1D fiber/yarn supercapacitors for wearable energy storage

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**1D FIBER/YARN SUPERCAPACITORS FOR WEARABLE
ENERGY STORAGE**

ZHAI SHENGLI

**SCHOOL OF CHEMICAL AND BIOMEDICAL ENGINEERING
NANYANG TECHNOLOGICAL UNIVERSITY**

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1D Fiber/Yarn Supercapacitors for Wearable Energy Storage

Zhai Shengli

School of Chemical and Biomedical Engineering

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List of abbreviation

1D	one-dimensional
2D	two-dimensional
3D	three-dimensional
AFM	atomic force microscopy
CNT	carbon nanotube
CV	cyclic voltammetry
DH	double hydroxide
EDLC	electrical double layer capacitor
EDS	energy-dispersive X-ray spectroscopy
ESR	equivalent series resistance
eV	electron voltage
FESEM	field emission scanning electron microscopy
F/YSC	fiber/yarn supercapacitor
FMSC	fiber micro-supercapacitor
GCD	galvanostatic charge/discharge
GO	graphene oxide
HGO	holey graphene oxide
LED	light-emitting diode
Li-ion	lithium-ion
MSCs	micro-supercapacitors
MWCNT	multi-walled carbon nanotube
NW	nanowire

PANI	polyaniline
PEDOT	poly (3, 4-ethylenedioxythiophene)
PET	polyethylene terephthalate
PPy	polypyrrole
PSS	poly(styrenesulfonate)
PVA	polyvinyl alcohol
Reference	Ref.
rGO	reduced graphene oxide
SWCNT	single-walled carbon nanotube
SEM	scanning electron microscope
TEM	transmission electron microscope
TGA	thermogravimetric analysis
TMD	transition metal dichalcogenide
TMH	transition metal hydrate
TMN	transition metal nitride
TMO	transition metal oxide
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
YSC	yarn supercapacitor

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Abstract

With the fast development of wearable electronics, there is an urgent demand for advanced wearable energy storage devices, which are stable, long-lasting, flexible, wearable, and safe to fulfil the requirements of emerging wearable electronics. As a new family of supercapacitors, fiber/yarn supercapacitors (F/YSCs) with one-dimensional (1D) cylindrically shaped fibers or yarns as electrodes have attracted significant interests as energy storage devices for wearable electronics since 2011. They show good potentials as either micro-devices to complement or even replace micro-batteries in miniaturized wearable electronics or being scaled up to macro-devices using textile technology to store large amounts of energy for larger wearable electronics or smart textiles. Thus, in this thesis, the research on 1D F/YSCs for wearable energy storage applications is divided into two directions: long yarn supercapacitors (YSCs) which is capable of being knitted or weaved into energy storage textiles and short fiber micro-supercapacitors (FMSCs).

Presently, state-of-art YSCs have achieved high electrochemical performance via elaborated yarn electrode materials selection and engineering. However, the length of most reported YSCs is limited to several centimeters. In contrast, practical textile yarns are orders of magnitude longer. The reported length dependent performance often doesn't increase linearly with the increase of length. Further, the cost of electrode materials has seldom been considered, while it can be expected that a large amounts of electrode materials are needed for fabricating long YSCs. Lastly, few works have demonstrated realistic knitted or woven energy storage textiles from YSCs. In these regards, the research focus for YSCs in this thesis is to fabricate long YSCs with high energy storage performance at reasonable cost, and develop the capability to be knitted or woven into practical energy storage textiles. To this end, all-carbon solid-state YSCs

using commercially available activated carbon and carbon fiber yarns were demonstrated. Activated carbon with large surface area serves as electrode materials, while carbon fibers with excellent electrical conductivity and mechanical strength act as current collectors and substrate for depositing activated carbon. Long YSCs up to 50 cm with a total capacitance of 1164 mF were successfully fabricated. Utilized three long YSCs, a wearable wristband was knitted which is capable of lighting up a light-emitting diode (LED) indicator, demonstrating good potentials for wearable energy storage.

On the other hand, previously reported FMSCs often suffer from inferior energy storage capacity to micro-batteries, and their production methods are also not scalable for commercialization. Moreover, few studies have investigated the integration strategy of FMSCs to meet a wide range of energy and power requirements by wearable devices. Therefore, the research focus for FMSCs in this thesis is to first improve their energy storage performance, followed by exploring scalable and time-energy-efficient fabrication methods of fiber electrodes, and subsequently new device integration strategies. To these perspectives, this study began with the demonstration of micro-nano-integrated core-sheath hybrid carbon fibers comprised of a microscale core made of commercial graphite fibers and a nanoscale hybrid sheath comprised of nitrogen-doped graphene oxide (GO) sheets and multi-walled carbon nanotubes (MWCNTs). The highly conductive graphite fiber core provides efficient pathways for fast electron transfer, while the high surface area nano-hybrid sheath with large surface area and enables large capacitance storage. The use of graphite fiber core dramatically improves the electrical conductive of the electrode which achieved a 6-times increase in capacitance retention compared to hybrid carbon fibers without graphite fiber core. To further improve the energy storage capacity, pseudocapacitive materials, RuO₂ nanoparticles with ultrahigh high mass loading (up to 42.5%) was uniformly

incorporated into hybrid carbon fibers derived from holey GO (HGO) sheets as the main components and single-walled carbon nanotubes (SWCNTs) as nanospacers. The composite fibers produced exhibited one of the highest volumetric capacitance of 1054 F cm^{-3} among reported fibers. Next, a new hydrothermal method was developed which allows the independent control of temperature and pressure in a wide range of subcritical and near-critical conditions. The near-critical hydrothermal conditions can dramatically shorten the hydrothermal assembly time of hybrid carbon fibers from several hours to 20 mins and achieve an 80% energy saving with enhanced physicochemical and capacitive performance compared to standard hydrothermal methods. Furthermore, a new concept of integration strategy of multiple FMSCs both in the X-Y plane and Z-axis direction to build a three-dimensional (3D) supercapacitors (SCs) was demonstrated, which could save 75% footprint compared to the typical strategy of integrating fiber devices on a flat substrate.

In conclusion, this thesis shows that rational electrode material design, synthesis, and architecture engineering can address several key challenges in developing high-performance F/YSCs. The scalable and economical fabrication methods demonstrated can facilitate the practical applications of F/YSCs for wearable energy storage.

Chapter I Introduction

1.1 Background

Wearable electronics are smart electronic devices that can be worn on human body as accessories.^{1, 2} They can be connected to internet to exchange data with the user and other connected devices, enabling wireless networking and mobile computing to assist and benefit people. Wearable electronics like Apple watch, Huawei wristband and Sony VR headset *et al.* are playing an increasingly important role in the field of fitness and sports monitoring, entertainment, fashion, medical, healthcare and military *et al.* (Figure 1.1a, c).

Figure 1.1 (a) Components, products, applications, and markets of wearable electronics. (b) North America wearable technology market size, 2012-2022 (USD billion). Retrieved July 19, 2018, from <https://www.grandviewresearch.com/industry-analysis/wearable-technology-market>. (c) Practical application cases of wearable electronics in different fields. Retrieved November 13, 2018, from <http://www.beautifulwomenhere.com/smart-options-for-the-new-dresses/>, <http://blog.jumpinshirt.com/touchscreen-t-shirts-only-a-few-years-away/>, <http://www.forbes.com/site/brucelee/2017/11/05/wearable-tech-emerging-for-chronic-pain-relief/>, <https://www.dancespirit.com/e-traces-pointe-shoes-2326468978.html>, <http://sylviaherbert.com/fabric-antenna-sensors-1/> and <https://www.army-technology.com/features/featurebae-broadsword-centralised-batteries-and-wire-free-textiles-for-soldiers-4383689/>.

Wearable electronics industry is an emerging but promising area evidenced by its huge and growing global market size, especially dominated by North America followed by European Union and Asia Pacific (Figure 1.1a, b). The growing consumer interests and fast development of advanced electronics as well as the booming internet mobility industry facilitate the innovation of wearable electronics by integration of more components to achieve multiple functions. For example, the emerging data-sharing function between wearable electronics with smartphones enables users to conveniently check and manage their interested data and information via apps in smartphones. Besides their traditional fitness data tracking function, new functions like message notification and music player functions are also integrated into up-to-date sports wristbands. To realize all these functions, it calls for stable and long-lasting power sources for their ever-expanding functionalities. Besides requirements in energy storage, future power sources of wearable electronics are also expected to be flexible, safe, and

even integrable with clothes to ensure their normal use in various shape-changing conditions like traditional textiles to achieve better wearability.^{1, 3, 4}

1.2 Challenges of current wearable energy storage devices

So far, wearable electronics are mainly powered by conventional, rigid lithium-ion (Li-ion) batteries. However, Li-ion batteries suffer from low power density, short cycle life, and high cost.^{5, 6} In addition, the use of Li-ion batteries may raise safety issues including leakage of organic electrolytes which are harmful to human body and fire or even explosion once short circuit happens. Moreover, all components of Li-ion batteries are sealed inside rigid metallic or plastic housing for safety reasons. Thus, they are large in size, heavy in weight and mechanically inflexible which significantly deteriorate their wearability, and thus restrict their application as power sources for wearable electronics.^{7, 8}

1.3 1D fiber/yarn supercapacitors (F/YSCs) as a solution

An emerging power solution to wearable electronics is 1D F/YSCs. Intrinsically, supercapacitors hold advantages of high power density, fast charge/discharge rate, long cycling life and high stability over batteries due to their distinct energy storage mechanism.^{5, 9} Besides, 1D cylindrically shaped structure render F/YSCs the following advantages: i) They can be easily scaled up from micro-devices to macro-devices by integration or applying existing knitting/weaving technology. This enables their applications either in miniaturized devices to replace micro-batteries or as macro-scale energy storage textile to meet large energy demand. ii) They are mechanically flexible

and deformable in various directions which can withstand harsh conditions *e.g.*, bending, twisting and even crumpling, enabling excellent wearability and safety. iii) They enable greater design versatility as they break the limit to shapes of energy storage devices. Thus, they can be fabricated into various desired shapes and located at different positions.³ iv) They can be easily integrated with other fiber-/yarn-based energy harvesting devices or other electronics to create integrated multifunctional systems.^{3, 10,}

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1.4 Research objectives

In this thesis, my research on F/YSCs applied in wearable energy storage divides into two directions: long yarn SCs (YSCs) and short fiber micro-supercapacitors (FMSCs). Although there is no clear definition of YSCs and FMSCs in this thesis, YSCs refer to cylindrically shaped supercapacitors which are long enough to be fabricated into energy storage textiles by existing textile technology for large energy storage. In contrast, FMSCs are defined as cylindrically shaped, miniaturized supercapacitors that are designed and fabricated as power sources in microelectronics. For FMSCs, their diameters normally range from several micrometers to millimeters and their lengths are in millimeter or even the centimeter scale which are too short to be fabricated. One overarching objective of my research is to design high-performance 1D F/YSCs to overcome the geometrical and flexible restrictions of traditional planar energy storage devices. The study mainly involves supercapacitor electrode materials selection and architectural engineering. For long YSCs, it is critical to find electrode materials with high capacitance and safety but low cost. In addition, as current collectors, weavable/knitable yarns are required to have excellent electrical conductivity to ensure

fast electron transfer and mechanical flexibility to withstand the harsh conditions during fabrication. Furthermore, it is also important to efficiently incorporate electrode materials into weavable/knitable yarns while preserving their good energy storage capacities. While for FMSCs, research in this thesis mainly focuses on the improvement of energy storage performance of FMSCs, such as energy density, power density and rate capability. In addition, it is also urgent to develop scalable, economical fabrication methods of electrodes of FMSCs and thus facilitates their practical applications in wearable energy storage.

1.5 Thesis outline

The thesis comprises seven chapters. A brief highlight of the rationales and key findings of each chapter is summarized as follows:

Chapter I: Introduction. The rapid evolution of wearable electronics asks for flexible, stable and long-lasting power sources. Then the challenges existing in currently-used energy storage devices for wearable electronics and the motivations of using 1D F/YSCs as alternatives are introduced. Lastly, the overall research objectives of this thesis are included in this chapter.

Chapter II: Literature review. The review starts off with the overview of three main electrochemical energy storage devices including electrical double layer capacitors (EDLCs), pseudocapacitors and batteries, in terms of their different energy storage mechanisms and corresponding electrochemical characteristics. Subsequently, the background information of F/YSCs, including their components, device configuration, asymmetric design, advantages as well as performance evaluation are provided. This is

followed by the summary and evaluation of fiber/yarn substrates, electrode materials as well as electrolytes used in F/YSCs.

Chapter III: All-carbon solid-state yarn supercapacitors from activated carbon and carbon fibers for smart textiles. This chapter is first few works demonstrated long YSCs up to 50 cm while possessing both high capacitive performance and reasonable cost which is favorable for large-scale production. Notably, a practically usable wristband was successfully knitted which is capable of lighting light-emitting diodes (LEDs), demonstrating their great practical application potential.

Chapter IV: Hydrothermal assembly of micro-nano-integrated core-sheath carbon fibers for high-performance all-carbon micro-supercapacitors. The focus of following chapters shifts to FMSCs. Specifically, this chapter aims to improve rate capability of hybrid carbon fibers comprised of graphene oxide (GO) sheets and multi-walled carbon nanotubes (MWCNTs) via the use of highly conductive graphite fibers as cores. The use of graphite fiber core dramatically improves the electrical conductive of hybrid carbon fibers which achieved a 6-times increase in capacitance retention compared to hybrid carbon fibers without graphite fiber core.

Chapter V: Nano-RuO₂-Decorated Holey Graphene Composite Fibers for Micro-Supercapacitors with Ultrahigh Energy Density. To increase the energy storage capacity of hybrid carbon fibers, this chapter is a pioneering attempt to incorporate pseudocapacitive material (RuO₂) into hybrid carbon fibers derived from holey GO (HGO) sheets as the main components and SWCNTs as nanospacers. Though an optimized two-step method, RuO₂ was uniformly incorporated into hybrid carbon fibers with high mass loading (up to 42.5%), resulting in an ultrahigh volumetric capacitance ever reported for FMSCs.

Chapter VI: Ultrafast hydrothermal assembly of nanocarbon microfibers in near-critical water for 3D micro-supercapacitors. Ultimately, this chapter is mainly to overcome two barriers of FMSCs for commercialization, including slowness in production and large footprint after integration. This chapter is a first attempt to regulate hydrothermal conditions and found that near-critical condition could dramatically accelerate the assembly process of hybrid carbon fibers comprised of GO and SWCNT. And simultaneously achieve large energy saving, as well as physicochemical and capacitive performance enhancement. Furthermore, a new concept of integration strategy of multiple FMSCs both in the X-Y plane and Z-axis direction to build a 3D supercapacitor was put forward which could save 75% footprint compared to the conventional strategy by integration on a flat substrate.

Chapter VII: Conclusions and outlook. Major achievements of each chapter are summarized here. Future research direction of YSCs and FMSCs are recommended and an outlook on basics of their future commercialization are provided.

Chapter II Literature review

2.1 Energy storage systems

Currently, rechargeable batteries and supercapacitors are the two most popular electrochemical energy storage systems. They typically consist of two electrodes, current collectors, a separator, and electrolyte. Supercapacitors can be further categorized into electrical double layer capacitors (EDLCs) and pseudocapacitors depending on their energy storage mechanisms. In this section, I mainly compared the differences between EDLCs, pseudocapacitors and rechargeable batteries, in terms of their energy storage mechanisms, charge transfer kinetics *et al.* Furthermore, electrochemical features, typically cyclic voltammetry (current *vs.* voltage curves, abbreviated as CV) and galvanostatic charge/discharge (voltage *vs.* time curves, abbreviated as GCD) of the three different electrochemical energy storage systems are provided, which could serve as a means to classify distinct mode of energy storage.

	Non-faradaic	Faradaic		
Types of energy storage device	Electrical double layer capacitor (EDLC)	Pseudocapacitor		Battery (based on intercalation)
		Surface redox	Intercalation	
Mechanism	Reversible ion adsorption/desorption without phase transition	Continuous change in oxidation state without phase transition	Intercalation and change in oxidation state without phase transition	Intercalation and change in oxidation state with phase transition
Kinetics		$i \sim v$ (surface confined)		$i \sim v^{0.5}$ (diffusion controlled)
Examples of 2D materials	Graphene, Activated carbon	Heteroatom-doped or functionalized graphene	TMO, TMDC, MXene	Bulk layered materials
Electrochemical features

Figure 2.1 A comparison of supercapacitors and batteries in terms of their characteristic metrics such as CV, GCD, key mechanism description, and various energy-storage materials following different charge storage mechanisms.¹² Reproduced with permission from ref. 12. Copyright 2018 John Wiley and Sons.

2.1.1 Supercapacitors

Electrical double layer capacitors (EDLCs). EDLCs store energy by separating charges at the interface between electrode materials and electrolyte without redox charge-transfer reactions and crystallographic phase transition. During the charging process by applying a voltage to an EDLC, the dissolved and solvated cations in the electrolyte travel from the positive electrode to the negative electrode while anions travel from the negative electrode to the positive electrode (see Figure 2.2b, c). As a result, electrical double layers will be generated at the surface of electrode materials,

and that is why the term “electrical double layer capacitors” is used. These double layers consist of two layers of charges, taking an example of the negatively charged electrode surface as shown in Figure 2.2a, in which the first layer is the surface lattice structure of the electrode, and the other layer, with opposite polarity, emerges from dissolved and solvated ions in the electrolyte. These two layers are separated by a monolayer of solvent molecules and we call this layer inner Helmholtz plane. Inner Helmholtz plane can be regarded as a molecular dielectric like in conventional capacitors. Dissolved and solvated ions from outer Helmholtz plane with counterbalancing charges match the amount of charge in the electrode. During the discharging process, the reverse processes take place.

EDLCs have unique electrochemical features, as shown in Figure 2.1. In response to CV scanning, EDLCs usually exhibit rectangular CV curves, a potential-independent capacitance, and thus potential-independent current.¹² In addition, galvanostatic charge/discharge of an EDLC results in symmetric and linear GCD plots. The ultrafast, surface-dominated charge transfer enables EDLCs charge/discharge even within seconds, and thus output ultrahigh power density. Electrode materials of EDLCs have been well studied, such as activated carbons, carbon nanotubes (CNTs) and graphene. In short, to achieve high electrical double layer capacitance, electrode materials with large surface area, high conductivity, hierarchical pore size distribution, and good wettability are favorable.

Figure 2.2 (a) Models of the electrical double layers at a negatively charged electrode surface. (b, c) Distribution of ions in a discharged/charged supercapacitor. Retrieved July 19, 2018, from <https://en.wikipedia.org/wiki/Supercapacitor>.

Pseudocapacitors: The energy storage mechanism of pseudocapacitors is different from that of EDLCs because they are faradic in origin. There are also two layers of charges between electrode surface and electrolyte when applying a voltage on pseudocapacitors. These two layers are separated by inner Helmholtz plane and a static electric field forms that result in double layer capacitance (Figure 2.2a). Besides electrical double layer capacitance, the capacitance of pseudocapacitors also arises from charge transfer between electrolyte and electrode. Some dissolved and solvated ions can penetrate the inner Helmholtz plane and transfer charge with the electrode. The ions in the electrolyte within the Helmholtz double layers also act as electron donors and transfer electrons to the electrode atoms. Because of the redox reactions involved, the energy storage capacity of pseudocapacitors is significantly enhanced compared to that of EDLCs. As reported by Conway et al., the capacitance of pseudocapacitors can be 10–1000 times higher than EDLCs.¹³

Pseudocapacitors could storage energy by two different mechanisms: (1) fast, reversible surface redox reactions, resulting in redox pseudocapacitance, and/or (2)

intercalation of cations into layered electrode materials with charge transfer, resulting in intercalation pseudocapacitance (see Figure 2.3a).

Figure 2.3 Charge storage mechanisms of two types of pseudocapacitors (a) and rechargeable batteries (b).⁵ Reproduced with permission from ref. 5. Copyright 2016 Royal Society of Chemistry.

The redox pseudocapacitance arises from the adsorption of electroactive ions onto the surface or near-surface region of electrode materials for faradic reactions with electron transfer and oxidation state change. Thus, charge transfer in this process is also surface-dominated, same with EDLCs. The most commonly known materials undergoing such surface redox reactions include some transition metal oxide (*e.g.*, RuO_2 , MnO_2), conducting polymers like polyaniline (PANI), polypyrrole and poly (3, 4-ethylenedioxythiophene) (PEDOT), as well as oxygen- or nitrogen-containing surface functional groups on some carbonaceous materials. As a new type of charge storage devices, intercalation-type pseudocapacitors store energy by intercalation/de-intercalation of cations (*e.g.*, H^+ , Li^+ , Na^+ and K^+) into the interlayer planes of layered

electrode materials with redox charge transfer with electroactive species. Typical intercalation-type pseudocapacitors materials are layered two-dimensional (2D) materials, such as MoS_2 , V_6O_{13} and the recently emerged transition metal carbide, MXenes. It should be noted this intercalation process is surface-dominated and without crystallographic phase transition, while cation intercalation involved in batteries are diffusion-controlled along with crystallographic phase transition. The detailed charge storage mechanisms of batteries will be discussed in the next section. Therefore, in intercalation-type pseudocapacitors, the advantage of batteries which store energy in the bulk of the electrode materials is united with the advantage of supercapacitors in which charge transfer is surface-dominated. Such a new class of 2D layered energy storage materials is classified as “extrinsic pseudocapacitive materials”, as defined by Dunn and co-workers.^{12, 14} As shown in Figure 2.1, in contrast to EDLCs, pseudocapacitors normally exhibit broadly peaked CV curves and non-linear GCD curves without obvious plateaus, indicating their faradic nature.

2.1.2 Batteries

Batteries store energy mainly by the intercalation/de-intercalation of cations, such as H^+ , Li^+ , Na^+ , and K^+ , within the crystalline structure of electrodes materials, accompanied with electron transfer and crystallographic phase transformation (see Figure 2.1 and 2.3b). Taking LiCoO_2 -graphite battery as an example, during the charging process, Li^+ is extracted from LiCoO_2 crystalline structure and inserts into graphite lattice (C_n), where LiCoO_2 cathode is transformed to $\text{Li}_{1-x}\text{CoO}_2$ and graphite anode to Li/graphite composite (Li_xC_n). The intercalation/de-intercalation of cations in these rechargeable battery materials result in crystallographic phase transition, which is

the key difference with intercalation-type pseudocapacitors. In addition, for batteries, the faradic reactions occur in the bulk electrode materials in which the cations need to diffuse deeply into the bulky electrode materials. While in pseudocapacitors, fast redox reactions occur on surface/near-surface region of electrode materials, or on the interlayer of layered materials. Therefore, charge transfer in batteries is diffusion-controlled, undergoing sluggish diffusion compared to pseudocapacitors, and especially EDLCs (Figure 2.1).

The distinct electrochemical features of batteries are evidenced by the intense, clearly separated oxidative and reductive peaks in their CV curves, and obvious plateaus in GCD curves which implies faradic reactions occur at a constant potential (Figure 2.1). In addition, the CV curve is also an efficient tool to clarify the kinetic difference between the surface-dominated and diffusion-controlled mode for charge transfer, and thus serve as an effective means to distinguish batteries with supercapacitors. The peak current (i) response of diffusion-controlled batteries will be proportional to the square root of potential scanning rate ($i \sim \nu^{1/2}$), while EDLCs and pseudocapacitors exhibit linear current response dependency on potential scan rate ($i \sim \nu$) (Figure 2.1).

2.1.3 Why supercapacitors for wearable energy storage?

Figure 2.4 Simplified Ragone plots of various energy storage systems.¹² Reproduced with permission from ref. 12. Copyright 2018 John Wiley Sons.

Because of their diverse energy storage mechanisms, EDLCs, pseudocapacitors, and batteries exhibit their unique energy storage features as shown in the Ragone plots in Figure 2.4. Batteries show high energy density but low power density and rate performance because of their sluggish, diffusion-controlled charge transfer which restricts their application in high power output. While for EDLCs, the fast, physical charge storage allows ultrahigh power output, but limited energy density at the same time. Pseudocapacitors are regarded as a trade-off between batteries and EDLCs. They have some advantages of batteries (high energy density) and some of EDLC (high power density and rate capability). Especially, the recently emerged intercalation-type pseudocapacitors have attracted great attention because of their superior energy storage performance.

After the comparison of these energy storage systems, supercapacitors are chosen for wearable energy storage devices based on the following considerations: i) Safety. Batteries, like Li-ion batteries, typically comprise of hazardous, organic electrolytes which is harmful to human body once leakage happens. And the failure of separation

between anode and cathode by the separator may ignite the organic electrolytes, which could cause fire or even explosion. In contrast, supercapacitors are commonly composed of non-toxic materials for wearable energy storage. ii) Lifetime. Supercapacitors can last 10000 to 100000 charge/discharge cycles with neglect capacity degradation, while batteries can only operate for hundreds or potentially thousands of cycles.^{5, 15} Thus, supercapacitors could outlast the lifetime of wearable electronics without the need of replacement. iii) Energy storage performance. Supercapacitors have ultrahigh power density, excellent rate capability compared to batteries. Their energy storage capacity gap between batteries is gradually narrowed with the exploration of new pseudocapacitive materials, such as intercalation-type pseudocapacitive materials, MXene.

2.2 Advantages of 1D F/YSCs for wearable energy storage

The emergence of wearable electronics over the last two decades provide us with great convenience and even change our lifestyle. Wearable electronics have evolved from life-saving devices to fashion accessories ranging from activity monitor bracelets, smart watches, and smart glasses to GPS-enabled shoes. Since wearable electronics are directly worn on human body, they need advanced power system which is safe, stable, long-lasting, flexible, and light-weight to maintain their usability in various conditions. Currently, commercial wearable electronics are normally powered by conventional batteries, especially Li-ion batteries, which are often bulky in size, mechanically rigid, potentially risky in use and poor in wearability.

An emerging power solution to wearable electronics is 1D F/YSCs with cylindrically shaped fibers/yarns as electrodes. Apart from the intrinsic advantages of supercapacitors

described above, their wire-shaped structures have the following advantages for wearable energy storage: i) They exhibit wide application potentials including as micro-devices to replace micro-batteries to power miniaturized electronics (see Figure 2.5a, b), and as macro-devices (energy storage textiles) by integration or applying existing textile technologies for smart textile or high energy-consuming wearable electronics (see Figure 2.5c, d). ii) Their excellent mechanical flexibility enables them to withstand harsh conditions (*e.g.*, bending, twisting and crumpling), and knitted/woven textile allow air and sweat pass through freely. All these features ensure excellent wearability.^{3, 16} iii) The highly flexible F/YSCs break the shape limits of energy storage devices, thus they can be fabricated into various desired shapes and located at different positions. iv) Integrated multifunctional systems could be created by easily integrating them with other fiber-/yarn-based energy harvesting devices or other electronics.^{3, 10, 11} For example, Wang's group reported a highly stretchable and washable all-yarn-based self-charging knitting power textile that enables both biomechanical energy harvesting and simultaneously energy storing by hybridizing fiber-based triboelectrical nanogenerator and supercapacitors into one fabric.¹¹

Figure 2.5 Applications of 1D F/YSCs as micro-devices or being knitted or woven into macro-scale energy storage textiles. Schematic illustration (a) and photo (b) of a FMSC.¹⁷ Reproduced with permission from ref. 17. Copyright 2017 Elsevier. (c) Schematic illustration of an energy storage textile fabricated by weaving or knitting 1D YSCs and (d) photo of woven clothes made by YSCs lighting 30 LEDs.¹⁸ Reproduced with permission from ref. 18. Copyright 2015 American Chemical Society.

2.3 1D F/YSCs performance evaluation

2.3.1 Performance of the electrodes

A three-electrode cell which consists of a working electrode containing studied electrode materials, a reference electrode (*e.g.*, silver chloride, saturated calomel electrodes) and a counter electrode (*e.g.*, Pt, graphite) is normally used to study the electrochemical performance of single electrode.

The capacitance of single electrode could be determined either by CV or GCD curves according to equation (2.1) and (2.2), respectively.

$$C_{electrode} = \frac{Q}{2V} = \frac{1}{2Vv} \int_{V_-}^{V_+} i(V) dV \quad (2.1)$$

where Q is the total charge obtained by integrating the enclosed area of CV curves, V is the voltage window ($V = V_+ - V_-$), v is the scan rate, and $i(V)$ is the current of CV curves.

$$C_{electrode} = \frac{i}{dv/dt} \quad (2.2)$$

where i is the discharge current in GCD curves, t is the discharge time and V is the voltage, dV/dt is the slope of the discharge curve.

Generally, the capacitance of the electrode is normalized to specific capacitance ($C_{sp,electrode}$) based on length, area, volume or mass according to equation (2.3):

$$C_{sp,electrode} = \frac{C_{electrode}}{B_{electrode}} \quad (2.3)$$

where $B_{electrode}$ can be the length (cm), area (cm²), volume (cm³) or mass (g) of single electrode, the resulting specific capacitance is termed as specific length capacitance (F cm⁻¹), specific areal capacitance (F cm⁻²), specific volumetric capacitance (F cm⁻³) and specific gravimetric capacitance (F g⁻¹), respectively. For 1D F/YSCs, their fiber-/yarn-shaped electrodes could be roughly regarded as cylinders. Therefore, their surface area (πDL), and volume ($\frac{\pi D^2}{4} L$) are used to estimate their specific areal and volumetric capacitance, respectively, where D and L are the diameter and length of fiber-/yarn-shaped electrodes, respectively.

2.3.2 Performance of the supercapacitor cells

The performance of supercapacitor cells is mainly evaluated by the following metrics: capacitance, energy density as well as power density. A supercapacitor cell with two electrodes can be treated as two capacitors connected in series.¹⁹ Supercapacitor cell (C_{cell}) can be calculated according to equation (2.4):

$$\frac{1}{C_{cell}} = \frac{1}{C_p} + \frac{1}{C_n} \quad (2.4)$$

where C_p and C_n is the capacitance of the positive and negative electrode, respectively.

In symmetric supercapacitors, in which positive and negative electrodes are identical,

$C_p = C_n$, thus the capacitance of the supercapacitor cell is half of that of each electrode, $C_{cell} = \frac{C_p}{2} = \frac{C_n}{2}$. While in asymmetric supercapacitors, the capacitance of supercapacitors cell is determined by the electrode with lower capacitance.

The capacitance of a supercapacitor cell (C_{cell}) could be determined either by CV or GCD curves according to equation (2.5) and (2.6), respectively.

$$C_{cell} = \frac{Q}{2V} = \frac{1}{2Vv} \int_{V_-}^{V_+} i(V) dV \quad (2.5)$$

where Q is the total charge obtained by integrating the enclosed area of CV curves, V is the voltage window ($V = V_+ - V_-$), v is the scan rate, and $i(V)$ is the current of CV curves.

$$C_{cell} = \frac{i}{dV/dt} \quad (2.6)$$

where i is the discharge current in GCD curves, t is the discharge time and V is the voltage, dV/dt is the slope of the discharge curve.

Generally, the capacitance of a supercapacitor cell is normalized to specific capacitance ($C_{sp,cell}$) based on total length, area, volume or mass of the supercapacitor cells according to equation (2.7):

$$C_{sp,cell} = \frac{C_{cell}}{B_{cell}} \quad (2.7)$$

where B_{cell} can be the total length (cm), area (cm²), volume (cm³) or mass (g) of the supercapacitor cell, the resulting specific capacitance is termed as specific length capacitance (F cm⁻¹), specific areal capacitance (F cm⁻²), specific volumetric capacitance (F cm⁻³) and specific gravimetric capacitance (F g⁻¹), respectively. It should be noted that the totally area, volume and mass including electrodes, electrolyte and separators are recommended to be counted to truly report the performance of an assembled supercapacitor cell.

The energy density (E) a supercapacitor cell can be calculated by equation (2.8):

$$E = \frac{1}{2} C_{sp,cell} V^2 \quad (2.8)$$

where V is the voltage window, $C_{sp,cell}$ is the specific capacitance obtained from equation (2.7):

The power density (P) of a supercapacitor cell can be estimated by equation or equation (2.9) and (2.10):

$$P = \frac{V^2}{4R_s} \quad (2.9)$$

$$P = \frac{E}{t} \quad (2.10)$$

where R_s in equation (2.9) is the equivalent series resistance which is determined by the intercept of Nyquist plot on x axis, and t is the discharge time of GCD curves.

From equation (2.8) to (2.10), it could be concluded that the performance of SC cells is mainly determined by $C_{sp,cell}$, V , R_s . Elaborated electrode design including capacitive materials selection and engineering is essential to achieving high $C_{sp,cell}$. In addition, R_s could be reduced by using electrode materials and electrolyte with high conductivity, enabling good wettability of electrode materials, *et al.* The operating voltage window (V) in aqueous electrolytes is normally limited to below 1 V, restricted by the water electrolysis voltage at 1.23 V. In this regard, asymmetric SCs with different electrodes which can cover the voltage window of both the negative electrode and the positive electrode, are designed to extend the voltage window up to 2 V in aqueous electrolytes.^{19,}
²⁰ In addition, organic and ionic electrolyte are adopted to replace aqueous electrode due to their wide voltage window even beyond 3 V.^{21, 22}

It should be noted that previously reported specific capacitance, energy and power density of F/YSCs are diverse in units including per length, area, volume or mass, and there is no widely accepted standard yet. Specifically, for FMSCs, their mass is very

small, and the limited space is a key constraint.²³ Hence, performances based on volume and area but not mass are recommended to be reported. While for long YSCs, performance based on length is more meaningful to estimate their potentials as building blocks to fabricate energy storage textiles.

Apart from specific capacitance, energy density, power density, and rate capacity (capacitance retention ability in a range of CV scan rates or GCD currents) are also important parameters to judge their performance at high current density. In addition, to match the long-life time of wearable electronics, cycling performance of 1D F/YSCs is critical and essential to be shown. Furthermore, to prove their potential in real applications, the performance stability of 1D F/YSCs under various mechanical test (*e.g.*, bending, twisting, stretching and tailoring) and the ability to withstand harsh environmental conditions (*e.g.*, fire, water, low temperature) are also suggested to be provided.

2.4 Device design of 1D F/YSCs

2.4.1 Symmetric and asymmetric 1D F/YSCs

Same with conventional SCs, the positive electrodes and negative electrodes of 1D F/YSCs could be identical and the resulting devices are termed as “symmetric F/YSCs”. And when two electrodes are different, the resulting devices are denoted as “asymmetric F/YSCs”. In fact, asymmetric F/YSCs are favorable because of their largely enhanced energy storage capacity by taking advantage of their wide operating voltage window compared to their symmetric counterparts.

The energy density (E) of supercapacitors is calculated according to the equation (2.8): $E = \frac{1}{2} C_{sp,cell} V^2$, where $C_{sp,cell}$ is the specific capacitance of the supercapacitors and V is their operating voltage. Thus, expanding operating voltage is one direct way to enhance the energy density of supercapacitors. However, the commonly reported supercapacitors have a limited voltage window below 1 V in aqueous electrolyte because the theoretical water electrolysis voltage is 1.23 V. Even though organic or ionic liquid electrolyte could push the operating voltage even above 3V, these electrolytes sometimes are toxic, environmentally unfriendly, and low in ionic conductivity which significantly limit their practical applications. In this regard, a new class of supercapacitors, asymmetric supercapacitors with two distinct electrodes, are proposed to extend the voltage window of supercapacitors. An asymmetric supercapacitor typically consists of one positive electrode containing pseudocapacitive materials, one negative electrode made from electrical double layer capacitive materials (mainly carbon-based materials). The working voltage window of asymmetric supercapacitors can cover the working window of the positive electrode and the negative electrode, with an expanded voltage window up to 2 V ever reported in aqueous electrolytes.^{20, 24} From equation (2.8): $E = \frac{1}{2} C_{sp,cell} V^2$, the specific capacitance of supercapacitors is another critical parameter apart from voltage window to achieve large energy storage. The specific capacitance of supercapacitors (C_{cell}) is calculated based on equation (2.4): $\frac{1}{C_{cell}} = \frac{1}{C_p} + \frac{1}{C_n}$, where thus carbon-based materials, with intrinsically low specific capacitance, dragging down the overall specific capacitance of supercapacitors. In this perspective, pseudocapacitive materials (*e.g.*, MoO_3 , Fe_2O_3) with much higher specific capacitance are recently proposed as new negative electrode materials. Overall, the

asymmetric supercapacitors can achieve higher energy density than their symmetric counterparts.

2.4.2 Three device configurations of 1D F/YSCs

1D F/YSCs typically have three device configurations as illustrated in Figure 2.6, including i) two fiber/yarn electrodes placed in parallel on a supporting substrate (Figure 2.6a). ii) two fiber/yarn electrodes twisted together (Figure 2.6b) as well as iii) single coaxial fiber/yarn configuration (Figure 2.6c). In regardless of different device configurations, they all keep the electrode/electrolyte/with or without separator/electrode sandwiched structure. The first device configuration is common in FMSCs. FMSCs are easy to be scaled up by integrating more supercapacitors in parallel or series to meet specific energy and power requirement. In contrast, two fibers/yarns twisted, and coaxial fiber/yarn structure do not need substrates. The freestanding fibers/yarns are easier to be knitted or woven into energy storage textiles. Coaxial configuration enables large contact area between the positive electrode and negative electrode, whereas for twisted configuration, the contact area of two electrodes is limited and the two electrodes are easy to detach upon shape changes. However, the single coaxial F/YSCs are technically difficult to manufacture which limit their practical applications.

Figure 2.6 Schematic illustration of three typical device configurations of 1D F/YSCs:

(a) two parallel fibers/yarns; (b) two twisted fibers/yarns and (c) single coaxial fiber/yarn.³ Reproduced with permission from ref. 3. Copyright 2015 Royal Society of Chemistry.

2.5 Electrolytes of 1D F/YSCs.

The electrolyte is one critical component of supercapacitors in determining their energy storage performance. They play a fundamental role in electrical double layer formation and provide electroactive species for reversible redox reactions.²¹ Liquid electrolyte used for conventional macro-scale supercapacitors can be categorized into three types: i) aqueous electrolytes. ii) organic electrolytes and iii) ionic liquid electrolytes. Aqueous electrolytes mainly include acid solutions (*e.g.*, H₂SO₄), alkaline (*e.g.*, KOH) and neutral solutions (*e.g.*, Na₂SO₄). They typically exhibit high ion conductivity, for example, 0.8 S cm⁻¹ for 1 M H₂SO₄ at 25 °C, but narrow operating voltage window below 1 V restricted by water electrolysis voltage of 1.23 V. Organic electrolytes are currently dominating the commercial supercapacitors because of their wide operating voltage of 2.5 to 2.8 V,²¹ and hence enhanced energy density. Ionic liquid electrolytes recently emerge as alternative electrolytes due to their large voltage window (> 3 V), thermal, chemical and electrochemical stability, negligible volatility. However, compared to aqueous electrolytes, organic electrolytes and ionic liquid electrolytes suffer from high cost, low ionic conductivity ($\sim 10^{-2}$ S cm⁻¹)³ and toxic, inflammable issues. In addition, to use liquid electrolytes in F/YSCs, they need to be sealed up into metal and/or plastic package to avoid leakage, which is technically difficult to manufacture. Therefore, liquid electrolytes are not recommended for F/YSCs.

In contrast, solid-state electrolytes have attracted great interests to be used in fabrication of F/YSCs. Solid-state electrolytes have the following advantages compared to liquid counterparts: i) They not only serve as ion conductive media but also function as separator to separate the positive and negative electrodes, thus achieve separator-free. ii) Solid-state electrolytes radically avoid leakage issue appeared in liquid electrolytes, thus dramatically increase safety factor and technically simplify the manufacture of F/YSCs and the further knitting/weaving process. iii) Solid-state electrolytes could function as binders to prevent the detachment of electrolyte materials on fiber/yarn substrates and the detachment of two fiber/yarn electrodes. Among various types of solid-state electrolytes, gel polymer electrolytes prepared by dissolving polymers (*e.g.*, PVA) in aqueous electrolyte (*e.g.*, H₂SO₄, H₃PO₄ and KOH) have been extensively used in F/YSCs because of their high ionic conductivity (10^{-4} – 10^{-3} S cm⁻¹), good mechanical strengths and stability under various environmental conditions.¹

2.6 Fiber/yarn substrates of 1D F/YSCs

Fibers/yarns are the scaffolds of F/YSCs which currently serve as substrates for electrode materials deposition and pathways for electron transport to the external circuit. Generally, there are two requirements of fiber/yarn substrates: i) High electrical conductivity along the axial direction is essential to enable efficient electron transfer from one end to the other in long fibers/yarns. Fibers/yarns without sufficient electrical conductivity are subjected to serious electrochemical performance deterioration with extended length and increased current densities.^{7, 24} ii) Fiber/yarn substrates need to have robust mechanical properties for flexible/wearable applications. Especially, when YSCs are used to weave or knit into energy storage textiles, standard weaving/knitting

methods used in the textile industry requires yarns to have enough mechanical characteristics to prevent breakage during processing.¹⁸ Until now, modified textile fibers/yarns, metal wires, and various carbon-based fibers/yarns (see Figure 2.7) are three dominated fibers/yarns used in assembly of F/YSCs, which will be introduced accordingly in the following sections.

Figure 2.7 Images of various conductive fibers/yarns and their corresponding surface SEM images. (a, b) SWCNTs-coated cotton yarns.²⁵ Reproduced with permission from ref. 25. Copyright 2013 John Wiley and Sons. (c, d) Stainless steel yarns.¹⁸ Reproduced with permission from ref. 18. Copyright 2015 American Chemical Society. (e, f) Carbon fibers.²⁶ Reproduced with permission from ref. 26. Copyright 2015 John Wiley and Sons. (g) SEM images showing a web being drawn from a CNT forest and then twisted into a yarn.²⁷ (h) SEM image of the surface morphology of as-spun CNT yarn.²⁷ Reproduced with permission from ref. 27. Copyright 2010 Elsevier. (i, j) rGO fibers.²⁸ Reproduced with permission from ref. 28. Copyright 2014 Springer Nature.

2.6.1 Modified textile fibers/yarns

Traditional textile yarns made of natural cotton fibers or synthetic nylon fibers are readily available in large quantity with good mechanical characteristics (*e.g.*, common cotton yarns have a tensile strength of about 200 MPa),²⁸ but they are usually nonconductive. Several studies have utilized textile yarns as substrates for depositing conductive materials to make these yarns conductive. For example, Kim *et al.* wrapped CNTs sheets, which were drawn from MWCNT forest, on nylon yarn, leading to an electrical resistance of 190 $\Omega \text{ cm}^{-1}$. SWCNT coated cotton yarns reported by Liu *et al.* have an electrical resistance less than 20 $\Omega \text{ cm}^{-1}$ (see Figure 2.7a, b), and nickel coated cotton yarn reported by Zheng exhibit much lower electrical resistance of 1.6 $\Omega \text{ cm}^{-1}$.

2.6.2 Metal wires

Metal wires (*e.g.*, Pt, Ti, Cu, and stainless steel) have electrical conductivity several orders of magnitude higher than modified textile yarns (see Figure 2.7c, d). In addition, they also have good mechanical strength. Thus, they can serve as both current collectors and substrates for depositing energy storage electrode materials for F/YSCs.

2.6.3 Carbon-based fibers/yarns

Textile fibers/yarns are nonconductive, and thus they cannot directly contribute to energy storage, which lower gravimetric performances of resulting devices. After the deposition of conductive materials, the conductivity of modified traditional textile yarns (*e.g.*, cotton and nylon yarns) is still not sufficient for efficient electron transfer. Metal wires are heavy in weight, leading to poor wearing comfortability. Moreover, some hard

metal yarns may cause permanent damages to textile machines. In contrast, various carbon-based fibers/yarns (carbon fiber, CNT yarns, rGO fibers/yarns) are usually conductive and light in weight, and some of them can concurrently contribute to energy storage by either electrical double layer capacitance or pseudocapacitance. Thus, they are attractive choices for fabricating F/YSCs.

i) Carbon fibers, made from polyacrylonitrile or pitch, are produced in large quantity with a billions-dollars market every year (see Figure 2.7e, f).²⁹ Carbon fibers have both high electrical conductivity (up to 10^6 S m^{-1})^{29, 30} and excellent mechanical characteristics (tensile strength of 5.69 GPa and a Young's modulus of 0.94 TPa).^{31, 32} Besides, carbon fibers are light in weight and nontoxic, which make them suitable for fabricating F/YSCs which may further to be knitted or woven into textile energy storage devices;

ii) CNTs are cylindrical hollow carbon nanostructures. Individual CNTs are both highly conductive and mechanically strong. But they are usually short with length in micrometers. Several methods have been developed to assemble individual short CNTs into long yarns, including wet-spinning of liquid CNT dispersions,³³ dry-spinning of CNT forests³⁴ or CNT aerogel,³⁵ and twisting of 3D CNT thin films into 1D yarns.³⁶ The most common CNT yarn formation method for energy storage textile is the dry spinning from MWCNT forests (see Figure 2.7g, h), which yields CNT yarns with an electrical conductivity of 1.5×10^4 to $5 \times 10^5 \text{ S m}^{-1}$,^{33, 34, 37-40} tensile strength in a range of 1–4.3 GPa, and Young's modulus up to 120 GPa;^{41, 42}

iii) rGO fibers/yarns can be formed by assembling individual GO sheets via wet-spinning⁴³ or hydrothermal synthesis (see Figure 2.7i, j).⁴⁴⁻⁴⁶ The reported electrical conductivity of rGO fibers/yarns goes up to $4 \times 10^4 \text{ S m}^{-1}$ depending on synthesis conditions,⁴⁷⁻⁵⁰ and can be further increased by incorporating more conductive CNTs.^{24, 28} Their tensile strength ranges from 180 to 420 MPa.^{24, 44, 50} Lian *et al.* recently reported a significant improvement in rGO fiber/yarn properties by assembling GO

sheets of different sizes together, followed by high-temperature annealing.⁵¹ The tensile strength and electrical conductivity now reach 820 MPa and $2.21 \times 10^5 \text{ S m}^{-1}$, respectively. The excellent properties of rGO fibers/yarns have attracted interests of exploring their applications in wearable energy storage.

2.7 Electrode materials of 1D F/YSCs

As discussed in the above sections, supercapacitors store electrical energy by physical adsorption of electrolyte ions on the electrode surface which is called electrochemical double layer capacitance and/or by reversible redox reactions, intercalation or electrosorption at or near the surface of electrodes which is called pseudocapacitance. Generally, they require the electrode materials to have large surface area with good surface wettability for electrolyte ions to access, hierarchical pore size distribution and well pore connectivity to enable efficient electrolyte ion diffusion, high electrical conductivity for fast electron transfer, and/or high pseudocapacitance from redox reactions.

For F/YSCs, electrode materials are either deposited on existing conductive fibers/yarns or serve as building blocks to form freestanding fibers/yarns. The length of fibers/yarns ranges several millimeters to meters. Electrons need to transfer all the way along the fibers/yarns axis to the external circuit. In contrast, electrons in their conventional 2D film-based counterparts only need to transfer along their thickness direction, normally with a micrometer or even nanometer-level. Their electron transfer distance is considerably longer in magnitudes, and thus F/YSCs have higher requirements of the conductivity of electrode materials to maintain high power, energy output, and rate performance. In addition, since F/YSCs are directly worn on human

body, safety of electrode materials is another crucial issue to be considered when design F/YSCs.

In general, electrode materials used in F/YSCs can be categorized into three types: i) carbon-based materials, such as activated carbon, graphene and CNTs. ii) conductive polymers, such as PPy, PANI, and PEDOT: PSS. iii) various metallic compounds including transition metal dichalcogenides (TMDs), transition metal oxides (TMOs), transition metal hydrates (TMHs), transition metal nitrides (TMNs). It should be emphasized that most reported F/YSCs contains several different materials with dedicated design for higher energy storage by taking the advantages of each component.

2.7.1 Carbon-based materials

Carbon-based materials are regarded as promising electrode materials due to their large specific surface area, nontoxicity, high thermal and chemical stability, and wide operating temperature.⁵² They store energy by physical adsorption of electrolyte ions on the electrode surface which is called electrochemical double layer capacitance. Graphene-family materials are most often used carbon-based electrode materials in F/YSCs, followed by CNTs and activated carbon. Therefore, in this section, more paragraphs will be dedicated to graphene-family materials.

Activated carbons: Activated carbons are the most widely used materials in commercialized supercapacitors because of their abundance, low cost and easy-processing apart from the shared advantages of carbon-based materials.⁵² Activated carbons are generally produced from thermal and/or chemical activation of various types of carbonaceous precursors (*e.g.*, wood, coal).¹⁵ The specific surface area of activated carbons can reach beyond 3000 m² g⁻¹, however, their specific capacitance is normally

below $10 \mu\text{F cm}^{-2}$, smaller than the theoretical electrical double layer capacitance of 15-25 $\mu\text{F cm}^{-2}$.⁵³ The unsatisfactory performance should be attributed to the difficulty in controlling parameters like pore size distribution, pore connectivity, and surface functionality which also significantly influence their energy storage performance. Most importantly, activated carbons suffer from low conductivity which restricts their applications in supercapacitors, especially F/YSCs which require high conductive electrode materials. In my recent study, I directly deposited activated carbons (as energy storage materials) on carbon fiber yarns (as current collectors) and fabricated an all-carbon solid-state YSC. The assembled device yields a high length capacitance up to 45.2 mF cm^{-1} at 2 mV s^{-1} in PVA/H₃PO₄ gel electrolyte. However, owing to the poor conductivity of activated carbons, the YSCs exhibited poor rate capability.²⁹ Gao *et al.* wet-spun SWCNTs/chitosan composite into yarns, followed by thermal treatment in which chitosan was transformed into activated carbons. The fine combination of SWCNTs and activated carbons provides the YSCs with more effective area for ion transportation and energy storage.⁵⁴ The achieved capacitance of assembled YSCs is 48.5 F cm^{-3} (74.6 F g^{-1}) at a scan rate of 2 mV s^{-1} , 42.4 F cm^{-3} (65.2 F g^{-1}) at a current density of 0.05 mA cm^{-2} . Due to the device in micro-scale and well connection between conductive SWCNTs yarns and activated carbons, the device shows improved rate capacitance, with a 42.86% capacitance retention when the scan rate was increased from 0.05 to 4.2 mA cm^{-2} .

Carbon nanotubes (CNTs): CNTs are allotropes of carbon with a cylindrical nanostructure. They can be categorized into SWCNTs and MWCNTs. SWCNTs (diameter: 0.5–1.5 nm; length: 100 nm to several micrometers) are formed by one rolled-up graphene sheet, while MWCNT (diameter: > 100 nm; length: 0.1 to 50 μm) consists of several rolled-up concentric graphene sheets (see Figure 2.8). The key advantage of

CNTs is their high electrical conductivity which is favorable to achieve high power density. Nevertheless, their surface area is generally limited to below $500 \text{ m}^2 \text{ g}^{-1}$, much lower than that of activated carbons, which restricts their application as electrical double layer capacitive materials. Therefore, CNTs are normally used in F/YSCs in two forms:

i) As introduced in section 2.6.3, CNTs were spun into yarns via various methods, and then serve as current collectors and substrates for deposition of capacitive materials. The capacitance contribution of CNTs yarns are very limited ($\sim 20 \text{ F g}^{-1}$ or $\sim 0.8 \text{ F cm}^{-3}$),⁵⁵ which should be attributed to their relatively compact structure which hinders ion diffusion and limits accessible surface area. ii) CNTs were also used as conductive additives and/or mechanical substrates to form hybrid composites, such as graphene/CNTs hybrids, TMOs/CNTs hybrids. Their roles in F/YSCs will be discussed together with other supercapacitor materials in the following sections.

Figure 2.8 Schematic representation of SWCNTs and MWCNTs.⁵⁶

Graphene-family materials: Graphene-family materials usually include graphene, graphene oxide (GO) and reduced graphene oxide (rGO). Their chemical differences are illustrated in Figure 2.9. Graphene, single-layer carbon atoms arranged in a hexagonal lattice with 2D properties, has shown many excellent properties including large specific

surface area ($\sim 2630 \text{ m}^2 \text{ g}^{-1}$), high Young's modulus ($\sim 1 \text{ TPa}$), good electron mobility at room temperature ($\sim 10000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), *etc.*⁵⁷ Graphene has a high theoretical electrical double layer capacitance of $\sim 550 \text{ F g}^{-1}$. GO is obtained by chemical oxidation of graphite before ultra-sonication to exfoliate into GO sheets.^{58, 59} Thus, GO possesses large amounts of oxygen-containing functional groups with carboxyl groups localized mainly at the edges while hydroxyl and epoxy groups are found at the basal planes. rGO, which is chemically reduced from GO, has most of the hydroxyl and epoxy groups removed from the basal planes, leaving only carboxyl groups at the edges and restoring back the π -network of the basal planes.⁶⁰ Despite their differences in their chemical structures, both the GO and rGO sheets retain the 2D structure of graphene. These oxygen-containing groups on GO and rGO sheets, on the other hand, greatly improve their wettability and simultaneously induce pseudocapacitance. These characters make graphene-family materials greatly suitable as electrode materials for F/YSCs.

Same with CNTs, graphene is widely used as mechanical substrate and conductive enhancer for pseudocapacitive materials. These application cases will be discussed in the following sections together with other supercapacitor materials. In another aspect, as introduced in section 2.6.3, graphene-family materials could also be used as building blocks to form freestanding fibers/yarns via various methods (*e.g.*, wet-spinning, hydrothermal assembly, and film conversion)^{51, 61-63} which exhibit good energy storage capacity. The fiber/yarn formation normally involves the use of GO, followed by the reduce GO to reduced rGO fibers/yarns. In this section, we mainly focus on how to achieve high supercapacitor and mechanical performance of these rGO fibers/yarns by tailoring physical, chemical properties of the building blocks, GO sheets.

Figure 2.9 Graphene materials. (a) Graphene; (b) GO; (c) rGO.

The re-stacking of rGO sheets make pure rGO fibers/yarns (with a specific surface area of $\sim 20 \text{ m}^2 \text{ g}^{-1}$) lose most of their potentially high specific surface area, far from the theoretical value of graphene ($2630 \text{ m}^2 \text{ g}^{-1}$).^{28, 64} Various approaches have been explored to prevent the re-stacking of rGO sheets in rGO fibers/yarns. Introducing spacers between rGO sheets such as CNTs (Figure 2.10 a, b), cellulose nanocrystal and TMOs,⁶⁵⁻⁶⁷ is the most popular method. The highest surface area reported for spacer-intercalated rGO fibers/yarns is $398 \text{ m}^2 \text{ g}^{-1}$ by using SWCNTs.²⁸ In addition, engineering the intrinsic structure of GO sheets, for example, creating nano-sized holes on GO sheet (termed as HGO) (Figure 2.10c, d),⁶⁹ and optimizing fabrication methods may also be effective ways to enhance specific surface area of rGO fibers/yarns.⁶⁸

Figure 2.10 (a, b) Cross-sectional SEM images of a rGO/SWCNTs fiber, showing SWCNTs intercalating between rGO sheets.²⁸ Reproduced with permission from ref. 28. Copyright 2014 Springer Nature. (c) High-magnification TEM images of holey GO. (d) Schematic illustration of ion diffusion pathway across the graphene paper (GP) made from normal GO and holey graphene paper (HGP) made from HGO.⁶⁹ Reproduced with permission from ref. 69. Copyright 2015 American Chemical Society.

The absence of metal current collectors and the long electron-transfer distance along fiber/yarn axis requires rGO fibers/yarns to have considerable high conductivity to enable high rate performance. Reported strategies so far to increase the electrical conductivity of rGO fibers/yarns can be classified into three categories: i) Introduce conductive additives including CNTs, conductive polymers and metal oxides.^{24, 28} For example, rGO/CNTs hybrid fibers could achieve a 5 to 9 times increase in electrical conductivity compared to pure rGO fibers.^{24, 28} ii) The electrical conductivity of nanocarbons depends on the presence of long-range-conjugated graphitic networks. Particularly, oxygen-containing functional groups (*e.g.*, hydroxyl, carboxyl) reduce the electrical conductivity of nanocarbons by localizing p-electrons. Hence, the electrical

conductivity of rGO fibers/yarns could also be enhanced by controlling oxygen content in the resulting rGO fibers. iii) Tailoring the physical properties of GO sheets. For example, fibers/yarns fabricated from large GO sheets give rise to higher electrical properties because it can reduce the number of graphene sheets ends in the fibers and graphene junctions, leading to lower contact resistance.^{51, 68}

Mechanical properties of rGO fibers/yarns are determined by the alignment, compactness and cross-link between adjacent rGO sheets. Upon reduction, the alignment and densification of fibers are enhanced with the decrease of oxygen-containing groups, leading to increased tensile strength. In addition, the tensile strength of rGO fibers/yarns could also be improved by incorporating spacers between neighbouring graphene sheets which could form interfacial intercalation. Zhu *et al.* used cellulose nanocrystal as spacers and the resulting rGO/cellulose nanocrystal fibers has a higher tensile strength of 199.8 MPa compared to pure rGO fibers of 157.5 MPa. They attributed it to the abundance of hydroxyl groups on cellulose nanocrystal which form hydrogen bonds with rGO sheets.⁶⁴ It should be mentioned that even though polymers are also reported to reinforce tensile strength of rGO-based fibers/yarns, polymers insulate the electrolyte ions to permeate, transfer within fibers/yarns and block the linkage of graphene sheets along fiber/yarn direction, leading to poor supercapacitor performance. Thus, polymers are not suggested to be used as spacers to enhance the tensile strength of rGO-based fibers/yarns. Furthermore, the tensile strength of rGO fibers/yarns are also sensitive to intrinsic properties of graphene sheets used. Substantial works have proved that graphene sheets with larger lateral size give rise to higher mechanical properties because of the reduction of graphene sheets end in fibers/yarns and their conjunction along fiber/yarn axis.

Heteroatom doping offers possibilities for tailoring the intrinsic properties of graphene. The invasion of heteroatoms inevitably altering the structural and electronics properties of graphene.⁷⁰ GO and rGO are the most often used graphene-family materials in electrochemical energy storage. The oxygen-containing groups on GO/rGO sheets render them improved wettability between electrode and electrolyte, additional pseudocapacitance and well sheet separation in contrast to chemically inert pristine graphene. However, these oxygen-containing groups, on the other hand, are electron scatters and counterproductively increase the electron transfer resistance, leading to poor rate performance. To address the conductivity issue, other atoms including B, N, P and S doped or their co-doped GO/rGO have also been synthesized and demonstrated with enhanced electrical conductivity in comparison to pure GO/rGO. So far, N-doped graphene have been widely applied in electrode materials and their supercapacitor performance enhancement mechanisms have been well studied.^{70, 71} Our previous works showed that a merely 2.8 at% N doping in rGO/CNTs composite fibers bring an over 50% increase in volumetric capacitance to 305 F cm^{-3} .²⁸ B, P, S or their co-doped graphene-family materials emerge as highly interesting and promising electrode materials, however still haven't been applied in rGO fibers. Moreover, a deep understanding of the doping and surface pseudocapacitive mechanisms of B, P and S remains elusive. Much efforts are still needed to be made to reveal their role in enhancing capacitance.⁷⁰

Throughout this section, we show how to engineer the nanostructure of rGO fibers/yarns by tailoring the physical, chemical properties of GO sheets to achieve better supercapacitor and mechanical performance. Nevertheless, we can't concurrently achieve large specific surface, high electrical conductivity, well wettability and tensile strength, *etc. al.* For example, we propose to use HGO to increase specific surface area,

but on the other hand, the holes on HGO sheets destroy the long-range-conjugated graphitic networks and thus reduce electrical conductivity. Again, the removal of oxygen-containing groups increases both electrical conductivity and tensile strength of rGO fibers, while it reduces hydrophilicity at the same time and thus deteriorates wettability between electrode and electrolyte. We believe the trade-off among different properties of rGO fibers render researchers great design versatility. And more elaborate and advanced rGO fibers/yarns with excellent supercapacitor and mechanical performance can be foreseen.

2.7.2 Conductive polymers

Conductive polymers are polymers with highly π -conjugated polymeric chains, which have been widely studied as pseudocapacitive materials because of their low cost, high conductivity in a doped state, easy processing by dispersion, environmental friendliness, high energy storage capacity and high reversibility, *et al.*⁹ Conductive polymers could be positively charged (termed as n-doped) or negatively charged (termed as p-doped) via reversible chemical or electrochemical reactions which is also called “doping”. The reversible doping process is achieved by the insertion/desertion of ions with opposite charges in polymer matrix to maintain its neutral state as shown in the following equation (2.11) and (2.12):

Where A^- represents anion and C^+ is cation.

Electrical conductivity and pseudocapacitance are induced simultaneously during above the process. Actually, high electrical conductivity is the key advantage of

conductive polymers over most transition metal compounds which are semiconducting. The electrical conductivity of conductive polymers could be tuned up to 10^4 S cm^{-1} through chemical or electrochemical doping, even though their conductivity is normally low (of $10^{-10} - 10^{-5} \text{ S cm}^{-1}$) in neutral states.⁷²

Among various conductive polymers, PANI, PPy, PEDOT: PSS are most often used in supercapacitors. Nevertheless, the easily occurred swelling and shrinking during redox reactions significantly deteriorate their rate performance, and thus restrict their applications in supercapacitors. It has been widely demonstrated that hybridizing conductive polymers with other materials (*e.g.*, carbon-based, TMOs), which can serve as mechanical support, could reduce their cycle degradation. In the meanwhile, conductive polymers function as conductive enhancers to facilitate the charge transfer in the composites. The synergistic effects greatly help to release the energy storage capacity of each component in the composites. Specifically, in F/YSCs, the role of conductive polymers reported could be summarized as: i) Conductive polymers are pre- or post-deposited on transitional metal based pseudocapacitive materials, as conductive enhancers, to improve their electrical conductivity and ii) as “glue” and “pressure buffer” to stabilize pseudocapacitive materials on fiber/yarn substrate. Their specific applications cases will be discussed together with transitional metal-based materials in the following sections.

2.7.3 Transition metal dichalcogenides (TMDs)

TMDs include a large group of layered 2D materials which are in the form of MX_2 where M is a transition metal of groups 4–10 and X is a chalcogen.⁷³ Transition metal atomic layer is sandwiched between two chalcogen layers via covalent bonding and van

der Waals forces emerge between their multi-layers. These layers provide large surface area and abundant active edge sites undergoing electrostatic adsorption and redox reactions. In addition, TMDs have multiple phases and their phase diversity offer them various electronic properties from insulating, semiconducting to metallic.⁷⁴ These properties make TMDs greatly suitable for electrochemical energy storage. Among various TMDs, MoS₂ is the most popular electrode materials for supercapacitors due to their high energy storage capacity. Especially, recently reported 1T metallic MoS₂ (Figure 2.11a) is 10⁷ times more conductive, with enlarged interlayer spacing, more electrochemically active sites, and much better hydrophilicity compared to their most often reported 2H phase counterpart.^{75, 76} In 2015, Chhowalla and co-workers reported a 1T MoS₂-based film which achieves capacitance values ranging from ~400 to ~700 F cm⁻³ in a variety of aqueous electrolytes (Figure 2.11b, c).⁷⁶ These unique features offer 1T phase MoS₂ intriguing benefits for energy storage, especially for F/YSCs. Inspired by these findings, Veerasubramani pioneeringly applied 1T MoS₂ in F/YSCs by brush coating few layered 1T MoS₂ on stainless steel wires. The few layered MoS₂ was prepared by ball milling bulk MoS₂. Two obtained MoS₂/stainless steel wires were placed in parallel and sandwiched by PVA/LiCl gel electrolyte. After that, the fabricated device was inserted into a flexible tube to keep the device from atmospheric impurities and external scratches. The fabricated FSCs delivered a specific capacitance of 119 $\mu\text{F cm}^{-1}$ and energy density of 8.1 nWh cm⁻¹. Apart from good energy storage capacity, the high conductivity, enlarged interlayer spacing and good wettability of 1T MoS₂ also lead to the excellent rate capability of the which was evidenced by the excellent phase angle of 80° and ~90% capacitance retention when the charge/discharge current increase from 2.5 to 25 μA .⁷⁷

Figure 2.11 (a) Top and side views of the 2H and 1T phases of the MoS₂ monolayer.⁷⁸

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(b) SEM image of an electrode made of 1T MoS₂ nanosheets by vacuum filtration. (c)

CV curves of 1T phase MoS₂ nanosheet paper in 0.5 M sulphate-based electrolyte solutions at scan rates of 20 mV s⁻¹.⁷⁶ Reproduced with permission from ref. 76.

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2.7.4 Transition metal oxides (TMOs)/Transition metal hydrates (TMHs)

TMOs emerge as promising supercapacitor materials because the pseudocapacitance arising from their intrinsic redox activity is much higher compared to electrical double layer capacitance induced by physical adsorption. For example, the theoretical capacitance of graphene arising from physical adsorption is 550 F g⁻¹,⁷⁹ while that of TMOs, *e.g.*, NiO, can reach up to 3750 F g⁻¹.⁸⁰ A main drawback of TMOs is that most TMOs are semiconducting, and thus undergo poor electrical conductivity, limiting their energy storage capacity especially at high current. To design high-performance TMOs-

based fiber electrodes, it calls for advanced strategies in tailoring nanosheets of TMOs and fiber/yarn architecture to i) improve electrical conductivity of TMOs-based materials. ii) achieve high mass loading. iii) enable large surface area and iv) facilitate ion diffusion to increase utilization rate of TMOs. In the following sections, we describe the development of TMOs in 1D F/YSCs.

RuO₂: RuO₂ is an excellent pseudocapacitive material due to its high theoretical specific capacitance ($\sim 1400 \text{ F g}^{-1}$), wide potential window, fast charging/discharging rate, high chemical stability, and especially its high electronic conductivity ($\sim 105 \text{ S cm}^{-1}$) which is superior to most other TMOs.^{9, 81} Considerable efforts have been made to study factors that influence the capacitive performance of RuO₂.⁹ It has been widely proved that hydrous RuO₂ with amorphous structure is favorable to achieve higher capacitance.⁸¹⁻⁸³ The price of RuO₂ is very high (about $\sim 2000 \text{ USD Kg}^{-1}$)¹⁴ and thus it is not suitable for large-scale energy storage applications. However, the absolute amount of RuO₂ used in small-scale energy storage devices is tiny. Therefore, we believe that RuO₂ has a great application potential in small-scale micro-devices including FMSCs.

MnO₂: MnO₂ have been extensively studied as pseudocapacitive material, and thus widely applied in F/YSCs due to its high theoretical capacitance of $\sim 1370 \text{ F g}^{-1}$, low cost as well as environmental safety. Crystallized MnO₂ have multiple crystalline structures including amorphous, α -, β -, γ - and δ -MnO₂. α -, β -, γ -MnO₂ have a tunnel structure while δ -MnO₂ have a relatively open layered structure. Among them, amorphous MnO₂ could facilitate the penetration of electrolyte ions, α -MnO₂ has relatively larger tunnels compared to β - and γ -MnO₂ and δ -MnO₂ relatively open layered structure which facilitate electrolyte ion transfer. Hence, amorphous, α - and δ -MnO₂ are most often used in F/YSCs.⁹ Since aggregated bulky MnO₂ suffers from poor ion diffusion compared to their 1D and 2D counterparts, and thus lead to low utilization rate

of MnO₂ and rate performance. Since then, considerable works have been made to synthesize MnO₂ with 1D wire or 2D thin layer morphology (see Figure 2.12a–d), including 1D nanowires,⁸⁴ 2D nanosheets,⁸⁵ and flower-like structure with nanoplates²⁸ *et al.* Compared to their bulky counterpart, 1D or 2D morphologies render i) lower ionic resistance due to shorter transport pathway for electrolyte ion diffusion. ii) larger active surface area for electrolyte ion to access and iii) higher electronic conductivity ensuring efficient electron transfer.

The surface area of most conductive fibers/yarns including metal wires, carbon fibers are too small (*e.g.*, $< 10 \text{ m}^2 \text{ g}^{-1}$ for carbon fibers) to host much MnO₂.⁸⁶ To increase MnO₂ loading, a popular solution is to pre-deposit a thin layer of rGO before MnO₂ deposition (Figure 2.12e, f). rGO layers possess large surface area, thus they can provide sufficient sites for MnO₂ anchoring. On the other hand, rGO with excellent conductivity also provide excellent interfacial contact between MnO₂ and rGO for fast electron transport. Besides, rGO can also provide more channels to facilitate electrolyte ions transfer.^{87, 88} As mentioned above, poor conductivity is one common drawback of most TMOs including MnO₂, which dramatically depresses their energy storage capacity, especially rate performance. Depositing a layer of conductive polymers on MnO₂ is one popular strategy to improve the conductivity (Figure 2.12f). Conductive polymers provide better interconnectivity within MnO₂ for fast electron transfer. Conductive polymers, on the other hand, contribute to the charge storage process through pseudocapacitance based on redox reactions. Furthermore, they can serve as the protective layer and stress buffer to avoid MnO₂ detaching from the fiber/yarn.^{25, 89} Figure 2.12g, h shows the photographs of the 15 cm × 10 cm woven clothes made of PPy/MnO₂/Rgo/ stainless steel yarns and a wrist band knitted with a pattern which can light LED panels, indicating the yarns' vast application potential.

Figure 2.12 MnO_2 with various morphology (a) bulky⁹⁰ (Reproduced with permission from ref. 90. Copyright 2012 American Chemical Society), (b) nanosheets⁸⁵ (Reproduced with permission from ref. 85. Copyright 2016 John Wiley and Sons), (c) flower-like²⁵ (Reproduced with permission from ref. 25. Copyright 2013 John Wiley and Sons) and nanowires⁶⁶ (Reproduced with permission from ref. 66. Copyright 2016 Elsevier), deposited on various fiber/yarn substrates. (e) Schematics of stainless steel yarn fabrication. (f) Illustration of the yarn modified by deposition of rGO, MnO_2 and PPy. (g) Photographs of the 15 cm $\times$ 10 cm woven clothes (energy storage textiles) made of yarns which can light 30 LEDs. (h) A wrist band knitted with a pattern (inset shows

the pattern powering a LED).¹⁸ Reproduced with permission from ref. 18. Copyright 2015 American Chemical Society. (i) Schematic illustration of the fabrication of amorphous MnO₂@MWCNT fiber. (j) Plot of volumetric energy density versus volumetric power density for MnO₂@MWCNT fiber supercapacitors and other reported MWCNT fiber supercapacitors. (k) Cycling and bending stability of amorphous MnO₂@MWCNT fiber supercapacitors.⁹¹ Reproduced with permission from ref. 91. Copyright 2017 American Chemical Society.

The commonly adopted core-sheath structure, in which conductive fibers/yarns as core backbone and MnO₂ as the sheath, limits the capacitance contribution of fiber/yarn core because the agglomerated layer of MnO₂ blocks the penetration of electrolyte ions to access fiber core. In addition, semiconducting MnO₂ with low conductivity suffers from unfavorable thickness-dependence and is associated with limitations in the transport of both electrons and ions. Only a very thin layer of MnO₂ could be utilized to participate in redox reactions. Further increased MnO₂ mass loading increases both electrical and ionic resistance and lowers down utilization rate of MnO₂. To address these issues, an emerging strategy is to directly incorporate MnO₂ into fibers along with the fiber fabrication process, forming an integrated composite fibers. The integrated structure with well MnO₂ dispersion enables high MnO₂ mass loading yet still with efficient electron and ion transportation and without sacrificing their utilization rate. Zhu's group reported a hierarchical MnO₂ NWs/rGO hybrid fibers by electrospinning MnO₂ and GO hybrid dispersion, followed by HI reduction (Figure 2.12i). rGO sheets inhibit the aggregation of MnO₂ NWs and ensuring a high MnO₂ mass loading of 40%. rGO sheets, on the other hand, serve as superhighways for facilitating electron and ion transfer, achieving high utilization rate of MnO₂. Flexible solid-state fiber

supercapacitors were assembled using the as-prepared hybrid fibers and they displayed a high volumetric capacitance of 66.1 F cm^{-3} , excellent cycling stability (96% capacitance retention over 10000 cycles), and high energy and power density (up to 5.8 mWh cm^{-3} and 0.51 W cm^{-3} , respectively). (Figure 2.12j, k).⁶⁶

Co₃O₄ and its isostructure: Co₃O₄ is another attractive pseudocapacitive material because of its high redox activity with an ultrahigh theoretical capacitance of 3560 F g^{-1} , as well as good reversibility.⁹² Nanostructured Co₃O₄ with size within hundreds of nanometers is preferred because the shorter ion diffusion pathways, larger surface area and higher electrical conductivity enabling fast electron transfer compared to its bulky counterparts, resulting in higher capacitance and utilization rate. However, relatively expensive and toxic in nature significantly limit Co₃O₄'s application in supercapacitors. Thus, tremendous attempts have been made to replace Co in Co₃O₄ partially by cheaper and environment-friendly elements (*e.g.*, Zn, Ni, Cu, Fe). The resulting isostructures of Co₃O₄ exhibit superior capacitive performance because of their stronger electrochemical activity and richer redox reactions. For example, ZnCo₂O₄, in which Zn²⁺ replaces Co²⁺ at the tetrahedral site in spinel Co₃O₄ has been widely investigated as a high-performance pseudocapacitive material (Figure 2.13a).⁹³ Especially, Ni-doping can surprisingly increase the electrical conductivity from $3.1 \times 10^{-5} \text{ S cm}^{-1}$ for Co₃O₄ to $0.1\text{--}0.3 \text{ S cm}^{-1}$ for Ni_xCo_{3-x}O₄. Such an increase in electrical conductivity could give rise to superior rate performance.⁹⁴ Jang's group introduced a 3D-NiCo₂O₄/Ni nanostructure by electrodepositing flower-like NiCo₂O₄ nanoflakes (with thicknesses in the range of $\sim 20\text{--}30 \text{ nm}$) on a pre-prepared 3D porous nickel (3D-Ni) architecture on a Ni-wire substrate (Figure 2.13b).⁹⁵ An asymmetric, all-solid-state fiber supercapacitors with PVA/KOH as gel electrolyte was assembled by using as-prepared fiber electrodes. The assembled device could deliver a high capacitance of 30 F g^{-1} and 3 F cm^{-3} at a

scan rate of 5 mV s^{-1} , gravimetric energy density of 2.18 W h kg^{-1} ($0.21 \text{ mW h cm}^{-3}$) and a power density of 21.6 W kg^{-1} (2.1 mW cm^{-3}). Even after 5000 cycles, it can still retain 100% of its initial capacitance, indicating its excellent reversibility.

Figure 2.13 (a) Crystal structure of spinel ZnCo_2O_4 . The Zn-ions occupy the tetrahedral sites and Co-ions occupy the octahedral sites.⁹³ Reproduced with permission from ref. 93. Copyright 2012 Royal Society of Chemistry. (b) Schematic illustration of the preparation of 3D- $\text{NiCo}_2\text{O}_4/\text{Ni}$ electrodes.⁹⁵ Reproduced with permission from ref. 95. Copyright 2016 Royal Society of Chemistry.

NiO/Ni(OH)₂ and their isostructures: NiO/Ni(OH)_2 have also attracted great interests as promising pseudocapacitive materials due to their ultrahigh theoretical capacitance ($> 3000 \text{ F g}^{-1}$), low cost and environmental friendliness and easy synthesis.²¹ The key limitations of NiO/Ni(OH)_2 in practical applications lie in their low electronic conductivity and short cycle life which is caused by degradation of its microstructure. To address these issues, nanostructured, highly porous NiO/Ni(OH)_2 in the form of nanosheets, nanoflakes, nanoflowers nanowires and nanowalls *et al.*, with size within hundreds of nanometers are preferred because the shorter ion diffusion pathways, larger surface area and higher electrical conductivity which enable fast

electron transfer compared to their bulk counterpart, resulting in higher capacitance and utilization rate. In addition, making NiO and/or conductive carbon materials or conductive polymer composites are also able to increase the conductivity of NiO/Ni(OH)₂, as well as prevent the degradation of NiO/Ni(OH)₂ since carbon materials or polymers can serve as support. Besides improving electrical conductivity via conductive carbon materials and conductive polymers, the conductivity of NiO/Ni(OH)₂ could also be enhanced by introduction Co ions into NiO/Ni(OH)₂ matrix. Ni/Co double hydroxides (DHs) have been widely explored and applied in capacitive energy storage. Apart from improved conductivity, Ni/Co DHs consist of two electrochemical active sites which provide richer redox activity both from Ni and Co ions, leading to superior energy storage capacity in contrast to metal mono-hydroxides. Lu *et al.* electrodeposited Ni/Co DHs nanosheets on highly conductive, Ni-coated carbon fibers (Figure 2.14a–c).⁹⁶ Subsequently, an asymmetric flexible solid-state fiber supercapacitors has been developed successfully via using Ni/Co DHs/Ni/carbon fibers as positive electrode, pen ink deposited Ni-coated carbon fibers as negative electrode, and PVA/KOH as gel electrode. The asymmetric fiber supercapacitors exhibited a specific capacitance of 28.67 mF cm⁻² and energy density of 9.57 μWh cm⁻² at corresponding power density as high as 492.17 μW cm⁻². After 5000 charge/discharge cycles at a current density of 20 A g⁻¹, the capacitance still remains at 95.6%, demonstrating a superior recyclability.

Figure 2.14 (a) Schematic illustration of fabrication for the flexible fiber-type solid-state asymmetric supercapacitor device. (b) Ni/Co DHs forms a decent conductive network with the porous ink film and abundant open space for electroactive surface sites. (c) High magnification FESEM images show that the rippled silk nanosheet is ultrathin.⁹⁶ Reproduced with permission from ref. 96. Copyright 2017 American Chemical Society.

MoO₃ and V₂O₅: Because of the intrinsic limitation of energy storage mechanism of carbon-based materials by electrostatic adsorption of electrolyte ions, the low energy storage capacity of carbon-based materials unmatched that of various positive materials with large capacity in asymmetric supercapacitors, resulting in unsatisfactory energy density. Hence, it calls for novel negative materials with high energy storage capacity to replace carbon-based materials in asymmetric supercapacitors. In this regard, MoO₃ is one emerging material with high capacitance as new negative electrode materials. MoO₃ are low in cost and have multiple valence states which provide abundant active sites for high capacitive performance, as well as high work function (6.9 eV) to widen voltage window between positive and negative electrode. However, like most other TMOs/TMHs, MoO₃ also suffers from low electrical conductivity ($10^{-5} \text{ S cm}^{-1}$)⁹⁷ and

performance degradation during cycling. To address these issues, carbon-based materials were used as support to provide large surface area, facilitate electron transfer and avoid the degradation of MoO_3 . In this regard, Zhu's group wet-spun rGO/ MoO_3 composite fibers as negative electrodes, and rGO/ MnO_2 composite fibers as positive electrodes (Figure 2.15).⁹⁶ The asymmetric, all-solid-state fiber supercapacitors delivered a superior volumetric energy density of 18.2 mWh cm^{-3} at a power density of 76.4 mW cm^{-3} and exhibited good cycling performance with a capacitance retention of 96.8% after 3000 cycles of charge/discharge at a fixed current density of 1 A cm^{-3} .

Figure 2.15 Schematic illustration of the design and fabrication of the fiber-based asymmetric supercapacitors with rGO/ MoO_3 fibers as negative electrodes and rGO/ MnO_2 fibers as positive electrodes.⁶⁷ Reproduced with permission from ref. 67. Copyright 2017 Elsevier.

Instead of relying on conductive carbon materials, the conductivity of MoO_3 could also be improved through the low-valence-state Mo doping into MoO_3 and N doping.⁹⁸ Yang's group demonstrated a new *in situ* N and low-valence-state Mo dual doping strategy that remarkably boosted the electrochemical performance of MoO_3 NWs. The author found that the co-doping of low-valence-state Mo and N into MoO_3 increase its wettability, electrical conductivity, ionic diffusion rate and provide more active sites to

achieve higher energy storage capacity. Especially, N doping was also found to play a dominant role in stabilizing MoO₃.²⁰

Besides MoO₃, V₂O₅ is another promising negative electrode material for asymmetric supercapacitors due to its layered structure which facilitates ion diffusion, variable oxidation state (from V²⁺ to V⁵⁺), low price and ease of synthesis.⁹⁹ Iron-based materials also hold great promise to replace carbon-based negative materials because of their large theoretical capacitance, wide voltage window at negative potential, rich abundance, low cost and environmental friendliness.¹⁰⁰

2.7.5 Transition metal nitrides (TMNs)

TMNs (*e.g.*, VN, TiN) hold great promise as negative electrode materials in asymmetric supercapacitors. The key advantage of TMNs compared to most other pseudocapacitive materials is its excellent electrical conductivity.¹⁰¹ Among TMNs, VN is the most well-studied materials for supercapacitors because of its high electrical conductivity of $1.6 \times 10^6 \text{ S cm}^{-1}$ and high gravimetric capacitance up to 1340 F g^{-1} .¹⁰² ¹⁰³ A plausible method to make full use of the high capacitance of VN is to enable its large surface area for electrolyte ions to access. Yao *et al.* introduced a facile and effective approach to directly grow well-aligned 3D VN NWs on CNT fibers, in which NWs could provide large electrochemically active surface and short paths for rapid ion diffusion and electron transport.¹⁰² However, irreversible electrochemical oxidation significantly deteriorates the cycling stability of VN. Previous research has proved that carbon coating could solve this problem.¹⁰⁴ Hence, they coated a thin layer of carbon on VN nanowires, resulting in a C/VN NWs/CNT fiber electrode. To make full use of the effective surface area and decrease the contact resistance between two electrodes, an

asymmetric, coaxial fiber supercapacitors was fabricated by wrapping $\text{MnO}_2/\text{PEDOT:PSS}/\text{CNT}$ sheets (positive electrode) on C/VN NWs/CNT fiber (negative electrode) with $\text{PVA}/\text{Na}_2\text{SO}_4$ gel electrolyte sandwiched (Figure 2.16a–g). The as-prepared device exhibited a high specific capacitance of 213.5 mF cm^{-2} and an exceptional energy density of $96.07 \text{ } \mu\text{Wh cm}^{-2}$. The capacitance of this device could reach 90% after 6000 cycles, demonstrating its excellent cyclic ability.

Figure 2.16 Schematic illustrations of (a) the fabrication of the asymmetric coaxial fiber supercapacitors, (b) the cross-sectional structure of the fiber supercapacitors, and (c) wrapping of an aligned CNT sheet around a modified CNT fibers. (d, e) SEM images of VN nanowires arrays on CNT fibers with increasing magnifications. (f) SEM image of the fiber supercapacitors tied into a knot. (g) Photograph of the as-prepared fiber supercapacitors woven into flexible textiles.¹⁰² Reproduced with permission from ref. 102. Copyright 2017 American Chemistry Society.

2.7.6 MXene

More recently, transition metal carbides, carbonitrides and nitrides (MXenes), a new 2D material family, have attracted great interest as supercapacitor electrode materials. MXenes have a general formula of $M_{n+1}X_nT_x$ ($n=1-3$), where M is an early transition metal (*e.g.*, Ti, Zr, and Mo), X stands for C or N, and T represents surface terminated groups of $-OH$, $-F$ or $-O$ (Figure 2.17a-c).¹⁰⁵ MXenes have exhibited several advantages over other supercapacitor electrode materials including ultrahigh electrical conductivity up to 9880 S cm^{-1} , rich chemistry, tunable surface termination and hydrophilicity, exceptional cation intercalation as well as excellent pseudocapacitive behavior with a highest capacitance over 1500 F cm^{-3} to date.^{106, 107} Since 2017, MXenes start to appear in FSCs because of their big success in planer SCs. In 2017, Kim *et al.* bush-coated synthesized titanium carbide on stainless steel wires, and a FSC was fabricated by twisted two as-prepared fiber electrodes separated by PVA/KOH gel electrolyte.¹⁰⁸ The assembled device exhibited a high length capacitance of 3.09 mF cm^{-1} , a high energy density of 210 nW h cm^{-1} , and an excellent cycling stability. The excellent conductivity of the resulting fiber electrodes was evidenced by its nearly rectangular shapes even at a CV scan rate up to 250 mV s^{-1} (Figure 2.17d, e). Besides stainless steel wires, researchers have also coated MXenes on other fiber substrates including silver-plated Nylon fibers and carbon fibers to assembled FSCs.^{109, 110} However, as we mentioned earlier, coatings active materials on existing conductive fibers gives rise to low mass loading, poor capacitance, rate performance and utilization rate. Processing MXenes into fibers is a possible way to solve these issues. Given the insufficient inter-sheet strength of MXenes to form fibers, Razal *et al.* used GO as host to wet-spun $Ti_3C_2T_x$ MXene/GO dispersion into MXene/GO fibers with a high MXenes mass loading of $\sim 88\%$ (Figure 2.17f, g).¹¹¹ MXene sheets are orderly aligned between

graphene oxides liquid crystalline templates. The wet-spun fibers showed a high volumetric capacitance ($\sim 341 \text{ F cm}^{-3}$ at 0.5 A cm^{-3}) and when used in a FSC device, generated maximum energy and power densities of $\sim 5.1 \text{ mW h cm}^{-3}$ and 1700 mW cm^{-3} , respectively. In addition, spinning conductive fibers by biscrolling activate materials-coated CNT sheets into highly flexible yarns could also ensure high mass loading, well particle connectivity. Rizal's group fabricated flexible yarn electrodes by biscrolling $\text{Ti}_3\text{C}_2\text{T}_x$ MXene with CNTs sheets referred to as "BMX yarns." (Figure 2.17h), achieving a highest MXene loading of $\sim 98 \text{ wt\%}$ and displaying record specific volumetric, aerial, gravimetric, and linear capacitance of 1083 F cm^{-3} , 3188 mF cm^{-2} , 428 F g^{-1} , and 118 mF cm^{-1} , respectively.¹¹² When the BMX yarns are made into freestanding asymmetric FSC prototypes by pairing with biscrolled RuO_2 yarns, the respective maximum energy and power densities of $61.6 \text{ mW h cm}^{-3}$ ($168 \text{ }\mu\text{W h cm}^{-2}$ and $8.4 \text{ }\mu\text{W h cm}^{-1}$) and 5428 mW cm^{-3} (14.8 mW cm^{-2} and $741 \text{ }\mu\text{W cm}^{-1}$) were achieved.

Figure 2.17 (a) Schematic diagram of the atomic structure of $\text{Mo}_2\text{TiC}_2\text{T}_x$, (b) a cross-sectional SEM image of $\text{Mo}_2\text{TiC}_2\text{T}_x$ film and (c) a TEM image of a single-layer $\text{Ti}_3\text{C}_2\text{T}_x$ flake.¹⁰⁵ Reproduced with permission from ref. 105. Copyright 2017, Springer Nature. (d, e) CV curves of a FSC assembled by two titanium carbide-coated stainless steel wires at different scan rates.¹⁰⁸ Reproduced with permission from ref. 108. Copyright 2017 RSC. (f, g) Schematic representation of the spinning formulation and fiber spinning of MXene/GO fiber.¹¹¹ Reproduced with permission from ref. 111. Copyright 2017 Royal Society of Chemistry. (h) Schematic of the fabrication process for BMX yarns. MXene dispersion was coated on CNT sheets and biscrolled to form a composite BMX yarn in which MXene is evenly distributed within the CNT framework.¹¹² Reproduced with permission from ref. 112. Copyright 2017 John Wiley and Sons.

Chapter III All-carbon solid-state yarn supercapacitors from activated carbon and carbon fibers for smart textiles

(This chapter is reproduced with permission from Zhai, S.; Jiang, W.; Wei, L.; Karahan, H. E.; Yuan, Y.; Ng, A. K. and Chen, Y*; All-carbon solid-state yarn supercapacitors from activated carbon and carbon fibers for smart textiles, *Materials Horizons*, 2015, 2, 598-605. Copyright 2015 Royal Society of Chemistry.)

3.1 Introduction

Smart textiles are intelligent devices integrated with various wearable electronics, which can sense and respond to environmental stimuli. They require integrated energy storage to power their functions. Many research efforts focus on either directly overlaying conventional batteries onto existing textiles or coating energy storage materials on fabrics.¹¹³⁻¹¹⁸ Such approaches face tremendous difficulties in connections, bulkiness, wearability, and safety.¹¹⁹ As discussed in Chapter II, an emerging approach is to build integratable 1D F/YSCs by directly incorporating supercapacitor materials at the formation stages of textile fibers. Next, multiple fibers are spun into energy storage yarns. These yarns can be further fabricated into energy storage fabrics.^{1, 120} Besides the intrinsic advantages of supercapacitors This new approach has several advantages: i) fibers/yarns are highly flexible, and they can be woven or knitted into textiles of various shapes at preferred locations, which render great design versatility in the development of smart textile products. ii) woven or knitted textiles allow moisture and air from a human body to pass through freely, leading to much better wearability compared to large surface area impermeable thin film devices. and iii) established textile technology can be utilized to address many challenges in scalable manufacturing.

Among different yarn-based energy storage devices, yarn supercapacitors (YSCs) are particularly attractive because of their high power density, long cycle life, and fast charge/discharge rates.^{3, 4, 121, 122}

Supercapacitors store energy based on two principles: electrical double-layer capacitance and pseudocapacitance. Recent research efforts have been focused on the development of novel electrode materials including carbon nanomaterials, such as carbon nanotubes and graphene, conducting polymers, and a few pseudocapacitive nanomaterials in form of nanosheets, nanoparticles, and nanofibers. These nanomaterials serve as building blocks for energy storage fibers due to their large surface area, high specific capacitance, and other unique electrical and mechanical properties.^{24, 28, 43, 47, 54, 84, 90, 123-142} However, the cost of nanomaterials is high, scalable production is often not available, and their potential health and environmental risks are uncertain,¹⁴³⁻¹⁴⁷ which hinder their realistic applications in the near future. In contrast, activated carbon derived from biomaterials or polymer precursors is the most widely used electrode material in commercial supercapacitors. The challenge is to efficiently incorporate activated carbon into weavable/knitable fibers while preserving their good capacitive energy storage properties. Furthermore, long yarns are needed to fabricate practical smart textile products. Recent research has found that the performance of fiber electrodes based on carbon nanomaterials often deteriorates significantly with the increase of fiber length due to their large electrical resistances.²⁴ Although metal wires, such as Au, Cu, and stainless steel, can be used as current collectors to reduce the equivalent series resistance (ESR) of YSCs, they do not directly contribute to capacitive energy storage.^{126, 127, 136, 137, 140} They are also heavy in weight and less flexible, leading to poorer wearability of resulting energy textiles. Carbon fibers, made from polyacrylonitrile or pitch, have excellent mechanical and electrical properties. They are

produced in large quantity with billions of dollars global market, which may act as alternatives to metal wires in YSCs.

In this work, I show that all-carbon solid-state YSCs can be fabricated using activated carbon and carbon fibers. The composition of carbon materials in yarn electrodes was optimized to enable YSCs to possess both high specific length capacitance and specific gravimetric capacitance. The electrochemical properties of the assembled YSCs in different lengths were evaluated; they demonstrate one of the highest specific length capacitances and total capacitances among all F/YSCs ever reported in the literature. Owing to their excellent mechanical flexibility, three long YSCs were knitted into a wearable wristband, which can light a light-emitting diode (LED) indicator, unveiling their potential in smart textile applications.

3.2 Experimental section

3.2.1 Electrochemical properties of pristine carbon fiber yarns and activated carbon

The electrochemical properties of pristine carbon fiber yarns were evaluated by the CV methods in the three-electrode configuration in 1 M H₂SO₄ electrolyte with a voltage window range of 0–1V on an electrochemical workstation (CHI, 660D). In the three-electrode configuration, a platinum wire served as counter electrode, an Ag/AgCl electrode as reference electrode and a 3.5 cm-long pristine carbon fiber yarn (1 mg cm⁻¹) as working electrode. The electrochemical properties of activated carbon were also evaluated by CV methods with the same three-electrode set-up except an activated coated carbon cloth as working electrode. Activated carbon (2 mg) and polyvinylidene

fluoride (binder) were mixed at a mass ratio of 9:1 in N-methyl pyrrolidone by sonication. The mixture was then coated on a 1×1 cm area on a rectangle carbon cloth (1×3 cm), followed by drying at $100\text{ }^{\circ}\text{C}$ overnight. The capacitance measurements of both pristine carbon fiber yarn and activated carbon were taken using CVs at 2, 5, 10, 20 mV s^{-1} .

The capacitance C of pristine carbon fiber yarn and activated carbon was determined using both CV curves according to equation (3.1):

$$C = \frac{Q}{2V} = \frac{1}{2\nu v} \int_{V_-}^{V_+} i(V) dV \quad (3.1)$$

Q is the total charge obtained by integrating the area within CV curves, V is the scanned voltage window ($V = V_+ - V_-$), ν is the scan rate of CV curves, and $i(V)$ is the current intensity.

The specific length capacitance C_L of pristine carbon fiber yarn is calculated using equation (3.2):

$$C_L = C/L \quad (3.2)$$

where L denotes the length of pristine carbon fiber yarn.

The specific gravimetric capacitance C_g of activated carbon is calculated using

$$C_g = C/m \quad (3.3)$$

where m denotes the mass of activated carbon on a carbon cloth.

3.2.2 Preparation of hybrid carbon yarn electrodes

The suspension of activated carbon was prepared by mixing activated carbon particle powders (YP-50F, Kuraray, Japan; pore volume: 0.7 mL g^{-1} , packing density: $\sim 0.4\text{ g cm}^{-3}$, and total surface area: $\sim 1600\text{ m}^2\text{ g}^{-1}$) at the concentration of 40 mg mL^{-1} with ethanol solution (deionized water and 99% ethanol in a 1: 3 volume ratio). Liquitex

matte medium was added (in the weight ratio of 5: 95 toward activated carbon) to increase the suspension viscosity so that it can be easily coated on carbon fibers. Carbon fiber yarns (Zoltek Panex 35) were concurrently used as current collectors for supercapacitors and as substrates for depositing activated carbon. The density (mass per length) of carbon fiber yarns was controlled at 1 mg cm^{-1} , resulting in a tightened yarn diameter (without most of voids among individual carbon fibers) of about 0.25 mm. Activated carbon suspension was dropped casting on loose carbon fiber yarns at different mass loadings (0.5, 1, 1.5, and 2 mg cm^{-1}). After loaded with activated carbon, hybrid carbon yarns were twisted using a handheld yarn spinner (“Lacis” Power, 4-ply Cord Marker and Fringe Twister) in a Z twist (turning right), until about 5 turns per inch to tighten them. Twisted hybrid carbon yarns were first dried in a vacuum oven at $80 \text{ }^{\circ}\text{C}$ for 8 hours. Subsequently, they were dipped in a polymer gel (polyvinyl alcohol (PVA)/ H_3PO_4) for 20 min, and then dried at room temperature. The polymer gel was prepared by dissolving PVA (10 g) in deionized water (100 mL). The PVA–water mixture was heated to $90 \text{ }^{\circ}\text{C}$ under constant stirring until it became clear. After it was cooled to room temperature, H_3PO_4 (10 g, > 99% pure) was added into it with mixing.

3.2.3 Scanning electron microscope

The morphology of activated carbon, carbon fiber yarns, and hybrid carbon yarns was examined using a scanning electron microscope (SEM, JEOL, JSM6701, 5 kV). Each sample was gold sputter-coated for five minutes prior to SEM analysis.

3.2.4 Assembling yarn supercapacitors (YSCs)

Two hybrid carbon yarns of the same length were used as electrodes. They were twisted together using the handheld yarn spinner at about 5 turns per inch in an S twist (left turn). The combination of Z (from the twisted hybrid carbon yarns) and S twisting helps to lock the two electrodes together. YSCs of different lengths at 5, 10, 20, and 50 cm were fabricated using yarn electrodes of lengths 5.5, 11, 22, and 55 cm. There is an approximately 9.1% length reduction when two electrodes were twisted together. The twisted 2-ply yarns were dipped into PVA/H₃PO₄ gel for another 20 min, and dried at room temperature until the polymer gel solidified. The diameter of as-prepared YSCs is about 1–2 mm depending on the packing density.

3.2.5 Electrochemical testing of YSCs

Assembled two-electrode YSCs were tested using an electrochemical workstation (CHI, 660D) by CV and GCD to determine their capacitance. EIS was carried out using a potentiostat (VersaSTAT 4) to determine ESR. All devices underwent CV at 20 mV s⁻¹ for 100 cycles to “pre-cycle” the devices, and then capacitance measurements were taken using CVs at 2, 5, 10, 20 mV s⁻¹, followed by GCD at 25, 50, 100, and 200 mA g⁻¹ based on an active material (activated carbon) in electrodes. All devices were tested in a 0.0–1.0 V window.

The capacitance C_D of YSCs was determined using both CV and GCD according to equation (3.4) and (3.5), respectively.

$$C_D = \frac{Q}{2V} = \frac{1}{2\nu} \int_{V_-}^{V_+} i(V) dV \quad (3.4)$$

Q is the total charge obtained by integrating the area within CV curves, V is the scanned voltage window ($V = V_+ - V_-$), ν is the scan rate of CV curves, and $i(V)$ is the current intensity.

$$C_D = i/(dV/dt) \quad (3.5)$$

i is the discharge current in GCD, t is the discharge time in GCD, and V is the voltage.

The specific length capacitance C_L of YSCs is calculated using

$$C_L = C_D/L_D \quad (3.6)$$

where L_D denotes the length of YSCs.

The specific gravimetric capacitance C_g is calculated using

$$C_g = 2C_D/m \quad (3.7)$$

where m denotes the mass of activated carbon in a single yarn electrode.

3.3 Results and discussion

3.3.1 Fabrication of hybrid carbon YSCs

Figure 3.1. Schematic illustration of the fabrication process of all-carbon solid-state YSCs (left) and corresponding photographs of carbon yarns of every fabrication step (right).

Figure 3.1 shows the fabrication process of all-carbon solid-state YSCs. Commercial carbon fiber yarns act as substrates for hosting activated carbon particles with high surface area. Due to the relatively high electrical conductivity of carbon fiber yarns, they also function as current collectors in YSCs. Carbon fiber yarns used in this study have bundles of graphite filaments (see the SEM image in Figure 3.2a) with an electrical conductivity of 679 S cm^{-1} . We used carbon fiber yarns with a density (mass per length) of 1 mg cm^{-1} , a diameter of 250 μm (without most voids among individual carbon fibers), and an electrical resistance of about $3.0 \Omega \text{ cm}^{-1}$. This particular density was used because i) they have relatively small electrical resistance, which we expected that long YSCs can be fabricated with low ESR and ii) there are sufficient numbers of individual carbon fibers. We can easily loose the carbon fiber yarn to a flattened layer of $\sim 5 \text{ mm}$ in width, as shown in Figure 3.1. It is easier to deposit activated carbon suspension evenly on such a flattened layer. Activated carbon suspension was prepared by mixing activated carbon particles with ethanol, water, and Liquitex matte medium in specific ratios as described in Experimental in order to achieve uniform and stable activated carbon coatings on carbon fiber yarns. Activated carbon suspension was dropped casting on loose carbon fiber yarns at different mass loadings (0.5 to 2 mg cm^{-1}). Owing to the empty space among individual graphite filaments (see Figure 3.3), activated carbon particles not only cover the surface of graphite filaments, but also fill up voids among them. After coating activated carbon, we reduced the space among individual graphite filaments by twisting hybrid carbon yarns until about 5 turns per inch. Twisted hybrid carbon yarns were further coated with PVA/ H_3PO_4 gel, which bound carbon materials together to improve the structural integrity of hybrid carbon yarns. YSCs were fabricated by twisting two hybrid carbon yarns together using the handheld yarn spinner. The twisted YSCs were further covered with an additional layer of PVA/ H_3PO_4 gel. The

solidified gel not only acted as an electrolyte in YSCs but also as a separator between two yarn electrodes.

Figure 3.2 Scanning electron microscope images of carbon fiber (a) and activated carbon (b) used in this study. (c) CV curves of pristine carbon fiber yarn. The specific length capacitance of the carbon fiber yarn determined from its CV curves is 0.141 mF cm^{-1} at the scan rate of 2 mV s^{-1} , 0.105 mF cm^{-1} at 5 mV s^{-1} , 0.090 mF cm^{-1} at 10 mV s^{-1} , and 0.080 mF cm^{-1} at 20 mV s^{-1} . (d) CV curves of activated carbon. The capacitance of activated carbon determined from its CV curves is 126.30 F/g at the scan rate of 2 mV s^{-1} , 100.87 F g^{-1} at 5 mV s^{-1} , 74.91 F g^{-1} at 10 mV s^{-1} , and 47.86 F g^{-1} at 20 mV s^{-1} .

3.3.2 Effect of activated carbon loading on hybrid carbon yarns

SEM was used to examine the morphology of hybrid carbon yarns. Figure 3.2a shows that individual graphite filaments have a diameter of about 6–7 mm. Activated carbon

particles have a wide range of sizes from less than 1 to 10 μm (also see Figure. 3.2b). Some activated carbon particles were directly deposited on graphite filaments, while more occupied voids among graphite filaments. With the increase of mass loading from 0.5 to 2 mg cm^{-1} in hybrid carbon yarns, more activated carbon particles stay in voids with some distance to graphite filaments. Activated carbon particles can provide considerable surface area for electrical double layer capacitance. However, their relatively low electrical conductivity would significantly limit electron transfer when they are away from current collectors.

Figure 3.3 SEM images of hybrid carbon yarns with different loadings of activated carbon. (a) 0.5 mg cm^{-1} , (b) 1.0 mg cm^{-1} , (c) 1.5 mg cm^{-1} , and (d) 2 mg cm^{-1} .

To optimize the mass loading of activated carbon in hybrid carbon yarns, electrochemical properties of 10 cm long YSCs assembled using hybrid carbon yarns that contain different amounts of activated carbon were compared. The activated carbon mass loadings of 0.5, 1, 1.5, and 2 mg cm^{-1} in hybrid carbon yarns produce YSCs containing 1.1, 2.2, 3.3, and 4.4 mg cm^{-1} of activated carbon (note that two 11 cm long hybrid carbon yarns were twisted into one 10 cm long YSC). Figure. 3.4a shows their

CV curves at 2 mV s^{-1} . The enclosed area of CV curves increases with higher activated carbon loading, indicating greater total apacitance. Figure. 3.2c suggests that the capacitance of carbon fiber yarns is very low (0.141 mF cm^{-1} at 2 mV s^{-1} measured in a $1 \text{ M H}_2\text{SO}_4$ electrolyte). Thus, most of the capacitance of the YSC can be attributed to activated carbon. Figure. 3.4b shows that the calculated specific length capacitance of the YSCs from their CV curves increases from 30.7, 45.2, 53.0, to 63.0 mF cm^{-1} when the mass loading of activated carbon in YSCs increases from 1.1 to 4.4 mg cm^{-1} . In contrast, the specific gravimetric capacitance corresponding to the mass of activated carbon in YSCs decreases from 111.7, 82.1, 64.2, to 57.3 F g^{-1} . Figure. 3.2d shows that activated carbon used in this work has a specific gravimetric capacitance of 126.3 F g^{-1} at 2 mV s^{-1} measured in a $1 \text{ M H}_2\text{SO}_4$ electrolyte. The decrease in specific gravimetric capacitance suggests that electrical double layer capacitance contributed by activated carbon becomes less efficient when activated carbon particles are away from current collectors. Although higher activated carbon loading can increase specific length capacitance, the efficiency of capacitive energy storage by activated carbon reduces significantly. Therefore, in the following studies, we focused on YSCs with activated carbon loading at 2.2 mg cm^{-1} , which provides both relatively high specific length capacitance at 45.2 mF cm^{-1} and specific gravimetric capacitance at 82.1 F g^{-1} .

Figure 3.4. (a) CV curves of 10 cm long YSCs with different activated carbon loadings at a scan rate of 2 mV s^{-1} . (b) The variation of specific length capacitance C_L of YSCs and specific gravimetric capacitance C_g corresponding to the mass of activated carbon in YSCs.

3.3.3 Electrochemical performance of YSCs

Figure 3.5 Electrochemical performances of a 10 cm long YSC. (a) CVs taken at 2, 5, 10, and 20 mV s^{-1} . (b) GCD curves at 25, 50, 100, and 200 mA g^{-1} . (c) Specific length capacitance at different CV scan rates and discharging current densities. (d) Specific energy and power densities. (e) Long term cycling at the scan rate of 20 mV s^{-1} for 10 000 cycles. (f) EIS result taken from 200 kHz to 10 mHz, with an inset displaying the enlarged plot at the high frequency region.

The electrochemical performance of the 10 cm YSCs containing 2.2 mg cm^{-1} activated carbon was further characterized by CV and GCD. CV curves of this device shown in Figure. 3.5a have a large enclosed area, indicating high capacitance. It

becomes spindle-shaped at higher scan rates. Correspondingly, GCD curves in Figure. 3.5b are symmetric triangular-shaped at lower discharge current densities. They become less symmetric with voltage drops at the beginning of the discharge process at higher discharge current densities. Figure. 3.5c shows that the specific length capacitance determined from CV curves of the device drops from 45.2, 28.0, 24.3 to 14.3 mF cm⁻¹ when the CV scan rates increases from 2, 5, 10 to 20 mV s⁻¹. Similarly, the specific length capacitance determined from GCD curves decreases from 46.8, 39.7, 34.9 to 21.3 mF cm⁻¹, when the discharge current density is increased from 25, 50, 100 to 200 mA g⁻¹. The gravimetric capacitance of the device was also calculated, which is shown in Figure. 3.6. The specific length capacitance of the device is much higher than many recently reported F/YSCs, which include multi-walled carbon nanotube/ordered mesoporous carbon composite fiber at 1.91 mF cm⁻¹,¹²⁸ polyelectrolyte-wrapped graphene/carbon nanotube core-sheath fiber at 5.3 mF cm⁻¹,⁴³ and multi-walled carbon nanotubes/carbon microfibers/carbon film at 6.3 mF cm⁻¹.¹²⁴ The specific length energy and power densities of the device are shown in Figure. 3.5d. At the current density of 25 mA g⁻¹, it has an energy density of 6.5 mW h cm⁻¹ and a power density of 27.5 mWcm⁻¹. It can retain an energy density of 3.0 mW h cm⁻¹ at a higher power density of 220 mW h cm⁻¹. These power and energy densities are higher than those of many reported F/YSCs containing various nanomaterials, such as reduced graphene oxide/MnO₂ nanosheets/polypyrrole deposited stainless steel current collectors at 1.4 mW h cm⁻¹ and 1.3 mW cm⁻¹,¹⁴⁰ activated carbon deposited natural fibers with stainless steel current collectors at 3.3 mW h cm⁻¹,¹³⁷ carbon fiber/polyaniline at 1.4 mW h cm⁻¹ and 119 mW cm⁻¹,¹⁴¹ carbon nanotube/MnO₂/ polymer fiber at 0.75 mW h cm⁻¹ and 19.3 mW cm⁻¹,¹⁴⁸ multi-walled carbon nanotubes/carbon microfibers/carbon film at 0.7 mW h cm⁻¹ and 13.7 mW cm⁻¹,¹²⁴ and polyelectrolyte-wrapped graphene/carbon

nanotube core-sheath fiber at $0.0471 \text{ mW h cm}^{-1}$ and 2.57 mW cm^{-1} .⁴³ Furthermore, the device reveals excellent cycling stability with 86.6% capacitance retentions after 10 000 cycles at the scan rate of 20 mV s^{-1} . We noticed that the rate capability of the YSCs is relatively poor at fast scan rates or high discharge current densities (see Tables 3.1 and 3.2), which can be attributed to that fact that activated carbon has lower electrical conductivity and the polymer gel electrolyte also has a slower ion transport. The rate capability can be improved by using more conductive nanomaterials, such as carbon nanotubes, graphene, and carbon onions.^{24, 114} However, considering the various issues of nanomaterials as discussed in Introduction, YSCs proposed in this work are based on commercially available and low-cost carbon materials with unique merits. ESR of the YSC was also measured using EIS. Figure. 3.5f shows that its ESR is $4.9 \Omega \text{ cm}^{-1}$. The relatively small ESR implies that longer YSCs can be fabricated, which are more beneficial for integrating YSCs into wearable fabrics.

Figure 3.6. Gravimetric capacitance of a 10 cm long YSC at different CV scans rates and discharging current densities. The weight of YSC per centimetre is about 26.3 mg/cm (including activated carbon, carbon fibers and gel electrolyte).

Table 3.1 Specific length capacitance at different CV scan rates

Scan rate (mV/s)	2	5	10	20	50	100	200	500
Capacitance per length (mF/cm)	45.2	28.0	24.3	14.3	9.8	6.5	3.2	1.5

Table 3.2 Specific length capacitance at different current densities

Current density (mA/g)	25	50	100	200	500	1000
Capacitance per length (mF/cm)	46.8	39.7	34.9	21.3	11.2	2.6

Table 3.3 Comparison of F/YSCs reported in the literature.

Ref.	Electrode Materials	Electrolyte	Measurement methods	Length (cm)	Specific length capacitance (mF/cm)	Total capacitance (mF)
This work	Activated carbon/carbon fibers	PVA/H₃PO₄	2-electrode CV, 2 mV/s	5	51.2	256
				10	45.2	452
				20	31.65	633
				50	23.28	1164
47	Graphene framework/graphene fiber	PVA/H ₂ SO ₄	2-electrode	4.5	0.018	0.081
124	MWCNTs/CMF bundles/CNT film	PVA/H ₃ PO ₄	2-electrode GCD, 2 mV/s	5	6.3	31.5
43	rGO/CNT	PVA/H ₂ SO ₄	2-electrode GCD, 0.1 mA/cm ²	40	5.3	
127	CNT/carbon fiber	PVA/H ₂ SO ₄	2-electrode	17	0.5	8.5
128	CNT/OMC	PVA/H ₃ PO ₄	2-electrode GCD, 0.5 μ A		1.91	
135	CNT/MnO ₂	PVA/H ₃ PO ₄	2-electrode GCD, 2 μ A		0.015	

136	PEDOT/MWCNT	PVA/H ₂ SO ₄	2-electrode CV, 1 V/s	5	0.46	2.3
137	Activated carbon/stainless steel/natural fiber	SiWA	2-electrode CV, 2 mV/s	6	37.2	223.2
24	CNT/rGO fiber	PVA/H ₂ SO ₄	2-electrode GCD, 50 mA/cm ³	3 6	0.351 0.288	1.053 1.73
18	PPy/MnO ₂ /rGO	PVA/H ₃ PO ₄	2-electrode GCD	10	15.5	155
141	PANI/functionalized carbon fiber	PVA/H ₃ PO ₄	2-electrode GCD	10	3.9	39
148	Coiled carbon nanotubes/MnO ₂ /polymer fiber	PVA/LiCl	2-electrode	1	5.4	5.4
149	PANI/CNT/Pt	PVA/H ₃ PO ₄	2-electrode CV, 5 mV/s		0.2413	
150	CNT/Ti fiber	PVA/H ₃ PO ₄	2-electrode GCD, 0.25 μ A		0.024	
151	ZnO nanowires/graphene	PVA/H ₃ PO ₄	2-electrode CV, 100 mV/s		0.025	

3.3.4 Performance of YSCs of different lengths

For applications in energy storage textiles, long yarns are required to build realistic weavable devices. Previous studies were often limited to devices with short lengths.^{54,}
⁵⁵ The performance of fiber electrodes often deteriorates significantly with the increase of their length due to large resistances of electrodes.²⁴ We assembled YSCs of lengths 5, 10, 20, and 50 cm containing 2.2 mg cm^{-1} activated carbon. Figure. 3.7a shows their CV curves at 2 mV s^{-1} . The total capacitance of YSCs increases from 256, 451.7, 632.9 to 1164 mF when their length increases from 5 to 50 cm. Figure. 3.7b shows that the total capacitance increases linearly with the extension of length up to 10 cm, and the trend apparently deviates from linearity when the length is further extended. This is consistent with their CV curves in Figure. 3.7a, where the CV curves of the 5 cm and 10 cm YSCs exhibit a more rectangular shape. Conversely, the CV curves of 20 cm and 50 cm yarn are spindle-shaped, suggesting higher resistances in the devices.

We further compared the specific length capacitance of YSCs at different lengths with various FSCs reported in the literature. As shown in Figure. 3.7c, YSCs reported here show the specific length capacitances of 51.2 mF cm^{-1} (5 cm), 45.2 mF cm^{-1} (10 cm), 31.65 mF cm^{-1} (20 cm), and 23.28 mF cm^{-1} (50 cm), which are much higher than many previous results. To the best of our knowledge, these values are among the highest specific length capacitances ever reported for FSCs. The details of previous studies and their measurement conditions are listed in Table 3.3. We also compared the total capacitance and the length of assembled FSCs. As shown in Figure. 3.7d, YSCs reported here demonstrate both high total capacitance and a large length.¹⁴⁹⁻¹⁵¹

Figure 3.7. (a) CV curves of YSCs of different lengths at a scan rate of 2 mV s^{-1} . All supercapacitors were assembled using hybrid carbon yarns containing 2.2 mg cm^{-1} activated carbon. (b) The correction between total device capacitance and device length. (c) Comparison of specific length capacitance among the literature data. (d) Comparison of total device capacitance and device length among the literature data.

3.3.5 Mechanical flexibility and wearable knitted wristband

Figure 3.8. Stress-strain curve of pristine single carbon fiber yarn used in this work. It has a Young's modulus of 255.7 GPa.

Figure. 3.8 shows that carbon fiber yarns used in this work have excellent mechanical strength with a Young's modulus of 255.7 GPa. They are mechanically strong enough to be knitted. The mechanical flexibility of YSCs was tested by bending a 10 cm device at different angles or crumpling the device as shown in Figure. 3.9. Figure. 3.9a shows that CV curves of the device have minimal changes under different conditions. It can retain nearly 100% of its initial capacitance upon bending at different angles, and only exhibited a small decrease (< 9%) when the whole device was crumpled. Figure. 3.9b shows that the device still retains 98% of its initial capacitance after 1000 bending cycles. Due to its excellent mechanical flexibility, we knitted one 30 cm and two 50 cm YSCs together into a wearable wristband by hand. The structure of this wristband is shown in Figure. 3.9c. The photo in Figure. 3.9d demonstrates its ability to light an LED indicator (for about 1 minute) and to be safely worn, just like other wearable devices. We believe that such a wearable wristband has vast applications in smart textile.

Figure 3.9. (a) Capacitance retention of a 10 cm YSCs under different mechanical deformation conditions. Inset: CV curves of the YSCs at a scan rate of 5 mV s^{-1} and photos taken under different deformation conditions. (b) Capacitance retention at different bending cycles. Inset: Photos of the YSC under flat (I) and bended 360° (II) conditions. (c) Schematic illustration of a wearable wristband integrated using one 30 cm and two 50 cm long YSCs. (d) Photo of our wristband worn together using a Fitbits wristband. Our wristband can light an LED.

3.4 Conclusions

I have successfully fabricated all-carbon solid-state YSCs using commercially available activated carbon and carbon fiber yarns. Conductive carbon fibers concurrently serve as current collectors in YSCs and as substrates for the deposition of activated carbon particles with large surface area. Two hybrid carbon yarn electrodes

were twisted together in PVA/H₃PO₄ polymer gel. A 10 cm YSCs with the optimum composition of 2.2 mg cm⁻¹ activated carbon and 1 mg cm⁻¹ carbon fibers shows a specific length capacitance of 45.2 mF cm⁻¹ at 2 mV s⁻¹, which is one of the highest specific length capacitances ever reported for FSCs. It also exhibits an energy density of 6.5 mW h cm⁻¹ and a power density of 27.5 mW cm⁻¹, and can retain an energy density of 3.0 mWh cm⁻¹ at a higher power density of 220 mW h cm⁻¹. Due to the low equivalent series resistance at 4.9 Ω cm⁻¹, long YSCs up to 50 cm were demonstrated with high total capacitance up to 1164 mF. The all-carbon solid-state YSCs also show excellent mechanical flexibility with small capacitance changes upon bending or being crumpled. Using three long YSCs, a wearable wristband was knitted, and it can light an LED indicator, demonstrating strong potential for smart textile applications. Moreover, the fabrication method demonstrated in this work is based on commercially available safe carbon materials, which can be further scaled up for commercial exploration in the near future.

Chapter IV Hydrothermal assembly of micro-nano-integrated core-sheath carbon fibers for high-performance all-carbon micro-supercapacitors

(This chapter is reproduced with permission from Zhai, S.; Karahan, H. E.; Wei, L.; Chen, X.; Zhou, Z.; Wang, X. and Chen, Y*; Hydrothermal assembly of micro-nano-integrated core-sheath carbon fibers for high-performance all-carbon micro-supercapacitors, *Energy Storage Materials*, 2017, 9, 221–228. Copyright 2017 Elsevier.)

4.1 Introduction

With the emergence of trendy devices, such as Google glass, Apple watch, Fitbit wristband, and Oculus VR headset, wearable electronic devices (WEDs) already became a reality rather than science fiction.^{2, 152} So far there are no other reliable alternatives that offer stable and long-lasting energy supply, small Li-ion batteries serve as the main energy storage solution for WEDs. However, batteries often suffer from sluggish charge/discharge rate and low power density.^{153, 154} In addition to these, common batteries are also limited in mechanical flexibility, which restricts the innovation of WEDs.^{118, 155-158} As introduced in chapter I and chapter II, being lightweight, highly flexible and 1D, fiber-based micro-supercapacitors (FMCSs) are regarded as promising alternative energy storage solutions for WEDs.^{90, 135, 159, 160} Apart from the intrinsically high power density, fast charge/ discharge rate, and long cycling life^{3, 23, 142, 161, 162}, FMSCs also offer a great flexibility for design, as they are compatible with weaving and knitting. Further, they can facilitate the integration of WEDs with textiles and other fiber devices.^{3, 23, 142, 161, 162}

Fiber electrodes are the key components of FMSCs, and they should possess large surface area (for charge storage), high conductivity (for fast charging/discharging), and mechanical flexibility for building high-performance WEDs. Graphene based materials have been explored as building blocks to fabricate fiber electrodes^{79, 163, 164}, due to their large specific surface area ($\sim 2630 \text{ m}^2 \text{ g}^{-1}$)¹⁴⁰, high electrical conductivity (up to 10^6 S cm^{-1})¹⁶³, and high mechanical flexibility¹⁶⁵. Several methods were used to assemble graphene-based materials into fiber electrodes, including wet-spinning^{43, 44, 51, 134, 166}, dry-spinning,^{28, 44, 46} rolling graphene films into fibers^{62, 167, 168}, to name a few. However still, it is challenging to translate the excellent nanoscale properties of graphene-based materials into their macroscale assemblies. One reason is that graphene layers often restack together leading to small surface area for charge storage. Also, the contact resistance among small individual graphene sheets results in low overall electrical conductivity.

A versatile new approach, *i.e.* space-confined hydrothermal assembly, to convert nanoscale materials into microscale fibers using capillary channels was recently reported^{28, 46, 159}. Using this method, graphene oxide (GO) and carbon nanotubes were effectively assembled into porous hybrid fibers. The surface area of hybrid fibers reaches $\sim 400 \text{ m}^2 \text{ g}^{-1}$. However, their electrical conductivity undesirably remained below 100 S cm^{-1} . Particularly, with the increase of hybrid carbon fiber diameter from around 20 to above $200 \mu\text{m}$, their electrical conductivity dropped to less than 20 S cm^{-1} ⁴⁶. It should be noted that electrodes with electrical low conductivity result in poor rate capability in SCs. The rate capability is a critical performance indicator for SCs since higher the rate capability wider the range of charge/discharge current densities with minor variation in capacitance, which is desirable for vast practical applications.⁵³

Previous studies have reported the integration of neat metal wires, such as Au, Pt, Ni, Ti, or metal-coated plastic fibers as current collectors into fiber electrodes for achieving high rate capability in FMSCs^{47, 127, 136, 169}. However, metal wires take up a considerable portion of the total weight and volume of FMSCs with limited contribution to the total device capacitance, which inevitably compromises the device gravimetric and volumetric energy/power density.³ Commercial carbon (graphite) fibers comprise many graphite filaments of typically around 5-10 μm in diameter, and importantly they have high electrical conductivity (up to 10^4 S cm^{-1}) with excellent mechanical properties⁷. Further, the density of graphite fibers (*i.e.* $\sim 1.7 \text{ g cm}^{-3}$) is around one tenth of the density of metal wires (*e.g.* Au is at around 20 g cm^{-3})^{29, 47}. They are commercially available at low cost. Thus, graphite fibers offer a good potential in creating practical fiber electrodes for FMSCs.

In this study, I describe the synthesis of micro-nano-integrated core-sheath fiber electrodes using the space-confined hydrothermal assembly method for solid-state all-carbon FMSCs. The “core-sheath” structures involve highly conductive microscale “cores” made of commercial graphite fibers and nanoscale porous “sheaths” comprised of the hybrid of nitrogen doped GO and multiple walled carbon nanotubes (MWCNTs). The fiber electrodes were assembled into solid-state FMSCs with high specific energy and power densities. Furthermore, multiple FMSCs were integrated as energy storage units to power light-emitting diodes (LEDs), unveiling their good potentials for applications in WEDs.

4.2 Experimental section

4.2.1 Preparation of GO dispersions

The expandable graphite powder (DL50, Qingdao Henglid Graphite Co., Ltd) was first thermally expanded at 1050 °C for around 15 s to obtain expanded graphite. GO sheets were prepared through a modified Hummers' method using expanded graphite particles.^{43, 170} Briefly, the expanded graphite powder (1 g) and 200 mL H₂SO₄ (Merck, 98%) were added to a round bottom flask (500 mL), followed by the dropwise addition of KMnO₄ (5 g). Then the mixture was stirred at 30 °C for 24 h. Afterwards, deionized water (200 mL) and H₂O₂ (50 mL) were added to the mixture in an ice-water bath under stirring for 30 min. Subsequently, the resulting brown colored slurry was washed via multiple cycles of centrifugation by HCl (1 M) and then with deionized water until the pH of supernatant reaches above pH 5. Finally, the concentration of the GO dispersion was adjusted to 10 mg mL⁻¹.

4.2.2 Functionalization of MWCNTs and graphite fibers

MWCNTs (FloTube 9000, CNano Technology) of ~10 nm in diameter and typically ~10 µm in length were functionalized by refluxing in HNO₃ (65%) for 4 h. Then, the functionalized MWCNTs were dispersed in deionized water, and its concentration was adjusted to 2.5 mg mL⁻¹. Graphite fibers (Zoltek Panex 35) were first dipped into concentrated H₂SO₄ (98%) for 15 min. Next, they were sonicated in a mixture of acetone and ethanol for 15 min, followed by washing with deionized water. Finally, treated graphite fibers were dried in vacuum oven at 30 °C before use.

4.2.3 Synthesis of micro-nano-integrated core-sheath fibers

The homogeneous GO/MWCNT dispersion at the mass ratio of 4:1 was prepared by mixing GO dispersion (10 mg mL^{-1}) and MWCNT dispersion (2.5 mg mL^{-1}) with the addition of ethylenediamine (EDA, $20 \text{ }\mu\text{L mL}^{-1}$). As illustrated in Figure 4.2, the dispersion was injected into one side sealed glass tubes of 80 mm in length and 2 mm in inner diameter. At the same time, a bundle of graphite fibers (diameter: $\sim 40\text{--}50 \text{ }\mu\text{m}$, length: $\sim 10 \text{ cm}$, and electrical conductivity: 680 S cm^{-1}) were inserted into the glass tubes. Subsequently, the glass tubes were filled vertically in a stainless steel autoclave bomb lined by Teflon, and additional water was added in the autoclave outside of glass tubes. Lastly, resulting stuffed glass tubes, which can be considered space-confined hydrothermal mini-reactors, were subjected to heat at $180 \text{ }^{\circ}\text{C}$ for 12 h. After cooling, the resulting core-sheath fibers were poured into a water reservoir; and then dried in open air at room temperature overnight. For comparison, GO/MWCNT/EDA-derived hybrid fibers without graphite fiber cores (in short, core-free hybrid fibers) were also synthesized.

4.2.4 Physicochemical characterization of fibers

The morphology of fibers was characterized by field-emission scanning electron microscope (SEM, JEOL, JSM-6701) at an electron accelerating voltage of 5 kV. X-ray photoelectron spectroscopy (XPS, PHI Quantera) and energy dispersive X-ray spectroscopy (EDS, JEOL, JSM-6701) were employed to determine the chemical composition of fibers prepared. The electrical conductivity of fibers was measured using

a four-point probe station (Keithley) with a probe pin diameter of 40.6 μm and the spacing between pins at 1.6 mm.

4.2.5 Electrochemical properties of fibers

The electrochemical properties of fibers were first evaluated by CV and GCD on an electrochemical workstation (CHI 660E). The tests were carried out in a 3-electrode configuration in H_2SO_4 (1 M) electrolyte, using the core-sheath fibers (1 cm in length) as working electrodes, an Ag/AgCl (3 M KCl) electrode as the reference electrode, and a platinum electrode as the counter electrode. The capacitance of carbon fiber electrodes ($C_{\text{electrode}}$) was determined via CV and GCD according to Equation. (4.1) and (4.2), respectively.

$$C_{\text{electrode}} = \frac{Q}{2V} = \frac{1}{2V\nu} \int_{V_-}^{V_+} i(V) dV \quad (4.1)$$

where Q is the total charge obtained by integrating the enclosed area of CV curves, V is the voltage window ($V = V_+ - V_-$), ν is the scan rate of CV curves, and $i(V)$ is the current of CV curves.

$$C_{\text{electrode}} = i/(dV/dt) \quad (4.2)$$

i is the discharge current of GCD curves, t is the discharge time, and V is the voltage.

The specific volumetric capacitance ($C_{V,\text{electrode}}$) of the carbon fiber electrode was calculated using Equation (4.3):

$$C_{V,\text{electrode}} = C_{\text{electrode}}/V_{\text{electrode}} \quad (4.3)$$

where $V_{\text{electrode}}$ is the volume of the carbon fiber electrode.

4.2.6 Fabrication of solid-state fiber-based micro-supercapacitors (FMSCs)

Symmetric FMSCs were fabricated using two fibers of the same length and diameter as electrodes in poly (vinyl alcohol) (PVA)/H₃PO₄ gel electrolyte. Two fiber electrodes were placed in parallel on a polyethylene terephthalate (PET) film with one end of the fiber attached to a conductive silver paint pad for external circuit connection, and then coated with the gel electrolyte, followed by drying in open air overnight. PVA/H₃PO₄ gel electrolyte was prepared by dissolving PVA (10 g) in deionized water (100 mL) at 90 °C under stirring. After the mixture became clear and cooled down to room temperature, H₃PO₄ (10 g) was added under stirring.

4.2.7 Performance tests of FMSCs

The performances of FMSCs were tested in a 2-electrode configuration on the electrochemical workstation. CV, GCD, and electrochemical impedance spectroscopy (EIS) tests were carried out. The total capacitance (C_{device}) of the FMSCs was calculated using Equation (4.4) or (4.5):

$$C_{device} = \frac{Q}{2V} = \frac{1}{2V\nu} \int_{V_-}^{V_+} i(V)dV \quad (4.4)$$

where Q is the total charge obtained by integrating the enclosed area of CV curves, V is the voltage window ($V=V_+ - V_-$), ν is the scan rate of CV curves, and $i(V)$ is the current of CV curves.

$$C_{device} = i/(dV/dt) \quad (4.5)$$

where i is the discharge current of GCD curves, t is the discharge time and V is the voltage.

The specific volumetric capacitance $C_{V,electrode}$ of fiber electrodes in the 2-electrode FMSCs can be calculated using the equation (4.6):

$$C_{V,electrode} = 2C_{device}/V_{electrode} \quad (4.6)$$

$V_{electrode}$ is the volume of one carbon fiber electrode.

The volumetric capacitance of the FMSCs ($C_{V,device}$) was calculated according to the equation (4.7):

$$E_{V,device} = \frac{1}{2} C_{V,device} V_{device}^2 \quad (4.7)$$

V_{device} is the total volume of FMSCs including both electrodes and gel electrolyte.

The volumetric energy density ($E_{V,device}$) of the FMSCs was obtained from equation (4.8):

$$P_{V,device} = E_{V,device}/t \quad (4.8)$$

where t is the discharge time.

4.3 Results and discussion

Figure 4.1 An atomic force microscope image of GO sheets used in this study and its corresponding height profile. (Scale bar: 2 μm)

As illustrated in Figure 4.2, GO and MWCNTs were used to form the nanoscale porous sheath. GO sheets used in this study have an average lateral size of $\sim 25 \mu\text{m}$ (see

Figure 4.1). Large GO sheets offer less random alignment leading to a macroscale order when assembled as fibers with an enhanced electrical conductivity and higher mechanical strength compared to fibers produced using small GO sheets.^{50, 166, 171} The other component of the sheath, MWCNTs, serves two purposes: (1) preventing the restacking of GO sheets, to maintain a larger surface area accessible for electrolyte ions, and (2) improving the electrical conductivity of the resulting hybrid. The mass ratio of GO to MWCNTs was set at 4:1 based on the optimization made in our previous studies.^{28, 46} Besides, EDA was added to the mixture to reduce and nitrogen-dope GO, as well as to crosslink GO sheets with MWCNTs.²⁸ The graphite fiber bundle is 10 cm long crossing the whole glass tubes.

Figure 4.2 Schematic illustration of the space-confined hydrothermal assembly of core-sheath fibers. (a) A glass tube sealed at one end. (b) GO/MWCNT/EDA dispersion injected into the glass tube together with a bunch of densely packed commercial graphite fibers. (c) Hydrothermal assembly inside the glass tube at 180 °C in an autoclave. (d) The dried carbon fiber with a graphite fiber core and GO/MWCNT hybrid sheath.

At each run, tens of glass tubes filled with GO/MWCNT/EDA dispersion and graphite fibers were loaded vertically in an autoclave; and the autoclave was heated to the desired hydrothermal condition at 180 °C. We previously studied the formation of GO/MWCNT

fibers in capillary channels in different diameters ranging from 0.3 to 2 mm.⁴⁶ It was found that larger channels could yield hybrid fibers with higher specific length capacitance, which are beneficial for increasing the energy storage capacity of FMSCs. However, because of smaller capillary pressure in large diameter channels, the packing density of large diameter hybrid carbon fibers is much smaller than that of smaller fibers, leading to their inferior performances at higher scanning or charge/discharge rates [30]. Thus, in this study, we focused on the synthesis of fiber electrodes using the large glass tube (*i.e.* 2 mm in diameter).

Figure 4.3 (a) Photograph of core-sheath fibers, the enlarged photo shows one end of the fiber with graphite fibers extending out. (b) Cross-sectional SEM image of the core-sheath fiber and (c, d) SEM images of the enlarged views of sheath layers. Scale bars are 20 μm in (b), 2 μm in (c), and 200 nm in (d). (Note that the interface of commercial carbon fiber core and GO/MWCNT-derived sheath is visible in (c)).

Figure 4.3a shows a photograph of several as-synthesized core-sheath fibers in water. As displayed in the enlarged photograph, a thick layer of GO/MWCNT-derived sheath is wrapped uniformly around the graphite fiber core. After drying, the sheath shrinks significantly due to capillary forces, and the graphite fiber bundle was packed densely in the middle (see Figure 4.3b). It is desirable to keep the volume fraction of graphite fibers small so that the whole fiber can have larger specific volumetric capacitance

values. The diameter of dried core-sheath fibers is $\sim 170\ \mu\text{m}$ whereas that of the graphite fiber bundle is $\sim 45\ \mu\text{m}$. Accordingly, graphite fibers only take up about 7% of the volume of the overall fiber. SEM images in Figure 4.3c and d show that graphene sheets are closely packed but not restacked together, which are beneficial to create larger surface area accessible for electrolytes. Further, MWCNTs fill the gaps and voids among graphene sheets and distribute uniformly throughout the sheath. For comparison, the core-free hybrid fibers were also synthesized under the same conditions. They have a larger diameter of $\sim 235\ \mu\text{m}$ after drying (see Figure 4.4a and b).

Figure 4.4 (a) Photography of (core-free) GO/MWCNT-derived hybrid fibers. (b) Scanning electron microscope (SEM) image of the cross-section of a GO/MWCNT-derived hybrid fiber. (Scale bar: $20\ \mu\text{m}$)

The porosity of core-sheath and core-free fibers was studied by measuring their nitrogen adsorption/desorption isotherms, and the results are presented in Figure 4.5. Since the surface area of graphite fiber core is negligible compared to that of the GO/MWCNT sheath. We peeled off the GO/MWCNT sheath from the graphite fiber core to compare with the core-free fibers. Their specific surface areas are similar, with the GO/MWCNT sheath at $264.6\ \text{m}^2\ \text{g}^{-1}$ and the core-free hybrid fibers at $238.4\ \text{m}^2\ \text{g}^{-1}$,

respectively. Hysteresis loops on their nitrogen adsorption-desorption isotherms indicate the existence of mesopores, which are beneficial for achieving fast ion transport.

Figure 4.5 (a) Nitrogen adsorption/desorption isotherm and (b) pore size distribution of core-sheath fibers (graphite fiber core was removed). (c) Nitrogen adsorption/desorption isotherm and (d) pore size distribution of core-free hybrid fibers.

EDS and XPS were used to study the chemical nature of the core-sheath fibers. EDS maps (see Figure 4.6a) show that C, O, and N are distributed uniformly throughout the sheath. Correspondingly, their XPS spectra (Figure 4.7) further illustrate chemical structures of C, O, and N in the fibers. Their core-level C 1s peak can be deconvoluted into five sub-peaks. Peaks centered at ~ 284.0 and ~ 284.9 eV correspond to carbon atoms in sp^2 - and sp^3 - hybridized structures, respectively; and peaks at ~ 286.3 , ~ 287.8 , and

~288.9 eV are associated with C–N/C–O, C=O, and O=C–O bonds, respectively.^{28, 172} These results reveal that some functional groups still remain after chemical and thermal reduction of oxygen functionalities. In addition to C1s, the analysis of N1s region is quite essential, as we also want to dope N into the fiber. The N atomic content is about 4.3%. N1s seen in Figure 4.7c can be deconvoluted into three sub-peaks at ~398.2, ~399.6, and ~402.0 eV. The peak at ~398.2 eV corresponds to pyridinic nitrogen and the peak at ~399.6 is associated with amine moieties or other sp³ carbon and nitrogen bonds. The peak at ~402.0 eV can be ascribed to pyrrolic and graphitic nitrogen.^{46, 157, 173} Overall, EDS and XPS results confirm that we have managed to successfully dope the GO-MWCNT sheaths with nitrogen functionalities, which is in agreement with our previous observations^{28, 46}

Figure 4.6 (a) SEM image of the cross-section of the core-sheath fiber and its corresponding EDS maps for C, O, and N. (b) SEM image of the core-free fiber and its corresponding EDS maps for C, O, and N.

Figure 4.7 (a) XPS spectra of the core-free and core-sheath fibers. (b) C1s XPS peak and (c) N1s XPS peak of the core-sheath fiber.

To evaluate the electrochemical performances of the core-sheath fibers, CV and GCD tests were carried out in a 3-electrode configuration in comparison with the core-free hybrid fiber. Figure 4.8a shows that CV curves of the core-free fiber are spindle-shaped, especially at higher scan rates, suggesting a slow charge transfer rate. Correspondingly, their GCD curves (Figure 4.8c) exhibit large voltage drops at the beginning of the discharge process, indicating their low electrical conductivity. In contrast, the CV curves of the core-sheath fibers (Figure 4.8b) maintain quasi-rectangular shapes with large enclosed areas at high scan rates up to 100 mV s^{-1} , indicating their much better rate capability as electrodes for FMSCs. This can also be observed in their GCD curves (Figure 4.8d) with much smaller voltage drops as compared to those of core-free hybrid fibers. Their specific volumetric capacitances at different scan rates were calculated from their CV curves. The results are summarized in Figure 4.8e. Because graphite fiber cores may have only a limited contribution to the total capacitance, the specific volumetric capacitance of the core-sheath fiber is slightly smaller than that of the core-free fibers at the scan rate of 2 mV s^{-1} . However, with the increase in scan rate, the specific volumetric capacitance of the core-sheath fiber becomes much larger than that of core-free fibers above 5 mV s^{-1} . From 2 to 100 mV s^{-1} , the core-sheath fiber preserves

more than 52% of its initial capacitance, which is six times higher compared to that of the core-free hybrid fiber keeps at 8.5%. The significantly improved rate capacity can be attributed to its conductive graphite fiber core with an electrical conductivity of $\sim 680 \text{ S cm}^{-1}$, which is much larger than that of the core-free hybrid fiber (*i.e.* $\sim 23 \text{ S cm}^{-1}$). Thus, as expected, the charge transfer is much more efficient through the graphite fiber core.

Figure 4.8 Electrochemical performances of the GO/MWCNT-derived core-free hybrid fiber and the core-sheath fiber measured using a 3-electrode configuration in 1 M H₂SO₄ electrolyte. Both fibers are cut into ~1 cm in length as working electrodes. CV curves of the core-free fibers (a) and the core-sheath fibers (b) at different scan rates. GCD curves of the core-free fibers (c) and the core-sheath fibers (d) at various charge/discharge current densities. (e) Specific volumetric capacitances of the two types of fibers at different scan rates calculated from their CV curves.

Next, a solid-state FMSC was fabricated using the core-sheath fibers as fiber electrodes. As illustrated in Figure 4.9a, two core-sheath fibers of ~1 cm in length were assembled into a symmetric FMSC using PVA/ H₃PO₄ as a gel electrolyte. Figure 4.9b shows that CV curves of this FMSC retain a quasi-rectangular shape at the high scan rate up to 100 mV s⁻¹, indicating fast charge transfer in its electrodes. Correspondingly, its GCD curves in Figure 4.9c have a symmetric triangular-shape at the charge/discharge current density from 0.05 to 2 A cm⁻¹. The specific volumetric capacitance of each electrode of the FMSC was calculated from both CV and GCD curves, and the results are presented in Figure 4.9d. It should be noted that capacitances calculated from CV depend on voltage scan rates, while those of GCD depend on current densities applied. Thus, the specific volumetric capacitances of each electrode obtained from CV and GCD curves are not exactly matching to each other. The specific volumetric capacitances vary from 112.7, 105.7, 98.6, 91.6, 84.1 to 78.4 F cm⁻³ when the discharge current density increases from 0.05, 0.1, 0.2, 0.4, 1.0 to 2.0 A cm⁻³. This FMSC can retain above 69% of its initial specific volumetric capacitance from 0.05 to 2.0 A cm⁻³ which is superior to many previously reported fiber based FMSCs with fiber electrodes in similar diameters, such as those made of wet-spun graphene fibers (100 μm in

diameter) ¹²⁹, wet-spun graphene fibers with a sheath of carboxymethyl cellulose (75 μm in diameter) ⁴³ and nitrogen-doped GO/MWCNT fibers (236 $\pm$ 10 μm in diameter)

46.

Figure 4.9 Performances of a symmetric all-solid-state FMSC assembled using two core-sheath fibers. (a) Schematic illustration of the FMSC assembled by two core-sheath fibers of ~1 cm in length in PVA/H₃PO₄ gel electrolyte on a PET substrate. (b) CV curves of the FMSC at different scan rates. (c) GCD curves of the FMSC at different charge/discharge current densities. (d) The specific volumetric capacitance of each fiber electrode of the FMSC at different scan rates and charge/discharge current densities. (e) Comparison of the specific length and volumetric capacitance of the FMSC in this study with those reported in previous literatures. (f) Comparison of the energy and power densities of the FMSC in this study with those reported in previous literatures.

The volume of this FMSC including both electrodes and the surrounding gel electrolyte is $\sim 4.74 \times 10^{-4} \text{ cm}^3 \text{ cm}^{-1}$ in length, and the total area of the device is estimated to be $\sim 1.07 \times 10^{-1} \text{ cm}^2 \text{ cm}^{-1}$ in length. Thus, the specific length capacitance, specific volumetric capacitance and specific areal capacitance of the FMSC were calculated to be 12.8 mF cm^{-1} , 27 F cm^{-3} and 119.6 mF cm^{-2} , respectively, at the current density of 0.05 A cm^{-3} . These performances are higher than many recent reported performance results of FMSCs.^{18, 47, 133, 141, 161, 162, 169, 174-176} Their comparison is shown in Figure 4.9e. The details of previous studies and their measurement conditions are listed in Table 4.1. The specific volumetric energy and power densities of the FMSC were calculated from its GCD curves, and the results are shown in Figure 4.9f. It achieves the high volumetric energy density of 3.75 mWh cm^{-3} , length energy density of $1.78 \text{ } \mu\text{Wh cm}^{-1}$ and areal energy density of $16.61 \text{ } \mu\text{Wh cm}^{-2}$ at the power density of 12 mW cm^{-3} , and retains the high energy density of 2.60 mWh cm^{-3} at the high power density of 612 mW cm^{-3} . These performance data are higher than those of a 5.5-V/100-mF commercial supercapacitor, and are one of the best among recently reported FMSCs,

such as those made of rGO/MnO₂ nanosheets/polypyrrole deposited on stainless steel current collector (1.1 mWh cm⁻³, 150 mW cm⁻³)¹⁸, rGO@carboxymethyl cellulose core-sheath structured fiber (3.5 mWh cm⁻³, 180 mW cm⁻³)⁴³, MWCNT/rGO fiber (3.4 mWh cm⁻³, 700 mW cm⁻³)²⁴ and nitrogen-doped rGO/MWCNT fiber (3.1 mWh cm⁻³, 400 mW cm⁻³)⁴⁶. It should be noted that many previously reported FMSCs could achieve a high energy density at low power densities. But they suffer from a significant drop in energy density with the increase of power densities, which limits their application potential. In contrast, the FMSC reported in this study can retain up to 69.3% of their initial energy density when its power density increases over fifty times, from 12 to 612 mWh cm⁻³. This is promising to develop practical high-performance FMSCs that will be useful for various WEDs.

Table 4.1 Comparison of fiber supercapacitors reported in the literature. (All measurements given are based on 2-electrode method.)

* These values are based on the actual devices built.

References [#]	Electrode materials	Diameter (electrode) (μm)	Electrolyte	Specific length capacitance* (mF cm^{-1})	Specific volumetric capacitance* (F cm^{-3})
This work	N-GO/MWCNT core-sheath fiber	170	PVA/H ₃ PO ₄	12.8	27.00
133	CNT sheets / CNT fiber	43*	PVA/H ₃ PO ₄	0.029	32.09
47	3D porous network-like graphene framework / graphene fiber	100	PVA/H ₂ SO ₄	0.018	0.115
174	MnO ₂ /CNT fibers	80	PVA/LiCl	1.36	8.65
176	CNT fibers	20	PVA/H ₃ PO ₄	0.02826	4.5
162	ZnO nanowires / Plastic wires	220	PVA/H ₃ PO ₄	0.2	0.26
141	PANI coated carbon fiber thread / functionalized carbon fiber thread		PVA/H ₃ PO ₄	3.5	5.8
161	rGO-GO	50	electrolyte free	0.225	11.44
294	CNT fibers	65	PVA/H ₂ SO ₄	0.51	18.12
175	MnO ₂ / CNT fiber	31	PVA/KOH	0.157	35.19
18	PPy / MnO ₂ / rGO	180-250	PVA/H ₃ PO ₄	15	12.4

The stability of the FMSC was evaluated by the CV at 100 mV s^{-1} for 10000 cycles. Figure 4.10a shows that the FMSC retains $\sim 96.5\%$ of its initial capacitance even after 10000 cycles, indicating excellent cycling stability. To evaluate its mechanical stability, the FMSC was fully bent (*i.e.* $\sim 180^\circ$) for 1000 times. The FMSC can retain its structural integrity after bending, and remarkably shows only $\sim 0.1\%$ of drop in its capacitance at 100 mV s^{-1} , which suggests excellent mechanical stability (Figure 4.10b). The capacitance retention was also monitored by the CV at 100 mV s^{-1} for 10000 cycles after the FMSC was bent at $\sim 180^\circ$ for 1000 times. Figure 4.10c shows that it retains $\sim 95.2\%$ of its initial capacitance.

Figure 4.10 (a) Cycling tests of the FMSC at the scan rate of 100 mV s^{-1} for 100000 cycles. (Inset is a photograph of the FMSC). (b) Capacitance retention test of the FMSC when bent at 180° for 1000 times. (Inset photograph shows the fully bent FMSC.). (c) Capacitance retention test of the FMSC after bent at 180° for 1000 times.

For practical WED applications, it is desirable to connect FMSCs in series or parallel to broaden their operating voltage and current. Figure 4.11a shows that when two or three FMSCs are connected in series, their charge/discharge voltage windows are expanded to 2 and 3 V, respectively, without changing discharge time. Figure 4.11b exhibits that when two or three FMSCs are connected in parallel, their output currents are doubled and tripled,

respectively, with the same voltage window. Both results demonstrate the excellent integratability and scalability of the FMSCs assembled using core-sheath fibers.

Figure 4.11 GCD curves of one, two or three FMSCs connected in series (a) and in parallel (b). (Note that the inset images show corresponding integration schematics in both figures).

To further demonstrate the potential for practical applications, as shown in Figure 4.12a, the energy storage unit was fabricated by integrating fifteen fibers together, with five connected in parallel first into the parallel array and then three parallel arrays were assembled in series. For comparison, we also fabricated another energy storage unit using the core-free fibers. Figure 4.12b shows the CV curves of the two energy storage units at the scan rate of 200 mV s^{-1} . The CV curve of the energy storage unit assembled from the core-sheath fibers has a much larger enclosed area and a more rectangular shape, indicating faster charge transfer and more energy stored. The energy storage unit integrated by core-sheath fibers has the energy density of 2.54 mWh cm^{-3} at the power density of $121.14 \text{ mW cm}^{-3}$. In contrast, the unit integrated by core-free hybrid fibers can only deliver the energy density of 1.17 mWh cm^{-3} at the power density of 65.22 mW cm^{-3} . We used them to light

a red LED to further compare their performances. Both were first charged at the same current intensity (3 mA). The energy storage unit assembled from the core-sheath fibers can light the red LED for 3 min (see Figure 4.12c) whereas the other unit can only power the same LED for around 1.5 min (see Figure 4.12d). Besides, the LED powered by the energy storage unit assembled from the core-sheath fibers is much brighter. Furthermore, the energy storage unit can also work under bending, twisting and stretching conditions as shown in Figure 4.12e and f.

Figure 4.12 (a) Photography of two energy storage units, integrated by the core-sheath fiber based FMSCs (upper), core-free hybrid fiber based FMSCs (middle) and their corresponding integration schematics (bottom): five FMSCs are integrated into a parallel array first, and then three parallel arrays are connected in series. The fibers are 1 cm in

length. (b) CV curves of the two energy storage units. Photography of a LED lightened by the energy storage unit integrated by the core-sheath fiber based FMSCs (c) and the core-free hybrid fiber based FMSCs (d). (e, f) Photographs show that the integrated energy storage unit can work under bending, twisting and stretching conditions.

4.4 Conclusions

Novel micro-nano-integrated core-sheath fibers were synthesized by space-confined hydrothermal assembly of nitrogen doped GO/MWCNT hybrids around commercial graphite fiber cores. The nanoscale GO/MWCNT hybrids provide large surface area (up to $400 \text{ m}^2 \text{ g}^{-1}$) and sufficient surface functional groups (4.3% of N) for capacitive energy storage. The microscale graphite fiber core with high electrical conductivity (680 S cm^{-1}) serves as fast electron transfer pathways. As a result, the core-sheath fiber preserves more than 52% of its initial capacitance from 2 to 100 mV s^{-1} , more than six times increase in rate capability compared to that of the core-free hybrid fiber. All-solid-state FMSCs assembled using these fiber electrodes show a high specific length capacitance of 12.8 mF cm^{-1} and a high specific volumetric capacitance of 27 F cm^{-3} at the current density of 0.05 A cm^{-3} . They can retain ~69.3% of their initial capacitances when the current density increases from 0.05 to 2 A cm^{-3} . They also exhibit the high energy density of 3.75 mWh cm^{-3} at the power density of 12 mW cm^{-3} , and can retain an energy density of 2.60 mWh cm^{-3} at the high power density of 612 mWh , which are higher than most of previously reported FMSCs. The FMSC in this study also show good long-term stability with the capacitance retention of ~96.5% after 10000 cycles, and excellent mechanical stability with ~99.9% capacitance retention after 1000 bending cycles. Furthermore, multiple FMSCs can

be assembled in parallel and/or in series to expand their working voltage window or/and current densities. An integrated energy storage unit comprising of 15 FMSCs was assembled to lighten an LED indicator, demonstrating its good potential in WED applications.

Chapter V Nano-RuO₂-decorated holey graphene composite fibers for micro-supercapacitors with ultrahigh energy density

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5.1 Introduction

In Chapter VI, we introduced that the fast development of wearable electronic devices (WEDs) creates a strong demand for highly efficient and miniaturized energy storage solutions. Micro-batteries currently dominate the field in actual applications.^{177, 178} But, because of their fast charge/discharge rate, high power density, and long cycling life, micro-supercapacitors (MSCs) are emerging fast as promising alternatives.^{3, 46, 179-182} Particularly, among various types of MSCs, fiber-based MSCs (FMSCs) that use 1D fibers as electrodes, have attracted significant interests due to their unique characteristics. For example, FMSCs are usually highly flexible and thus can be knitted or woven into textiles, which not only offers excellent wearability but also provides device design flexibility.^{3, 46} Further, multifunctional WEDs can be created by integrating FMSCs with fiber-based energy harvesting and/or environmental sensing devices.^{3, 46}

Graphene materials is a promising material candidate for fabricating 1D electrodes for FMSCs due to their large surface area and high electrical conductivity.^{3, 17, 63, 183, 184} Graphene fibers have been assembled using several methods, such as wet-spinning,^{24, 41, 43,}

⁵¹ hydrothermal assembly,^{17, 44, 46} film conversion,^{167, 168} and electrophoretic deposition.¹⁸⁵

Although graphene fiber electrodes usually deliver high power and long cycle life, their energy storage capacity based on the physical adsorption mechanism of double layer capacitance is limited by their surface area (about 100-300 F g⁻¹).^{63, 185-188} In comparison, pseudocapacitive materials store energy via reversible redox reactions at electrode-electrolyte interfaces,¹⁸⁹ which may have 10-100 times higher specific capacitance than that of materials based on double layer capacitance alone.¹⁸⁹ In order to increase energy storage capacity, significant research efforts have been devoted to incorporating various pseudocapacitive materials into graphene fibers. They include conductive polymers (*e.g.*, poly(3,4-ethylenedioxythiophene), poly(styrenesulfonate), polyaniline and polypyrrole),^{190, 191} transition metal oxides/hydroxides (*e.g.*, RuO₂, MnO₂, MoO₂, V₂O₅, Ni(OH)₂, Co(OH)₂)^{146, 154, 159, 188, 192-195} and metal sulfides (*e.g.*, NiCo₂S₄, MoS₂)^{191, 196, 197}. However, until now the energy storage capacity of fiber electrodes is still not satisfactory.

There are mainly three challenges in integrating pseudocapacitive materials into graphene fibers for FMSCs. First, most of the graphene fibers have been formed by the wet-spinning process.^{63, 198} The addition of pseudocapacitive material precursors often significantly changes the ionic strength or pH of graphene or graphene oxide (GO) dispersions, which strongly affects the formation of structurally stable graphene fibers.^{63, 199} Second, although increasing mass loading of pseudocapacitive materials in graphene fibers usually leads to higher total capacitance in composite fibers, it often causes extensive aggregation of pseudocapacitive materials inside graphene fibers, leading to uneven distribution and lower specific capacitance.^{192, 197} Third, high mass loading of pseudocapacitive materials also often block small pores in graphene fibers, which limits the

efficient electrolyte ion diffusion, leading to lower rate capability of the resulting fiber electrodes.^{142, 159, 192, 197}

In this study, ruthenium oxide (RuO₂) is selected as the pseudocapacitive material due to its high theoretical specific capacitance ($\sim 1400 \text{ F g}^{-1}$), high electrical conductivity ($\sim 10^5 \text{ S cm}^{-1}$), a wide potential window, fast charging/discharging rate and high chemical stability.^{200, 201} We synthesized a novel holey graphene oxide (HGO)/ RuO₂ composite fibers using a two-step procedure. Hybrid HGO fibers were first synthesized by a space confined hydrothermal synthesis method. Next, three different routes were explored to efficiently incorporate a large amount of amorphous hydrous RuO₂ into the porous HGO fiber scaffold. The resulting composite fibers were characterized by various techniques to determine their optimum composition, including scanning electron microscope (SEM), energy-dispersive X-ray spectroscopy (EDS), transmission electron microscope (TEM), Raman spectroscopy, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA) and electrochemical tests. The optimized composite fibers were used to assemble solid-state FMSCs, resulting in the highest energy storage capacity ever reported for FMSCs together with good rate capability. Furthermore, a self-power energy system was demonstrated using multiple FMSCs and commercial flexible solar cells. Overall, our results unveil the good potential of HGO/RuO₂ composite fibers for FMSC applications.

5.2 Experimental section

5.2.1 Preparation of carbon precursors

GO was synthesized from natural graphite flakes (Sigma-Aldrich) by the modified Hummers' method. Homogeneous GO aqueous dispersion was prepared using as-prepared GO, and its concentration was adjusted to 2 mg mL⁻¹. HGO was prepared using the previously reported method.²⁰² In brief, 10 mL H₂O₂ (30 %) was mixed with 100 mL GO dispersion (2 mg mL⁻¹) and then heated at 95 °C under stirring for 2 h. The as-prepared HGO was further purified by centrifugation and washing with deionized water three times to remove residual H₂O₂ before being re-dispersed in deionized water at the concentration of 8.0 mg mL⁻¹. Commercial SWCNTs (Carbon Solutions, Inc., AP-SWNT, with the diameter of ~1.4 nm) were functionalized by refluxing in HNO₃ (65 %) for 4 h. Afterwards, functionalized SWCNTs were dispersed in distilled water at the concentration of 2 mg mL⁻¹ by the tip sonication (Sonics, VCX 130PB).

5.2.2 Synthesis of HGO/RuO₂ composite fibers

The HGO/RuO₂ composite fibers were synthesized in two steps. In the first step, the wet HGO fiber scaffold was prepared by the space-confined hydrothermal synthesis. A homogeneous HGO and SWCNTs mixture at the mass ratio of 4:1 was prepared by mixing 1 mL HGO dispersion (8 mg mL⁻¹) and 1 mL SWCNTs dispersion (2 mg mL⁻¹), followed by adding 30 μL EDA. The mixture was injected into one side sealed glass tubes with the total length of 80 mm and an inner diameter of 0.5 mm. Afterwards, these glass tubes were vertically loaded in a Teflon-lined autoclave bomb with additional water outside the glass tubes. Subsequently, the autoclave bomb was placed into an electric oven at 220 °C for 6 h. After cooled down to the room temperature, the wet HGO fibers formed inside the glass tubes were poured into a water reservoir. In the second step, three different routes were used

to anchor Ru ions on the HGO fiber scaffold. In the first route, the wet HGO fibers were first dried in air at 25 °C for 24 h before emerged in the RuCl₃ aqueous solutions (0.005 to 0.03 M) for 12 h. Afterwards, the Ru³⁺ adsorbed HGO fibers were emerged in 1 M NaOH solution for 1 h to form Ru(OH)₃. The resulting composite fibers were then annealed in air at 150 °C for 2 h to transform Ru(OH)₃ to RuO₂. In the second route, the wet HGO fibers directly emerged in RuCl₃ aqueous solutions followed by being dried in air. In the third route, the wet HGO fibers were first freeze-dried for 24 h before emerging in the RuCl₃ aqueous solutions. The rest of the treatment procedures in the last two routes were kept the same as what used in the first route.

5.2.3 Characterization of physicochemical properties

The morphology of composite fibers was examined by a field emission SEM (ULTRA Plus, Zeiss) at the electron accelerating voltage of 5 kV and a TEM (JEOL, JEM-2100F). Their chemical composition was analyzed by XPS (PHI 5000 VersaProbe, ULVAC-PHI) and EDS (ULTRA Plus, Zeiss). Their Raman spectra were recorded on a Raman microprobe (inViaTM Reflex, Renishaw) under a 633-nm laser excitation. The TGA measurements were carried out on a TGA analyzer (SDT Q600) from 25 to 800 °C at the heating rate of 10 °C /min in air. The fibers were considered as cylinders. SEM was used to measure their diameters, and a ruler was used to measure their lengths. Their volumes were calculated according to $V = \frac{\pi D^2}{4} \times L$ (where V is the volume, D is the diameter, and L is the length of fibers). The balance of the TGA analyzer was used to determine their weights.

5.2.4 Characterization of electrochemical properties

The electrochemical properties of composite fibers were first evaluated by the CV and GCD methods in the three-electrode configuration in 1 M H₂SO₄ electrolyte on an electrochemical workstation (CHI660E). A single composite fiber (2000 μ m in length) was used as the working electrode, an Ag/AgCl (3 M KCl) electrode and a platinum mesh (2 $\times$ 2 cm) were employed as the reference electrode and counter electrode, respectively. The capacitance of fiber electrodes was determined by their CV curves and GCD curves according to the equation (5.1) and (5.2), respectively.

$$C_{electrode} = \frac{Q}{2V} = \frac{1}{2Vv} \int_{V_-}^{V_+} i(V) dV \quad (5.1)$$

where Q is the total charge obtained by integrating the enclosed area of CV curves, V is the scanned voltage window ($V = V_+ - V_-$), v is the CV scan rate, and $i(V)$ is the current of the CV curves.

$$C_{electrode} = \frac{i}{dV/dt} \quad (5.2)$$

where i is the discharge current, t is the discharge time and V is the voltage, dV/dt is the slope of the discharge curve.

The specific volumetric capacitance of fiber electrodes was calculated using the equation (5.3).

$$C_{V,electrode} = C_{electrode} / V_{electrode} \quad (5.3)$$

where $V_{electrode}$ is the volume of the fiber electrodes.

5.2.5 Fabrication and evaluation of solid-state FMSCs

PVA/H₃PO₄ gel electrolyte was prepared by dissolving 10 g PVA (molecular weight 89,000-98,000, Sigma) in 100 mL deionized water at 90 °C under stirring. After the mixture became clear, it was cooled to the room temperature, and then 10 g H₃PO₄ was added under stirring. Two fiber electrodes with same length were placed in parallel on a polyethylene terephthalate (PET) film with the two ends in the opposite direction connected to the external circuits via conductive silver paste. Afterwards, gel electrolyte was coated on the two fiber electrodes and dried in air overnight. The device performances were tested in the two-electrode configuration. Their CV and GCD curves were recorded on the electrochemical workstation. The total capacitance of the FMSCs was calculated from their CV and GCD curves by the equation (5.4) and (5.5), respectively.

$$C_{device} = \frac{Q}{2V} = \frac{1}{2Vv} \int_{V_-}^{V_+} i(V) dV \quad (5.4)$$

where Q is the total charge obtained by integrating the enclosed area of CV curves, V is the voltage window ($V = V_+ - V_-$), v is the scan rate, and $i(V)$ is the current of CV curves.

$$C_{device} = \frac{i}{\left(\frac{dV}{dt}\right)} \quad (5.5)$$

where i is the discharge current, t is the discharge time and V is the voltage, dV/dt is the slope of the discharge curve.

The specific volumetric capacitance $C_{V,electrode}$ of fiber electrodes used in FMSCs is calculated by the equation (5.6):

$$C_{V,electrode} = 2 \frac{C_{device}}{V_{electrode}} \quad (5.6)$$

where $V_{electrode}$ is the volume of one fiber electrode in FMSCs.

The volumetric capacitance of FMSCs ($C_{V,device}$) is calculated according to the question (5.7):

$$C_{V,device} = \frac{C_{device}}{V_{device}} \quad (5.7)$$

where V_{device} is the total volume of FMSCs including two electrodes and the surrounding gel electrolyte.

The volumetric energy density ($E_{V,device}, Wh\ cm^{-3}$) of FMSCs is calculated by the equation (5.8):

$$E_{V,device} = \frac{1}{2} C_{V,device} \frac{V^2}{3600} \quad (5.8)$$

where V is the applied voltage window.

The volumetric power density ($P_{V,device}, W\ cm^{-3}$) of FMSCs is obtained from the equation (5.9):

$$P_{V,device} = 3600 \frac{E_{V,device}}{t} \quad (5.9)$$

where t is the discharge time.

5.3 Results and discussion

Our initial attempt was to directly synthesize HGO/RuO₂ composite fibers by adding RuCl₃ aqueous solutions in carbon material dispersions, and then the mixture went through a conventional one-pot hydrothermal synthesis. However, this approach was unsuccessful, because Ru³⁺ ions significantly interrupt the assembly of HGO sheets, resulting in scattered large particles other than stable 1D fibers. Therefore, as illustrated in Figure 5.1, HGO/RuO₂ composite fibers were then synthesized in the two-step procedure: first, a porous HGO fiber scaffold was hydrothermally assembled, and next RuO₂ was incorporated into the fiber scaffold.

In the first step, HGO was used as the building block for the fiber because of three considerations: i) HGO has a large surface area, which can not only host a significant amount of RuO₂, and also provide a high double layer capacitance. ii) HGO can boost the utilization rate of supported RuO₂ by preventing the severe aggregation of RuO₂ and providing conduction paths for protons to access RuO₂.^{193, 201, 203} iii) More importantly, the nanoscale holes on the graphene basal plane are expected to facilitate the rapid ion transport required in FMSCs.^{202, 204} Single-walled carbon nanotubes (SWCNTs) were added because our previous studies showed that SWCNTs could prevent the complete restacking of GO sheets to enable larger ion accessible surface area. SWCNTs are also beneficial for enhancing the electrical conductivity of the interconnected GO network.²⁸ The mass ratio between HGO and SWCNTs was set at 4 to 1, following the previously optimized recipe used for GO and SWCNT.^{28, 46} Small amount of ethylenediamine (EDA) was also added as a nitrogen dopant for HGO and a crosslinking agent for enhancing the binding between HGO and SWCNTs.²⁸ The HGO/SWCNTs/EDA aqueous mixture was injected into one end closed glass tubes. Subsequently, the glass tubes were loaded vertically in an autoclave bomb and served as the space-confined hydrothermal reactor. The hydrothermal assembly was carried out at 220 °C for 6 h. Wet HGO fibers were formed inside the glass tubes, which were poured into a water reservoir (see the photo in the Figure 5.2).

Figure 5.1 Schematic illustration of the synthesis of HGO/RuO₂ composite fibers.

Figure 5.2 Photos of HGO fibers in a water reservoir.

In the second step, the critical task is to efficiently incorporate RuO₂ into the porous HGO fiber scaffold with uniform distribution and high mass loading. We explored three different routes. As illustrated in Figure 5.1, in the first route, the wet HGO fibers were first dried in air, and then dipped into the RuCl₃ aqueous solution (0.02 M) to absorb Ru³⁺ ions. Next, the adsorbed Ru³⁺ ions were transformed into RuO₂ by reacting with NaOH. Afterwards, Ru(OH)₃ was converted to RuO₂ by annealing in air at 150 °C.¹⁹³ The resulting

composite fibers were denoted as “air dry-HGO/RuO₂”. In the second route, the wet HGO fibers directly emerged in the RuCl₃ aqueous solution before being dried in air followed by the other treatments the same as what used in the first route. The resulting composite fibers were denoted as “wet-HGO/RuO₂”. The third route used freeze-dried HGO fibers to load Ru³⁺ ions in the RuCl₃ aqueous solution. The other treatments were also kept the same. The resulting composite fibers were denoted as “freeze dry-HGO/RuO₂”.

Figure 5.3 Cross sectional and enlarged SEM images and the corresponding (C or Ru) elemental maps (a, b, c) air-dried HGO fiber, (d, e, f) air dry-HGO/RuO₂, (g, h, i) wet-

HGO/RuO₂, and (j, k, l) freeze dry-HGO/RuO₂. Scales bars in the first and third rows are at 10 μ m. Scales bars in the second row are at 2 μ m.

Figure 5.4 (a, b) EDS elemental (O, N) maps of the air-dried HGO fiber in Figure 5.3a.

We first evaluated the efficiency of the three different synthesis routes according to the distribution uniformity and mass loading of RuO₂ in the resulting HGO/RuO₂ composite fibers. The morphology of the fibers was examined by SEM, and their elemental composition was determined by EDS. TGA was further carried out to determine the Ru mass loadings. The cross-section of fracture ends of the fibers and their EDS elemental maps are shown in Figure 5.3 and Figure 5.4. Figure 5.3a and 5.3b show that HGO sheets are densely packed along their central axis, and SWCNTs interpose between HGO sheets. EDS elemental maps (Figure 5.3c and Figure 5.4a, b) indicate that C, N, O elements are uniformly distributed throughout air-dried HGO fibers. After incorporating RuO₂, the diameter of air dry-HGO/RuO₂ fiber remains similar to that of air-dried HGO fiber at 35 μ m with the densely packed structure (see Figure 5.3e). The wet-HGO/RuO₂ fiber also has a same densely packed structure (see Figure 5.3h) with a slightly larger diameter of 37 μ m. In contrast, the freeze dry-HGO/RuO₂ fiber has an interconnected 3D porous structure (see

Figure 5.3k) with a much larger diameter of 135 μm . TGA results (see Table 5.1) show that the Ru mass loading in the air dry-HGO/RuO₂ fiber is only 0.7 wt.%. The freeze dry-HGO/RuO₂ fiber has a relatively higher Ru mass loading of 4.6 wt.%. However, its EDS elemental map (Figure 5.3l) indicates that Ru is not uniformly distributed in the fiber with most of Ru staying near to the outer surface. In comparison, the wet-HGO/RuO₂ fiber has a much higher Ru mass loading of 36.8 wt.%, which is 52 times higher than that in the freeze dry-HGO/RuO₂ fiber and 7 times higher than that in the air dry-HGO/RuO₂ fiber. More importantly, Ru is uniformly distributed throughout the wet-HGO/RuO₂ fiber (see Figure 5.3i).

We propose that the high mass loading and uniform distribution of Ru in the wet-HGO/RuO₂ fiber can be attributed to the following three factors. First, the wet HGO fiber has the interconnected 3D porous structure similar to that of the freeze-dried HGO fiber. The open channels are beneficial for the transport of Ru³⁺ ions throughout the fiber when the wet fiber was immersed in the RuCl₃ aqueous solution. In comparison, it is much harder to transfer Ru³⁺ ions into the closed packed air-dried HGO fibers. Second, the filled water in the wet HGO fiber serves as a natural “canal” for Ru³⁺ ions diffusion. In comparison, even though the freeze-dried HGO fiber also has a similar porous structure, it is harder for the RuCl₃ aqueous solution to enter the dried fiber. Figure 5.5 shows that the air-dried HGO fiber has much better wettability than the freeze-dried HGO fiber in the contact angle measurement. Third, the holes on HGO sheets facilitate the diffusion Ru³⁺ ions into the fiber. We carried out a comparable study by substituting HGO with non-hole GO while all other experimental conditions were kept the same. Table 5.1 and Figure 5.6 show that the Ru mass loading decreases by ~6.8 wt.% to 30.0 wt.% when non-hole GO was used.

Figure 5.5 A Photograph showing the meniscus curvatures between air-dried HGO fiber and water (a), freeze-dried HGO fiber and water (b).

Figure 5.6 (a) Cross-section SEM image of wet-GO/RuO₂ fiber and (b) its EDS elemental map of Ru. Scales bars are 10 μ m. (c) CV curves of the wet-GO/RuO₂ and wet-HGO/RuO₂

fiber measured at the scan rate of 10 mV s^{-1} using a 3-electrode configuration in $1 \text{ M H}_2\text{SO}_4$ electrolyte. (d) Ru mass loading of fibers and their corresponding volumetric capacitance.

To better understand their chemical characteristics, the wet-HGO/RuO₂ fiber was further characterized by Raman spectroscopy, X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). Raman spectrum of the fiber (see Figure 5.7) shows two distinct peaks at ~ 502 and 608 cm^{-1} , which originate from RuO₂.^{193, 205, 206} The existence of SWCNTs is confirmed by the radial breathing mode (RBM) peak at $\sim 161 \text{ cm}^{-1}$.^{207, 208} The D-band peak at $\sim 1350 \text{ cm}^{-1}$ and the G-band peak at $\sim 1580 \text{ cm}^{-1}$ indicate the coexistence of HGO and SWCNTs.^{207, 208} XRD spectra in Figure 5.8 shows that there are two main peaks, which can be assigned to the (002) and (100) diffraction peaks of disordered GO sheets.^{192, 193} No crystalline diffraction peaks from RuO₂ (e.g., JCPDS file 40-1290) were observed, even though the mass loading is high, which suggests that amorphous RuO₂ was formed in the fiber. Previous studies have reported that amorphous RuO₂ possesses higher capacitance than its crystalline structure.^{83, 209}

Figure 5.7 Raman spectra of the wet-HGO/RuO₂ fiber.

Figure 5.8 XRD patterns of air dry-HGO/RuO₂ fiber, wet-HGO/RuO₂ fiber and RuO₂ particles (XRD patterns of RuO₂ particles is digitalized form ref. 188).

XPS survey scan of the fiber (see Figure 5.9) indicates the existence of C, N, O, and Ru in the fiber. The core-level O1s spectrum can be deconvoluted into 6 sub-peaks (see Figure 5.9b). The three peaks centered at 531.3, 532.4 and 533.3 eV are associated with C-O, C=O, and O-C=O, respectively, which originate from oxygen-containing groups on HGO sheets.²¹⁰ These oxygen-containing groups are beneficial for stabilizing RuO₂ particles on HGO sheets via chemical and Van der Waals interactions.¹⁹³ The other three peaks are from RuO₂ at ~529.5 eV, Ru-O-H at ~530.5 eV and H₂O at 531.8 eV.^{205, 211} Figure 5.9c shows a typical Ru3p_{1/2} peak at 485 eV and Ru3p_{3/2} peak at 462.5 eV from RuO₂.^{205, 211} The Ru3p_{3/2} peak can be deconvoluted into two peaks at 461.5 eV from RuO₂ and 463.5 eV from Ru(OH)₂.^{205, 209} Overall, the XPS results suggest that RuO₂ in the fibers is hydrated, which is beneficial for ionic transportation.²⁰⁵

Figure 5.9 (a) XPS survey scan of the wet-HGO/RuO₂ fiber and its O1s (b) and Ru3p (c) XPS spectra.

The electrochemical performances of the fibers were first evaluated by cyclic voltammetry (CV), galvanostatic charge and discharge (GCD) and electrochemical impedance spectra (EIS) in 1 M H₂SO₄ electrolyte using a standard three-electrode configuration (see Figure 5.10 and Figure 5.11). Figure 5.11 shows that the composite fibers have two redox peaks, which is the typical pseudocapacitive behavior of RuO₂.^{193, 212} The wet-HGO/RuO₂ fiber has the highest volumetric capacitance, indicating by the largest enclosed CV curve area. Table 5.1 summarizes the specific volumetric capacitance and specific gravimetric capacitance of the fibers. The wet-HGO/RuO₂ fiber also has the highest gravimetric capacitance. In contrast, air dry-HGO/RuO₂ fiber shows a negligible capacitance increase compared to HGO fiber because of the low Ru loading. Although freeze dry-HGO/RuO₂ fiber has a higher Ru loading, its large volume leads to the lowest specific volumetric capacitance. The preliminary electrochemical test results indicate that incorporating RuO₂ via the wet HGO fibers yields the best electrochemical performances among the three different routes explored.

Figure 5.10 CV (at scan rate of 2, 5, 10, 20, 50, 100 mV s^{-1}), GCD curves and specific capacitance of HGO and HGO/RuO₂ composite fibers at various scan rates and current densities. (a, b, c) air-dried HGO fiber; (d, e, f) air dry-HGO/RuO₂ fiber; (g, h, i) wet-HGO/RuO₂ fiber; (j, k, l) freeze dry-HGO/RuO₂ fiber and (m, n, o) wet-GO/RuO₂ fiber.

Figure 5.11 (a) CV curves of HGO and HGO/RuO₂ composite fibers measured at the scan rate of 10 mV s^{-1} using a 3-electrode testing configuration in $1 \text{ M H}_2\text{SO}_4$ electrolyte. (b) Nyquist plots of HGO and HGO/RuO₂ composite fibers.

Table 5.1 Physical and chemical properties of HGO, HGO/RuO₂ and GO/RuO₂ composite fibers.

Fiber	Diameter (μm)	Ru content (wt.%)	Density (g cm^{-3})	Volume of a single electrode ($\text{cm}^3 \text{ cm}^{-1}$)	Weight of a single electrode (g cm^{-1})	§Specific volumetric capacitance (F cm^{-3})	§Specific gravimetric capacitance (F g^{-1})
Air-dried HGO fiber	35.0 ± 1.0	0	0.85 ± 0.03	9.62×10^{-6}	8.18×10^{-6}	203	239
Air dry-HGO/RuO ₂ fiber	35.0 ± 2.0	0.7	0.86 ± 0.05	9.62×10^{-6}	8.27×10^{-6}	229	266
Wet-HGO/RuO ₂ fiber	37.0 ± 3.0	36.8	1.36 ± 0.05	1.07×10^{-5}	1.46×10^{-5}	811	596
Freeze dry-HGO/RuO ₂ fiber	135.0 ± 6.0	4.6	0.045 ± 0.005	1.43×10^{-4}	6.44×10^{-6}	11	244
Wet-GO/RuO ₂ fiber	36.5 ± 2.5	30.0	1.26 ± 0.05	1.05×10^{-5}	1.32×10^{-5}	569	452

§Specific volumetric and gravimetric capacitances are determined by CV curves at the scan rate of 10 mV s^{-1} in three-electrode tests.

Figure 5.12 SEM images of the surface side view of (a-b) HGO, (c-d) HGO/RuO₂-1, (e-f) HGO/RuO₂-2, (g-h) HGO/RuO₂-3 and (i-j) HGO/RuO₂-4. (b, d, f, h, and j) are enlarged views of (a, c, e, g, i), respectively. Scales bars are 10 μm in (a, c, e, g and i) and 2 μm in (b, d, f, h, and j).

Next, we further optimized the Ru mass loading in the HGO fiber scaffold via the wet HGO fiber route. Five wet-HGO/RuO₂ fibers were prepared by emerging wet HGO fibers in RuCl₃ aqueous solutions at the concentration of from 0 to 0.03 M (denoted as HGO, HGO/RuO₂-1, HGO/RuO₂-2, HGO/RuO₂-3 and HGO/RuO₂-4, respectively), and all other experimental parameters were kept the same. SEM images of the resulting fibers are shown in Figure 5.12. The outer surface of all fibers has wrinkled GO sheets enfolding SWCNTs, similar to hybrid carbon fibers reported before.^{28, 46} With the increase of RuCl₃ solution concentration, some aggregated RuO₂ particles appear in HGO/RuO₂-3 (Figure 5.12h), and they are more visible on HGO/RuO₂-4 (Figure 5.12j). As listed in Table 5.2, the diameter of the fibers increases slightly from 35 to 38 μm , while their density rises significantly from 0.85 to 1.52 g/cm³. The Ru mass loadings were determined by TGA, which are 0, 20.5, 30.6, 36.8, and 42.5 wt.% for the five fibers, respectively (shown in Figure 5.13 and Table 5.2). TEM image of the HGO/RuO₂-3

fiber in Figure 5.14a illustrates the holey structure of GO sheets. Based on the analysis of more than 50 pores in HGO sheets, their pore size was found to range from 0.2 to 1.4 nm with the average size of 0.8 nm (Figure 5.14b). The size of RuO_2 particles ranges from 0.5 to 2.0 nm, and they are uniformly distributed on HGO sheets. Selected area electron diffraction images give two rings, which correspond to (002) and (100) diffraction of disordered GO sheets, respectively. The absence of diffraction rings corresponding to crystalline RuO_2 suggest amorphous RuO_2 is produced, which agrees with the XRD results in Figure 5.8.

Figure 5.13 TGA curves of HGO/RuO₂-2 and HGO/RuO₂-3.

Figure 5.14 (a) TEM image of HGO/RuO₂-3 fiber with 36.8 wt.% Ru. (b) Pore size distribution of pores in HGO sheets.

We further characterized the electrochemical properties of the five HGO/RuO₂ fibers with different Ru mass loadings. Their CV curves in Figure 5.16a show the enclosed area increases with the rising of Ru mass loading. Their specific volumetric and gravimetric capacitance were calculated both from their CV curves at different scan rates and GCD curves at different current densities (see Figure 5.15). The results are presented in Figure 5.16b, c, and summarized in Table 5.2. Both specific volumetric and gravimetric capacitance calculated from CV and GCD curves increase continuously with the Ru mass loading. The HGO/RuO₂-4 fiber has the highest capacitance of 1054 F cm⁻³ at the scan rate of 2 mV s⁻¹, to our knowledge, this is also the highest capacitance ever reported for fiber electrodes used for FMSCs (see the comparison of results in recent literature in Table 5.4).^{17, 28, 46, 88, 91, 100, 159, 191, 213-216} Figure 5.16b shows that the HGO/RuO₂-3 fiber has the 60% capacitance retention when the CV scan rate increases from 2 to 100 mV s⁻¹. In comparison, the HGO/RuO₂-4 has the lower 51% capacitance retention. We propose that the decrease in the capacitance retention can be attributed to the aggregation and formation of large RuO₂ particles at the high Ru loading of 42.5 wt.%. These aggregated RuO₂ particles may block the efficient diffusion of electrolyte ions into the composite fiber.

EIS was further carried out to characterize the influence of the Ru mass loading on the capacitive performance of HGO/RuO₂ fibers (see Figure 5.16d). A modified Randles circuit²¹¹ (see the inserted circuit in Figure 5.16d) was used to fit the EIS Nyquist spectra using the ZVIEW program. Semi-infinite transport was considered in the model. The fitted parameters were listed in Table 5.3. The real axis intercepts on Nyquist plots in

the high-frequency region are related to the equivalent series resistance (R_s), which combines the ohmic resistance of electrolytes, the internal resistance of electrode materials and their contact resistances.^{217, 218} In the high- to mid-frequency region, the width of the arc indicates the charge transfer resistance (R_{CT}) at the electrolyte/electrode interface.^{217, 218} HGO/RuO₂-2 has the lowest R_s and R_{CT} (see Figure 5.16d and Table 5.3), which suggests efficient electrolyte ion transfers and sufficient contacts between electrolyte ions and electrodes. R_s and R_{CT} of HGO/RuO₂-3 slightly increase compared to those of HGO/RuO₂-2 while HGO/RuO₂-4 shows a noticeable jump. This observation supports our hypothesis that aggregated RuO₂ particles may block the efficient diffusion of electrolyte ions into HGO/RuO₂-4 fiber. Constant phase element (CPE) is an equivalent electrical circuit component that simulates the behavior of capacitors.²¹⁹ If $n = 0$, the CPE is a pure resistor, and when $n = 1$, CPE is a ideal capacitor.²¹⁹ CPE_{DL} is the constant phase element of double layers, which occurs at interface between solids and ionic solutions due to the separation of ionic and/or electronic charges.¹³ From table 5.3, CPE_{DL} of HGO/RuO₂-4 is smaller than that of HGO/RuO₂-3 even with a higher Ru mass loading. Since CPE_{DL} represents the accessible surface area of electrode materials,¹³ the heavily loaded RuO₂ in HGO/RuO₂-4 may limit the accessible surface area of electrolyte ions, which agree with our hypothesis. The tail from the end of high-frequency arc to the mid-frequency region represents Warburg element (W_o). It can be expressed as $A/(j\omega)^n$, where A is the Warburg coefficient, ω is the angular frequency ($\omega = 2\pi f$, f is the frequency in Hertz) and n is an exponent.²¹⁹ W_o represents the diffusion of electrolyte ions into the inner porous structure of electrode materials.²²⁰ HGO/RuO₂-4 has the highest A and lowest n among HGO/RuO₂ fibers, which is correlated with its poor rate capability as evident by its spindle-shaped CV curves at 100 mV s⁻¹. R_L is the leakage resistance, which is placed in parallel with CPE_L . R_L normally is very high, and

thus is ignored in the circuit.²¹¹ CPE_L represents the constant phase element of pseudocapacitance origins from faradic charge transfer processes.²¹¹ CPE_L increases continuously with the increase of Ru mass loadings, which is consistent with the larger enclosed area of CV curves in Figure 5.16a. Furthermore, Bode plots show that HGO/RuO₂-4 has the highest relax time constant (τ_0), which also indicates its poor rate capability.²¹¹ Bode plots together with Nyquist plots indicate the inefficient ion diffusion in the HGO/RuO₂-4 fiber.

In the meanwhile, the ion diffusion coefficient in HGO and HGO/RuO₂ fibers were also calculated based on the equation (5.10).²²¹

$$D = R^2 T^2 / 2 S^2 n^4 F^4 C^2 \sigma^2 \quad (5.10)$$

where D is the ion diffusion coefficient, R is the gas constant, T is the absolute temperature, S is the geometric surface area of the electrode, n is the number of electron transfer, F is Faraday constant, C is the concentration of H⁺ ions, and σ is the Warburg factor which can be obtained through the equation (5.11).²²¹

$$Z' = R_s + R_{ct} + \sigma \omega^{-1/2} \quad (5.11)$$

where Z' is the real part of impedance, R_s is the equivalent resistance, R_{ct} is the charge transfer resistance, σ is the Warburg factor and ω is the frequency in Hertz.

As listed in Table 5.3, HGO/RuO₂-2 has the highest ion diffusion coefficient and the value slightly decrease for HGO/RuO₂-1 and HGO/RuO₂-3. However, with the further increase in Ru mass loading, the ion diffusion coefficient of HGO/RuO₂-4 suddenly drops by 35%. These results agree with the findings from EIS measurements and indicate the inefficient ion transfer in HGO/RuO₂-4. Overall, the HGO/RuO₂-3 fiber was selected as fiber electrodes for assembling FMSCs in consideration of its good rate capability and high specific volumetric capacitance.

The utilization rate of RuO₂ in HGO/RuO₂ fibers was calculated based on the equation (5.12):

$$r = C_{RuO_2}^{Cal} / C_{RuO_2}^{The} \quad (5.12)$$

where $C_{RuO_2}^{The}$ is the theoretical specific gravimetric capacitance of RuO₂ (~1400 F g⁻¹),²⁰⁰ $C_{RuO_2}^{Cal}$ is the calculated specific gravimetric capacitance of RuO₂ in HGO/RuO₂ fibers according to the equation (5.13):

$$C_{electrode} = C_{HGO} \left(1 - \frac{Ru_{wt}\%}{75.9\%}\right) + C_{RuO_2}^{Cal} \times \frac{Ru_{wt}\%}{75.9\%} \quad (5.13)$$

where $C_{electrode}$ is the total specific gravimetric capacitance of HGO/RuO₂ fibers, C_{HGO} is the specific gravimetric capacitance of HGO (301 F/g), $Ru_{wt}\%$ is the Ru mass loading in HGO/RuO₂ fibers, and 75.9% is the weight fraction of Ru in RuO₂. The HGO/RuO₂-3 fiber has the utilization rate of RuO₂ of 76.4%, which is higher than most of previously reported RuO₂/carbon-based supercapacitors, for example RuO₂/graphene (~35.7%)¹⁹³ and RuO₂/multi-walled carbon nanotubes (~23.0%).²²²

To further explore the charge storage mechanism in HGO/RuO₂ fibers, CV sweep analysis was conducted on the HGO/RuO₂-3 fiber to quantitatively differentiate the capacity contribution from surface capacity effect and diffusion-controlled process by the following equations:^{223, 224}

$$i_V = k_1 v + k_2 v^{1/2} \quad (5.14)$$

or

$$i_V / v^{1/2} = k_1 v^{1/2} + k_2 \quad (5.15)$$

where i is the current density at a voltage (V), v is the scan rate (mV s⁻¹), $k_1 v$ is the current contribution from the surface capacity effects, including electrical double layer capacitance and fast surface faradic reactions, $k_2 v^{1/2}$ represents the current contribution from the slow diffusion-controlled insertion.^{223, 224} k_1 and k_2 can be

derived from the slope and intercept, respectively, of a linear plot of $i_v/v^{1/2}$ versus $v^{1/2}$. As shown in Figure 5.16g, the surface capacity accounts for 81.8% of the total capacity at 2 mV s^{-1} , and the ratio rises to 95.5% at 100 mV s^{-1} , which indicate the surface-dominant nature of HGO/RuO₂ within the wide scan range of 2 to 100 mV s^{-1} . Therefore, the high surface capacity ratio accounts for the high rate capability of HGO/RuO₂-3 fiber.

Figure 5.15 CV and GCD curves of HGO and HGO/RuO₂ composite fibers. (a, b) HGO fiber; (c, d) air dry-HGO/RuO₂ fiber; (e, f) wet-HGO/RuO₂ fiber; (g, h) freeze dry-HGO/RuO₂ fiber and (i, j) wet-GO/RuO₂ fiber.

Figure 5. 16 (a) CV curves of HGO, HGO/RuO₂-1, HGO/RuO₂-2, HGO/RuO₂-3 and HGO/RuO₂-4 fibers at the scan rate of 10 mV s⁻¹ measured using 3-electrode tests in 1 M H₂SO₄ electrolyte. The specific volumetric capacitance of the fibers at different scan

rates calculated from their CV curves (b) and at various current densities calculated from their GCD curves (c). (d) The variation of the specific volumetric capacitance and the capacitance retention from 2 to 100 mV s⁻¹ at different Ru mass loadings in the fibers. (e) Nyquist plots of HGO and HGO/RuO₂ fibers. The inset is the modified Randles equivalent circuit used to simulate EIS spectra, where R_S is the equivalent series resistance (ESR), R_{CT} is the charge transfer resistance, R_L is the leakage resistance, CPE_{DL} is the constant phase element of double layers, CPE_L is the constant phase element of pseudocapacitance, W_0 is the Warburg element. (f) Bode plots of HGO and HGO/RuO₂ fibers. Differentiation of the capacity contribution from the surface capacity effect and diffusion-controlled process at the CV scan rate of 2 mV s⁻¹ (g) and 100 mV s⁻¹ (h).

Table 5.2 Physiochemical and electrochemical properties of HGO and wet-HGO/RuO₂ fibers.

Fiber	Ru content (wt%)	Diameter (μm)	Density (g cm^{-3})	Volume of a single electrode ($\text{cm}^3 \text{cm}^{-1}$)	Weight of a single electrode (g cm^{-1})	‡Specific volumetric capacitance (F cm^{-3})	‡Specific gravimetric capacitance (F g^{-1})
HGO	0.0	35.0 ± 2.0	0.85 ± 0.03	9.62×10^{-6}	8.17×10^{-6}	256	301
HGO/RuO ₂ -1	20.5	35.5 ± 1.5	1.05 ± 0.02	9.62×10^{-6}	1.00×10^{-5}	485	461
HGO/RuO ₂ -2	30.6	36.5 ± 2.0	1.25 ± 0.06	1.05×10^{-5}	1.31×10^{-5}	694	555
HGO/RuO ₂ -3	36.8	37.0 ± 3.0	1.36 ± 0.09	1.07×10^{-5}	1.46×10^{-5}	912	670
HGO/RuO ₂ -4	42.5	38.0 ± 3.0	1.52 ± 0.10	1.13×10^{-5}	1.72×10^{-5}	1054	693

§Specific volumetric and gravimetric capacitances are determined by CV curves at the scan rate of 10 mV s^{-1} in three-electrode test.

Table 5.3 Equivalent circuit parameters obtained by fitting Nyquist plots using a modified Randles equivalent unit.

Fiber	R_S (Ω)	R_{CT} (Ω)	CPE_{DL} (F)	n_{DL}	$W_0 = A/(j\omega)^n$		D (cm ² s ⁻¹)	CPE_L (F)	n_L
					$A/\Omega \text{ s}^{-n}$	n			
HGO	642.4	58.5	8.4×10^{-5}	0.76	370.2	0.42	1.33×10^{-14}	2.0×10^{-4}	0.81
HGO/RuO ₂ -1	464.7	48.7	8.2×10^{-5}	0.74	363.1	0.43	1.35×10^{-14}	9.0×10^{-4}	0.87
HGO/RuO ₂ -2	367.6	34.2	8.6×10^{-5}	0.78	351.0	0.47	1.37×10^{-14}	1.5×10^{-3}	0.86
HGO/RuO ₂ -3	584.6	50.1	8.1×10^{-5}	0.80	377.0	0.41	1.15×10^{-14}	1.8×10^{-3}	0.83
HGO/RuO ₂ -4	872.4	67.4	7.1×10^{-6}	0.79	421.5	0.35	8.80×10^{-15}	2.1×10^{-3}	0.83

Figure 5.17 (a) Schematic illustration of the FMSC structure. (b) CV curves of the FMSC at different scan rates. (c) GCD curves of the FMSC at different charge/discharge current densities. The specific volumetric capacitance of the FMSC and its individual electrode at different scan rates (d) and at different current densities (e). (f) Cycling performance and coulombic efficiency of the FMSC at the current density of 5000 mA cm⁻³ for 10000 cycles. Nyquist plots (g) and Bode plots (h) of the FMSC after 1st and 10000th cycles. (i) Comparison of the specific volumetric energy and power densities reported for FMSCs and other MSCs in recent literatures.

As illustrated in Figure 5.17a, the two-electrode symmetric solid-state FMSC was fabricated using two HGO/RuO₂-3 fibers (2000 μm in length and 36.6 μm in diameter) supported on a flexible polyethylene terephthalate (PET) film. The fibers were covered with poly(vinyl alcohol) (PVA)/H₃PO₄ gel electrolytes and used as both current collectors and active electrodes. Figure 5.17b shows the FMSC's CV curves, which have

a quasi-rectangular shape at the scan rate from 2 to 100 mV s⁻¹. The redox peaks of RuO₂ disappear, indicating fast redox reactions occurred on the surface RuO₂ particles, which is similar to previous studies.²²⁵ Figure 5.17c shows the galvanostatic charge and discharge (GCD) curves of the device at various current densities (300-6000 mA cm⁻³), which has a symmetric triangular shape, indicating the fast charge transfer in the FMSC. The specific volumetric capacitance of the fiber electrode ($C_{V,electrode}$) was calculated from both the FMSC's CV and GCD curves and are shown in Figure 5.17d and e, respectively. The fiber electrode has the capacitance of 903 F cm⁻³ at the CV scan rate of 2 mV s⁻¹ or 889 F cm⁻³ at the current density of 300 mA cm⁻³. The total volume of the FMSC, including two fiber electrodes and their surrounding gel electrolytes, is about 2.44×10^{-5} cm³ cm⁻¹ in length. The total area of the device is estimated to be 2.32×10^{-2} cm² cm⁻¹ in length. Correspondingly, the specific volumetric capacitance, length capacitance and areal capacitance of the FMSC ($C_{V,device}$) is 199.2 F cm⁻³, 4.86 mF cm⁻¹ and 0.21 F cm⁻², respectively, at 2 mV s⁻¹ or 196.1 F cm⁻³, 4.78 mF cm⁻¹ and 0.21 F cm⁻², respectively, at 300 mA cm⁻³.

Figure 5.17f shows that the FMSC retains 88.9% of its initial capacitance after 5000 charge/discharge cycles and 78.7% after 10000 cycles. The coulombic efficiency after 10000 cycles is around 98%, indicating the highly stable structure of the fiber electrodes.²²⁶ To explore the reasons for the capacitance decay after the long-term cycling, we compared Nyquist plots of the FMSC after 1 cycle and 10000 cycles in Figure 5.17g. The width of the high-frequency arc and the ESR after the 10000 cycles are both higher than those after 1 cycle. The inclined line with a slope of ~45° in the mid-frequency region represents the Warburg impedance, and its length indicates the electrolyte ion diffusion distance.^{217, 218} The length of the inclined line increases after 10000 cycles. Overall, these results suggest inefficient charge transfer and electrolyte

ion diffusion in the electrode after the long-term cycling. We also compared the Bode plots in Figure 5.17h. The FMSC shows a slower relax time constant after 10000 cycles compared to its initial value, suggesting an increased charge transfer resistance and poorer ion diffusion. These findings agree with the results obtained from Nyquist plots. Pseudocapacitive materials usually have relatively short cycling life because redox reactions are not completely reversible.^{227, 228} Therefore, we propose that non-reversible Faradic reactions after the long-term cycling would cause less efficient charge transfers and hinder the electrolyte ion transport.

The FMSC's volumetric energy and power density were calculated from its GCD curves. Figure 5.17i shows that it has the maximum energy density ($E_{V,device}$) of 27.3 mWh cm⁻³ (corresponding to a length energy density of 0.7 μWh cm⁻¹ and a areal energy density of 29.2 μWh cm⁻²) at the power density ($P_{V,device}$) of 147.7 mW cm⁻³, and retains more than half of its energy density of 15.9 mW cm⁻³ at the high power density of 2954.1 mW cm⁻³. To our knowledge, this performance is among one the best results reported for FMSCs (see Figure 5.17i and Table 5.5),^{17, 18, 28, 43, 46, 88, 91, 100, 131, 159, 175, 181, 191, 213-215, 229-232} such as those made of GO/multi-walled carbon nanotube (MWCNT) fiber (3.1 mWh cm⁻³, 400 mW cm⁻³),⁴⁶ GO/PEDOT core-sheath fiber (7.0 mWh cm⁻³, 88 mW cm⁻³),¹⁹¹ MnO₂/SWCNT fiber (11.7 mWh cm⁻³, 167.7 mW cm⁻³),²¹³ MWCNT/V₂O₅/MWCNT fiber (2.1 mWh cm⁻³, 1500 mW cm⁻³).¹⁸¹ Its performance is also superior to other MSCs, including phosphorene and graphene interdigital in-plane MSC (11.6 mWh cm⁻³, 1500 mW cm⁻³)²³³ and Ni/MnO₂ 2D MSC (4.7 mWh cm⁻³, 80.0 mW cm⁻³)¹⁸² *etc.*

Table 5.4 Comparison of recently reported fiber electrodes of FMSCs. (All measurement results listed belong to one fiber electrode measured using the 3-electrode method).

Ref.	Electrode materials	Electrolyte	Voltage window (V)	Specific volumetric capacitance (F cm^{-3})	Specific gravimetric capacitance (F g^{-1})
This work	HGO/RuO₂	1 M H₂SO₄	0-1	485-1054 at 2 mV s⁻¹	461-693 at 2 mV s⁻¹
28	Nitrogen doped-SWCNT/rGO	1 M H ₂ SO ₄	0-1	295 @ 2 mV s ⁻¹	NA
17	Nitrogen doped-GO/MWCNT /carbon fiber	1 M H ₂ SO ₄	0-1	123 @ 2 mV s ⁻¹	NA
159	rGO	1 M Na ₂ SO ₄	0-0.9	137 at 5 mV cm ⁻³	NA
88	MnO ₂ /rGO/carbon fiber	1 M Na ₂ SO ₄	0-0.8	13.7 at 0.5 mA cm ⁻³	NA
214	Carbon fiber@NiP _x	6 M KOH	0-0.4	817 at 2 mA cm ⁻³	NA
131	MnO ₂ /carbon fiber	1 M Na ₂ SO ₄	0-0.8	58.7 at 0.1 A g ⁻¹	428 at 0.1 A g ⁻¹
101	FeOOH/PPy@carbon fiber	5 M LiCl	-0.8-0	30.2 at 10 mV s ⁻¹	NA
213	MnO ₂ /CNT fiber	1 M Na ₂ SO ₄	0-1	97.7 at 2 mV s ⁻¹	NA
91	MnO ₂ @MWCNT fiber	6 M LiCl	0-1	63.9 at 0.2 A cm ⁻³	NA
215	PPy/rGO/MWCNTs	4 M LiCl	0-0.8	25.9 at 0.01 V s ⁻¹	NA
216	FeSN-C	6 M KOH	-0.8-0.3	1320.4 at 0.1 A g ⁻¹	NA

112	MXene/CNT yarn	3 M H ₂ SO ₄	-0.55-0.1	1083 at 2 mA cm ⁻²	428 at 2 mA cm ⁻²
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Table 5.5 Comparison of recently reported FMSCs. (All measurement results listed belong to actual supercapacitors measured using the two-electrode method).

Ref.	Electrode materials	Electrolyte	Voltage window (V)	Specific volumetric capacitance (F cm ⁻³)	Specific gravimetric capacitance (F g ⁻¹)	Energy density (mWh cm ⁻³)	Power density (mW cm ⁻³)
This work	HGO/RuO₂	PVA/H₃PO₄	0-1	199.2 at 2mV s⁻¹			
				196.1 at 300 mA cm⁻³	NA	27.2	2954
28	N-SWCNT/rGO	PVA/H ₃ PO ₄	0-0.9	45 at 26.7 mA cm ⁻³	NA	6.3	1085
46	N-MWCNT/rGO	PVA/H ₃ PO ₄	0-1	29.7 at 2 mV s ⁻¹	NA	3.2	440
17	N-rGO/MWCNT /carbon fiber	PVA/H ₃ PO ₄	0-1	27 at 2 mV s ⁻¹	NA	3.75	612
43	rGO/CNT@ carboxymethyl	PVA/H ₃ PO ₄	0-0.8	NA	NA	3.5	18
18	PPy / MnO ₂ / rGO	PVA/H ₃ PO ₄	0-0.8	12.4	NA	1.1	160
131	Polyaniline /CNT fiber	PVA/H ₂ SO ₄	0-0.8	2.5	NA	0.22	400
159	N-rGO/SWCNT// MnO ₂ -rGO/SWCNT	PVA/H ₃ PO ₄	0-1.8	11.1 at ~25 mA cm ⁻³	NA	5	1000
175	MnO ₂ /CNT fiber	PVA/KOH	0-1.5	35.19 at 10 mV s ⁻¹	NA	0.69	260
215	PPy/rGO/MWCNT	PVA/H ₃ PO ₄	0-0.8	~8 at 1 mV s ⁻¹	NA	0.94	117.12

230	Activated carbon fiber	PVA/H ₃ PO ₄	0-0.8	27.6 at 13 mA cm ⁻³	48.3 at 13 mA cm ⁻³	2.5	NA
191	rGO @PEDOT	PVA/H ₃ PO ₄	0-0.8	78.8	NA	7	88
88	MnO ₂ /rGO/carbon fiber//rGO hydrogel/copper wire	PAAK/KCl	0-1.6	2.54 at 0.2 mA cm ⁻³	NA	0.9	200
231	Nickel fiber/Co ₃ O ₄ //carbon fibers/graphene	PVA/KOH	0-1.5	2.1 at 20 mA cm ⁻³	NA	0.62	1470
214	Carbon fiber@NiP _x	PVA/KOH	0-1.4	33 at 2 mA cm ⁻³	NA	8.97	3510
86	MnO ₂ /carbon fiber	PVP/Na ₂ SO ₄	0-1	NA	NA	3.8	89
101	FeOOH/PPy/carbon fiber// MnO ₂ /carbon fiber	PVA/LiCl	0-1.5	5.5 at 5 mA cm ⁻³	NA	2	NA
181	MWCNT/V ₂ O ₅ /MWCNT fiber	PVA/LiCl	0-0.8	31 at 2 mA cm ⁻³	NA	2.1	1500
213	MnO ₂ /SWCNT fiber	PVA/LiCl	0-1	156 at 0.2 A g ⁻³	152.4 at 0.2 A g ⁻¹	11.7	167.7
91	MnO ₂ @MWCNT fiber	PVA/LiCl	0-1	10.9 at 0.1 A cm ⁻³	NA	1.5	2500
232	(CNT)@MnO ₂ //CNT@PPy	PVA/KOH	0-1.5	9.45 at 10 mV/s	8.35 at 10 mV s ⁻¹	9.45	253.56
233	Phosphorene/graphene	BMIMPF ₆	0-3	37.5 at 5 mV s ⁻¹	NA	11.6	1500
182	Ni/MnO ₂	LiClO ₄ /PVA	0-0.8	0.0532 at 0.1 mA cm ⁻²	NA	4.7	80
112	MXnene/CNT yarn//RuO ₂ /CNT yarn	PVA/H ₂ SO ₄	0-1.5	203 at 2 mA cm ⁻²	123 at 2 mA cm ⁻²	61.6	358

Figure 5.18 GCD curves of one, two or three FMSCs connected in series (a) and in parallel (b). The inset images illustrate the electric circuit drawings of the FMSCs.

In order to meet various power and energy requirements in practical application, it is desirable to connect FMSCs in series and in parallel to widen their operating voltage and/or current density. Figure 5.18a shows that when two or three our FMSCs were connected in series, their operating voltage window is doubled or tripled, respectively, while the discharge time nearly doesn't change. When two or three FMSCs were connected in parallel (see Figure 5.18b), their discharge time increases by a factor of two or three, respectively, with the same operating voltage window. These results indicate the excellent integrability and scalability of the FMSCs assembled using the HGO/RuO₂ fibers.

To demonstrate the practical application of the FMSCs as a high-power energy storage device for wearable electronics, an energy storage unit was fabricated by connecting five FMSCs in parallel first, and then four of the parallel arrays were assembled in series (schematically shown in Figure 5.19a). Subsequently, we constructed a self-powered system. Two solar panels (SANYO, AM-5302) were connected in series as the energy generation unit, which can provide a maximum output voltage of ~4 V. The energy generation unit was connected with the FMSC based

energy storage unit to power a red LED panel as illustrated in Figure 5.19. The result highlights the potential of integrating FMSCs for practical application.

Figure 5.19 (a) Schematic drawing of the FMSC based energy storage unit integrating multiple HGO/RuO₂ fibers. (b-c) Electronic circuit diagrams of the FMSC based energy storage unit together with solar cell-based energy generation unit. (d) Photo of the energy storage unit charged to ~4 V by two solar cells. (e) Photo of the charged energy storage unit lighting a red LED panel. (f) GCD curve (at ~1 A cm⁻³) of the FMSC based energy storage unit.

5.4 Conclusion

I have demonstrated a facile two-step synthesis method to uniformly incorporated ultrahigh mass loading of RuO₂ nanoparticles (up to 42.5 wt.%) in HGO hybrid fibers. The interconnected 3D porous structure, the filled water, and holes on HGO sheets facilitate the transportation of Ru³⁺ ions into the fibers. The composite fiber has the specific volumetric capacitance of 1054 F cm⁻³ at 2 mV s⁻¹, which is the highest ever reported for fiber electrodes. Solid-state FMSCs were assembled using the optimized

fiber with 36.8 wt.% Ru loading. The FMSC has a specific volumetric capacitance of 199 F cm^{-3} at 2 mV s^{-1} and 196 F cm^{-3} at 300 mA cm^{-3} . It also delivers an ultrahigh energy density of 27.3 mWh cm^{-3} . To our knowledge, both the volumetric capacitance and the energy density of the FMSCs are the highest among those reported for FMSCs to date. The maximum power density of the FMSC is $2954.1 \text{ mW cm}^{-3}$, which is comparable to commercial supercapacitors. Furthermore, multiple FMSCs can be connected in series or parallel to expand the operating voltage window or current density. An integrated self-power energy system was demonstrated comprising of 20 FMSCs and flexible solar cells, which can be used to light a LED panel. Overall, the HGO/RuO₂ composite fibers have excellent scalability and ease of integration with other complex electronics for practical applications.

Chapter VI Ultrafast hydrothermal assembly of nanocarbon microfibers in near-critical water for 3D micro- supercapacitors

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6.1 Introduction

In Chapter III, IV and V, I have demonstrated all-carbon, YSCs or FMSCs as promising alternatives to conventional batteries for wearable energy storage. Carbon-based nanomaterials (nanocarbons) are promising electrode materials due to their unique and tunable physical and chemical properties^{183, 184}. Hybrids of graphene-family materials and carbon nanotubes (CNTs) have shown excellent performances as microfiber electrodes^{28, 234}. However, despite pristine graphene nanosheets and certain CNTs are among the most electrically conductive materials with large surface area^{15, 235, 236}, the microfiber electrodes prepared out of those often exhibit markedly inferior results^{46, 63, 123}. Because, the architectural aspects, physical defect levels, and chemical functionalities all greatly influence the electrical conductivity as well as ion-accessibility to their surface^{3, 179, 237}. For assembling high-performance electrodes using graphene-family materials and/or CNTs, it is crucial to i) maintain interparticle connectivity but prevent restacking/rebundling, ii) create large surface area and porosity but avoid loose packing, and iii) introduce desirable chemical functionalities but

preserve graphitic lattice without extensive defect formation ^{3, 63}. Last but not least, it is important to achieve these in a scalable and time-energy-efficient manner for increasing the commercialization potential ^{28, 238}. In my understanding, this challenge is a nanoarchitectonic task beyond the realm of conventional material synthesis since it requires the harmonization of multiple nanoscale properties and behaviors into macroscopic structures ²³⁹. Accordingly, we focused on the technicality of nanocarbon microfiber assembly.

Several methods are available for the fabrication of nanocarbon microfibers, such as rolling of GO/CNT films ^{167, 168}, dry-spinning of CNT forests ^{240, 241}, and wet-spinning ^{24, 41, 43, 51, 61, 142, 161, 166, 242}, electrophoretic deposition ²⁴³, or hydrothermal processing ^{17, 28, 44, 46, 159, 190} of graphene oxide (GO) and/or CNT dispersions. Thin-film-rolling suffers in diameter control and practicality, and dry-spinning is currently limited to CNTs and polymer-derived carbon fibers ^{3, 128, 133, 244}. Wet-spinning is practically appealing due to its fast production of microfibers via coagulation process ^{43, 61, 179, 245}. Nevertheless, it often involves polymeric additives and requires extensive post-reduction ^{48, 49, 61}. Electrophoretic deposition works without additives but arguably not suitable for scale-up and again requires post-reduction ^{3, 63, 243}. Hydrothermal assembly inside confined space, on the other hand, have unique advantages owing to its precise and versatile morphological control, great flexibility in building material precursor selection, and enabling of simultaneous thermal/chemical reduction and heteroatom doping of nanocarbon microfibers ^{17, 28, 44, 46, 159, 190, 246}.

The hydrothermal assembly of nanocarbon microfibers ^{17, 28, 44, 46, 159, 190} shares some similarity to the widely used hydrothermal synthesis/crystallization of substances in hot-compressed aqueous environments ²⁴⁷⁻²⁵⁰. Based on the practices applied so far, the first step is the preparation of a stable and processable nanocarbon material dispersion. For

taking the advantage of colloidal stabilization induced by electrostatic repulsion, well-mixed dispersions of charged nanocarbons such as GOs and oxidized CNTs are employed as the nanoscale precursors (with or without crosslinkers and/or polymeric additives). Then, the precursor dispersion is typically transferred inside microtubes for shape-confinement. Subsequently, stuffed microtubes are placed inside Teflon-lined autoclave bombs and heated. And finally, during the high-temperature treatment, the oxidized nanocarbons get reduced and interlocked as well-defined microfibers. However, despite its advantages explained above, the technique suffers from its slowness. Under the mild subcritical conditions applied in typical hydrothermal systems (*i.e.*, $180\text{ }^{\circ}\text{C} \leq T \leq 230\text{ }^{\circ}\text{C}$), the whole process takes 12 to 24 hours for the complete assembly of microfibers. Otherwise, when the treatment duration is kept shorter, either freestanding microfibers do not form, or extensive post-annealing is needed for improving the electrical conductivity. Thus, bearing in mind that the solvent and reactant behavior of water particularly changes above $250\text{ }^{\circ}\text{C}$ toward its supercritical point ($T_{\text{critical}} = \sim 374\text{ }^{\circ}\text{C}$, $P_{\text{critical}} = \sim 221\text{ bar}$)²⁵¹⁻²⁵⁴, we propose that subcritical hydrothermal assembly could lead the production of nanocarbon microfibers with improved conductivity in a shorter time for improved performance and productivity.

In this contribution, the ultrafast hydrothermal assembly of nanocarbon microfibers is demonstrated using a new easily applicable nonequilibrium subcritical hydrothermal method, which is significantly different from various commonly used hydrothermal reactors. We systematically investigate how the hydrothermal conditions (temperature, pressure and time) can regulate the packing density, reduction level, and conductivity of resulting microfibers. The optimized microfibers were used to fabricate FMSCs, which display the high specific volumetric energy densities comparable to that of commercial thin-film Li-ion batteries. Further, by integrating multiple FMSCs in both

X-Y plane and Z-axis direction, we built a new 3D energy storage device having a wide operation voltage and current window together with a reduced device footprint.

6.2 Experimental section

6.2.1 Preparation of carbon precursors

GO was synthesized from natural graphite flakes (Sigma-Aldrich) following a modified-Hummers method ²⁸. As-produced slurry was homogenized thoroughly applying magnetic shaking for days, and then the concentration of homogenized dispersion was adjusted to 8 mg mL⁻¹. SWCNTs (Carbon Solutions, Inc., AP-SWNT, with a diameter of ~1.4 nm) were first functionalized by refluxing in HNO₃ (65%) for 4 hours and then dispersed in deionized water at the concentration of 4 mg mL⁻¹ by applying 2 hours of tip-sonication at 80% amplitude (Sonics, VCX 130 PB).

6.2.2 Hydrothermal assembly of nanocarbon microfibers

A homogeneous GO/SWCNT (at 1 to 1 mass ratio) dispersion was prepared by mixing 1 mL of GO dispersion (8 mg mL⁻¹) and 2 mL of SWCNT dispersion (4 mg mL⁻¹), followed by addition of 30 μ L of N-doping crosslinker, ethylenediamine (EDA). As illustrated in Figure 6.1, the dispersion was added to multiple capillary quartz tubes (with one end closed at the inner diameter of 0.5 mm) hosted in the stainless reactor vessel. The reactor was then purged several times with N₂ before pressurization with the same gas to a pressure (as listed in Table 6.1) in the range of 75 to 108 bars by connecting to a high-pressure N₂ cylinder. Substantially, the hydrothermal reactor was quickly

heated to a temperature ranging from 180 to 340 °C (to 200 °C under 3 minutes and 360 °C under 4 minutes) in the high-temperature fluidized bed sand bath (Techne, SBL-2D) and kept at that temperature for the various durations. After the hydrothermal assembly, the reactor was cooled down to the room temperature and depressurized to the atmospheric pressure. The hybrid carbon fibers formed inside the quartz tubes were poured into a water reservoir. The fibers in gel-state were then dried in an environmentally controlled drying chamber at 25 °C in 0.7 bar air (humidity: ~40%) for 0.5 hours.

6.2.3 Characterization of physicochemical properties

The morphology of the carbon-based hybrid microfibers was examined by a field emission SEM (ULTRA Plus, Zeiss) at the electron accelerating voltage of 5 kV. Their specific surface area and porosity were characterized using a surface area analyzer (Autosorb-1, Quantachrome Instruments). The chemical composition of the fibers was analyzed by XPS (PHI 5000 VersaProbe, ULVAC-PHI, Inc.), and EDS (ULTRA Plus, Zeiss). Their Raman spectra were recorded on a Raman microscope (inVia™ Reflex, Renishaw) under a 514-nm laser excitation. Their electrical conductivity was measured using a four-point probe station (Keithley Instruments) with a probe pin diameter of 40.6 μm and a probe spacing of 1.6 mm.

6.2.4 Evaluation of electrochemical properties

The electrochemical properties of the hybrid carbon fibers were evaluated in a three-electrode cell in 1 M H_2SO_4 electrolyte, using an Ag/AgCl (3 M KCl) electrode as the

reference electrode, a platinum mesh as the counter electrode, and a single hybrid carbon fiber as the working carbon fiber electrode. The CV and GCD curves were recorded on an electrochemical workstation (CHI660E, CH Instruments, Inc.). The capacitance of the fiber electrode was calculated from their CV curves by the equation (6.1).

$$C_{electrode} = \frac{Q}{2V} = \frac{1}{2Vv} \int_{V_-}^{V_+} i(V) dV \quad (6.1)$$

where Q is the total charge obtained by integrating the enclosed area of CV curves, V is the scanned voltage window ($V=V_+ - V_-$), v is the CV scan rate, and $i(V)$ is the current density.

The specific volumetric capacitance ($C_{V,electrode}$) of the fiber electrodes was calculated by the equation (6.2):

$$C_{V,electrode} = C_{electrode} / V_{electrode} \quad (6.2)$$

where $V_{electrode}$ is the volume of the fiber electrode.

6.2.5 Fabrication of solid-state FMSCs

PVA/H₃PO₄ gel electrolyte was first prepared by dissolving 10 g of PVA (molecular weight 89,000-98,000, Sigma-Aldrich) in 10 mL deionized water at 90 °C under stirring. After the mixture turns clear, it was cooled to room temperature, and then 10 g H₃PO₄ was added under stirring. Two microfibers assembled at 340 °C were dipped into the gel electrolyte (with one end staying outside the electrolyte) for 5 minutes, and then dried in an environmentally controlled drying chamber at 25 °C in air (humidity: ~40%) for 1 hour. Subsequently, the gel-coated fibers were placed in parallel on a PET film with the two fiber ends free of gel electrolytes placed in the opposite direction. Last, the two ends of the fibers without gel electrolytes were connected to external circuits via conductive silver pastes. Furthermore, multiple microfibers were integrated in parallel

and in series to fabricate a 3D energy storage unit. As schematically illustrated in Figure 6.19, first, four fibers were placed in the X-Y plane to form a four-fiber flat array, which is equivalent to two FMSCs connected in parallel. Next, four layers of four-fiber flat arrays were stacked together layer by layer in the Z-axis direction. The sixteen-fiber array constitutes a 3D block with its two ends connected to external circuits. Last, two 3D blocks were connected in series, resulting in the 3D energy storage unit with the total thickness of five pieces of piled up 5-cent coins.

6.2.6 Performance tests of solid-state FMSCs

The performance of solid-state FMSCs was evaluated in the two-electrode configuration on the electrochemical workstation by CV and GCD. The total device capacitance is calculated using the equation (6.3) or (6.4):

$$C_{device} = \frac{Q}{2V} = \frac{1}{2Vv} \int_{V_-}^{V_+} i(V) dV \quad (6.3)$$

where Q is the total charge obtained by integrating the enclosed area of CV curves, V is the voltage window ($V = V_+ - V_-$), v is the scan rate, and $i(V)$ is the current density.

$$C_{device} = \frac{i}{\left(\frac{dV}{dt}\right)} \quad (6.4)$$

where i is the discharge current, t is the discharge time and V is the voltage, dV/dt is the slope of the discharge curve.

The specific volumetric capacitance $C_{V,electrode}$ of fiber electrodes used in FMSCs is calculated according to the equation (6.5):

$$C_{V,electrode} = 2 \frac{C_{device}}{V_{electrode}} \quad (6.5)$$

where $V_{electrode}$ is the volume of one fiber electrode used in FMSCs.

The volumetric capacitance of the FMSCs ($C_{V,device}$) is calculated using the equation (6.6):

$$C_{V,device} = \frac{C_{device}}{V_{device}} \quad (6.6)$$

where V_{device} is the total volume of the FMSCs including two electrodes and surrounding gel electrolytes.

The volumetric energy density ($E_{V,device}, Wh\ cm^{-3}$) of the FMSCs is obtained from the equation (6.7):

$$E_{V,device} = \frac{1}{2} C_{V,device} \frac{V^2}{3600} \quad (6.7)$$

where V is the applied voltage window.

The volumetric power density ($P_{V,device}, W\ cm^{-3}$) of the FMSCs is calculated using the equation (6.8):

$$P_{V,device} = 3600 \frac{E_{V,device}}{t} \quad (6.8)$$

where t is the discharge time.

6.3 Results and discussion

6.3.1 Novel hydrothermal reactor

Commonly used hydrothermal reactors (*i.e.*, Teflon-lined fixed-volume autoclave bombs) are typically operated below 250 °C without a precise control over the pressure and hence phase behavior of water, which mainly depends on the vessel filling ratio^{246, 249}. Here, we designed a new hydrothermal reactor capable of controlling the temperature and pressure of water independently. As illustrated in Figure 6.1a and Figure 6.2, the hydrothermal system consists of four main units: i) a cylindrical stainless

steel reactor vessel (316 SS, ½ inch outer diameter) with a total internal volume of ~20 mL connected to a valve-controlled T-shaped stainless steel tube (T-tube, ¼ inch diameter), ii) a set of tip-sensitive temperature (K-type) and pressure sensors attached to the T-tube, iii) a high-pressure gas cylinder regulated with a pressure controller, and iii) a high-temperature fluidized sand bed furnace. The pressure of the reactor vessel can be regulated up to ~265 bars by filling it with N₂ gas from the high-pressure gas cylinder attached. And, the temperature can be varied quickly (up to ~360 °C) by directly inserting the reactor vessel into the sand bed furnace. This system enables the hydrothermal assembly of nanocarbon materials in aqueous reaction media under subcritical and near-critical conditions (see the illustrative water phase diagram given in Figure 6.1b and Figure 6.14a for the temperature-pressure conditions explored). It should be noted that near-critical hydrothermal conditions have been widely used in the conversion of biomass to fuels or other chemicals ^{255, 256}. These reaction conditions (similar temperatures and pressures carried out in this work) have been proved to be safe and easy to operate. The proposed system has a good potential for realizing scalable material production.

Figure 6.1 Hydrothermal assembly of nanocarbon microfibers under subcritical conditions. (a) Schematic of the hydrothermal system with independently controlled high-temperatures and -pressures. (b) Illustrative temperature-pressure phase diagram of water with the subcritical hydrothermal conditions studied in this work (marked by solid spheres). Temperature (T_{tp}) and pressure (P_{tp}) at triple point of water. Temperature (T_c) and pressure (P_c) at critical point of water. (c) The electrical conductivity of nanocarbon microfibers assembled at different subcritical conditions.

Figure 6.2 The chemical process diagram of the hydrothermal system with independently controlled high-temperature and -pressure. HV = hand valve. PR = pressure regulator. PI = pressure indicator. TI = temperature indicator. NRV = non-return valve. PRV = pressure relief valve. Atm = atmosphere.

Table 6.1 Simulated and real pressures that the hydrothermal reactor need to be initially pressurized to at different fiber synthesis conditions.

Fiber	T180- P160- t360	T220- P160- t240	T260 P160- t180	T300- P160- t060	T340- P150- t020	T340- P160- t020	T340- P160- t180	T340- P180- t020
*Simulated pressure (bar)	105	97	90	83	73	78	78	88
Real pressure (bar)	108	100	92	84	75	79	79	89

*Simulated by Aspen HYSYS[®] based on the ideal gas equation. Real pressures measured by pressure gauge is slightly different with simulated pressures.

6.3.2 Hydrothermal assembly of nanocarbon microfibers

Following the previously optimized recipe for the preparation of hybrid carbon electrodes via hydrothermal assembly²⁸, I mixed GO and oxidized SWCNTs in 1 to 1 mass ratio. And, to enhance the binding between GO and SWCNTs, and chemically reduce and dope the resulting structures, we have also added ethylenediamine (EDA), a nitrogen-doping crosslinking agent, to the mixture (GO/SWCNT/EDA)²⁸. Nitrogen doped reduced GO (rGO) provides a large surface area for achieving high electrical double layer capacitance and pseudocapacitance. SWCNTs, on the other hand, prevent the restacking of rGO formed during the assembly and drying steps, increase the electrical conductivity and ensure ion-accessibility through the formation of nanochannel pores. It should be noted that the ratio among GO/SWCNT/EDA has been previously studied²⁸. The focus of this work is on the new hydrothermal system, thus, we did not change the previously optimized recipe in this work.

I have explored three main parameters of the hydrothermal assembly process, *i.e.*, temperature, pressure, and time. Accordingly, we have denoted the microfibers fabricated with a tertiary labeling system as “fiber-T-P-t”, where “T”, “P”, and “t” refer to the temperature (in Celsius degrees, °C), pressure (in bars), and time (in minutes), respectively, in digit form without decimal numbers (for example: 360, 020, etc.). To test how fast the microfibers can be assembled by increasing the temperature from 180 to 340 °C (at a fixed pressure of 160 bar), we have performed the process for different durations from 10 minutes to 12 hours. For assessing the successful completion of assembly process, we have used electrical conductivity measurements conducted on dried microfibers as an indicator.²⁵⁷ As shown in Figure 6.1c, the electrical conductivity of microfibers initially increases with the extension of process duration, and reach a

different maximum at each temperature. The time needed for reaching the maximum value is much lower at higher temperatures: while 180 °C needs minimum 6 hours for completion, 340 °C takes only 20 minutes to peak. More importantly, the peak electrical conductivities of the microfibers synthesized at higher temperatures are much higher. For instance, the fiber-T340-P160-t020 has an electrical conductivity of 126.2 S cm^{-1} , which is ~78% higher than that of the fiber-T180-P160-t360.

Figure 6.3 Photograph of wet and dry T340-P160-t020 microfibers. (a) wet microfibers dispersed in a water reservoir, (b) a single wet (bottom) and dry (top) microfibers next to a ruler.

Despite being produced much faster, the fiber-T340-P160-t020 exhibits one of the highest electrical conductivity among the hydrothermally assembled nanocarbon microfibers demonstrated to date^{17, 28, 44, 46, 47, 63, 258}. Therefore, performing hydrothermal assembly under near-critical conditions is greatly beneficial for the fabrication of nanocarbon electrodes for FMSCs. However, it is worth noting that the extension of processing duration beyond the completion of assembly process becomes quite

detrimental at under near-critical conditions. For example, while the changes in the peak electrical conductivity values are negligible below 260 °C even after hours of extra treatment, the electrical conductivity of the fiber-T340-P160-t020 drops ~13% in less than 3 hours of further exposure (comparing T340-P160-t020 and T340-P160-t180 in Table 6.4). We have also tested the role of pressure in near-critical hydrothermal conditions at 340 °C. As given in Table 6.4, varying the pressure in between 150 and 180 bar did not change the conductivity of microfibers significantly produced in 20 minutes. Overall, increasing the temperature from 180 °C to near-critical 340 °C (at and above 150 bar) enables the successful completion of hydrothermal assembly expeditiously, much faster than all the previous studies in the field of hydrothermal processing of nanocarbons (Figure 6.4 and Table 6.2).

Figure 6.4 Comparison of the temperature and duration of hydrothermal processes employed for the preparation of nanocarbon architectures for different applications. (For the references, see Table 6.2 below)

Table 6.2 Comparison of the temperature and duration of hydrothermal processes employed for the preparation of nanocarbon architectures for different applications.

Ref.	Application Area	Material Composition	Hydrothermal Conditions (temp. [°C] time [h])	Remarks (if any)
This work	energy storage (micro-supercapacitors)	N-doped rGO/SWCNT (N-rGO/SWCNT)	180~340 0.33~6 (@ 150~180 bar)	using near-critical conditions for microfiber assembly for the first time
283	energy storage (lithium-ion battery)	N-doped holy rGO	180 6	high volumetric capacity for lithium-ion battery
28	energy storage (micro-supercapacitors)	(N-rGO/SWCNT)	220 6	development of a scalable method to continuously produce microfiber via a linear hydrothermal microreactor
284	energy storage (film supercapacitor)	RGO/ Ni(OH) ₂	210 24	N.A.
285	catalysis	rGO/TiO ₂ nanotubes	120 24	photocatalyst
286	catalysis	N-rGO/NiCo DH	150 12	catalyst for oxygen evolution reaction
287	catalysis	Au/rGO	180 12	catalyst for reduction of 4-nitrophenol
288	sensing	SnO ₂ /rGO	120 8	good sensing properties to NH ₃
289	sensing	rGO	180 10	potential application in pressure sensing
290	sensing	Au/rGO	180 12	excellent selectivity for NO sensing
291	antibacterial	Ag/rGO	120 20	application in water disinfection

6.3.3 Physicochemical properties of microfibers

Morphology and pore structures by SEM and physisorption: To better understand the effect of processing conditions on hydrothermal assembly, I have thoroughly characterized the physicochemical properties of microfibers using microscopic and spectroscopic techniques. Figure 6.5 shows the scanning electron microscopy (SEM) images of the microfibers with peak electrical conductivities produced in mild subcritical and near-critical conditions: T180-P160-t360, and T340-P160-t020. The average diameter of the microfibers decreases from ~ 72 to $\sim 60 \mu\text{m}$ when the temperature increases from 180 to 340 °C (Figure 6.5a, d). Accordingly, the fiber-T180-P160-t360 (Figure 6.5b, c) has a less compact structure than the fiber-T340-P160-t020 (Figure 6.5e, f). While the T180-P-160-t360 microfibers give an average density of $\sim 0.85 \text{ g cm}^{-3}$, the T340-P160-t020 microfibers have a higher density of $\sim 1.13 \text{ g cm}^{-3}$. Despite the steady densification of microfibers by increased temperature (Table 6.4), the specific surface area values fluctuated in a narrow range of around $380\text{-}390 \text{ m}^2 \text{ g}^{-1}$ (see Figure 6.7 for physisorption measurements). We attribute this to the success of SWCNTs as spacers for rGO (see Figure 6.5c, f and Figure 6.6, aligned SWCNTs interposed between rGO layers)^{28, 259}, which prevented restacking and provided large specific surface area. A steep uptake at the low pressure and hysteresis loop in the nitrogen adsorption/desorption isotherm (Figure 6.7a) suggest the existence of micropores ($< 2 \text{ nm}$) and mesopores ($2\text{-}50 \text{ nm}$), respectively²⁶⁰. The hierarchical porous structure is shown by the pore size distribution ranging from ~ 0.5 to $\sim 27.3 \text{ nm}$ with three main peaks at ~ 0.7 , ~ 1.3 , $\sim 2.9 \text{ nm}$ and a broad peak after $\sim 4.0 \text{ nm}$. Carbon dioxide adsorption/desorption was also performed to study micropores (Figure 6.7c, d). Micropores contribute to the high specific surface area and provide abundant active sites

²⁶¹, which mesopores facilitate ion transport ^{261, 262}. The hierarchical porous structure in the microfibers is beneficial to supercapacitive energy storage. SEM images in Figure 6.8 compares the surfaces of the hybrid fibers synthesized with different assembly time (fiber-T340-P160-t020 vs. fiber-T340-P160-t180). The fiber-T340-P160-t020 has a rough surface with wrinkled rGO sheets enfolding SWCNTs, similar to rGO/SWCNT fibers reported in the literatures ^{17, 28, 46}. When the assembly time is extended to 3 hours, fewer wrinkled rGO sheets are observed on the surface of the fiber-T340-P160-t180, SWCNT bundles are exposed instead. This suggests that rGO sheets may decompose when exposed to superheated water for a long duration ²⁶³.

Figure 6.5 Microscopic and spectroscopic characterization of nanocarbon microfibers. (a-f) Microstructures of the hybrid fibers. SEM images of the full-view, cross-sectional, and enlarged area of (a-c) fiber-T180-P160-t360, and (d-f) fiber-T340-P160-t020. Scale bars are 20 μm , 10 μm , and 500 nm in (a,d), (b,e), and (c,f), respectively. (g) Raman, and (h) X-ray photoelectron spectroscopy (XPS) spectra of microfibers.

Figure 6.6 SEM images of the outer surface of (a) fiber-T180-P160-t360, (b) fiber-T340-P160-t020, (c) fiber-T220-P160-t340, (e) fiber-T260-P160-t180 and (g) fiber-T300-P160-t060. Enlarged view of cross-sectional SEM images of (d) fiber-T220-P160-t340, (f) fiber-T260-P160-t180 and (g) fiber-T300-P160-t060. Scale bars are all at 500 nm.

Figure 6.7 Physisorption isotherms and pore size analysis of microfibers fabricated under near-critical conditions. (a) Nitrogen adsorption/desorption isotherms, and (b) pore size distribution of fiber-T340-P160-t020. (c) Carbon dioxide adsorption/desorption isotherms, and (d) pore size distribution of fiber-T340-P160-t020.

Figure 6.8 SEM images of the full-view and outer surface of microfibers assembled under near-critical conditions (340 °C and 160 bar) by applying the hydrothermal assembly for different durations. (a,b) T340-P160-t020 (20 minutes), and (c,d) T340-P160-t180 (3 hours). Scale bars are 20 μm and 200 nm in (a,c) and (b,d), respectively.

Chemical properties by Raman and XPS: Subsequently, we performed Raman measurements to compare the graphitic quality of microfibers with peak electrical conductivities at each temperature condition (Figure 6.5g). Based on the intensity ratio of defect-related D band ($\sim 1350\text{ cm}^{-1}$) and graphitic G band ($\sim 1590\text{ cm}^{-1}$)^{201, 264, 265}, defect level of microfibers shows an overall decreasing trend from 180 to 340 °C (see the I_D/I_G values in Table 6.4). This suggests that higher temperatures remove more surface functional groups of oxidized nanocarbons in favor of conjugated graphitic structures. However, when the assembly duration is extended from 20 minutes to 3 hours, the I_D/I_G value of microfibers produced at 340 °C (and 160 bar) increases, which suggest structural corrosion in the graphitic network (Figure 6.9)²⁶³. In contrast, the microfibers synthesized under different pressures (fiber-T340-P150-t020, fiber-T340-P160-t020, and fiber-T340-P180-t20) have the same I_D/I_G values (also see Figure 6.9). Notably, all these Raman results agree with the electrical conductivity results given in Figure 6.1c (see Figure 6.10c).

Figure 6.9 Raman spectra of microfibers assembled at 340 °C under different pressures and processing durations: fiber-T340-P160-t180, fiber-T340-P180-t020, and fiber-T340-P150-t020.

Figure 6.10 Correlation between hydrothermal conditions of nanocarbon microfibers and their electrical, chemical properties. (a) Assembly time and electrical conductivity of nanocarbon microfibers at different subcritical conditions. (b) I_D/I_G and C/O ratio of nanocarbon microfibers at different subcritical conditions. Electrical conductivity corresponds to I_D/I_G (c) and C/O ratio of nanocarbon microfibers (d).

Furthermore, to characterize the chemical content of the microfibers, we carried out energy dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS) measurements. EDS elemental maps show that C, O, and N distribute uniformly throughout the whole microfiber structures (Figure 6.11). Correspondingly, XPS survey scans show that all microfibers contain C, O, and, N (Figure 6.5h). The C/O atomic ratio determined from XPS spectra are used to quantify the chemical properties of GO^{63, 257}. We observed that as the processing temperature increases, C/O values also increases, in agreement with the trend of I_D/I_G values (see Table 6.4 for C/O values). The comparison of the C/O ratio observed at mild and near-critical conditions shows that the fiber-T340-P160-t020 gives a C/O ratio of 11.7, which is more than twice of that of the fiber-T180-P160-t360 at 5.7.

Figure 6.11 SEM images and corresponding EDS elemental maps (C, N, and O) of microfibers. (a) fiber-T180-P160-t360, (b) fiber-T220-P160-t240, (c) fiber-T260-P160-t180, (d) fiber-T300-P160-t060, and (e) fiber-T340-P160-t020, (f) fiber-T340-P150-t020, (g) fiber-T340-P180-t020, and (h) fiber-T340-P160-t180. Scale bars are 100 μm in all images.

For comparing the functional group profiles of microfibers assembled under mild subcritical and near-critical conditions, we have further analyzed the high-resolution C1s, O1s, and N1s spectra of the fiber-T180-P160-t360 and fiber-T340-P160-t020 (Figure 6.12). The C1s peaks of both microfibers were deconvoluted into five sub-peaks with different intensities. The peaks centered at 284.4 eV correspond to the carbon atoms in sp^2 - hybridized structures^{266, 267}. And, the peaks 285.5, 286.2, 287.8, and 288.7 eV are associated with C-N, C-O, C=O and O=C-O bonds, respectively.²⁶⁶⁻²⁶⁸ The O1s peak can be deconvoluted into three peaks at 531.3, 532.4, 533.3 eV corresponding to C-O, C=O and O-C=O bonds, respectively²⁶⁷. The observation of these O-involving peaks in both microfibers indicates that 20 minutes of near-critical processing do not completely reduce the oxidized nanocarbon precursors. The N1s peak is resolved into four main peaks: pyridinic N at 398.4 eV, amine moieties or other sp^3 C and N bonds at 399.5 eV, pyrrolic N at 400.1 eV and graphitic N at 401.2 eV²⁶⁸. Despite the near-

critical processing does not make a huge impact on the total N-doping level of microfibers (see Table 6.4), the composition of N-containing functional groups shows a considerable variation in favor of graphitic N (see Figure 6.13 for the effect of processing temperature on the composition of O- and N-containing functional groups).

Figure 6.12 XPS analysis spectra of the fiber-T180-P160-t360 and fiber-T340-P160-t020. (a) C1s, (c) O1s and (e) N1s spectra of fiber-T180-P160-t360, and (b) C1s, (d) O1s and (f) N1s spectra of fiber-T340-P160-t020.

Figure 6.13 The abundance changes of atoms in different states in nanocarbon microfibers at different subcritical conditions. (a) O and (b) N.

6.3.4 Potential effects of hydrothermal assembly conditions

The electrical conductivity of nanocarbons depends on the presence of long-range-conjugated graphitic networks^{269, 270}. Particularly, O-containing functional groups (*e.g.*, hydroxyl, carboxyl) reduce the electrical conductivity of nanocarbons by localizing π -electrons²⁵⁷. Therefore, the successful reduction of O-containing groups is arguably the most critical event in the hydrothermal assembly of oxidized nanocarbons for obtaining electrical conductivity structures eventually. The assembly process utilized water at subcritical temperature and under sufficiently high pressures to maintain a liquid phase to act as the reaction medium. With higher temperatures, the dielectric constant of water decreases in addition to a greater degree of dissociation into H_3O^+ and OH^- ions. H^+ ions (H_3O^+) abundantly present in subcritical water are important players for the reduction of oxidized nanocarbons by subcritical hydrothermal processing as they protonate and dehydrate hydroxyl/carboxyl groups^{257, 271}. However, the abundance of H^+ ions in mild subcritical (ca. $160\text{ }^\circ\text{C} < T < 230\text{ }^\circ\text{C}$, $P_{\text{saturation}} < P$) and near-critical (ca.

320 °C < T < 374 °C, $P_{\text{saturation}} < P < 221$ bar) water is comparable (Figure 6.14f) ^{251, 253, 272}. Accordingly, the concentration of H⁺ ions cannot solely explain the role of near-critical condition. However, while the temperature increases from 180 to 340 °C, density, viscosity, and dielectric constant of water show a dramatic linear-like reduction (see Figure 6.14b, c and g) ^{251-254, 273}. Such changes in the solvent quality of water likely speed up the reactions involved including H⁺-induced reduction of oxidized species. Beyond, since the near-critical water dissolves nonpolar species too ^{251, 254, 274}, enhanced solvation effect at higher temperatures might be increasing the specific surface area of the microfibers via suppressing the restacking/rebundling of nanocarbons.

It is well established that the effect of pressure on the phase behavior of water is lower than the effect of temperature in subcritical region (see water property changes under different temperatures and pressures in Figure 6.14b-g) ^{246, 251-253, 272, 274}. Accordingly, we observed the changes in the physicochemical properties of microfiber with 20% increase in the processing pressure (from 150 to 180 bar) at 340 °C (Table 6.4) is not big. In contrast, less than 15% increase in the processing temperature from 300 to 340 °C (at 160 bar) made a dramatically beneficial impact on the properties of microfibers and the time required for reaching peak electrical conductivity (20 minutes instead of 1 hour). However, it should be noted that the ability to manipulate the pressure independently for a hydrothermal system is still critical. In order to reach the subcritical states at certain temperatures, the pressure must be kept above its saturation vapor pressure as shown in the temperature-pressure phase diagram of water in Figure 6.14. It is not possible to enter the near-critical conditions without the independent pressure control.

Figure 6.14 Properties of pure water as a function of temperature. (a) Temperature-pressure phase diagram of water with the subcritical hydrothermal conditions studied in

this work. (b-e) Density and viscosity of water at different pressures as a function of temperature. (f) Ion product of water under (1) 1 bar or saturated pressure and (2) 250 bar as a function of temperature. (e) Static dielectric constant of water or vapor at (1) 100 bar and (2) 200 bar as a function of temperature. (a-e) is based on the data obtained from National Institute of Standards and Technology (NIST). (f1) is based on the data obtained from ref. 292. (f2) is digitization of figure in ref. 251. (g) is based on the data obtained from ref. 293. The insert figures in (b-g) shows the corresponding properties of water within a narrow temperature range from 180 to 340 °C. Ion product and static dielectric constant data of water under 150, 160, 180 bar are not available, so properties under two most adjacent pressure (obtained from ref. 251, 292 and 293) are presented in (f) and (g) to speculate these two properties under 150, 160 and 180 bar. It is clearly seen in (f) and (g) that ion product and static dielectric constant both share similar trend under the two adjacent pressures. And the trend is even applicable in a wider range of pressure (Ref. 251, 292 and 293).

6.3.5 Energy consumption of hydrothermal assembly process

Furthermore, we have compared the energy consumption in the formation of microfibers. The energy consumption is calculated based on the total energy consumption of the high-temperature fluidized sand bed furnace at different synthesis conditions. The energy consumption for synthesizing fiber-T180-P160-t360 (the typical hydrothermal temperature) is set as 100%. The detailed calculation is listed in Table 6.3. The results in Table 6.4 show that the formation of microfibers in 20 mins only uses 19.4% of the energy of that used in the typical hydrothermal condition, which is more than 80% of energy saving. In a short summary, as we clearly demonstrated, the short

application of near-critical conditions gives the optimum results in hydrothermal assembly of nanocarbons, which can be maintained with a simple and expectedly scalable hydrothermal setup (see Figure 6.15 for an envisioned scalable process for the synthesis of FMSCs electrodes based on near-critical hydrothermal microfiber assembly process).

Table 6.3 Output power of and total energy of the high-temperature fluidized sand bed furnace at different fiber synthesis conditions.

Fiber	T180- P160- t360	T220- P160- t240	T260 P160- t180	T300- P160- t60	T340- P150- t20	T340- P160- t020	T340- P160- t180	T340- P180- t20
Output power* (kW)	0.49	0.63	0.95	1.29	1.71	1.71	1.71	1.71
Duration (min)	360	240	180	60	20	20	180	20
Total Energy consumption† (kWh)	2.94	2.52	2.85	1.29	0.57	0.57	5.13	0.57

*The output power (P) of the furnace is determined by the equation $P = UI$, where U is the working voltage of the furnace (220 V) and I is the current. The current was measured by a digital multimeter (ISO-TECH IDM91E).

†The totally energy consumption (E) is determined by the equation of $E = Pt$, where P is the output power of the furnace and t is the duration of the hydrothermal assembly.

Table 6.4 Physical and chemical properties of nanocarbon microfibers and the energy efficiency of the hydrothermal assembly processes. The average values are based on the data collected by minimum three measurements performed on separate samples.

Sample label (temp.-press.-time)	Diameter (μm)	Density (g cm^{-3})	Surface area ($\text{m}^2 \text{g}^{-1}$)	N doping (at.%)	I_D/I_G ratio	C/O ratio	Conductivity (S cm^{-1})	Energy consumption*
T180-P160-t360	72.0 ± 2.0	0.85 ± 0.03	391 ± 7	4.0	1.14	5.7	71 ± 2.0	100%
T220-P160-t240	68.0 ± 1.5	0.92 ± 0.02	383 ± 10	4.1	1.10	6.8	77.6 ± 1.5	85.7%
T260-P160-t180	65.0 ± 1.0	0.99 ± 0.03	389 ± 8	4.5	1.05	9.5	86.1 ± 2.0	96.9%
T300-P160-t060	63.0 ± 1.0	1.08 ± 0.02	381 ± 10	4.6	0.96	10.8	98.9 ± 1.5	43.9%
T340-P150-t020	60.0 ± 1.0	1.14 ± 0.02	379 ± 6	4.6	0.88	11.4	128.1 ± 4.0	19.4%
T340-P160-t020	60.0 ± 2.0	1.13 ± 0.02	385 ± 11	4.8	0.88	11.7	126.2 ± 2.0	19.4%
T340-P160-t180	59.0 ± 3.0	1.16 ± 0.02	368 ± 13	4.3	0.92	11.1	114.4 ± 2.5	174.5%
T340-P180-t020	60.0 ± 2.5	1.13 ± 0.01	387 ± 7	4.7	0.87	11.6	127.5 ± 2.0	19.4%

*Energy consumption is calculated based on the total energy consumption of the high-temperature fluidized sand bed furnace at different synthesis conditions. The energy consumption for synthesizing fiber-T180-P160-t360 (the typical hydrothermal temperature) is set as 100%. The detailed calculation results are listed in Table 6.3.

Figure 6.15 Schematics of an envisioned scalable process for the synthesis of FMSCs electrodes based on near-critical hydrothermal microfiber assembly process. Nanocarbon microfibers are synthesized by injecting homogeneous GO/SWCNT/EDA mixture into numerous reactors with multiple channels in every reactor in turns (number of reactors and diameter of channels can be customer-designed according to different requirements) through a pump, followed by pressurizing the reactor system through a pressurization system. Then the reactor was instantly heated to near-critical condition for 20 minutes before vent the system and push nanocarbon microfibers into a water reservoir by a pressurized gas flow. Once fiber synthesis is completed in one reactor, this reactor is re-fed with a new batch of feeding solution. At the same time, fiber synthesis continues in other reactors.

6.3.6 Electrochemical properties of the hybrid microfibers

The electrochemical properties of the hybrid microfibers synthesized at different temperatures with peak electrical conductivities were first tested using the three-electrode configuration in 1 M H₂SO₄. Cyclic voltammetry (CV) curves obtained at the scan rate of 20 mV s⁻¹ are shown in Figure 16f. The reversible anodic and cathodic peaks at 0.3-0.5 V come from the pseudocapacitance by oxygen-containing groups and/or nitrogen heteroatoms^{28, 275}. The redox peaks disappear in the neutral electrolyte (1 M Na₂SO₄) (see Figure 6.17), suggesting that the pseudocapacitance was induced by oxygen-containing functional groups and/or nitrogen heteroatoms²⁷⁵. The enclosed area of CV curves increases with the hydrothermal temperature, indicating that the fiber-T340-P160-t020 has the highest electrochemical capacitance. The CV curves of the fiber-T340-P160-t020 at the scan rates ranging from 2 to 100 mV s⁻¹ are collected in Figure 6.16e. The fiber-T340-P160-t020 maintains a quasi-rectangular shape at high scan rates, suggesting its high rate capability. In contrast, the CV curves of the microfibers synthesized at lower temperatures are spindle-shaped at high scan rates (Figure 6.16a-d). Since the total weight of microelectrodes used in microscale devices like MSCs is typically so small, we preferred comparing the specific volumetric capacitance values other than gravimetric capacitances^{28, 46, 276}. Figure 6.16c summarizes the specific volumetric capacitance ($C_{V,electrode}$) values of the microfibers at different scan rates determined from their CV curves. The fiber-T340-P160-t020 has the highest capacitance of 322 F cm⁻³ at the scan rate of 2 mV s⁻¹, which is one of the highest volumetric capacitance reported for carbon-based microfiber electrodes (see Table 6.5)^{17, 28, 43, 46, 84, 159, 258}. And, in line with the electrical conductivity and specific surface area values shown above in Table 6.4, the volumetric capacitance of the

microfibers decreases with the decrease of processing temperature. Furthermore, the fiber-T340-P160-t020 retains > 64% of its capacitance when the scan rate increases from 2 to 100 mV s⁻¹, while the capacitance retention rates of the other fibers drop in between ~58 to ~44% for other microfibers.

To compare the charge transfer and ion diffusion resistance of microfibers, we have carried out electrochemical impedance spectroscopy (EIS) measurements. As shown in Figure 6.16d, the Nyquist plot of the fiber-T340-P160-t020 shows a steeper response in the low-frequency region, which indicates an ideal capacitive behavior^{217, 218}. And, as evidenced by the observation of an inconspicuous arc in the high-frequency region, the charge transfer resistance of the fiber-T340-P160-t020 is low as well^{217, 218}. Besides, the comparison of Warburg impedances, *i.e.*, the inclined lines with a slope of ~45° in medium-frequency region of Figure 6.16d, provide further insight regarding the effect of processing temperature on the diffusion behavior of ions inside microfibers^{217, 218}. Based on the decrease in the length of Warburg curves by the increase of temperature, the diffusion distance of the electrolytes should be much lower in fiber-T340-P160-t020 compared to fiber-T180-P160-t360^{217, 218}. Besides, the equivalent series resistance (ESR) values calculated from the real axis intercept on Nyquist plots also decreases significantly (from 526.7, 430.9, 366.3, 272.1 to 181.3 Ω) with the increase of temperature. This observation indicates that increasing the temperature of hydrothermal assembly process improves significantly the electrical conductivity of resulting microfibers, which is in agreement with the four-probe-based conductivity results given in Table 6.4.

CV- and EIS-based electrochemical characterizations collectively indicate that the high temperatures boost the capacitive performance of microfibers produced by hydrothermal assembly. This outcome can be attributed to three main reasons. First,

unless the processing duration is optimized, the microfibers assembled at higher temperatures get reduced more efficiently and possess higher electrical conductivity. And, as the electrical conductivity increases, the charge transfer in microfiber electrodes also gets faster. Second, the microfibers assembled at higher temperatures have higher densities due to their compacted structures, improving their specific volumetric capacitance. Third, compacted microfibers also have smaller diameters while retaining similar large specific surface areas, which can shorten the diffusion distance of electrolyte ions.⁴⁶ As a result, the microfibers expeditiously assembled under near-critical conditions (T340-P160-t020) offer a great potential for applications with their optimal features.

Figure 6.16 Electrochemical performances of hybrid carbon fibers tested using the three-electrode configuration in 1 M H₂SO₄ electrolyte. CV curves of (a) fiber-T180-

P160-t360, (b) fiber-T220-P160-t240, (c) fiber-T260-P160-t180, (d) fiber-T300-P160-t060 and (e) fiber-T340-P160-t360. (f) CV curves of microfibers measured at the scan rate of 20 mV s^{-1} . (g) The specific volumetric capacitance of microfibers at different scan rates calculated from their CV curves. (h) Nyquist plots of microfibers.

Figure 6.17 Comparative CV curves of fiber-T340-P160-t020 at the scan rate of 100 mV s^{-1} in $1 \text{ M H}_2\text{SO}_4$ and Na_2SO_4 electrolytes.

6.3.7 Two-electrode solid-state FMSCs

As illustrated in Figure 6.18a, using two 0.5 cm long fiber-T340-P160-t020 as both current collector and electrode embedded in gel electrolyte (poly(vinyl alcohol) (PVA)/ H_3PO_4), we have built two-electrode symmetric solid-state FMSCs supported on a flexible polyethylene terephthalate (PET) film (device-T340-P160-t020). CV curves of these FMSCs remained in a rectangular-like shape at the high scan rates up to 100 mV s^{-1} (Figure 6.18b). Correspondingly, the galvanostatic charge and discharge (GCD) curves at a wide range of current densities ($98.6\text{--}1970.2 \text{ mA cm}^{-3}$) display a symmetric

triangular shape, with no significant IR drops (Figure 6.18c). Both CV and GCD observations indicated the fast charge transfer along the microfiber electrodes.

Based on the CV and GCD curves of FMSCs, we calculated the specific volumetric capacitance ($C_{V,electrode}$) of the microfiber electrodes (Figure 6.18c and d). At the scan rate of 2 mV s^{-1} (CV), and the current density of 98.6 mA cm^{-3} (GCD current density), the volumetric capacitances of the microfibers were 308 and 301 F cm^{-3} , respectively. The distance between two microfiber electrodes is $\sim 18\text{-}20 \text{ }\mu\text{m}$. The total volume of the FMSCs, including two fiber electrodes and their surrounding gel electrolytes, is about $8.3 \times 10^{-5} \text{ cm}^3 \text{ cm}^{-1}$ in length. The total area of the device is estimated to be $3.8 \times 10^{-2} \text{ cm}^2 \text{ cm}^{-1}$ in length. Correspondingly, the specific volumetric capacitance, length capacitance and areal capacitance of the FMSC ($C_{V,device}$) is 52 F cm^{-3} , 4.3 mF cm^{-1} and 113.6 mF cm^{-2} , respectively, at 2 mV s^{-1} and 51 F cm^{-3} , 4.2 mF cm^{-1} and 111.4 mF cm^{-2} , respectively, at 98.6 mA cm^{-3} . Thus, achieved performance of FMSCs is one of the best among all MSCs fabricated using carbon-based fiber electrodes to date (see comparison given in Table 6.6)^{17, 28, 43, 46, 140, 159, 169, 175, 215, 230, 277}. After cycles of 10000 charge/discharge loops, the FMSCs could retain $\sim 96\%$ of their initial capacitance, demonstrating an excellent cycling stability (Figure 6.18f). We have also calculated the volumetric energy and power density of FMSCs using GCD curves. Figure 6.18g shows that device-T340-P160-t020 has an energy density of 7.1 mWh cm^{-3} (corresponding to a length energy density of $0.6 \text{ }\mu\text{Wh cm}^{-1}$ and an areal energy density of $15.5 \text{ }\mu\text{Wh cm}^{-2}$) at the power density of 83.6 mW cm^{-3} , and retains more than half of its energy density with 3.9 mWh cm^{-3} at a power density of $1645.7 \text{ mW cm}^{-3}$. This performance is again among of the best values reported so far for FMSCs^{17, 28, 43, 46, 140, 159, 169, 175, 215, 230, 277, 294}. For comparison, the energy density of device-T340-P160-t020 is 10 times higher than that of $5.5 \text{ V}/100 \text{ mF}$ and $2.75 \text{ V}/44 \text{ mF}$ commercial supercapacitors at a similar

power density^{278, 279}. It is even more important to note for benchmarking purposes that the energy density of device-T340-P160-t020 is comparable with 4 V/500 μ Ah Li thin-film battery^{28, 278-280}, while delivering a power density of three orders higher^{28, 280}.

Figure 6.18 Electrochemical performances of the solid-state FMSCs assembled using two identical fiber-T340-P160-t020 (device-T340-P160-t020). (a) Schematic illustration of a FMSCs assembled by two fiber-T340-P160-t020 in PVA/H₃PO₄ gel electrolyte on a PET substrate. (b) CV curves of the FMSCs at the different scan rates. (c) GCD curves of the FMSCs at the different charge/discharge current densities. Specific volumetric capacitances of the FMSCs and its individual electrode at the different scan rates (d) and at various current densities (e). (f) The cycling test of the FMSCs at the current density of 1970.2 mA cm⁻³ for 10000 cycles. (The inset figure shows the GCD curves after 10,000 cycles). (g) Energy and powder densities of the FMSCs compared with previously reported FMSCs and commercial batteries, and capacitor

Table 6.5 Comparison of recently reported carbon-based fiber electrodes of FMSCs.

Ref.	Electrode Composition	Fabrication Method	Conductivity (S m^{-1})	Electrolyte System	Voltage Window (V)	Specific Volumetric Capacitance (F cm^{-3})
This work	N-rGO/SWCNT	Hydrothermal	12620	H_2SO_4 (1 M)	0-1.0	322 (@ 2 mV s^{-1})
				PVA/ H_3PO_4	0-1.0	308 (@ 2 mV s^{-1}) 301 (@ 98.6 mA cm^{-3})
28	N-SWCNT/rGO	Hydrothermal	10200	H_2SO_4 (1 M)	0-1.0	295 (@ 2 mV s^{-1})
46	N-MWCNT/rGO	Hydrothermal	2290	PVA/ H_3PO_4	0-1.0	125 (@ 2 mV s^{-1})
17	N-GO/MWCNT (core-sheath design)	Hydrothermal	N.A.	H_2SO_4 (1 M)	0-1.0	123 (@ 2 mV s^{-1})
84	rGO	Wet-spinning	N.A.	PVA/ H_3PO_4	0-1.0	3.8 (@ 0.1 mA cm^{-2})
43	rGO@carboxymethyl cellulose(CMC)	Wet-spinning	N.A.	PVA/ H_3PO_4	0-0.8	114 (@ 0.1 mA cm^{-2})
43	rGO/CNT@CMC	Wet-spinning	N.A.	PVA/ H_3PO_4	0-0.8	158 (@ 0.1 mA cm^{-2})
43	rGO/CNT@CMC	Wet-spinning	N.A.	H_2SO_4 (1 M)	0-0.8	239 (@ 0.1 mA cm^{-2})
133	CNT-sheet/CNT-fiber	Dry-spinning	N.A.	PVA/ H_3PO_4	0-1.0	32.09 (power density: N.A.)
159	N-SWCNT/rGO	Wet-spinning	10000	Na_2SO_4 (1 M)	0-0.9	137 (@ 5 mV s^{-1})

Table 6.6 Comparison of recently reported FMSCs. (All measurement results listed belong to actual devices based on the two-electrode method.)

Ref.	Electrode Composition	Conductivity (S m^{-1})	Electrolyte System	Voltage Window (V)	Specific Volumetric Capacitance (F cm^{-3})	Energy Density (mWh cm^{-3})	Power Density (mW cm^{-3})
This work	N-rGO/SWCNT	12620	PVA/H ₃ PO ₄	0-1.0	52 (@ 2 mV s ⁻¹)	7.1	1645.7
28	N-SWCNT/rGO	10200	PVA/H ₃ PO ₄	0-0.9	45 (@ 26.7 mA cm ⁻³)	6.3	1085
46	N-MWCNT/rGO	2290	PVA/H ₃ PO ₄	0-1.0	29.7 (@ 2 mV s ⁻¹)	3.2	440
17	N-GO/MWCNT (core-sheath design)	N.A.	PVA/H ₃ PO ₄	0-1.0	27 (@ 2 mV s ⁻¹)	3.75	612
43	rGO/CNT@CMC	N.A.	PVA/H ₃ PO ₄	0-0.8	N.A.	3.5	18
18	Polypyrrole/MnO ₂ /rGO	N.A.	PVA/H ₃ PO ₄	0-0.8	12.4	1.1	160
131	MnO ₂ -decorated carbon fiber	N.A.	PVA/H ₂ SO ₄	0-0.8	2.5	0.22	400
159	N-rGO/SWCNT, MnO ₂ -rGO/SWCNT	10000	PVA/H ₃ PO ₄	0-1.8	11.1 (@ ~25 mA cm ⁻³)	5	1000
175	MnO ₂ /CNT-fiber	N.A.	PVA/KOH	0-1.5	35.19 (@ 10 mV s ⁻¹)	0.69	260
229	CNT-fiber	10000	PVA/H ₃ PO ₄	0-1.0	18.12	N.A.	N.A.
215	Polypyrrole/rGO/MWCNT	N.A.	PVA/H ₃ PO ₄	0-0.8	~8 (@ 1 mV s ⁻¹)	0.94	117.12
230	activated carbon	1800	PVA/H ₃ PO ₄	0-0.8	27.6 (@ 13 mA cm ⁻³)	2.5	100

6.3.8 3D integration of FMSCs

FMSCs have the potential of serving as high-power energy storage units in miniaturized electronic devices^{278, 280-282}. Previous studies devoted to FMSCs mainly focused on the development of electrode materials, only a few studies investigated the integration of FMSCs with miniaturized devices²⁸². Connecting multiple FMSCs in series and/or in parallel on a flat surface is a commonly employed strategy for broadening the operating voltage and current, which is desired for meeting the specific requirements of practical applications. As a result, multiple fiber electrodes often occupy a large surface area, making it difficult, if not impossible; to integrate FMSCs in miniaturized electronic devices. To address this problem, here we explored the integration of our multiple device-T340-P160-t020 FMSCs in both the X-Y plane and the Z-axis directions. Such integration allowed us to build a new type of 3D energy storage device, which can reduce the footprint of FMSCs and expand their operating voltage and current window. We first overlaid FMSCs on top of another along the Z-axis without using PET substrates between each other and then connected them both in parallel. Figure 6.19a shows that the total output current of the overlaid FMSCs containing four pieces of microfiber electrodes is doubled compared to the individual two-electrode FMSCs (charged/discharged at 147.9 mA cm^{-3}). Next, we connected two overlaid four-electrode FMSCs in series. Figure 6.19b shows that the charge/discharge window of the integrated eight-electrode device is expanded to 2 V (charged/discharged at the same current density as that used for individual two-electrode FMSCs). These two steps demonstrate the feasibility of integrating multiple FMSCs in both the X-Y plane and the Z-axis direction. In a subsequent demonstration, we fabricated a 3D energy storage device by integrating 32 microfiber electrodes, which we call 3D-FMSCs. The

structure of 3D-FMSCs is schematically illustrated in Figure 6.19e. Fabrication process of the 3D-FMSCs is schematically shown in Figure 6.19c. Four fibers were first placed in the X-Y plane to form a four-fiber flat array, which is equivalent to two FMSCs connected in parallel. Next, four layers of the four-electrode FMSCs were stacked together layer by layer in the Z-axis. Finally, we connected two sixteen-electrode FMSCs in series and obtained 3D-FMSCs, which has a thickness similar to that of five pieces of piled up 5-cent coins (~ 10 mm) (Figure 6.19e). As described in the Experimental section, fiber-T340-P160-t020 were first dipped into the gel electrolyte for 5 mins, and then dried in an environmental chamber with controlled temperature at $25\text{ }^{\circ}\text{C}$ in air and a humidity of $\sim 50\%$. As the concentration of the gel electrolyte is fixed, the diameter of fiber-T340-P160-t020 after coated with gel electrolytes is within a narrow range of $\sim 78\text{-}80\text{ }\mu\text{m}$ (see Figure 6.19d). Considering the diameter of fiber-T340-P160-t020 before gel coating is $\sim 60\text{ }\mu\text{m}$, so when two gel-coated fibers were placed side by side in parallel, the distance between two adjacent fiber electrodes is $\sim 18\text{-}20\text{ }\mu\text{m}$. Similarly, when different layers are stacked together, the distance between two adjacent layers is also around $\sim 18\text{-}20\text{ }\mu\text{m}$. A single charged 3D-FMSC could light up a red LED for more than 5 minutes (Figure 6.19f). Importantly, the integration of 16 two-electrode FMSCs as a 3D-FMSCs reduced the device footprint by around 75%, which may help FMSCs designs compete with micro-batteries for emerging wearable/portable electronics applications.

Figure 6.19 3D integration of microfiber electrodes as stacked and enlarged FMSCs. (a) GCD curves of one and two fiber-T340-P160-t020 based FMSCs connected in parallel along the Z-axis. (b) Two parallelly connected FMSCs arrays are further connected in series, and the inserted images show the corresponding schematic illustrations. (c) Schematic illustration of the fabrication process of a 3D energy storage unit integrated by fiber-T340-P160-t020-based FMSCs: four fibers were placed in the X-Y plane to form a four-fiber flat array which is equivalent to two FMSCs connected in parallel,

then four parallel arrays are stacked together layer by layer in the Z-axis with the external circuit connected. Last, two of these 3D device arrays are connected in series. (d) SEM images of fiber-T340-P160-t020 after coating PVA/H₃PO₄ gel electrolyte. (e) Schematic illustration of the 3D energy storage unit in (c). (f) Photography of a red LED lightened by the 3D energy storage unit with the thickness of five 5-cent coins. The three parts labeled with numbers corresponding to the areas in (e).

6.4 Conclusions

In conclusion, I have presented a new hydrothermal method that allows the independent control of temperature and pressure in a wide range of subcritical and near-critical conditions. This serves as a practical nanoarchitectonic platform for optimizing the physicochemical properties of nanocarbon microfiber electrodes for FMSCs applications. Exploring through a wide range of temperature-pressure-time conditions, we demonstrated that near-critical hydrothermal conditions allow the fabrication of high-performing nanocarbon microfibers from GO, oxidized SWCNTs, and EDA rapidly within 20 minutes. The resultant microfibers exhibit a high packing density of 1.13 g cm⁻³, a large ion-accessible surface of 385 m² g⁻¹, and an excellent electrical conductivity of 126.2 S cm⁻¹. These properties lead to one of the highest volumetric capacitance reported for carbon-based fiber electrodes, 322 F cm⁻³ at the scan rate of 2 mV s⁻¹. And, using such electrodes, we built a two-electrode symmetric solid-state FMSCs that gives a specific volumetric capacitance of 52 F cm⁻³, and an energy density of 7.1 mWh cm⁻³ at the power density of 83.6 mW cm⁻³, which is one of the best among all MSCs fabricated based on carbon-based fiber electrodes. Furthermore, we demonstrated the first integration of multiple FMSCs in both the X-Y plane and the Z-

axis direction to build a 3D energy storage device. A 3D-FMSCs unit can fit to ~25% of the space required for fitting flat 2D FMSCs of same electrode number while expanding the operating voltage and current window. The new hydrothermal assembly method provides a new nanoarchitectonic tool for assembly of various structures from nanoscale building blocks. The demonstrated FMSCs and 3D-FMSCs hold a great promise for the development of innovative applications for future wearable/portable electronics.

Chapter VII Conclusions and outlook

7.1 Conclusions

1D F/YSCs, with their unique energy storage mechanism and structural advantages, are emerging as a promising energy solution to wearable electronics. They may find applications either as micro-devices to power miniaturized wearable electronics or be scaled up to macro-devices for smart textiles and high energy-consuming wearable electronics. The recent advances in electrode materials of supercapacitors, including carbon-based materials and pseudocapacitive materials, facilitate the fast development of 1D F/YSCs. This thesis presents several projects on the design, synthesis, and engineering of electrode materials to fabricate 1D fiber/yarn electrodes with a high electrochemical performance for F/YSCs.

An emerging approach to building energy storage devices for wearable electronics is to incorporate energy storage materials into textiles fibers directly and then integrate multiple fibers into wearable textiles. In chapter III, I demonstrated all-carbon solid-state YSCs using commercially available activated carbon and carbon fiber yarns. Activated carbon with large surface area serves as electrode materials, while carbon fibers with excellent electrical conductivity and mechanical strength act as current collectors and substrate for depositing activated carbon. The all-carbon solid-state YSCs exhibit good capacitive performance and scalability. Long YSCs up to 50 cm in length were successfully demonstrated, yielding a high total capacitance up to 1164 mF. The YSCs also shows excellent mechanical flexibility with minor capacitance decrease upon bending or being crumpled. Utilized three long YSCs, a wearable wristband was knitted which is capable of lighting up an LED indicator.

In contrast to long YSCs as textile energy storage, FMSCs are promising energy storage solutions for miniaturized electronics because of their mechanical flexibility, small size, and good integrability. In Chapter IV, I synthesized micro-nano-integrated core-sheath fibers comprised of a microscale core made of commercial graphite fibers and a nanoscale hybrid sheath comprised of nitrogen doped GO sheets and MWCNTs. The highly conductive graphite fiber core provides efficient pathways for fast electron transfer, while the functionalized nano-hybrid sheath with large surface area and enables large capacitance storage. The use of graphite fiber core dramatically improves the electrical conductive of the electrode which achieved a 6-times increase in capacitance retention compared to hybrid carbon fibers without graphite fiber core. Solid-state FMSCs assembled using two identical core-sheath fibers as electrodes, which concurrently possess high length capacitance of 12.8 mF cm^{-1} , and volumetric capacitance of 27 F cm^{-3} , showing an energy density of 3.75 mWh cm^{-3} and a power density of 612 mW cm^{-3} . 15 FMSCs were connected in parallel or series to expand their current densities or voltage window, demonstrating excellent integrability for practical applications.

Because electrical double layer capacitance serves as the main charge storage mechanism, the capacitance of hybrid carbon fibers comprised of graphene and CNTs is unsatisfactory. In contrast, pseudocapacitive materials normally have 10-100 times higher specific capacitance than electrical double layer capacitive materials. Thus, in Chapter V, based on an optimized two-step synthesis method, high-capacitance RuO_2 nanoparticles with ultrahigh high mass loading (up to 42.5%) was uniformly incorporated into hybrid carbon fibers derived from HGO sheets as the main components and SWCNTs as nanospacers. The composite fibers produced exhibited an ultrahigh volumetric capacitance of 1054 F cm^{-3} . Solid-state FMSCs assembled using

composite fibers with optimized Ru mass loading of 36.8% have a high specific capacitance of 199 F cm^{-3} , delivered the ultrahigh energy density of 27.3 mWh cm^{-3} and the power density of $2954.1 \text{ mW cm}^{-3}$.

Hybrid carbon fibers described in Chapter IV and V both were synthesized in a traditional Teflon-lined autoclave bomb. Under the mild subcritical application applied in typical hydrothermal systems ($180\text{--}220^\circ\text{C}$), it takes ~ 12 hours to complete the assembly of hybrid carbon fibers. The slow assembly process in traditional hydrothermal reactors is not suitable for scalable production. In chapter VI, I described a new nonequilibrium subcritical hydrothermal method capable of independently manipulating the temperature and pressure to create unique assembly conditions crossing the commonly used liquid-vapor boundary. It was found that near-critical hydrothermal conditions shorten the hydrothermal assembly time of graphene and CNT composite fibers into 20 mins and simultaneously achieve an 80% energy saving compared to standard hydrothermal methods. In addition, the role of hydrothermal temperature and pressure was studied. I found that the temperature plays a dominated role in determining the assembly of hybrid carbon fibers. Furthermore, a new strategy was demonstrated to integrate multiple FMSCs both in the X-Y plane and Z-axis direction to build a 3D SCs, which can save 75% footprint compared to the typical strategy by aligning many fibers on a flat substrate.

7.2 Outlooks

Overall, my research on wearable energy storage focuses on two directions: long YSCs capable of being knitted or weaved into energy storage textiles and short FMSCs serving as energy storage solutions for miniaturized electronics. Despite their vast

difference in size, YSCs and FMSCs both need new electrode materials (*e.g.*, intercalation-type pseudocapacitive materials, such as MXenes) and novel designs for electrodes and device configurations to achieve higher electrochemical performance. Narrowing the energy density gap with batteries while preserving their high-power density and ensuring well rate performance is the main research target.

Figure 7.1 Outlook of future YSCs (a) and FMSCs (b).

7.2.1 YSCs for textile energy storage

Because long YSCs up to several kilometers are required to knit or weave practical textiles, I propose that future studies of YSCs should focus on the following directions (Figure 7.1a): i) Safety is the most critical feature for YSCs. Non-toxic materials are preferred, and careful packaging is needed if harmful substances are utilized. ii) It is urgent to develop scalable fabrication processes for YSCs, including efficient electrode materials deposition, electrolyte deposition, and device assembly methods. iii) Because the long electron transfer distance in YSCs is expected to significantly deteriorate their

rate performance, besides high capacitance, novel electrode materials with high electrical conductivity are needed to enable fast electron transfer. iv) To fabricate long YSCs, large amounts of electrode materials are required. Thus, the cost of electrode materials is essential. Even though the use of pseudocapacitive materials could diametrically boost the electrochemical performance of YSCs, the high cost of some pseudocapacitive materials may hinder their practical applications. v) In YSCs, gel electrolytes (mostly PVA-based) are commonly used to replace liquid electrolytes to avoid electrolyte leakage. Gel electrolytes also serve as separators to prevent short circuits. A simple short circuit on one site may cause the entire failure of YSCs. However, current commonly used gel electrolytes are not stable under hot, wet environmental or mechanically harsh conditions. Besides, they also suffer from low ionic conductivities and limited voltage window. Therefore, it is vital to develop new solid-state electrolytes with better stability under various conditions, higher ionic conductivity, and broader voltage windows. vi) Washability is the essential attribute of textiles. The washing of energy storage textiles posts many technical challenges because washing conditions are both chemically and mechanically demanding. Future work on energy storage textiles should develop strategies to address this issue. vii) Clothes in direct contact with human skins have even higher wearability requirements, which place critical constraints on the design of practical textile energy storage devices. Nevertheless, the exact wearability requirements for textile energy storage devices fabricated from YSCs are still not well defined. Besides the aforementioned six aspects, flame-resistance, mechanical flexibility, stretchability, abrasion resistance, moisture penetrability, fatigue lifetime, mass density, thermal conductivity, and wettability are all needed to be carefully studied.

7.2.2 FMSCs for miniaturized devices

As discussed in Chapter II, carbon-based materials hold several advantages as the building blocks of the electrodes for FMSCs. However, translating the advantages of carbon nanomaterials into electrodes of FMSCs is challenging because of the desirable nanoscale properties often disappear during the assembly process. For example, the specific surface area of graphene-based fibers is normally $< 400 \text{ m}^2 \text{ g}^{-1}$ and their conductivity are below 100 S cm^{-1} , which are much inferior to the theoretical value of graphene. To this end, as shown in Figure 7.1b, I propose that future studies on FMSCs should focus on how to preserve the intrinsic properties of carbon-based materials when we assemble them into macroscale devices. This task involves materials selection and engineering as well as the innovation in assembly methods.

On the other aspect, because the absolute mass loading of pseudocapacitive materials in FMSCs is low, their high-cost becomes less important. My studies in Chapter V have demonstrated that the incorporation of pseudocapacitive materials (RuO_2) into electrical double layer-type hybrid carbon fibers can significantly boost the electrochemical performance of FMSCs. Therefore, it is useful to further explore various novel pseudocapacitive materials to be incorporated into hybrid carbon fibers, especially new intercalation-type pseudocapacitive materials (*e.g.*, MXene). Since the chemical and physical properties of various carbon-based fibers and pseudocapacitive materials are different, it is important to optimize their incorporation methods. Furthermore, physiochemical properties of pseudocapacitive materials, such as crystallographic phase, particle size, heteroatom doping, should also be optimized. The same as YSCs, other critical issues, such as scalable production, high-performance solid-state electrolyte, safety, lifetime, are also important for realizing the practical applications of FMSCs.

Publications

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