and lead to higher PCE. Among all the PSCs based on meso- TiO_2 layer, the PSC-4000 rpm shows the lowest PL intensity as the partially enlarged PL spectra, as shown in Figure 4.13 b, which means that the PSC-4000 rpm group exhibits the fastest extraction/transport of electrons.

Figure 4.13 (a) PL spectra and (b) partially enlarged PL spectra of the control and hollow rice grain-shaped TiO_2 NSs based samples

Figure 4.14 can better explain the electron transportation mechanism within the meso- TiO_2 layer based PSCs with different distribution densities of the rice grain-shaped TiO_2 NSs. To be more specific, the distribution density is related to the spin

coating speed. When higher speed is adopted, the distribution of the rice grain-shaped TiO_2 NSs is more dispersed, while lower speed will cause the denser distribution of the rice grain-shaped TiO_2 NSs. The meso- TiO_2 layer plays a role as an active scaffold to enable the electron transportation from the perovskite light absorber to the FTO layer through its conduction band (CB), as shown in Figure 4.14 a. Photoinduced electrons generated in perovskite tend to inject into the CB of the nearest TiO_2 NS and the electrons transport/inject more efficiently into the TiO_2 CB with more TiO_2 NSs, which will reduce the recombination probability, thus enhance the V_{OC} of the device. So, when the population of the hollow rice grain-shaped TiO_2 NSs is small in relative terms of the substrate area, the performance of the TiO_2 NSs based PSCs is enhanced with the increasing quantity of the rice grain-shaped TiO_2 NSs. Thus, the enhanced J_{SC} and FF can be obtained in the PSC-4000rpm. However, when using a lower spin coating speed to fabricate the meso- TiO_2 layer, the hollow rice grain-shaped TiO_2 NSs tend to be denser and start to pile up, resulting in no direct contact with the substrate, as shown in Figure 4.14 b. In this case, some photogenerated electrons must pass through the interface between the upper and lower TiO_2 NSs before they can finally reach the substrate. Therefore, the distance, in which electrons need to transport to the substrate, is extended and more free electrons might be annihilated during this period, which leads to a reduction in the number of electrons that finally reach the outer circuit. Besides, the protuberances in Figure 4.4 c compromise the integrity of the device structure, which also limits the device performance. Therefore, the performance of the PSC-2000 rpm is worse than that of the PSC-4000 rpm. And these reasons also apply to the trend of IPCE curves and PL spectra.

Figure 4.14 Photogenerated electrons transporting mechanism within PSCs based on different hollow rice grain-shaped TiO_2 NS distribution density.

4.3.3 FDTD Simulation

Figure 4.15 Meso- TiO_2 layer model building for FDTD simulation.

FDTD is a commonly used method to explore optical related effect within PSCs²⁷⁸. To further verify the optical power distribution modulation effect of isolated TiO_2 NSs²⁸⁸, FDTD simulations were carried out on the compact- TiO_2 /perovskite models with and

without rice grain-shaped TiO₂ mesoporous layer. The meso-TiO₂ (grain-shaped) model is built based on the area selected from Figure 4.3 b, as shown in Figure 4.15.

Figure 4.16 FDTD simulation results. Simulated optical power distribution within the perovskite layer with incident wavelength at (a, b) 450 nm (c, d) 550 nm and (e, f) 650 nm. (a, c, and e) are PSC-Control device structure and (b, d, and f) are PSC-4000 rpm device structure.

Figure 4.16 shows the simulated optical power distribution at the meso-TiO₂/perovskite interface of rice grain-shaped TiO₂ NSs based model and the identical position in the control model. As can be seen, the introduction of rice grain-shaped TiO₂ NSs caused a remarkable local optical field enhancement (Figure 4.16 b, d, and f) compared to the plain control model (Figure 4.16 a, c and e), especially at shorter incident wavelength region, which is in well agreement with the IPCE results in Figure 4.10 a. This local optical enhancement can benefit the optical absorption of the perovskite layer, as discussed in the previous results^{249,278,288}. And the FDTD simulation result also indicates that the optical transmittance of rice grain-shaped TiO₂ NSs based model at meso-TiO₂/perovskite interface is also better than that of the plain control model as shown in Figure 4.17.

Figure 4.17 Simulated optical transmittance at meso-TiO₂/perovskite interface.

4.4 Conclusion

In summary, we have exploited an electrospinning method using TTIP solution to fabricate the hollow rice grain-shaped TiO₂ NSs with an average diameter of 200-300 nm. The electrospun hollow rice grain-shaped TiO₂ NSs have been further employed as the isolated distributed mesoporous TiO₂ layer of CH₃NH₃PbI₃ based large area PSCs. Detailed electron transportation mechanisms have been discussed based on the difference of TiO₂ NSs distribution condition with various spin-coating speeds. FDTD optical model simulation has been carried out to study the optical power distribution and transmittance in different TiO₂/perovskite models, and enhanced light absorption of perovskite film has been observed in the rice grain-shaped TiO₂ NSs based sample. The PSC-4000 rpm offers an optimized PCE of 14.2% with the J_{SC} of 21.6 mA cm⁻², V_{OC} of 1.07 V and FF of 0.61, which is superior to the plain structure based control group with the PCE of 9.6%. PL spectra indicate that carriers' recombination within the TiO₂/perovskite system with the rice grain-shaped TiO₂ NSs is substantially suppressed, exhibiting notably efficient carrier injection/transportation from the perovskite layer to the carrier transporting layer. This is due to the better infiltration of the perovskite light absorber and the increased contact area between the perovskite and TiO₂ provided by

this unique TiO_2 NSs network and the optimized overall device structure. This work suggests that in the future explorations, various of isolating distributed nanostructures are good choices for the electron transport layer in PSCs.

Chapter 5: Highly Oriented Electrospun P(VDF-TrFE) Fibers via Mechanical Stretching for Wearable Motion Sensing

Advances in functional fabrics enable the realization of wearable smart devices in the form factor of fibers that can be seamlessly adapted in our daily lives. For mechanical-related sensing and power generation, piezoelectric materials are particularly favorable because they can convert mechanical shape changes into electric outputs. Electrospinning is a widely applied technique to produce extended length of fiber-shaped piezoelectric devices. However, this versatile process normally results in randomly distributed fibers with poor electrical properties and limited response to mechanical stimuli.

In this chapter, a stretching induced alignment method is demonstrated to achieve highly oriented electrospun poly[(vinylidene fluoride-co-trifluoroethylene)] P(VDF-TrFE) fibers on a large scale. And both the piezoelectric property and mechanical endurance are investigated. Furthermore, the resulting highly oriented electrospun P(VDF-TrFE) fibers are further twisted into fiber bundles and then woven into a daily outfit. The functional fiber bundles can be used both individually and combinedly to monitor body gestures including angles of elbow bending and directions of the swing arm.

5.1 Introduction

Fibers are one of the most fundamental material forms, made by nature or humans. The integration of materials with disparate electrical or mechanical properties into a single fiber with diverse functionalities presents new opportunities for extending fiber applications in numerous fields, especially the realization of fiber-based wearable electronics^{25,289–295}, apart from their conventional applications as optical devices.^{296–301} Among all the applicable functional materials, piezoelectric materials, which can convert mechanical shape changes into electric outputs, are particularly favorable to

fabricate wearable devices for mechanical related sensing and power generation.^{302–304} According to material molecular compositions, piezoelectric materials are generally divided into ceramics and polymers. Indeed, even though inorganic piezoelectric materials offer high piezoelectric property, they are mechanically hard and brittle, which have difficulties to be directly applied to wearable devices. Besides, many piezoelectric ceramics contain heavy metal elements such as lead, that are harmful to human and environment.^{305–307} On the other hand, piezoelectric polymers, represented by polyvinylidene fluoride (PVDF) and its copolymer poly[(vinylidene fluoride-co trifluoroethylene) (P(VDF-TrFE))], are more preferable for wearable devices as they are lightweight, stretchable, environment-friendly and chemically stable.^{308,309}

To construct piezoelectric polymer fibers, electrospinning, as a representative template-free method,^{310,311} is a versatile technique to produce an extended length of fiber-shaped structures with a number of advantages such as large surface area, tunable surface morphologies, and enhanced mechanical performance.^{172,280,312,313} With electrospinning, when the droplet of the polymer solution is charged by the high applied voltage, the liquid droplet is pulled into a thin fiber and then collected by the grounded electrode. However, this liquid-to-solid transferring process normally results in randomly distributed fibers with poor electrical properties and limited response to mechanical stimuli. Therefore, to improve the performance of electrospun fibers, several methods have been demonstrated to obtain aligned electrospun fibers^{52,314–317} as discussed in Section 2.1.2. Two most frequently adopted methods are: (1) using a high-speed rotating collector with a very sharp edge,^{42,43,50} and (2) using two separated parallel electrodes.^{51,318} A very high rotating speed (>3000 rpm) is necessary for the rotating collector method, which brings high requirements to the fabrication facilities and increases electricity consumption. Also, the necessary role of sharp edge further restricts the amount of highly aligned electrospun fibers that can be collected. The parallel electrode method, on the other hand, can only fabricate aligned electrospun fibers in a very limited length, typically on the millimetre scale.

In this chapter, we demonstrate a simple dynamical mechanical stretching process that enables the formation of large-scale highly oriented electrospun P(VDF-TrFE) fibers obtained under low rotation speed. As a result, these globally parallel fibers exhibit enhanced mechanical and piezoelectric properties. Furthermore, the resulting

fibers are twisted into fiber bundles and then woven into a daily outfit for body motion sensing.

5.2 Fabrication and Characterization

5.2.1 Materials

Unless specified, all materials are from Sigma-Aldrich. 15 wt% P(VDF-TrFE) (Piezotech, 70/30, Mw 450,000.) solution is prepared by adding 1.5 g P(VDF-TrFE) in 10 mL mixed organic solvent (Dimethylacetamide (DMAC)/acetone = 3/7), magnetic stirred at 75 °C for an hour, and then cooled down to room temperature to obtain a homogenous clear solution.

5.2.2 Fabrication of Electrospun P(VDF-TrFE) Fibers

Figure 5.1 Schematic of the electrospinning process.

Figure 5.1 illustrate the schematic diagram of a far-field electrospinning process. During the electrospinning process, a high static voltage is applied between the metal needle and the collector to generate a strong electric force that draws charged droplets of P(VDF-TrFE) solution into thin fibers. Different from a conventional electrospinning setup with a flat collector, we use a low speed rotating drum wrapped with aluminum foil as the collector. P(VDF-TrFE) solution is prepared and transferred into a syringe, and then loaded in electrospinning setup (ET-2535, Ucalery). The electrospinning process is conducted with an applied voltage of 20 kV, the feed rate of 2 mL/h. The

distance between needle tip and the collector is 10 cm, and the rotating speed of collecting drum is fixed at 300 rpm. A dehumidifier is used to accelerate the solvent evaporation.

The as-spun P(VDF-TrFE) thin film consists of fibers with an average diameter of 1.1 μm is shown in Figure 5.2 which is very flexible and can be wrapped on different curved surfaces.

Figure 5.2 As-spun flexible P(VDF-TrFE) thin film and the corresponding SEM image.

5.2.3 Dynamical Mechanical Stretching

Electrospinning is a simple and scalable way to fabricate P(VDF-TrFE) fibers for piezoelectric applications because this process can eliminate the need for direct contact poling or corona poling to induce spontaneous dipolar orientation.³¹⁹ The piezoelectric charge coefficient d , defined as the ratio of the change in polarization to the change in applied pressure, is given by

$$d_{3j} = \frac{\partial P}{\partial \sigma_j} = \frac{1}{A} \left[\frac{\partial}{\partial \sigma_j} \left(\frac{\mu}{z} \right) \right] = \frac{1}{A} \left[\frac{\partial \mu}{\partial \sigma_j} \left(\frac{1}{z} \right) - \frac{\mu}{z^2} \frac{\partial z}{\partial \sigma_j} \right] = P \left[\frac{\partial \ln \mu}{\partial \sigma_j} - \frac{\partial \ln z}{\partial \sigma_j} \right]$$

where $P = \frac{\mu}{V} = \frac{Q}{A}$ represents the polarization, μ is the total dipole moment, V is the volume of the fiber with surface area A , and Q is the magnitude of the surface charge given by $Q = \frac{\mu}{z}$, z is the thickness. When $j = 1$ the stress is normal to the fiber direction and when $j = 3$ the stress is along the fiber direction. Thus, the piezoelectric output voltage can be expressed as follows³²⁰

$$V_{33} = \frac{\sigma_3 d_{33} t}{\epsilon_0 \epsilon^T}$$

where σ_3 is the mechanical stress component along fiber direction, t is the distance between two electrodes, ε_0 is the permittivity of vacuum, and ε^T is the relative permittivity under constant stress. And

$$V_{31} = \frac{\sigma_1 d_{31} t}{\varepsilon_0 \varepsilon^T}$$

where σ_1 is the stress component normal to the fiber direction.

Therefore, the total induced an open-circuit output voltage V_{OC} from the electrospun fiber under stretching is

$$V_{OC} = V_{33} + V_{31} = (\sigma_3 d_{33} + \sigma_1 d_{31}) \frac{t}{\varepsilon_0 \varepsilon^T}$$

Because for P(VDF-TrFE) the d_{33} value is larger than d_{31} , the maximum value of V_{OC} is obtained when all the fibers are aligns along the stress direction, which means make full use of d_{33} . In our case, to stretch P(VDF-TrFE) fibers enables the alignment of these fibers to along the stress direction, thus achieving an enhanced piezoelectric response.

Since the drum is rotating while collecting, the as-spun fibers fallen on the surface of the collector possess similar initial orientations along the rotating direction. Meanwhile, the as-spun P(VDF-TrFE) fibers still contain some residual solvent, thus they are easy to deform under applied external force.³²¹ The electrospun P(VDF-TrFE) thin film is then peeled off the aluminum foil and mounted in the clamps of a linear travel stage driven by a controller for the following mechanical stretching process, as shown in Figure 5.3. The drawing velocity is precisely controlled at 2 mm/s. As a result, the initial orientations can be globally unified, which leads to the realignment of a large amount of electrospun P(VDF-TrFE) into highly oriented fiber bundles.

Figure 5.3 Mechanical Stretching process of electrospun P(VDF-TrFE) fibers.

As shown in Figure 5.4 a, this mechanical stretching process is so simple and feasible that could be completed without the assistance of any equipment. The proportion of parallel aligned electrospun P(VDF-TrFE) fibers increases with the extension of the sample, eventually reaching a globally aligned state for the entire sample, as SEM images shown in Figure 5.4 b.

Figure 5.4 Images of electrospun P(VDF-TrFE) fibers during mechanical stretching process under axial stress (scale bar is 5 μm).

To explore the best condition for this mechanical stretching process, we also investigate the temperature effect on the stretching process. We have measured the average force needed to achieve the same align proportion of the samples under different temperatures. As the results shown in Figure 5.5, a larger force is required to conduct

the stretching process for electrospun fibers at higher processing temperature to achieve the same align proportion. This is due to the fact that the easy deformation caused by the stretching process is mainly due to the residual solvent within the as-spun P(VDF-TrFE) fibers as we have discussed above. But, at a higher processing temperature, the evaporation of residual solvent becomes faster, which makes these fibers harder to be stretched to achieve the same align proportion processed at a lower temperature.

We can use the Antoine equation, which is a mathematical expression of the relation between the vapor pressure of the solvent and the temperature, to explain how temperature affects the solvent evaporation

$$\log P = A - \frac{B}{T}$$

where P is the absolute vapor pressure, T is the temperature, A and B are material-related coefficients. So the higher the temperature is, the higher the vapor pressure will be, and the faster the solvent will evaporate.

Figure 5.5 Average applied force for stretching electrospun fiber after treated by different temperature.

5.2.4 Characterization

To better observe the stretching-induced alignment processing, organic dyes (Rhodamine 590 Chloride, Exciton) are doped into P(VDF-TrFE) solution, and

fluorescence images of the electrospun P(VDF-TrFE) fibers are obtained by using Olympus fluorescence microscope with a 100 W mercury lamphouse and a U-MWGS3 mirror cube. Scanning electron microscope (SEM) images are obtained using a field emission SEM (FESEM 6340F) at 5 kV, and X-ray diffraction (XRD) experiments are conducted by a Shimadzu XRD-6000 X-ray diffractometer with Cu K α radiation ($\lambda = 1.54 \text{ \AA}$). The mechanical property of the electrospun P(VDF-TrFE) fibers is measured by a force meter (YISIDA, DS2-5N) while extending by the same linear travel stage at a constant speed of 1 mm/s. The aligned P(VDF-TrFE) fibers are twisted into fiber bundles manually and woven into a sweater and a sports suit. Both the bending response and the real-time motion monitoring signal are measured by a Keithley 6517B electrometer/high resistance meter and data is recorded by customized software.

5.3 Results and Discussion

5.3.1 Material Property

Figure 5.6 XRD patterns of electrospun P(VDF-TrFE) fibers before and after mechanical stretching process.

To verify that P(VDF-TrFE) in the fibers is indeed in the ferroelectric phase, X-ray diffraction (XRD) patterns of the electrospun P(VDF-TrFE) fibers before and after the stretching process are shown in Figure 5.6, and fitting of the patterns can reveal the quantification of each phase (shown in Figure 5.7).³²²

Figure 5.7 XRD peaks fitting of electrospun P(VDF-TrFE) fibers.

Both samples exhibit identical peaks at $2\theta = 17.14^\circ$ corresponding to (200)/(110) peak of the α -phase, $2\theta = 19.98^\circ$ corresponding to (200)/(110) peak of the β -phase, and $2\theta = 18.73^\circ$ corresponding to an amorphous phase, respectively. These results show that the electrospun P(VDF-TrFE) fibers consist of both paraelectric and ferroelectric crystal forms as well as a small amount of amorphous phase, but the ferroelectric β -phase is a majority (>60%), thus confirming the piezoelectric property of this electrospun P(VDF-TrFE) fiber. The piezoelectric coefficient d_{33} is measured using an atomic force microscopy (AFM, Asylum MFP-3D) with PFM mode, the measured d_{33} value is -25.3 pm/V, which is similar as previously reported results.³²³

5.3.2 Stretching Analysis

Figure 5.8 Fiber distribution at different stages of the mechanical stretching process (scale bar is 50 μm). The percentage value in each image indicates the aligned fiber proportion.

To better observe the stretching-induced alignment process, a small number of organic dyes (RH590) are doped into the P(VDF-TrFE) solution and then fabricated into electrospun P(VDF-TrFE) fibers. The organic dyes emit red light when illuminated by a light source with a wavelength of 532 nm due to its fluorescence effect. Figure 5.8 is the fluorescence optical microscope images of electrospun P(VDF-TrFE) fiber films at different stages of mechanical stretching. As revealed in Figure 5.8 a, the distribution of as-spun P(VDF-TrFE) fibers is extremely random that it is very difficult to indicate the major orientation of these fibers. However, with the mechanical stretching process proceeding, the P(VDF-TrFE) fibers begin to show different levels of unified orientation towards the direction of stretching, as shown in Figure 5.8 b and c. When the mechanical stretching process is completed, the majority of the electrospun P(VDF-TrFE) fibers are aligning in a highly paralleled way, as illustrated in Figure 5.8 d.

To quantify the alignment level of electrospun P(VDF-TrFE) fibers, we use aligned fiber proportion. To be more specific as long as the orientation of a fiber falls in the range from -5° to $+5^\circ$ to a certain direction, this fiber is regarded as along this certain direction, as indicated in Figure 5.9.

Figure 5.9 Direction definition of P(VDF-TrFE) fibers.

Based on this, we can define the aligned fiber proportion as the ratio of the fiber population with a certain direction to the total fiber population (shown as Figure 5. 10).

Figure 5. 10. Quantity and proportion of different fiber status at different stages of the stretching process.

Next, the aligned fiber proportion is calculated at different stages of mechanical stretching process of the electrospun P(VDF-TrFE) fiber by counting both the aligned fiber number and the total number, and the result is shown in Figure 5. 11. The distribution of as-electrospun P(VDF-TrFE) fibers is random that we can hardly find a certain direction of the fibers. If the electrospun P(VDF-TrFE) fibers are completely random, the theoretical value of the aligned fiber proportion in any direction should be $\sim 5\%$ (10° out of 180° totally). But the average aligned fiber proportion along the drum rotating direction is $\sim 10.3\%$ which is slightly higher due to the fact that the drum is rotating while collecting. After being stretched along the rotating direction, the aligned fiber proportion has substantially increased to $\sim 38.4\%$ at stage 2 (stretched to 150% of its original length) and $\sim 78.6\%$ at stage 3 (stretched to 200% of its original length). Finally, a highly aligned fiber proportion of $\sim 91.4\%$ is achieved globally when stretched to 400 % of its original length.

Figure 5. 11 Aligned proportions of different experimental groups.

5.3.3 Mechanical and Electrical Characterization

To investigate the effect of mechanical stretching process on mechanical property of electrospun P(VDF-TrFE) fibers, the strain and stress curves are measured as plotted in Figure 5.12. With the increasing of aligned fiber proportion, the electrospun P(VDF-

TrFE) fibers can withstand larger external stress under the same strain, which means the shape change of better aligned electrospun P(VDF-TrFE) fibers is smaller than its random distributed counterpart under the same applied tension. This advantageous mechanical property makes highly aligned P(VDF-TrFE) fibers more suitable for wearable motion sensors.

Figure 5.12 Strain and stress curve of electrospun fiber at different aligned proportions

But electrospun P(VDF-TrFE) fibers with alignment proportion exceeding 90% show poorer mechanical endurance. This is because, when the aligned fiber proportion is high (>80%), most of fibers are well aligned and under a tightened status (as Figure 5.13 a shows). When further processed by stretching to increase the aligned proportion, tightened fibers start to break up (as Figure 5.13 b shows), which will weaken the mechanical endurance of the electrospun fibers. So the mechanical property of extremely paralleled electrospun P(VDF-TrFE) fibers is inferior to that of ~80% aligned counterpart, which means the upper limit of stretching of fibers shall be when aligned fiber proportion is around 80%. Therefore, the stress drops sharply for G4 when the strain exceeds 150%.

Figure 5.13 SEM image of (a) ~80% aligned electrospun P(VDF-TrFE) fibers and (b) ~90% aligned electrospun P(VDF-TrFE) fiber.

Then, the electrical property is characterized by applying external periodical positive and negative forces (shown in Figure 5.14) and then measuring the corresponding output voltage. Figure 5.15 a is the output voltage curve of electrospun P(VDF-TrFE) fibers with different aligned fiber proportions. These curves indicate that at the beginning, the electrical respond increases with the increase of aligned fiber proportion.

Figure 5.14 (a) Loose and (b) bending state of aligned P(VDF-TrFE) fibers.

Figure 5.15 (a) Voltage output curves and (b) average output of four groups of aligned proportions

This trend is well agreed with the simulation study using finite-element method (COMSOL). Figure 5.16 shows the voltage potential distribution of both well-aligned and nonaligned P(VDF-TrFE) fibers under a bending deformation caused by same displacement, respectively. The output voltage of well-aligned P(VDF-TrFE) fibers is 522.9 V, higher than its nonaligned counterpart (457.3 V).

Figure 5.16 Simulated output of (a) aligned and (b) non-aligned electrospun P(VDF-TrFE) fiber.

However, when the electrospun P(VDF-TrFE) fibers become highly paralleled (aligned fiber proportion $> 80\%$), the output would drop. As summarized in Figure 5.15 b about the average output regarding the aligned fiber proportion, the highest output of

84.92 mV is achieved by P(VDF-TrFE) fibers with ~80% aligned proportion, about 266% of their randomly distributed counterpart (31.92 mV).

This is because, for randomly distributed fibers, the increase in fiber alignment proportion is mainly attributed to the stretch of originally coiled fibers from the electrospinning process (Figure 5.8 a), while highly aligned fibers (aligned fiber proportion >80%) start to break when the strain is further increased as observed in Figure 5.13 b. This leads to the decrease in the voltage output.

5.3.4 Applications in Wearable Motion Sensing

To use the resulting 80% aligned P(VDF-TrFE) fibers as wearable sensors, they are further twisted into bundles and yarns. Figure 5.17 illustrates the details of these P(VDF-TrFE) fiber bundles and the way they are woven into fabrics acting as motion sensors. From the SEM image in Figure 5.17, the P(VDF-TrFE) fibers within each bundle are highly parallel to each other and following the twisting direction, which provides the enhanced performance in both mechanical and electrical aspects due to their highly oriented nature and efficient signal conduction.³¹³

Figure 5.17 Twisted electrospun P(VDF-TrFE) fiber bundle woven into an outfit.

To demonstrate the motion sensing function, we firstly use a single P(VDF-TrFE) fiber bundle to monitor the bending angle of the elbow. Figure 5.18 a shows the three different bending angles of the elbow, 45°, 90°, and 135°, which are three representative gestures, respectively. At each angle, the elbow repeats to bend and extend periodically. The corresponding voltage signals are plotted in Figure 5.18 b and c, and the average output is 10.6 mV, 20.3 mV, and 42.5 mV, respectively. The reason that the responding output is not increasing linearly with the elbow bending angle is that, with the increasing of the bending angle, the functioning length of the P(VDF-TrFE) fiber bundle also increases, leading to a higher output voltage under 135° bending angle. These results

prove that the change of gesture can be reconstructed using a single wearable P(VDF-TrFE) fiber bundle. The detection limit of this single P(VDF-TrFE) fiber bundle based gesture sensor is less than few degrees, mainly due to the way that fiber bundle is integrated into the outfit.

Figure 5.18 (a) Monitoring different bending angles of elbow movement (45°, 90°, and 135°) using twisted P(VDF-TrFE) fiber bundle. (b) Corresponding voltage outputs and (c) their average values.

Furthermore, multiple P(VDF-TrFE) fiber bundles can be used in a combined way to monitor the direction of the arm swing. As demonstrated in Figure 5.19 a, two P(VDF-TrFE) bundles are woven separately into the front side and back side of a sportswear's shoulder parts. When the demonstrator's arm is swing backward, the P(VDF-TrFE) bundle attached to the front side is stretched and the one on the back side is loose. So, a signal pulse generated by the front side bundle indicates the backward direction of the swing. Similarly, the forward direction of swing is recorded by the back side bundle, as shown in Figure 5.19 b. The average voltage outputs of backward and forward motion are 8.87 mV and 8.38 mV, respectively. The slight difference is due to the motion-induced distinction between backward and forward swings. Therefore, together with the sensing of bending angle of the elbow, these wearable P(VDF-TrFE) fiber bundles can be woven into multi-dimensional fabrics to achieve gesture recognition, such as motion-tracking technology for virtual reality (VR).

Figure 5.19 (a) Two directions of the arm swing (forward and backward) and (b) their corresponding voltage outputs.

5.4 Conclusion

In summary, we have developed a stretching-induced alignment method to fabricate highly oriented electrospun P(VDF-TrFE) fibers on a large scale. These globally aligned electrospun P(VDF-TrFE) fibers exhibit an enhanced piezoelectric property. The average output voltage of 80% aligned electrospun P(VDF-TrFE) fibers is 84.96 mV, about 266% of their original randomly distributed counterpart. Also, highly oriented electrospun P(VDF-TrFE) fibers possess better mechanical endurance. When woven into an outfit, the aligned electrospun P(VDF-TrFE) fiber bundle can work both individually and combinedly to monitor body gestures including angles of elbow bending and directions of the swing arm, which may lead to the further development of motion-tracking technology.

Chapter 6: Conclusion and Future Work

6.1 Conclusion

In this project, we have applied electrospinning technique to the solar energy harvesting and motion sensing for wearable smart devices.

The first contribution is to exploit an electrospray method to fabricate TiO_2 NHSs with an average radius of ~ 200 nm. The TiO_2 NHSs have been further employed as a mesoporous layer of $\text{FA}_{0.81}\text{MA}_{0.15}\text{Pb}(\text{I}_{0.836}\text{Br}_{0.15})_3$ based PSCs. The detailed electron transporting mechanisms are discussed based on the difference of TiO_2 NHSs distribution densities with various electrospraying collecting time. The PSC with the collecting period of 60 s demonstrates an optimized 19.3% PCE with J_{SC} of 23.8 mA cm^{-2} , V_{OC} of 1.14 mV and FF of 0.71, which is superior to the TiO_2 NPs based control group with the PCE of 17.0%. TPV measurement indicates that PSC-60 s, compared to the PSC from control group adopting 30 nm TiO_2 NPs, exhibits notably efficient carrier injection/transport from $\text{FA}_{0.81}\text{MA}_{0.15}\text{Pb}(\text{I}_{0.836}\text{Br}_{0.15})_3$ to both TiO_2 NHS and HTM layers. This is due to the increase of the contact area between $\text{FA}_{0.81}\text{MA}_{0.15}\text{Pb}(\text{I}_{0.836}\text{Br}_{0.15})_3$ and TiO_2 caused by this unique TiO_2 NHS network and optimized overall device structure.

The second contribution is to exploit an electrospinning method using TTIP solution to fabricate the hollow rice grain-shaped TiO_2 NSs with an average diameter of 200-300 nm. The electrospun hollow rice grain-shaped TiO_2 NSs have been further employed as the isolated distributed mesoporous TiO_2 layer of $\text{CH}_3\text{NH}_3\text{PbI}_3$ based large area PSCs. Detailed electron transportation mechanisms have been discussed based on the difference of TiO_2 NSs distribution condition with various spin-coating speeds. FDTD optical model simulation has been carried out to study the optical power distribution and transmittance in different TiO_2 /perovskite models, and enhanced light absorption of perovskite film has been observed in the rice grain-shaped TiO_2 NSs based sample. The PSC-4000 rpm offers an optimized PCE of 14.2% with the J_{SC} of 21.6 mA cm^{-2} , V_{OC} of 1.07 V and FF of 0.61, which is superior to the plain structure based control group with the PCE of 9.6%. PL spectra indicate that carriers' recombination within the TiO_2 /perovskite system with the rice grain-shaped TiO_2 NSs is substantially suppressed,

exhibiting notably efficient carrier injection/transportation from the perovskite layer to the carrier transporting layer. This is due to the better infiltration of the perovskite light absorber and the increased contact area between the perovskite and TiO_2 provided by this unique TiO_2 NSs network and the optimized overall device structure. This work suggests that in the future explorations, various of isolating distributed nanostructures are good choices for the electron transport layer in PSCs.

The third contribution is to develop a stretching-induced alignment method to fabricate highly oriented electrospun P(VDF-TrFE) fibers on a large scale. These globally aligned electrospun P(VDF-TrFE) fibers exhibit an enhanced piezoelectric property. The average output voltage of 80% aligned electrospun P(VDF-TrFE) fibers is 84.96 mV, about 266% of their original randomly distributed counterpart. Also, highly oriented electrospun P(VDF-TrFE) fibers possess better mechanical endurance. When woven into an outfit, the aligned electrospun P(VDF-TrFE) fiber bundle can work both individually and combinedly to monitor body gestures including angles of elbow bending and directions of the swing arm, which may lead to the further development of motion-tracking technology.

6.2 Recommendation for Future Work

In the future work, we plan to continue on the following two projects:

1. Explore electrospun isolating distributing metal oxide nanostructures as the mesoporous layer of large area PSCs. As we have discussed in Chapter 3 and 4, the traditional meso- TiO_2 layer constructed by small radius nanoparticles has its limitation for fabricating large-area PSC as the surface states generated from a large number of grain boundaries can trap the photogenerated free electrons, resulting in the degraded device performance. On the other hand, the isolating distributed nanostructures consisting of relatively big TiO_2 nanoparticles with reduced grain boundaries, larger contact area which can decrease the charge carrier recombination center, can address this issue for efficient transport of the photogenerated free electrons. Furthermore, such optical wavelength-scale

structure can adjust optical power distribution within the system, thus benefit the optical absorption. So in the future, we plan to utilize the electrospinning method for fabrication of the multiple metal oxide materials used for large area PSCs, such as SnO_2 , SiO_2 , and ZnO besides TiO_2 , to further improve the performance and PCE of large area PSCs, in seek of better commercialization of photovoltaic devices.

2. Investigate multifunctional electrospun polymer nanofibers for wearable smart devices. As we have discussed in Chapter 1, a wearable smart device must possess multiple functions simultaneously for a better monitor of body status. So besides the motion sensing function using piezoelectric polymer, we are expecting to integrate multiple functions within a single device using multiple functional materials. For example, using thermoelectric materials for harvesting energy from body heat and measuring the body temperature. In our previous work, we have investigated inorganic thermoelectric materials like p-type $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ and n-type Bi_2Se_3 ³²⁴ and organic thermoelectric materials like PEDOT:PSS polymer³²⁵, and we also tried to combine the organic and inorganic materials together to utilize the flexibility of polymer while using the inorganic thermoelectric materials to enhance the thermoelectric property³²⁵. In the future, we plan to use electrospinning technique to process the thermoelectric polymer materials and we can also introduce inorganic nanoparticles during the processing to improve the thermoelectric response. Figure 6.1 is our initial attempt to fabricate PEDOT:PSS nanofibers using electrospinning method.

Figure 6.1 (a) Photo, (b,c) optical images and (d) SEM images of electrospun PEDOT:PSS/PVA nanofibers.

Publication List

Journals

- **S. Ma**, T. Ye, T. Wu, Z. Wang, Z. Wang, S. Ramakrishna, C. Vijila, and L. Wei, Hollow rice grain-shaped TiO₂ nanostructures for high-efficiency and large-area perovskite solar cells, *Solar Energy Materials and Solar Cells* 191, 389-398 (2019).
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Conferences

- **Ma S**, Ye T, Wei L. Electrospayed TiO₂ nanoporous hemisphere arrays for enhanced efficiency of perovskite solar cells[C]// Conference on Lasers and Electro-Optics (CLEO), 2017 San Jose, US. (oral presentation)
- **Ma S**, Wei L. Electrospun PVDF Nanofiber Mat with Additional BaTiO₃ Nanoparticles Used as Dynamic and Static Piezoelectric Sensor[C]// Pacific Rim Conference on Lasers and Electro-Optics (CLEO-PR), 2017 Singapore. (poster presentation)
- **Ma S** and Wei L. Mechanical Induced Aligned P(VDF-TrFE) Fibers via Electrospinning for Wearable Motion Sensing. Materials Research Society (MRS) Fall Meeting & Exhibit, 2018 Boston, US. (poster presentation)

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