Electrospinning-derived hybrid nanofibers with tailored morphologies : mechanism and electrochemical properties

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NANYANG
TECHNOLOGICAL
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**ELECTROSPINNING-DERIVED HYBRID NANOFIBERS
WITH TAILORED MORPHOLOGIES: MECHANISM AND
ELECTROCHEMICAL PROPERTIES**

KONG JUNHUA

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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WITH TAILORED MORPHOLOGIES: MECHANISM AND
ELECTROCHEMICAL PROPERTIES**

KONG JUNHUA

School of Materials Science and Engineering

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List of Abbreviations and Acronyms

Alkali metals.....	Na_xK_y
Ammonia.....	NH_3
Anodic alumina membrane.....	AAO
Atomic force microscope.....	AFM
Bismuth titanates with La-substituted.....	$\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$
Carbon nanofibers.....	CNFs
Carbon nanofiber.....	CNF
Carbon nanotubes.....	CNTs
Carbon oxide.....	CO
Carbon dioxide.....	CO_2
Carbonized polydopamine.....	C-PDA
Catalytic chemical vapor deposition.....	CCVD
Cobalt.....	Co
Copper.....	Cu
Copper acetate.....	$\text{Cu}(\text{CH}_3\text{COO})_2$
Cyclic voltammetry.....	CV
Decomposition temperature in atmosphere environment.....	T_o
Decomposition temperature in oxygen-free environment.....	T_i
Dehydration temperature.....	D_h
Dimethylformamide.....	DMF
Dopamine chloride.....	DOPA
Electrochemical impedance spectroscopy.....	EIS
Field emission scanning electron microscopy.....	FESEM
Fluorine-doped tin oxide.....	FTO
Fourier transform infrared spectroscope.....	FTIR
Glass transition temperature.....	T_g
High resolution TEM.....	HRTEM
Hydrogen.....	H/H_2
Iron.....	Fe

Iron acetylacetonate.....	Fe(AcAc) ₃
Iron carbide.....	Fe ₃ C
Lithium ions.....	Li ⁺
Lithium ion batteries.....	LIBs
Lithium ion battery.....	LIB
Manganese oxide.....	MnO ₂
Mussel adhesive proteins	MAPs
Melting temperature.....	T _m
Nickel.....	Ni
Nitrogen.....	N/N ₂
One-dimentional.....	1D
Plasma-enhanced chemical vapor deposition.....	PECVD
Polyacrylonitrile.....	PAN
Polyamic acid.....	PAA
Polybenzimidazol.....	PBI
Polydopamine.....	PDA
Poly ethylene.....	PE
Poly (ethylene oxide).....	PEO
Polyimide.....	PI
Poly-L-lactic acid.....	PLLA
Poly(methyl methacrylate).....	PMMA
Polypyrrole.....	PPy
Polystyrene.....	PS
Poly(vinyl-idene fluoride).....	PVDF
Ruthenium chloride.....	RuCl ₃
Ruthenium oxide.....	RuO ₃
Silica.....	SiO ₂
Silicon.....	Si
Solid electrolyte interphase.....	SEI
Specific surface area.....	SSA
Scanning transmission electron microscope-energy dispersive X-ray spectroscopy	STEM-EDX
Thermo gravimetric analyzer.....	TGA
Three-dimensional	3D

Tin.....	Sn
Tin(II) acetate.....	Sn(CH ₃ COO) ₂
Tin(II) chloride.....	SnCl ₂
Tin chloride dihydrate.....	SnCl ₂ · 2H ₂ O
Tin oxide.....	SnO ₂
Tin sulphate.....	SnSO ₄
Tin sulphide.....	SnS
Titanium dioxide.....	TiO ₂
Transmission electron microscopy.....	TEM
High-resolution TEM.....	HRTEM
Tris-(hydroxymethyl) aminomethan.....	Tris
Wide angle X-ray diffraction.....	WAXD
X-ray photoelectron spectroscopy.....	XPS
Zero-dimensional.....	0D
Zinc acetate.....	Zn(CH ₃ COO) ₂
Zinc chloride.....	ZnCl ₂
Zinc oxide.....	ZnO

Abstract

Carbon-based hybrid nanofibers, which are composites derived from incorporation of organic or inorganic nanofillers into one-dimensional carbon matrix, have attracted tremendous attention for applications in lithium ion batteries (LIBs) due to their large aspect ratio, high specific surface area and fast lithium ion intercalation/de-intercalation rate. The organic or inorganic materials could be embedded in or wrapped over the amorphous or graphitized carbon phase, depending on the preparation method. Electrospinning followed by carbonization is one of the most powerful techniques to prepare CNFs since it allows mass production, morphology and structure control, and extremely large aspect ratio. Inorganic components have been combined with electrospinning-derived CNFs to further improve the electrochemical performance, for which the morphologies and structures of the hybrid nanofibers are critical for the improvement. Although different morphologies have been formed via electrospinning, leading to varied performance, the tailoring of morphologies of carbon-based hybrid nanofibers through carbonization is not yet well understood. Thus in this work, a systematic study was conducted on the effect of carbonization on morphologies and structures of carbon-based hybrid nanofibers. Their electrochemical properties were studied as anode of LIBs and correlated to the morphologies.

First of all, randomly orientated carbon-SnO₂ hybrid nanofibrous mats were prepared via conventional single-spinneret electrospinning followed by carbonization. Various tin-containing salts, including tin acetate (Sn(CH₃COO)₂), tin chloride dihydrate (SnCl₂ · 2H₂O), tin sulphate (SnSO₄), tin sulphide (SnS), were used as precursors of SnO₂, and polyacrylonitrile (PAN) was used as carbon source. The morphologies and structures of the hybrid nanofibers were investigated. It is shown that under the same carbonization conditions, carbon-SnO₂ hybrid nanofibers with different morphologies are formed from different SnO₂ precursors. The SnO₂ nanoparticles are uniformly distributed in CNFs in SnSO₄ and SnS-derived hybrid CNFs, while a carbon-SnO₂ core-shell morphology is achieved in Sn(CH₃COO)₂ and SnCl₂ · 2H₂O-derived ones. Corresponding SnO₂ nanofibers with varied structures, in either solid or hollow, are

also produced through simply burning out the carbon phase. When the carbon phase is completely removed, the nanoparticles touch each other, forming 1D aggregates. Thus, the hollow SnO₂ nanofibers actually consist of small SnO₂ nanoparticles.

The underlying mechanism for the formation of the varied morphologies was then discussed. Morphological evolution during carbonization was tracked. It is verified that Kirkendall effect is responsible for the formation of carbon-SnO₂ core-shell morphology. The Kirkendall effect is largely dependent on the melting point and decomposition behavior of the precursors. Utilizing Kirkendall effect during carbonization of single-spinneret electrospun hybrid nanofibers, novel core-shell morphology are created for the carbon/metal oxide hybrid nanofibers by choosing proper metal oxide precursors, providing greater opportunities to widen the applications of such hybrid systems.

The electrochemical properties of the carbon-SnO₂ core-shell hybrid nanofibers were further investigated as anode of LIBs. To accommodate the large volume change of SnO₂ shell, a thin carbon skin was further deposited onto the surface of carbon-SnO₂ core-shell nanofibers via hydrothermal treatment. Carbon-SnO₂-carbon sandwich-like hybrid nanofibers with largely improved electrochemical performance were achieved. The improvement is ascribed to the enhanced structural stability and electrical conduction induced by the carbon core and carbon skin. The small size of de-aggregated embedded SnO₂ nanoparticles, which is induced by the applied high temperature and pressure during hydrothermal coating, also ensures complete alloying with lithium ions.

To further enhance electrochemical properties of LIB anodes, encapsulation of Si nanoparticles in hollow graphitic CNFs was achieved by electrospinning of PAN/Si mixture followed by deposition of a polydopamine (PDA) shell, leaching out PAN and carbonization. Higher cycled capacity and rate capacity was achieved compared with carbonized PAN/Si NFs, which is due to the accommodation of the volume change of Si by carbonized PDA (C-PDA) shell and voids, high electrical conductivity of C-PDA owing to its graphitic structure and heteroatoms, and the hollow nature of the nanofibers.

In summary, the effect of carbonization on the morphologies and structures of single-spinneret electrospun carbon-tin salt hybrid nanofibers was investigated. It is found that during the carbonization, Kirkendall effect plays critical role in determining the morphologies of the produced carbon-SnO₂ hybrid nanofibers. By choosing precursors with proper melting and decomposition behaviors, uniform distribution of SnO₂ nanoparticles in carbon or carbon-SnO₂ core-shell morphologies can be obtained. Both the uniform distribution and core-shell morphologies can be further facilely modified to achieve improved electrochemical properties.

1 Introduction

1.1 Background

Carbon, amorphous or graphitic, is one of the most widely used material in both industries and scientific research. The good mechanical, thermal and electronic properties of carbon make it a promising material for a rich variety of applications. The reduction of size of carbon materials down to nanometer scale opened a new era for their further applications due to the enormously large surface area and distinctly improved properties of the nano-sized carbon materials. Among all the nano-sized carbon, one dimensional (1D) carbon nanostructures, including carbon nanofibers (CNFs) and nanotubes (CNTs), are of particular interest. Their improved mechanical strength, higher electrical and thermal conductivities and excellent optical properties in comparison with that of bulky carbon are due to their unique cylindrical nanostructure with extremely large aspect ratio, high surface area, one-dimensional (1D) transport and high defects content.

There are some popular strategies to prepare CNFs and/or CNTs, including catalytic chemical vapor deposition (CCVD), plasma enhance chemical vapor deposition (PECVD), templated method, and electrospinning. In CCVD and PECVD, gaseous carbon sources decompose due to the supplied high thermal or electronic energy. The decomposed carbon sources then deposit onto metallic nanoparticles, which act as catalyst, and continuously grow into 1D nanostructure, i.e., CNFs. To achieve relatively high aspect ratio is, however, a challenge for

CCVD and PECVD-derived CNFs. Via template-assisted routes, soft or hard templates are used as structure-directing agent to form CNFs or their arrays. The templates are then removed chemically or thermally. Although CNFs with uniform size could be obtained using a template with fine nano-sized channels, the complete removal of the template is yet difficult, and the residue would be the one to worsen the properties of the formed CNFs. Compared with the above mentioned methods, electrospinning is considered as the most effective one for the preparation of high-aspect ratio CNFs. During electrospinning a high voltage is provided to electrify polymer solutions or melts which are continuously fed into the needle tip. The electrified polymer drop will be stretched out and elongated into long thread with small diameter, forming randomly orientated or aligned polymer nanofibers upon solvent evaporation or cooling down. The polymer nanofibers can be then carbonized into CNFs. The aspect ratio of electrospinning-derived CNFs could be extremely high since the process of spinning nanofibers is theoretically uninterrupted, and the diameter can be facilely controlled by adjusting the electrospinning parameters and carbonization conditions. No template is needed in electrospinning. Furthermore, the as-prepared CNFs are in free-standing, flexible mat form, which is suitable for device fabrication.

Another unique advantage of electrospinning-derived CNTs is that inorganic materials can be easily incorporated in the electrospinning process. Such carbon-based hybrid nanofibers, as well as pure CNFs, have been widely used in electrochemical devices, for example, lithium ion batteries (LIBs). In the past few years, LIBs have been attracting increasing attention due to great demand for portable electronic devices and clean energy vehicles. Being the anode materials,

the morphologies and structures of CNFs and carbon-based hybrid nanofibers play critical role in determining the electrochemical performance of LIBs, including capacity, cyclability and efficiency. Therefore the research focus is on the design of anode with suitable morphologies and structures to achieve better electrochemical properties. For pure CNFs, non-woven mat with enclosed solid CNFs has been directly used as anode of LIBs.^[1] Highly porous and hollow CNFs were also produced by utilizing sacrificed template or co-axial spinneret,^[2, 3] to facilitate charge transfer during discharge/charge process. The capacity of pure CNFs, however, is normally less than 500 mAh g⁻¹. Materials with high theoretical capacity, including Si, metal, metal oxide, are thus incorporated into CNFs to form their uniform distribution in carbon matrix through in-situ electrospinning,^[4] or deposited onto the surface of CNFs to form core-shell morphology through chemical deposition route.^[5] The improved electrochemical performance results from the integrated interaction between components. High capacity is mainly provided by the introduced active material, while good cyclability is ensured by the relatively stable structure of hybrids. Carbon is used to accommodate the volume change of active material, which is common for most of active materials during lithium ion insertion/extraction, as well as lower the charge diffusion resistance.

To tailor the morphologies of electrospinning-derived carbon-based hybrid nanofibers, most of effort was, however, put onto the refinement of electrospinning process. It has been verified that the architecture of hybrids could be purposely adjusted by the assistance of external forces during electrospinning. As the examples, rotating disc and two conducting strips were used to align the

nanofibers, and a co-axial spinneret was also used to collect core-sheath hybrid nanofibers. The effect of another critical treatment, carbonization, on morphologies of hybrid nanofibers has never been studied. For hybrid nanofibers, in addition to the conversion from polymer to carbon, the transformation from metal/metal oxide precursors to the targeted materials occurs simultaneously during the carbonization. Since complicated chemical and physical transformations, which are strongly dependent on properties of the precursors, are involved in the carbonization process, it is hypothesized that morphologies of the hybrid nanofibers could be manipulated by varying carbonization process and/or applying other post treatment process. Thus, despite that there are many reports on electrospinning/carbonization-derived carbon-based hybrid nanofibers and their application in LIBs, it is still of intensive interest to systematically investigate the morphologies and structures of electrospinning-derived hybrid nanofibers, and understand the underlying mechanisms from a scientific point of view. Moreover, such studies would provide high possibility to achieve improved electrochemical properties, paving the way for development of high-performance LIB anode materials.

1.2 Objectives

The main objectives of this work are to manipulate the morphologies and structures of carbon-metal oxide and carbon-metal hybrid nanofibers through electrospinning and post heat treatment as well as understand the underlying mechanisms for the formation of various morphologies and structures of the hybrid nanofibers. On the basis of the above, electrochemical properties of the carbon/metal oxide hybrid nanofibers as anode materials for LIBs are

characterized to establish morphology-property relationships. That of carbon-metal hybrid nanofibers is not investigated in this work.

1.3 Work scope and thesis organization

This work is divided into two major parts. The first part is focused on structural and morphological studies of carbon-SnO₂ hybrid nanofibers prepared by electrospinning and carbonization as well as the underlying mechanisms. The obtained carbon-SnO₂ hybrid nanofibers with varied hybrid morphologies and phase structures are further modified and demonstrated as anode in LIBs. The second part is focused on the modification of electrospinning-derived carbon-Si hybrid nanofibers with uniform distribution of Si in carbon matrix, and its application as anode in LIBs.

The thesis is organized into the following chapters in sequence: first of all, the research background of this work is reviewed in chapter 2. This review includes the structure and preparation of CNFs, the principle of electrospinning, the nanostructures that can be obtained from electrospinning, the CNFs from electrospinning and carbonization, the applications of normal CNFs and electrospinning-derived CNFs as anode in LIBs. The hybrid morphologies and phase structures of carbon-SnO₂ hybrid nanofibers that can be achieved by the electrospinning and carbonization will be presented in chapter 3, and the underlying mechanisms for the formation of different hybrid morphologies will be discussed in chapter 4. The potential application of carbon-based hybrid nanofibers with varied hybrid morphologies and phase structures, as stated in chapter 3, will be modified and demonstrated as anode of LIBs in chapter 5 and 6.

Finally, the major findings of this work will be summarized in chapter 7, and the recommendations for the future work will be given in chapter 8.

2 Literature review

2.1 Carbon nanofibers: preparation routes and structures

The preparation and investigation of CNFs were firstly launched in 1889 by Hughes and Chambers, and the structure and morphology of CNFs were first observed under electron microscopy by a Russian group in 1950.^[6, 7] CNFs are nanometer-sized stacks of graphene layers in solid cylindrical form. CNFs can be categorized into different types considering the ordering of the graphene layers. The structures, size and defects of CNFs vary with different preparation routes.

2.1.1 Structures of carbon nanofibers

Comparing with bulk carbon materials, CNFs have unique structures and morphologies, including their unique micro-structures, high length to volume ratio resultant from one-dimension architecture and large specific surface area (SSA) due to the nanometer-scale size. The unique physical and chemical properties of CNFs are largely determined by the ordering and dimension of the graphene layers. Depending on the structure of the carbon source, applied decomposition energy from heat treatment or electrons, the nature of catalyst or template, the alignment of graphene layers can be perpendicular, parallel or tilted to the fiber axis,^[8, 9] leading to highly ordered CNFs or disordered CNFs with graphitic domains. The induced advanced properties qualify CNFs as promising candidates for mechanical, electrical and thermal management applications, such as energy storage (LIBs, supercapacitors, fuel cells, hydrogen storage),^[10 - 14] biosensors and gene delivery,^[15 - 17] field emission,^[18, 19] and reinforcements in composites.^[20]

2.1.2 Preparation of carbon nanofibers

The properties of CNFs are controlled by their morphology and structure. Till date, several strategies have been reported to fabricate a rich diversity of CNFs with different morphologies and structures. Some popular routes include CCVD and PECVD,^[21 - 24] template method,^[25 - 27] and as a particular one, electrospinning,^[28 - 32] which will be discussed in the following section.

During the processing of CCVD, a catalyst is used to decompose the flow of gas mixture, which acts as carbon precursor, at relatively high temperature in inert atmosphere. The decomposed gas will deposit onto the catalytic seeds and grow into 1D nanostructure to form CNFs. Some metals and their alloys, such as iron (Fe),^[33 - 36] iron carbide (Fe₃C),^[37 - 40] nickel (Ni),^[41, 42] and alkali metals (Na_xK_y),^[43] have been used as catalyst for the growth of CNFs, while as the carbon sources, those carbon-containing gases like methane, ethyne, ethene, carbon monoxide, H₂/CO mixture, acetylenes, methylpropiolate, 2-pentyne, and 1-heptyne have been employed. The morphologies, including size and shape, and structure, i. e., degree of crystallinity and ordering of graphene layers, of CNFs are largely determined by the morphology and chemical activity of catalyst, temperature as well as the type of carbon source. For example, under the combined effect of catalyst/temperature of Na_xK_y/450 °C, Fe/600 °C and Fe₃C/600 °C, the graphene layers could be highly disordered, perpendicular and parallel to the fiber axis.^[33, 41, 43]

Instead of the high temperature that is required in CCVD, the high-energy electrons are utilized in PECVD to activate the decomposition of gaseous carbon source on the surface of catalyst. The activation generally occurs in the non-equilibrium plasma. Compared with CCVD, PECVD is widely employed to prepare aligned CNFs, even

free-standing individual one, which is regulated by the formed electric field.^[44] Another advantage of PECVD over CCVD is that low temperature growth of carbon nanostructures on substrate can be realized via this route. Several reports have successfully obtained carbon nanostructures at relatively low temperature since the activation energy is provided by electron impact,^[45 - 47] although in some cases the temperature of substrate in PECVD was yet found to be similar as that in CCVD.^[48]

CNFs can also be prepared with the assistance of template. Generally, the template used is categorized into two main types, hard template and soft template. In hard template route, a carbon source is firstly impregnated into the nano-sized channels of template. The infiltrated carbon source is then converted to carbon through polymerization or carbonization. Finally the template was removed by certain treatment such as chemical etching, yielding CNFs. In order to produce CNFs, the hard template is required to be thermally and chemically stable and feasible for dissolution. Some popular ones include anodic alumina membrane (AAO),^[49 - 51] silica (SiO_2) with ordered 1D pores.^[52] In contrast, for the soft template method, some materials, such as triblock copolymer,^[53] amphiphilic block copolymer surfactant,^[54] and zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2$),^[55] are used as morphology director and mixed with carbon precursor, normally organic species. Simultaneous chemical reactions of morphology director and carbon precursor occur under certain condition, in which assemble of both is coordinated by each other. Therefore the morphologies of produced carbon nanostructures are somewhat adjustable and largely dependent on the assemble conditions, such as temperature and solvent, as well as the physical and chemical properties of soft template and carbon precursor. The template-derived CNFs, which are normally in highly disordered graphitic form, possess high porosity

with pores in controllable size and regularity in some cases. This makes CNFs be of great interests in electrochemical application since various ions, atoms or molecules can easily diffuse into carbon matrix through the nano-sized pores and interact with the carbon or carbon-supported active materials.

2.2 Carbon nanofibers from electrospinning

2.2.1 Electrospinning and its principle

Electrospinning is a popular technique used to convert polymeric bulky materials into polymer nanofibers. Originally, it was improved from another process called electrospray which was observed and recorded firstly by W. Gilbert in the 1550S'. The electrospinning process was firstly patented by J. F. Cooley and W. J. Morton, separately, in 1902. Hereafter a series of related patents about electrospinning, processed from polymer solutions or melts, were published, e.g., by A. Formhals during the period of 1934 to 1944, and C. L. Norton in 1936. All these creative works commercialized the fabrication of electrospinning-based fibers for various applications from 1939 onwards. Although the term, electrospinning, was not settled down until 1995,^[56] the research work of this process were on its way at a much earlier time when another pioneer, J. Zeleny, studied the electrospinning from a scientific point of view in 1914 by mathematically modeling the spinning behavior of fluids.^[57] As a foundation of electrospinning, taylor cone, which is used to model the shape of fluid droplet under electric field, was found and built by Taylor in 1970s'.^{[58-}^{60]} This critical phenomenon was further studied by another group in 2004.^[61] Since 1990s', many groups have been working on electrospinning focusing on the mechanism of the process itself and the properties of as-spun polymer fibers and hybrid fibers, indicated by the increasing publications year by year.

Principally, the polar polymer solution, or melting polymer in some cases,^[62 - 64] is used as source. It is electrified by an applied high voltage, stretched out, and elongated to nanofibers. The typical setup of electrospinning is displayed schematically in Figure 1. Polymer solution with suitable viscosity is prepared and loaded into syringe firstly. The solution is then delivered by a pump system and continuously fed to the metallic needle with a certain feeding rate. Under a sufficient applied voltage, the solution is charged and the electrostatic repulsion offsets the surface tension of solution. The solution droplet can therefore be stretched and ejected

Figure 1. Schematic showing of a typical electrospinning setup.

out from the needle tip at a critical point. If the molecular cohesion of the polymer solution is strong enough, the ejection will not breakup and form continuous fibrous structure in the most stable shape, i.e., cylindrical one. The solvent in the fibrous polymer solution evaporates during its flight towards substrate and finally the polymer nanofibers are collected on the aluminum foil.

Compared with nanofibers derived from other techniques, the electrospun nanofibers have shown some distinct advantages. Firstly, the diameter of nanofibers is facilely controllable. Generally, the diameter of the electrospun polymer nanofibers is largely dependent on solution properties, such as the molecular weight and distribution of

polymer, the viscosity and electrical conductivity of solution, the polarity of solvent, and operational conditions, such as applied voltage, feeding rate, distance between the needed tip and collector.^[65 - 67] An typical example is that if the concentration of polymer solution is increased, the diameter of the corresponding as-spun nanofibers can be largely increased from a few hundred nanometers to even micrometers. Secondly, the length of electrospun nanofibers could be up to several centimeters due to the continuous spinning process. Thirdly, a rich variety of polymers with different physical and chemical properties, such as polyacrylonitrile (PAN),^[68 - 70] poly(vinylidene fluoride) (PVDF),^[71] polystyrene (PS),^[72] poly ethylene (PE),^[73] poly (ethylene oxide) (PEO),^[74] polyimide (PI),^[75] polybenzimidazol (PBI),^[76, 77] polyamic acid (PAA),^[78] can be electrospun into corresponding nanofibers. The diversity in materials option broadens the application areas of electrospinning-derived nanofibers. Among all the polymers which have been used for electrospinning, PAN is the most popular one since it possess high dielectric constant and can be flexibly processed, and it is an excellent carbon precursor due to the high carbon yield and good thermal stability. Last but not least, the as-spun nanofibers are in flexible, free-standing membrane form, which can be directly used as electrode or host for other materials. Furthermore, the orientation of nanofibers in the membrane can be in non-woven form or highly aligned, depending on the type of collector that used.^[79] Typically, when a stationary plate collector is used, the as-spun nanofibers are randomly attached onto the collector. However, under the assistance of external mechanical, electrical or magnetic strength, for example, rotating disk with sharp edge,^[80] rotating drum,^[81] adjacent conductors with gap in-between,^[82, 83] highly aligned nanofibers could be easily produced.

Nanofibers and the nanofiber-based hybrids with different morphologies could be facilely controlled by electrospinning. Besides the solid nanofibers from electrospinning of single polymer, the ones with high porosity could also be produced when a pore-creating component is introduced into polymer phase for electrospinning and selectively removed thereafter.^[84 - 86] The uniform distribution of discontinuous nano-sized component in continuous main matrix during solidification in electrospinning process is believed to be the cause of pores formation.

2.2.2 Electrospinning of hybrid nanofibers

Many inorganic or organic species have been combined with polymer nanofibers via electrospinning and post-treatment. As the examples, carbon nanotubes (CNTs),^[87, 88] iron acetylacetonate ($\text{Fe}(\text{AcAc})_3$),^[89] poly(methyl methacrylate) (PMMA),^[90] have been incorporated into PAN and PEO nanofibers to form uniform distribution morphology, while some other materials, such as polypyrrole (PPy),^[91] titanium dioxide (TiO_2),^[92] have been deposited onto the surface of as-spun nanofibers, forming a shell. Through single-capillary electrospinning a mixture of two immiscible components, polymer-polymer hybrid nanofibers with core-shell morphology are also obtained.^[93, 94] Alternatively, by using a special accessory, spinneret comprising two coaxial capillaries, uniform organic-inorganic core-sheath hybrid nanofibers can be obtained as well.^[86, 95, 96] Corresponding 1D inorganic nanofibers, in either hollow or solid form, can be easily prepared via simply burning out the organic phase from the above-mentioned electrospun hybrid nanofibers, or directly electrospinning of sol-gel. Some examples are zinc oxide (ZnO),^[97, 98] zinc oxide-tin oxide (ZnO-SnO_2),^[99] TiO_2 ,^[100, 101] and bismuth titanates with La-substituted ($\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$) nanofibers.^[102]

The nanofibers derived from electrospinning have wide applications due to the many superiorities, including high aspect ratio and surface area, controllable size, rich diversity in materials, facile tailoring of morphology. The produced nanofibers can be used as template to prepare other organic or inorganic hollow nanofibers, i.e., nanotubes.^[103 - 105] The combination of polymer-polymer, polymer-inorganic material in nanofibrous form have been found great use in a rich variety of areas, including catalyst supporting,^[106 - 108] energy storage,^[109 - 111] nanocomposite reinforcement,^[28, 112, 113] tissue engineering and drug delivery.^[114 - 116]

2.2.3 Carbon nanofibers from electrospinning-derived nanofibers

The as-spun polymeric nanofibers can be subsequently converted to CNFs by a heat treatment process, i.e., carbonization. Despite the several strategies to fabricate CNFs as aforementioned, electrospinning is a more efficient technique since this route allows mass production of CNFs membrane, and the diameter and micro-structure of the CNFs can be tailored by controlling the electrospinning parameters and carbonization conditions, as well as the physical and chemical properties of precursors that selected.

Among the rich variety of electrospun polymer nanofibers, some of them are suitable for being used as the precursor of CNFs, including PI, PAA, PBI, and PAN. For a complete conversion from polymer nanofibers to CNFs, the carbonization process is generally divided into the following several steps: stabilization, carbonization and in some cases, graphitization.^[70, 117, 118]

Taking as-spun PAN nanofibers as an example, the stabilization of PAN is used to avoid melting and maintain the orientation of nanofibers.^[119 - 122] It usually occurs

between 180~300 °C under atmospheric conditions.^[123] A very slow heating rate, normally 1 °C/min, is required to stabilize the polymer since the fast heating speed will produce large amount of heat, destroying the nanofibrous morphology. During stabilization, PAN is converted to an infusible stable ladder polymer by transforming $C\equiv N$ bonds to $C=N$ bonds,^[124] whilst the molecules are cross-linked and therefore the carbon vaporization could be minimized at further elevated temperatures.^[125] This ladder structure, as a result of cyclization, dehydrogenation, aromatization and oxidation of nitrile groups in the acrylic molecule, enhances the thermal stability of PAN nanofibers.

In the process of carbonization, the stabilized PAN is heated to a higher temperature of up to 1600 °C in inert atmosphere, such as flowing argon, nitrogen, or vacuum. At this stage, the nanofibers undergo aromatic growth as well as further polymerization. Most of the heteroatoms, including hydrogen (H), nitrogen (N), are removed as in the form of gaseous by-products, for example, H_2 , N_2 and NH_3 (ammonia), leading to the formation of carbon-based structure with high carbon content of typically more than 95 wt%. At 400~600 °C, hydrogen atoms are removed from PAN, while at a temperature range of 600~1300 °C, nitrogen atoms will be removed.^[126] The structure of residual carbon is at the same time transformed to a honeycomb-like one via reorganization and coalescence. Shrinkage of the diameter of the nanofibers by normally tens of nanofibers, as well as wrinkle of the nanofibers, can be observed during carbonization process. In some cases, the formed honeycomb structured carbon is graphitized into the one with highly ordered graphitic structure via thermal treatment with a temperature as high as 1600~3000 °C.^[127] The introduction of well aligned hexagonal, i.e., honeycomb structures primarily made up of carbon atoms,

improves mechanical and electrical properties of CNFs. However, high energy consumption is an issue due to the extremely high temperature that required.

In addition to the conversion from polymer to carbon, complex physical and chemical transformation also occurs simultaneously during carbonization in carbon-based hybrid nanofibers. For example in polymer-metal salt system, carbon and metal/metal oxide are formed separately along with the increasing temperature. The structure of carbon is largely determined by the set top temperature, which gives rise to disordered graphitic carbon (at low temperature) or highly ordered graphitized one (at high temperature). In some cases, the produced metal, such as Fe, Co, can catalyze the graphitization of surrounded carbon at relatively low temperature.^[128] This could be considered as a good alternative to high temperature for the preparation of carbon with highly ordered graphene layers. The formation of metal/metal oxide is dependent on the thermal stability of metal salt which acts as precursor. Normally metal oxide is formed firstly from the decomposition of metal salt at proper temperature. The metal oxide could be carbothermally reduced to corresponding metal when the temperature is high enough. The crystallinity of form metal/metal oxide, including crystal size, inter-layer spacing, slightly varies with the temperature. The morphology of formed carbon-metal/metal oxide hybrid nanofibers is much related to that of electrospun hybrid nanofibers, which will be discussed later. Although it has been demonstrated in most of the references that the inorganic material distributes on the surface or inside the CNFs, the morphology of carbon-based hybrid nanofibers that can be obtained from the carbonization of as-spun hybrid nanofibers has not been investigated till now.

2.3 Carbon nanofibers-based materials as anodes in lithium ion batteries

2.3.1 Principles of LIB

As the one with high energy density, high voltage, large rate capacity and good rechargeability, LIBs have attracted increasing attention in the past few years since they are considered as very promising alternative power source for portable devices, such as laptops, cell phones, and hybrid electric vehicles. Basically, a lithium ion battery (LIB) consists of an anode, a cathode, and electrolyte. As shown in Figure 2, a separator is used to avoid the direct contact of two electrodes, while electrolyte is used to conduct the diffusion of lithium ions. During charging process, the lithium ions from cathode are inserted and stored in the anodic active materials under the

Figure 2. A schematic demonstration of the charging process of a typical lithium ion battery.

driving of applied electrical force. During discharging process, the lithium ions are extracted from the anode and diffuse back to cathode, simultaneously electrons flow through the external circuit to neutralize the charge balance, forming current as the

power to electronic devices. In a LIB, anode is the most important component since its capability of absorbing/desorbing lithium ions dominates the performance of the LIB. Many materials, including polymers, ceramics, transitional metals and metal oxides, metal alloys, and carbon, can be used as anode.^[4, 129 - 131]

Since 1990s, carbon materials have become one of the most promising candidates for anode of LIBs due to their stable electrochemical properties, light-weight, adjustable micro-structure and low cost.^[132 - 135] The mechanism of the intercalation of lithium ion into carbon materials has been reported.^[136, 137] Till now, one of the carbon host, graphite, has been commercialized by Sony in 1990 due to the low, stable electrochemical potential.^[138] Despite the relatively low capacity, 372 mAh g⁻¹ for graphite for instance, which is hardly to meet the raising commercial requirement, carbon materials are still under intensive research interests since they offer a reasonably good balance of cost, capacity and cycle life (cyclability). In contrast for many other materials, although they have been found to be active to lithium ions intercalation/de-intercalation, the low capacity (for polymers), or unsatisfied stability due to the large volume change during discharge/charge process (for metals, metal oxides, alloys, silicon (Si)), or high, unstable electrochemical potential, are main obstacle for their practical use.

As aforementioned, the electrochemical process in LIBs is essentially a reversible insertion/extraction of lithium ions between electrodes. The capacity is therefore largely dependent on the adsorption ability of anode materials while the cyclability relies on reversibility of insertion/extraction process. In order to improve the electrochemical properties of carbon-based anode, the following factors are believed to be critical: morphology, including size, dimension, architecture; structure,

including crystallinity, electrical conductivity, porosity and surface area; and the effective integrated combination with other active materials.

CNFs have gained great interests for decades in the area of energy storage. This is due to, firstly, the nano-scaled size achieves high SSA, which provides more reaction sites and shorter diffusion path for lithium ion. The charge transfer ability is thus enhanced. Secondly, the reduced internal resistance and extremely large length to diameter ratio further facilitate the charge transfer. Despite the great interests on CNTs currently, CNFs, which have comparable electrochemical performance with CNTs while faster lithium ion intercalation/de-intercalation than that in CNTs,^[139, 140] are worthwhile to be studied extensively.

2.3.2 Pure carbon nanofibers in lithium ion batteries

The electrochemical properties of pure CNFs, prepared from various methods, have been studied extensively in LIBs. Varied capacities from CNFs with different structure and morphology were achieved. Some examples are: amorphous CNFs with size of 80 nm in diameter and tens of micrometers in length were prepared by co-catalyst deoxidization.^[10] The CNFs show capacity of around 220 mAh g⁻¹ with high reversibility. Mesopores were introduced into disordered graphitic CNFs which were obtained via a CVD route.^[139] Higher capacity of about 460 and 170 mAh g⁻¹ was delivered at 0.1 C and 1C, respectively. It is believed that the improvement compared with amorphous CNFs is due to the structural and surface defects on the resultant porous CNFs. Graphitized CNFs were also obtained via high temperature treatment or high voltage-assisted spray pyrolysis.^[141, 142] Reversible capacity of 320~340 mAh g⁻¹ is achieved in such CNFs, in which the intercalation of lithium ions occurs in the region of the inter-layer spaces of the layered carbon.

Compared with other CNFs which require binder and/or conducting agent to form electrode, the electrospinning/carbonization-derived CNFs show great advantage in simplifying the preparation process of electrode since they are in free-standing membrane form and can be directly used as electrode. The electrochemical performance of electrospun CNFs in LIBs is largely determined by the electrospinning parameters, which lead to varied morphologies, and carbonization conditions, which give varied structures. Solid CNFs with diameter of 200~300 nm were prepared by electrospinning and carbonization of PAN.^[1] The effect of carbonization temperature on electrochemical performance was investigated. It was shown that the CNFs obtained at 1000 °C have a reversible capacity of 450 mAh g⁻¹. Some thermally or chemically unstable materials have been incorporated into PAN nanofibers during electrospinning to form porous CNFs, such as poly-L-lactic acid (PLLA),^[2] SiO₂ nanoparticles.^[143] The reversible capacity is slightly increased to about 490 mAh g⁻¹ due to the easier diffusion of lithium ions in carbon and higher SSA. CNFs with increased disordered content were obtained when a bicomponent, PAN and PPy, was used as precursor.^[144] Reversible capacity of higher than 450 mAh g⁻¹ is achieved, which is attributed to the unusual surface properties and structural features. Very recently, hollow CNFs were prepared by co-axial electrospinning and used as anode in LIBs.^[3] It is shown that the higher carbonization temperature decreases the initial irreversible capacity due to the resultant larger crystal size, and the one that carbonized at 800 °C shows the highest reversible capacity of around 400 mAh g⁻¹ than the others.

2.3.3 Carbon nanofibers-based hybrids in lithium ion batteries

As aforementioned, the low capacity of carbon materials, including CNFs, is always a challenge to meet the rising demand despite their excellent cyclability. Many efforts have been put into this area, in which one of the most effective strategies is to form hybrids.

CNFs have been combined with many active materials for the application in LIBs. In carbon-based hybrid nanofibers, carbon phase acts more as a buffering supporter to enhance the structure stability of active material which in most cases suffers from a large volume change during discharge/charge process. The high electrical conductivity of carbon also helps to facilitate the charge diffusion in hybrids. CNFs have been combined with graphene and Si via chemical vapor deposition or growth.^[5, 145 - 147] Improved capacity as well as cyclability is achieved from such hybrids compared with that of bare materials.

Electrospinning followed by post heat treatment is a powerful technique for the preparation of carbon-based hybrid nanofibers in LIBs. Generally, polymer, as the source of CNFs, and a salt, as the precursor of active material, is mixed together to form homogeneous solution or suspension. The solution or suspension is then electrospun into polymer-based hybrid nanofibers which is finally carbonized into carbon-based hybrid nanofibers. The conversion of precursor to target active material is completed simultaneously as well after carbonization. Several groups, especially X. Zhang's group, have done many works of introducing various components with high theoretical capacity into CNFs. Till now, Si,^[148] copper (Cu),^[149] Co,^[150] Ni,^[151] Fe₃O₄,^[152] manganese oxide (MnO₂),^[153] and zinc chloride (ZnCl₂),^[154] have been reported to be combined with CNFs and used as anode of LIBs. Discrete inorganic nanoparticles were observed to be deposited on or dispersed inside the nanofibers.

High capacity have been achieved with these hybrid nanofibers in comparison with that of pure CNFs without worsening the cycle life, indicating the positive influence that imported by the active components.

One special component that has been widely studied as anode of LIBs and combined with CNFs is SnO_2 , an n-type semiconductor with wide band gap ($E_g = 3.6 \text{ eV}$ at 300 K). Due to its high theoretical capacity (790 mAh g^{-1}), low toxicity and good processibility, nano-sized SnO_2 , including nanospheres,^[155, 156] nanotubes,^[157] nanowires,^[158] and nanorods,^[159] has found tremendous use in LIBs. Carbon/ SnO_2 hybrids have also been prepared via physical blending or chemical deposition for electrochemical applications.^[160 - 171] The initial capacity of nano-sized SnO_2 materials could reach over 2000 mAh g^{-1} , while that of carbon/ SnO_2 hybrids is also more than 1500 mAh g^{-1} , depending on the voltage window and the current density that applied. As stated above, carbon-based hybrid nanofibers from electrospinning and subsequent heat treatment are of great potential for LIBs. Considering the advantages of SnO_2 , fabrication of carbon- SnO_2 nanofibers is definitely an exciting research area worthwhile to explore. This is due to that the solution-based electrospinning route can induce a strong interaction between active phase and the carbon matrix, and realize more flexible morphology and structure control compared with other methods such as physical blending or chemical deposition. Some works concerning electrospun carbon- SnO_2 hybrid nanofibers as anode of LIBs have been attended.^[172 - 175] Various Sn-containing compound, including tin(II) chloride (SnCl_2), tin(II) acetate ($\text{Sn}(\text{CH}_3\text{COO})_2$), tin sulphate (SnSO_4), have been used as precursors of SnO_2 , which lead to slightly different electrochemical performance due to the varied composition of hybrids and structure of SnO_2 .

2.4 Remarks

In summary, electrospinning followed by carbonization is a useful strategy to obtain 1D carbon and inorganic nanostructures, and their hybrids. The produced free-standing nanofibrous mats have shown great potential in various areas especially energy storage, for which morphology and structure of the nanofibers play critical role in determining the electrochemical properties. Although the morphology of hybrid nanofibers could be tailored via the combination of electrospinning and other external force, the effects of carbonization on the morphology and structures have not yet been well studied. Moreover, the creation of 1D carbon-based hybrid nanostructures with tailored morphology is worthwhile to be explored due to the rising demand for high-performance energy storage devices.

3 Carbon-SnO₂ and SnO₂ nanofibers/nanotubes: the tunable morphologies via single-spinneret electrospinning and carbonization

3.1 Introduction

For carbon-based hybrid nanofibers, the improvements of functional properties are frequently resulted from the integration of distinct features of all components and interaction-evoked effects. Specially tailored morphologies may give rise to significant enhancements in properties. Besides the normal uniform distribution morphology of hybrid carbon nanofibers as aforementioned, there has been a growing interest in core-shell nanofibers as such morphological characteristics could further enhance material properties for a rich variety of applications. For example, amorphous silicon has been coated onto carbon nanofibers to form a core-shell structure for improving cycle capacity of the nanofibers in LIBs.^[5] Core-shell organic-inorganic hybrid nanofibers are also popular intermediates for preparation of nanotubes. Till now, methods that have been demonstrated for creating core-shell morphologies include template synthesis,^[176] self-assembly,^[177] partial extraction,^[178] and selective-area metalorganic vapor-phase epitaxy.^[179] Electrospinning is a facile technique for producing nanofibers, potentially at large scale, from either organic polymer solutions or inorganic sol-gels.^[32] By using a spinneret comprising two coaxial capillary, uniform core-sheath hybrid nanofibers can also be obtained.^[86, 95] Very recently, polymer-polymer core-shell morphology has been obtained via single-capillary electrospinning owing to the rapid occurrence of phase separation during solvent evaporation.^[93, 94] In this case, however, the immiscibility-induced phase

separation, and the viscosity and surface-tension differences between the components are crucial for the formation of the core-shell morphology. A stringent component matching is thus necessary.

In this chapter, aiming at investigating the morphologies of hybrid nanofibers that can be achieved by the electrospinning and post-treatment, we fabricated carbon-SnO₂ hybrid nanofibers using different SnO₂ precursors with widely varied chemical and physical properties. Furthermore, the tunability of the morphology of the hybrid nanofibers allows us to prepare 1D SnO₂ nanostructures by burning out the carbon. The unique morphological and structural features of these high-aspect-ratio 1D SnO₂ nanostructures are also presented.

3.2 Experimental

3.2.1 Chemicals

PAN ($M_w = 150000$), tin chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$), SnSO_4 and tin sulphide (SnS) were obtained from Aldrich Chemistry (USA). $\text{Sn}(\text{CH}_3\text{COO})_2$ was purchased from Strem Chemicals (USA). Dimethylformamide (DMF) was purchased from Tedia Company Inc (USA). All materials were used as received.

3.2.2 Electrospinning of PAN/tin compound suspensions

PAN/tin compound suspensions were prepared by dispersing the tin compounds into PAN/DMF solution. As a typical example, 0.53 g $\text{Sn}(\text{CH}_3\text{COO})_2$ powder was firstly added into 7.30 g DMF in an N₂ filled glove box. Vigorous stirring and mild ultrasonication were applied to disperse $\text{Sn}(\text{CH}_3\text{COO})_2$. 0.50 g PAN was then added into the $\text{Sn}(\text{CH}_3\text{COO})_2$ /DMF mixture. The concentration of PAN and $\text{Sn}(\text{CH}_3\text{COO})_2$

in the final suspension was 6.0 and 6.4 wt%, respectively. After magnetic stirring at 60 °C for 24 hrs, the mixture was cooled down to room temperature naturally under continuous stirring. Suspensions of PAN/SnCl₂·2H₂O/DMF, PAN/SnSO₄/DMF and PAN/SnS/DMF were also prepared following the same procedure, in which the concentration of PAN is 6.0, 6.5 and 7.0 wt%, and that of SnCl₂·2H₂O, SnSO₄ and SnS is 6.1, 6.3 and 4.8 wt%, respectively.

Electrospinning of the above suspensions was carried out using a conventional single-spinneret electrospinning setup (MECC nanon-01A, Japan). The needle tip-to-plate collector distance was 15 cm. The type of the spinneret used was 27^{1/2} G with inner diameter of 200 µm. The working voltage (DC supply from AC power source) and flow rate for the above four suspensions was optimized and set as shown in Table 1 to

Table 1. The working voltage (kV) and flow rate (mL h⁻¹) for different suspensions

Suspension	PAN/Sn(CH ₃ COO) ₂ /DMF	PAN/SnCl ₂ ·2H ₂ O/DMF	PAN/SnSO ₄ /DMF	PAN/SnS/DMF
Working voltage	12.0~13.0	12.0~13.0	10.5~11.5	10.0~11.0
Flow rate	0.40	0.30	0.50	0.50

obtain uniform nanofibers. The electrospun nanofibers were collected on aluminum foil and dried in a vacuum oven at 60 °C for 72 hrs. The electrospun fibrous mats from the suspension of PAN/Sn(CH₃COO)₂/DMF, PAN/SnCl₂·2H₂O/DMF, PAN/SnSO₄/DMF and PAN/SnS/DMF are denoted as P-SnAc, P-SnCl, P-SnSO₄, and P-SnS, respectively.

3.2.3 Carbonization of electrospun hybrid nanofibers

A two-step carbonization process consisting of stabilization and carbonization, which is commonly used condition as stated in literature review (section 2.2.3), was conducted with the as-spun hybrid nanofibers in a Carbolite tube furnace with a temperature controller (Type 201). The dried electrospun nanofibers were firstly stabilized by heating from room temperature to 280 °C at heating rate of 1 °C/min in air followed by annealing for 1 hr. They were then carbonized by increasing the temperature to 550 °C (10 °C/min) in argon (argon flow: 100 sccm) followed by annealing at 550 °C for 2.5 hrs before cooling down to room temperature. The carbonized hybrid fibers obtained from P-SnAc, P-SnCl, P-SnSO₄ and P-SnS are denoted as C-SnAc, C-SnCl, C-SnSO₄ and C-SnS, respectively.

3.2.4 Preparation of SnO₂ nanofibers

SnO₂ nanofibers were produced through burning out carbon from carbonized hybrid nanofibers. The carbonized hybrid nanofibers were heated up to 700 °C at a heating rate of 10 °C/min and kept at 700 °C for 1 hr in air. The SnO₂ nanofibers prepared from C-SnAc, C-SnCl, C-SnSO₄ and C-SnS are denoted as S-SnAc, S-SnCl, S-SnSO₄ and S-SnS, respectively.

3.2.5 Characterization

Morphologies of the hybrid nanofibers were observed using field emission scanning electron microscopy (JEOL FESEM JSM 6700) and transmission electron microscopy (JEOL TEM 2100). SEM images were obtained under accelerating voltage of 5 kV and working distance of 8 mm. All samples were coated with a thin layer of gold before imaging. The diameter of the hybrid nanofibers was measured statistically from their SEM images using a size measurement software ImageJ. The as-spun nanofibers were adhered onto holey carbon coated Cu grid directly for TEM study.

For carbonized nanofibers, they were dispersed into DMF using mild ultrasonication followed by casting onto holey carbon coated Cu grid. To observe cross-sectional morphology, hybrid nanofibers were embedded into epoxy and cut into ultra-thin slices using microtome (Leica) before attaching onto copper grid. TEM images were obtained under an accelerating voltage of 200 kV. Thermo gravimetric analyzer (TGA, Q500) was used to determine the content of Sn-compound in hybrid nanofibers. The samples were heated from room temperature to 700 °C at 10 °C/min in air atmosphere, and kept at 700 °C for 10 min. Wide angle X-ray diffraction (WAXD) and Raman measurement was performed using a Bruker D8 Discover GADDS X-ray diffractometer with Cu K α radiation and a Witec confocal Raman microscope, respectively. The SSA of SnO₂ nanofibers was measured using Micromeritics ASAP 2020 system.

3.3 Results and discussion

3.3.1 Electrospun hybrid nanofibers

For electrospinning, the PAN/tin compound ratio of the suspensions is varied in order to prepare carbon-SnO₂ nanofibers with SnO₂ content of 50 wt%; the calculation is based on the assumption of complete conversion of PAN to carbon and the tin compounds to SnO₂ after carbonization. The morphologies of the electrospun PAN/tin-compound hybrid nanofibers were examined using FESEM and TEM, and the corresponding images are shown in Figure 3. With all the precursors, uniform nanofibers with average diameter of 280 to 390 nm (Table 2) are obtained from the PAN/tin compound suspensions (Figure 3a₁~3d₁). In addition, nanometer-sized aggregates of tin compounds are uniformly distributed in the as-spun hybrid nanofibers, as shown by the TEM images (Figure 3a₂~3d₂). The homogeneous

Table 2. Average diameters (nm) of the as-spun and carbonized hybrid nanofibers

Nanofibers	Precursor			
	Sn(CH ₃ COO) ₂	SnCl ₂ ·2H ₂ O	SnSO ₄	SnS
As-spun	390±80	284±80	340±90	327±80
Carbonized	354±80	218±80	316±90	268±80

distribution is further confirmed by the corresponding cross-sectional TEM images of a single hybrid nanofiber, which are shown in Figure 4. The size of SnCl₂·2H₂O aggregates is around 20 nm and larger than that of the others, which is only about 10 nm or less. The size difference is probably because that SnCl₂·2H₂O is soluble in DMF, while the others can only be dispersed into DMF. Upon evaporation of DMF during electrospinning, pre-dissolved SnCl₂·2H₂O is able to precipitate to form larger nanoparticles, while the others show similar size (≤ 10 nm) as that in PAN suspensions, as shown in Figure 5 taking Sn(CH₃COO)₂ and SnSO₄ as typical examples.

3.3.2 Carbon-SnO₂ hybrid nanofibers

The electrospun hybrid nanofibers were subsequently carbonized into carbon-SnO₂ hybrid nanofibers. The carbonized mat shows good toughness for being tailored into different shapes without cracking. The structures of the carbonized nanofibers were studied by WAXD. Highly disordered graphitic carbon was obtained as confirmed by Raman spectrum and WAXD result (Figure 6) of neat CNFs, which were obtained by carbonizing neat PAN nanofibers under exactly the same conditions as that for PAN/tin compound hybrid nanofibers. Rutile-type tetragonal SnO₂ was formed in the hybrid carbon nanofibers derived from Sn(CH₃COO)₂, SnCl₂·2H₂O and SnSO₄ during

carbonization (Figure 7a).^[180] However, no SnO₂ is formed in that derived from PAN/SnS hybrid nanofibers (Figure 7b). This is due to the high thermal stability of

Figure 3. FESEM (left) and TEM (right) micrographs showing the morphologies of the electrospun PAN hybrid nanofibers incorporated with (a) Sn(CH₃COO)₂, (b) SnCl₂ · 2H₂O, (c) SnSO₄ and (d) SnS.

Figure 4. The TEM cross-sectional views of the a single electrospun PAN hybrid nanofiber incorporated with (a) $\text{Sn}(\text{CH}_3\text{COO})_2$, (b) $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, (c) SnSO_4 and (d) SnS , showing the distribution of tin compounds in PAN matrix.

Figure 5. TEM images of (a) $\text{Sn}(\text{CH}_3\text{COO})_2$ and (b) SnSO_4 dispersed in PAN/DMF solution, indicating the size of tin salt nanoparticles is about 10 nm or less. The TEM samples were prepared by casting corresponding dispersion of tin salt/PAN/DMF onto the copper grid.

SnS that does not decompose till 550 °C. The contents of SnO_2 or SnS in the carbon-based hybrid nanofibers were estimated from their TGA curves in air. Although the

nominal SnO₂ content calculated based on the assumption of complete conversion of PAN to carbon and the tin compounds to SnO₂ is 50 wt%, the actual values are 50, 36, and 43 wt% for Sn(CH₃COO)₂, SnCl₂ · 2H₂O, and SnSO₄-derived carbon-SnO₂ hybrid nanofibers (Figure 7c), respectively, and the content of SnS in C-SnS is about 45 wt% (Figure 7d). The lower SnO₂ content in carbon-SnO₂ hybrid nanofibers derived from

Figure 6. (a) Raman spectrum and (b) WAXD pattern of the neat CNFs, showing that the carbon is in amorphous form containing disordered graphene sheets.

Figure 7. (a and b) WAXD patterns and (c and d) TGA curves of carbon-SnO₂ hybrid nanofibers from different precursors and C-SnS.

Figure 8. FESEM (left) and TEM (right) images showing the morphologies of carbon-SnO₂ hybrid nanofibers derived from (a) Sn(CH₃COO)₂, (b) SnCl₂ · 2H₂O and (c) SnSO₄, and (d) the morphology of C-SnS.

SnCl₂ · 2H₂O is due to partial evaporation of SnCl₂ · 2H₂O in carbonization. The typical morphologies of the carbon-SnO₂ hybrid nanofibers are shown in Figure 8a₁~8d₁. The fibrous morphology is perfectly maintained in all carbon-SnO₂ nanofibers and C-SnS but the diameters are reduced (Table 2). The reduction in diameter is because of the removal of nitrogen and hydrogen from PAN during the carbonization. Uniform

darkness is observed in side-view TEM images (Figure 8a₂~8d₂), indicating that SnO₂ and SnS are distributed uniformly in the fiber axis and circumference directions.

Figure 9. Cross sectional TEM images and corresponding STEM-EDX line analysis of carbon-SnO₂ hybrid nanofibers derived from (a) Sn(CH₃COO)₂, (b) SnCl₂ · 2H₂O and (c) SnSO₄, and (d) that of C-SnS.

The cross-sectional TEM images of the carbon-SnO₂ hybrid nanofiber and C-SnS are shown in Figure 9. It is clearly seen that the morphology of Sn(CH₃COO)₂ and SnCl₂ · 2H₂O-derived carbon-SnO₂ nanofibers have typical core-shell morphology with carbon-rich core (light area) and SnO₂-rich shell (dark area) (Figure 9a and 9b). The corresponding line analysis along the abscissa of the cross-section of a carbon-SnO₂ hybrid nanofiber by scanning transmission electron microscope-energy dispersive X-ray spectroscopy (STEM-EDX) confirms the core-shell morphology. It is worth noting that there is no distinct boundary between the carbon-rich core and SnO₂-rich shell; the composition change is gradual and continuous in both cases. In contrast to the Sn(CH₃COO)₂ and SnCl₂ · 2H₂O-derived carbon-SnO₂ hybrid nanofibers, a uniform distribution of SnO₂ in carbon matrix is observed in SnSO₄-derived carbon-SnO₂ hybrid nanofibers (Figure 9c), and it is also verified by STEM-EDX line analysis on corresponding cross-section of hybrid nanofiber. Similar uniform distribution of SnS in carbon nanofibers is also observed in carbonized PAN/SnS hybrid nanofibers (C-SnS, Figure 9d).

Therefore through simply carbonizing electrospun PAN/tin compound hybrid nanofibers, carbon-SnO₂ hybrid nanofibers with different morphologies, either carbon core @ SnO₂ shell or uniform distribution of SnO₂ in carbon, can be obtained from proper SnO₂ precursors. The physical and chemical properties of SnO₂ precursors play critical role in determining the formation of various morphologies, which will be discussed in detail in next chapter. The configuration of carbon and SnO₂ in carbon-SnO₂ hybrid nanofibers could be conveniently tailored via simple annealing process. Taking Sn(CH₃COO)₂-derived carbon-SnO₂ core-shell hybrid nanofibers as an example, if they were further annealed at a higher temperature of 700 °C for 4 hrs in

argon atmosphere, carbon-Sn hybrid nanofibers, in which Sn is homogeneously distributed in carbon matrix, can be obtained (Figure 10a~10d). This is due to that SnO₂ is thermally reduced to metallic Sn by carbon when the temperature goes higher than 600 °C and melts since the melting point of Sn is as low as 232 °C. This is confirmed by the corresponding WAXD pattern as shown in Figure 10e. Simultaneously, the melting Sn will flow back into the carbon matrix through the

Figure 10. Morphology of carbon-Sn hybrid nanofibers, which were obtained via further annealing carbon-SnO₂ core-shell hybrid nanofibers at 700 °C in argon atmosphere, from (a) FESEM side view, (b) TEM side view and (c) TEM cross-sectional view. (d) STEM-EDX Sn elemental mapping of cross-section of a single carbon-Sn hybrid nanofiber. (e) WAXD pattern of obtained carbon-Sn hybrid nanofibers. (f) A schematic demonstration of the conversion from carbon-SnO₂ core-shell to carbon-Sn hybrid nanofibers with uniform distribution.

created nano-channels as showed schematically in Figure 10f, resulting in the conversion to homogeneous morphology for carbon-Sn hybrid nanofibers. It is worth noting that the nano-channels are generated in carbon matrix due to the release of gaseous by-products like H₂, carbon oxide (CO) and carbon dioxide (CO₂) during carbonization process.

3.3.3 SnO₂ nanofibers/nanotubes

As shown in Figure 11 (FESEM images) and Figure 12 (TEM images), uniform SnO₂ nanofibers/nanotubes with average diameter of about 100 nm were obtained after burning out carbon in the carbon-SnO₂ hybrid nanofibers and carbonized PAN/SnS nanofibers (C-SnS). SnO₂ nanotubes are obtained from Sn(CH₃COO)₂ and SnCl₂ · 2H₂O-derived carbon-SnO₂ hybrid nanofibers, while SnO₂ nanofibers are obtained from SnSO₄ and SnS-derived ones. This is consistent with the morphologies of the corresponding hybrid nanofibers; the first two exhibit the core-shell morphology whereas the other two have uniform distribution of tin compounds in the carbon matrix. The length of SnO₂ nanofibers/nanotubes can reach up to tens of microns, which is much longer than similar 1D hybrid nanostructures fabricated using templating and chemical growth processes. The WAXD results (Figure 13) indicate that tetragonal rutile phase of SnO₂ is produced from all the hybrid nanofibers.

The high resolution TEM (HRTEM) images (Figure 12a₂~13d₂) demonstrate that the SnO₂ nanofibers, either hollow or solid, are essentially composed of SnO₂ single nano-crystals. The size of single crystal in SnCl₂ · 2H₂O-derived SnO₂ nanotubes is about 20 nm, while that in those derived from Sn(CH₃COO)₂, SnSO₄ and SnS is less than 10 nm. This is further confirmed by their WAXD results (Figure 13). The grain sizes of the SnO₂ nanocrystals calculated from peaks (110) using Scherrer equation

are listed in Table 3. They match well with the sizes observed from the HRTEM images, verifying that each particle is a single nanocrystal. The nanocrystals are

Figure 11. SEM images of SnO₂ nanofibers/nanotubes derived from (a) Sn(CH₃COO)₂, (b) SnCl₂ · 2H₂O, (c) SnSO₄ and (d) SnS-derived hybrid nanofibers after burning out carbon, respectively.

Figure 12. TEM images and corresponding diffraction patterns of SnO₂ nanofibers/nanotubes derived from (a) Sn(CH₃COO)₂, (b) SnCl₂ · 2H₂O, (c) SnSO₄ and (d) SnS after burning out carbon, respectively.

randomly oriented. The SnO₂ nanofibers/nanotubes are hence polycrystalline as further confirmed by the diffraction patterns shown in Figure 12a₃~12d₃.

Figure 13. Wide angle X-ray diffraction patterns of SnO₂ nanofibers/nanotubes derived from different precursors.

Some functional properties of metal oxides are dependent on their facet structures. For example, high index faces provide high surface energy and high electrochemical activity for various applications such as gas sensing and lithium batteries.^[181, 182] The facet structure of the obtained SnO₂ nanofibers/nanotubes was investigated using WAXD. The four most intensive peaks, (110) at 26 °, (101) at 34 °, (200) at 38 ° and (211) at 52 °, are taken as references. Their integrated areas were measured and the relative intensity in percentage is listed in Table 3. For the SnCl₂-derived nanotubes, the (211) peak is the strongest peak, indicating that (211) facet is dominant, while the others have more low- index faces.

Table 3. Relative intensity of intensive peaks and grain size calculated from phase (110)

Precursor	Relative intensity (%)				Gran size (nm)
	(110)	(101)	(200)	(211)	
Sn(CH ₃ COO) ₂	38.1	27.0	8.4	26.5	8.07
SnCl ₂ ·2H ₂ O	32.5	21.9	8.5	37.1	18.91
SnSO ₄	26.0	11.8	32.2	30.0	7.47
SnS	43.1	17.1	7.7	32.1	11.37

The surface area, average pore size and pore volume of the SnO₂ nanofibers were studied by BET technique. The results are listed in Table 4, and N₂ adsorption/desorption isothermal profiles are shown in Figure 14. It is shown that the SnS-derived SnO₂ nanofibers have much higher surface area and smaller pore size than the others, despite that all have similar pore volume. The variation is resulted from the diameter of the nanofibers/nanotubes and the size and packing of the SnO₂ nano-crystals. Higher surface area provides more reaction sites for ions, indicating potential applications of these porous 1D SnO₂ nanostructures in areas such as energy storage and gas sensing, which are not investigated in this work.

Table 4. Surface area of SnO₂ nanofibers/nanotubes from different precursors

Precursor	Sn(CH ₃ COO) ₂	SnCl ₂ ·2H ₂ O	SnSO ₄	SnS
Surface area (m ² g ⁻¹)	42.3	37.5	52.2	148.4
Average pore size (nm)	14.2	15.5	7.5	5.2
Pore volume (cm ³ g ⁻¹)	0.15	0.17	0.13	0.16

Figure 14. N₂ adsorption/desorption isothermal profiles of SnO₂ nanofibers/nanotubes from different precursors. Typical isothermal profiles are observed for SnO₂ nanofibers/nanotubes derived from all precursors, in which SnS-derived SnO₂ nanofibers clearly shows the highest surface area.

3.4 Conclusions

Carbon-SnO₂ hybrid nanofibers were prepared via single-spinneret electrospinning followed by carbonization. With different SnO₂ precursors, different morphologies could be obtained under the same processing procedure. Carbon-rich core @ SnO₂-rich shell morphology is formed with Sn(CH₃COO)₂ and SnCl₂·2H₂O as the precursor, while a uniform distribution of SnO₂ in carbon nanofibers is achieved with SnSO₄ as the precursor. SnO₂ nanofibers and nanotubes can be produced from the hybrid nanofibers with uniform tin compound distribution and the core-shell hybrid nanofibers, respectively, through burning out the carbon. The obtained SnO₂ nanofibers/nanotubes consist of SnO₂ single nanocrystals whose size and facet structure are determined by their precursors. With length of up to tens of micrometers, the porous SnO₂ nanofibers/nanotubes are promising candidates for applications such as gas sensing and energy storage.

4 Core-shell carbon-metal oxide hybrid nanofibers: the underlying mechanism for the tunable morphologies

4.1 Introduction

As demonstrated in chapter 3, tailored morphology can be achieved for carbon-SnO₂ hybrid nanofibers via electrospinning and carbonization. Carbon core @ SnO₂ shell hybrid nanofibers are obtained when using Sn(CH₃COO)₂ and SnCl₂ · 2H₂O as precursors of SnO₂, while the ones with homogeneous distribution of SnO₂ in carbon matrix are obtained when using SnSO₄ and SnS as precursors of SnO₂ under the same carbonization conditions. The varied morphologies are supposed to be formed at the stage of carbonization since it is of the similar uniform distribution morphology for the electrospun hybrid nanofibers. In order to understand the mechanism behind the morphological variation, which is believed to be essential for the widening of the application of such hybrids, we conducted a systematic study on the morphological evolution along with carbonization process. Herein we analyze and reveal the essential material parameters for the formation of the core-shell morphology and provide critical insights into the underlying mechanism.

4.2 Experimental

4.2.1 Chemicals

Ruthenium chloride (RuCl₃) and copper acetate (Cu(CH₃COO)₂) were obtained from Aldrich Chemistry (USA). The other chemicals, including PAN (M_w = 150000), SnCl₂ · 2H₂O, SnSO₄, SnS, Sn(CH₃COO)₂, DMF, were the same as those mentioned in section 3.2.1, chapter 3. All materials were used as received.

4.2.2 Electrospinning of PAN/tin compound suspensions

The PAN/Sn(CH₃COO)₂, PAN/SnCl₂·2H₂O, PAN/SnSO₄ and PAN/SnS hybrid nanofibers, which are denoted as P-SnAc, P-SnCl, P-SnSO₄, and P-SnS, respectively, were prepared using the same suspensions and electrospinning conditions as aforementioned, referring to section 3.2.2, chapter 3.

Following the same procedure, PAN/RuCl₃ and PAN/Cu(CH₃COO)₂ hybrid nanofibers were prepared and collected after drying. The concentration of PAN and RuCl₃ in PAN/RuCl₃/DMF solution is 8 and 2.1 wt%, respectively. The concentration of PAN and Cu(CH₃COO)₂ in PAN/Cu(CH₃COO)₂/DMF solution is 7 and 7.3 wt%, respectively.

4.2.3 Sampling of carbonized hybrid nanofibers

The carbonization of electrospun hybrid nanofibers, including P-SnAc, P-SnCl, P-SnSO₄, and P-SnS, was the same as aforementioned, referring to section 3.2.3, chapter 3. In order to study the morphological evolution along with the carbonization

Table 5. The collected samples and corresponding naming from different precursors

Precursor	Temperature (°C)					
	25 (as-spun)	120	200	250	280 (after annealing for 1 hr)	550 (carbonized)
Sn(CH ₃ COO) ₂	a ₁ (P-SnAc)		a ₂	a ₃	a ₄	a ₅ (C-SnAc)
SnCl ₂ ·2H ₂ O	b ₁ (P-SnCl)	b ₂	b ₃		b ₄	b ₅ (C-SnCl)
SnSO ₄	c ₁ (P-SnSO ₄)				c ₂	c ₃ (C-SnSO ₄)
SnS	d ₁ (P-SnS)				d ₂	d ₃ (C-SnS)

process, including stabilization and carbonization, sampling of hybrid nanofibers at different temperature was carried out. The samples collected at certain temperature and their corresponding naming from different precursors is shown in Table 5.

Following the same carbonization condition, the electrospun PAN/RuCl₃ and PAN/Cu(CH₃COO)₂ hybrid nanofibers were carbonized for further study.

4.2.4 Characterization

The cross-section of the hybrid nanofibers was observed by TEM. The hybrid nanofibrous mat was embedded into epoxy, which was cured and then cut into ultra-thin slices using a microtome. The slices were attached onto carbon-coated copper grid for cross-sectional observation. Corresponding STEM-EDX elemental mapping and line analysis was carried out. The thermal behavior of precursor was studied by TGA under the same condition as that for carbonization: the samples were heated from room temperature to 280 °C at 1 °C/min in air atmosphere, and kept at 280 °C for 1 hr, then further heated to 550 °C at 10 °C/min in argon atmosphere followed by annealing at 550 °C for 2.5 hrs. The structure of hybrid nanofibers was investigated by WAXD. The equipment details and operation conditions can be found in section 3.2.5, chapter 3.

4.3 Results and discussion

4.3.1 The morphological evolution of core-shell hybrid nanofibers and underlying mechanism

As demonstrated, a carbon-SnO₂ core-shell morphology is formed during carbonization when using Sn(CH₃COO)₂ and SnCl₂·2H₂O as precursor of SnO₂.

The mechanism behind the formation of core-shell morphology is presented here, taking $\text{Sn}(\text{CH}_3\text{COO})_2$ -derived carbon- SnO_2 core-shell hybrid nanofibers as an example.

The distribution of the Sn-based materials and morphological evolution of the $\text{Sn}(\text{CH}_3\text{COO})_2$ -derived hybrid nanofibers during the heat treatment were probed using TEM and STEM-EDX element mapping, as shown in Figure 15. The cross-sectional TEM image taken before the heat treatment (at point a_1) shows that $\text{Sn}(\text{CH}_3\text{COO})_2$ nanoparticles (dark dots) are uniformly distributed in PAN across the diameter, as demonstrated in section 3.3.1, chapter 3, and the corresponding STEM-EDX element mapping image confirms the uniform distribution of Sn element in the as-spun nanofibers. In the subsequent ramping-up process, it is clear from the TEM images taken at 200 °C and 250 °C (at points a_2 and a_3) that the distribution of the Sn-containing components becomes heterogeneous with a lower Sn content in the core region. At the end of the stabilization process at 280 °C (at point a_4), a sharp dark ring in surface region was observed from the corresponding cross-sectional TEM image, and the STEM-EDX element mapping results show that most Sn and O atoms are located in the exterior regions, indicating a distinct core-shell morphology at the end of the stabilization. After carbonization at 550 °C (at point a_5), the morphology of the hybrid nanofibers is still core-shell, which is confirmed by cross-sectional STEM-EDX line analysis along the diameter of a carbon/ SnO_2 nanofiber.

The glass transition temperature (T_g) and melting temperature (T_m) of PAN are 85 °C and 317 °C, respectively, hence the stabilization is carried out at temperatures

between the T_g and T_m . Thus, on one hand, the fibrous morphology can be perfectly maintained during the stabilization since the treatment temperature is well below T_m . On the other hand, the hybrid nanofibers are heated up to temperatures well above its T_g , which renders the PAN chains in amorphous regions fairly high mobility so that the $\text{Sn}(\text{CH}_3\text{COO})_2$ component is able to diffuse fairly freely.

To clarify why SnO_2 forms the shell, the heat treatment process is further divided into three zones: A (below 182 °C, the T_m of $\text{Sn}(\text{CH}_3\text{COO})_2$), B (182 ~ 280 °C) and C (above 280 °C) (Figure 15). In atmospheric environment and under exactly the same thermal condition as the stabilization, TGA study on pure $\text{Sn}(\text{CH}_3\text{COO})_2$ powder demonstrates that $\text{Sn}(\text{CH}_3\text{COO})_2$ degrades almost completely up to 182 °C (Figure 15-TGA). Differently, in the absence of oxygen, only partial decomposition occurs at a higher temperature of 240 °C.^[183] Therefore, in Zone A, the $\text{Sn}(\text{CH}_3\text{COO})_2$ in the surface region of the as-spun nanofibers, which is in contact with air, is decomposed and oxidized into SnO_2 , whereas most $\text{Sn}(\text{CH}_3\text{COO})_2$ located inside in the as-spun fibers remain unreacted due to the absence of oxygen. The reactions result in a negative concentration gradient of $\text{Sn}(\text{CH}_3\text{COO})_2$ from the core to surface as well as a positive concentration gradient of SnO_2 in the same direction. As a result, the unreacted $\text{Sn}(\text{CH}_3\text{COO})_2$ in the core region tends to diffuse to the exterior while SnO_2 in the surface region tends to diffuse to the interior. Below 182 °C, the diffusion is very slow since all the materials are in solid state. In Zone B, the outward diffusion rate of interior melting $\text{Sn}(\text{CH}_3\text{COO})_2$ becomes much higher than the inward diffusion rate of solid SnO_2 formed on the surface, i.e. Kirkendall effect, which is associated with

Figure 15. Morphological evolution of the $\text{Sn}(\text{CH}_3\text{COO})_2$ -derived hybrid nanofibers in the heat treatment.

the phenomenon of atoms/compounds moving in or out of a sphere/rod as a diffusion couple caused by their different diffusion rates,^[184] becomes significant. Once $\text{Sn}(\text{CH}_3\text{COO})_2$ molecules are diffused to the surface region, they can be quickly oxidized into SnO_2 at elevated temperature, resulting in the build-up of

SnO_2 in the surface region. The concentration gradients remain until most $\text{Sn}(\text{CH}_3\text{COO})_2$ molecules are migrated to the surface, forming a SnO_2 shell after annealing at 280°C for 1 hr (point a_4), as have demonstrated by TEM and STEM-EDX.

WAXD studies were carried out on samples taken from different Zones (Figure 15-WAXD). The pattern corresponding to point a_1 confirms that in as-spun nanofibers the Sn-containing component exists mostly as $\text{Sn}(\text{CH}_3\text{COO})_2$ with characteristic reflection at $2\theta = 17^\circ$. The WAXD patterns taken at points a_2 and a_3 show the decreased intensity of the $\text{Sn}(\text{CH}_3\text{COO})_2$ peak in Zone B. In Zone C, the peak at $2\theta = 17^\circ$ disappears at the point a_4 , indicating that $\text{Sn}(\text{CH}_3\text{COO})_2$ has completely decomposed. The weak peak at $2\theta = 30^\circ$ corresponds to SnO derived from the reaction of $\text{Sn}(\text{CH}_3\text{COO})_2$ with trace moisture and decomposition of some $\text{Sn}(\text{CH}_3\text{COO})_2$ in core region.^[183] At the point a_5 , SnO is converted to Sn and SnO_2 in Ar, and the molten Sn flows back to the core region. Thus, the distribution of Sn atoms becomes less segregated towards outside of the nanofibers (Figure 15, TEM image a_5). Indeed, a very weak diffraction peak corresponding to metallic Sn can be observed at $2\theta = 45^\circ$ although all the intensive peaks can be assigned to rutile-type tetragonal phase of SnO_2 .^[180]

To confirm that Kirkendall effect is the key mechanism responsible for the formation of the core-shell morphology, the as-spun nanofibers were treated in argon environment instead of air under the same stabilization condition. No core-shell morphology was observed (Figure 16), indicating that the oxidation of $\text{Sn}(\text{CH}_3\text{COO})_2$ plays a vital role in the formation of the core-shell morphology. Furthermore, if $\text{Sn}(\text{CH}_3\text{COO})_2$ is exposed to air for some time before electrospinning, SnO_2 is

Figure 16. Cross-sectional TEM view of the PAN/Sn(CH₃COO)₂ hybrid nanofibers stabilized at 280 °C for 1 hr in Ar environment, showing uniform distribution of Sn-based particles rather than core-shell morphology.

uniformly distributed in the nanofibers even after the same heat treatment. This is because most Sn(CH₃COO)₂ molecules have been oxidized into SnO₂ in air before the heat treatment, hence no concentration gradient can be built up to drive the outward diffusion of the Sn-containing component.

It should be noted that the melting temperature of SnO₂ is high enough to avoid melting and back diffusion of SnO₂ into the core of the nanofibers. Therefore the formation of the core-shell morphology is determined by the melting and decomposition behaviors of SnO₂ precursors. Firstly, the decomposition temperature of SnO₂ precursor in atmosphere environment (T_o) must be lower than that in oxygen-free environment (T_i), which will build up the concentration gradient and act as the driving force for the diffusion of SnO₂ precursor to the surface region. Secondly, the melting temperature of SnO₂ precursor (T_m) should be between T_o and T_i to speed up its outer diffusion and ensure the formation of distinct core-shell morphology during stabilization. As can be seen from the decomposition of Sn(CH₃COO)₂ under the same condition as carbonization (Figure 15-TGA). The decomposition starts at about 70 °C in air. Its decomposition in the

absence of oxygen occurs at 240 °C, and melting temperature is 182 °C. The cross-sectional TEM images of $\text{Sn}(\text{CH}_3\text{COO})_2$ -derived hybrid nanofiber at point a_1 - a_5 shown in Figure 15 clearly show the morphology evolution which is ascribed to Kirkendall effect.

4.3.2 Verification of Kirkendall effect for other Sn-containing precursors

The decomposition behavior of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ under the same condition as the carbonization is studied by TGA and the curve is shown in Figure 17, and the cross-sectional TEM images of the corresponding hybrid nanofibers at different stages of the stabilization are also shown in Figure 17. In the as-spun hybrid nanofibers, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ is homogeneously distributed (image b_1). As shown by the TGA curve, PAN/ $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ hybrid nanofibers are dehydrated to PAN/ SnCl_2 nanofibers at 100 °C and below (D_h). The decomposition temperature of SnCl_2 in air is 160 °C as determined by TGA (T_o), which is much lower than that in oxygen-free environment (350 °C, T_i).^[185] Thus similar to that occurs in PAN/ $\text{Sn}(\text{CH}_3\text{COO})_2$ hybrid nanofibers, obvious outer diffusion of SnCl_2 can be

Figure 17. Morphological evolution of hybrid nanofibers derived from $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ during carbonization.

observed (image b₂, b₃ and b₄) after SnCl₂ melts at 247 °C (T_m) due to the concentration gradient created and fast diffusion of molten SnCl₂, forming a distinct SnO₂ shell.

The decomposition temperature of SnSO₄ in air is about 230 °C (T_o on the TGA curve of SnSO₄ in Figure 18), while its melting point is as high as 378 °C (T_m on the curve of SnSO₄). Although SnSO₄ decomposes at 230 °C that could result in concentration gradient of SnSO₄ from interior to exterior, no core-shell morphology is formed (TEM images c₁ and c₂) because of the very slow diffusion of SnSO₄ that is in solid state during the stabilization.

Figure 18. Morphological evolution of hybrid nanofibers derived from SnSO₄ and SnS during carbonization.

As SnS has even higher melting temperature of 882 °C, no decomposition of SnS to SnO₂ is observed during the whole carbonization process as determined by TGA (curve of SnS in Figure 18). Thus no concentration gradient is generated to drive the diffusion from interior to exterior. The uniform distribution is maintained

during stabilization (TEM image d₂), which is the same as that of the as-spun PAN/SnS nanofibers (TEM image d₁).

The above results verify that Kirkendall effect is responsible for the formation of core-shell morphology. The morphology of the carbon-SnO₂ hybrid nanofibers can therefore be tuned by choosing SnO₂ precursors with proper melting and decomposition behavior as these characteristics determine their diffusion behaviors in the PAN nanofibers during the stabilization process.

4.3.3 Carbon-RuO₂ and carbon-Cu hybrid nanofibers

On the basis of the underlying mechanism stated above, it is possible to prepare other carbon-metal oxide core-shell hybrid nanofibers from carbonization of corresponding single-spinneret electrospun PAN-metal salt hybrid nanofibers, wherever the decomposition and melting behaviors of the chosen metal salt meet the requirement of Kirkendall effect. Therefore the approach is a generic one for the preparation of carbon-metal oxide hybrid nanofibers with core-shell morphology. To verify this, we successfully prepared core-shell carbon-RuO₂ nanofibers (Figure 19a₁) from electrospun PAN/RuCl₃ hybrid nanofibers following the same procedure. The heterogeneous Ru distribution is confirmed by STEM-EDX line analysis (Figure 19a₂). Furthermore, the approach can also be used to prepare core-shell carbon-metal nanofibers in cases where metal oxides are reduced by carbon at temperatures below their T_m. An example demonstrated here is core-shell carbon-Cu hybrid nanofibers (Figure 19b₁) with metallic Cu in the surface region (Figure 19b₂ and b₃) from PAN/Cu(CH₃COO)₂ hybrid nanofibers. However, the electrochemical properties of carbon-metal hybrid nanofibers are not investigated in this work.

Figure 19. Cross-sectional TEM images of (a₁) carbon-RuO₂ and (b₁) carbon-Cu hybrid nanofibers obtained following the same procedure, and (a₂ and b₂) their corresponding STEM-EDX line analysis on cross-section, and (b₃) WAXD pattern of the carbon-Cu hybrid nanofibers, showing that the Cu component has been reduced to metallic Cu during carbonization. The RuO₂ and Cu contents are 20 wt% and 35 wt%, respectively.

4.4 Conclusions

Kirkendall effect, which strongly depends on the melting points and decomposition behaviors of the precursors, is verified as the cause for the formation of core-shell morphology. In order to obtain core-shell morphology, the SnO₂ precursor should

possess: 1) much lower decomposition temperature in air (T_o) than that in oxygen-free environment (T_i) for building up concentration gradient, which acts as the driving force for outward diffusion of the tin compounds; 2) a melting point between T_o and T_i , allowing fast diffusion for the formation of distinct core-shell morphology. It has been also verified that this approach can be a generic one to prepare carbon-metal oxide and carbon-metal hybrid nanofibers with core-shell morphology, wherever the physical and chemical properties of the precursors of metal oxides or metals meet the above requirements.

5 Carbon-SnO₂-carbon sandwich-like hybrid nanofibers: improved electrochemical performance as anode of lithium ion batteries

5.1 Introduction

SnO₂ is an outstanding candidate as anode in LIBs due to the relatively high theoretical capacity, low toxicity and easy processing as aforementioned. The use of SnO₂ as the anode material is, however, hampered by its enormous volume change of more than 200 % during lithiation/delithiation and poor electrical conductivity. The huge volume change collapses the structure and damages the electrical conduction pathways. Thus, the LIBs with bulk SnO₂ as the anode suffer rapid capacity decay from the resultant pulverization and electrical contact loss.

To alleviate the negative effect of the volume change, various approaches have been put forward to modify the morphology and structure of SnO₂, including fabricating nano-sized SnO₂,^[155, 159, 186 - 188] introducing mesopores,^[156] and incorporating SnO₂ into other active or inactive materials to form composites.^[164, 173, 189 - 191] A more effective way is to combine these approaches. For example, Lou *et al.* reported that SnO₂/carbon core/shell hollow nanospheres exhibit improved reversibility for lithium storage.^[161] Wang *et al.* prepared SnO₂-carbon core-shell coaxial nanotubes that show higher cycle capacity than that of pure carbon nanotubes.^[169] In both aforementioned examples, the nanometer-sized SnO₂ provides high capacity and largely reduced diffusion length for lithium ions, while the carbon shell enhances electrical contact, facilitating charge transfer and also acts as buffering phase to accommodate the

volume change of SnO₂. The hollow structures however, allow free inward expansion of the SnO₂ that may cause detachment of the SnO₂ core from the carbon shell.^[192]

Therefore, the electrochemical performance, especially the reversibility and high-rate capacity, of these anode materials need to be further enhanced to meet rising demands.

A possible approach to further enhance the cyclability and high-rate capacity of the SnO₂-based anodes is to create carbon-SnO₂-carbon sandwich-like nanostructures. The volume change of SnO₂ may be more effectively buffered by the carbon core and shell from both sides. In addition, better electrical conduction may be achieved by sandwiching a layer of SnO₂ between carbon, and the lithium ion insertion/extraction would not be hindered if the carbon skin is thin enough and “breathable”. In principle, this design concept can be applied to both 1D nanostructures such as nanofibers and zero-dimensional (0D) nanostructures such as nanospheres. For LIB anodes, 1D conductive nanostructures are preferred because they can form free-standing mats that could be used as anodes directly without adding in any conductive agent and binder, largely simplifying the fabrication process. Thus, in this chapter, carbon-SnO₂-carbon sandwich-like hybrid nanofibers based on PAN/Sn(CH₃COO)₂-derived carbon-SnO₂ core-shell hybrid nanofibers were fabricated, and their structures and electrochemical properties as the anode material for LIBs were investigated.

5.2 Experimental

5.2.1 Chemicals

The chemicals, including PAN ($M_w = 150000$), Sn(CH₃COO)₂, DMF, were the same as those mentioned in section 3.2.1, chapter 3. Glucose was supplied by Sigma-Aldrich Chemistry (USA). All chemicals were used without further purification.

5.2.2 Synthesis of carbon-SnO₂-carbon sandwich-like hybrid nanofibers

Carbon-SnO₂ core-shell hybrid nanofibers were prepared via electrospinning followed by carbonization as demonstrated previously, referring to section 3.2.2 and 3.2.3, chapter 3. The sample is denoted as HF50 here since the weight percentage of SnO₂ is 50 wt% in the hybrid nanofibers. The carbon-SnO₂-carbon sandwich-like hybrid nanofibers were then prepared from HF50 through hydrothermal treatment in the presence of glucose. In a typical experiment, 40 mg glucose was dissolved in 40 ml deionized (DI) water. The glucose solution and 50 mg HF50 nanofibrous mat were then placed in a Teflon-lined stainless steel autoclave. After treated in an oven at 200 °C for 20 hrs, the hybrid nanofibrous mat was washed with DI water three times before dried at 60 °C for 48 hrs in a vacuum oven. The dried nanofibrous mat was calcinated at 550 °C for 3 hrs in argon atmosphere. Following the same procedure, 0, 40, 100, 200 and 400 mg glucose was used to produce carbon coatings of 0, 2, 5, 15 and 30 nm, respectively. To measure the capacity of the pure carbon used in this study, nanofibrous carbon mat hydrothermally coated with a carbon skin of 15-nm thickness was also prepared following the procedures described above.

5.2.3 Characterization

The morphologies of the hybrid nanofibers were observed under a FESEM and a TEM. STEM-EDX element mapping was also conducted. The compositions of the hybrid nanofibers were determined via TGA. WAXD measurement was carried out to study the structure of hybrids. X-ray photoelectron spectroscopy (XPS, Thetaprobe, Thermo Scientific) was used to characterize the elemental composition. The SSA was measured using a Micromeritics ASAP 2020 system. The equipment details and operation conditions can be found in section 3.2.5, chapter 3.

5.2.3 Electrochemical measurement

The hybrid nanofibrous mats, round lithium flakes with thickness of 0.6 mm and diameter of 1.0 cm, 1 M LiPF₆ in the mixture of ethylene carbonate and dimethyl carbonate with 1/1 volumetric ratio, and porous PP/PE/PP membrane (Celgard[®] 2325, USA) were used as the working electrode, counter electrode, electrolyte, and separator, respectively. All parts were carefully assembled into 2032 button cells in an argon-filled glove box with moisture and oxygen level of less than 1 ppm. Cycle and rate capacity were measured by connecting the button cells to a battery test system (4200, MACCOR) in a voltage range of 3.0~0.005 V. Cycle test at current rate of 0.1C was carried out under following conditions: discharging at 1C rate to 0.005V, then standby for 5 min, and finally discharging at 0.2C rate to 0.005V followed by charging at 0.1C rate to 3V. Cycle test at 1C was carried out under following conditions: discharging at 1C rate to 0.005V, then standby for 5 min, and finally discharging at 0.1C rate to 0.005V followed by charging at 1C rate to 3V. For rate capacity test, the battery was discharged at 0.1C rate and charged at various current rates. Cyclic voltammetry (CV) test was performed on an electrochemical workstation (PGSTAT302, Autolab) within a voltage window of 3.0~0 V and at the scan rate of 0.01 mV/s. The electrochemical impedance spectroscopy (EIS) study was conducted using the same electrochemical workstation in a frequency range of 10⁵~10⁻² Hz and at the a.c. amplitude of 5 mV.

5.3 Results and discussion

5.3.1 Morphology and structure study of hybrid nanofibers

Figure 20 illustrates the preparation process for the hybrid nanofibers. Firstly, PAN/Sn(CH₃COO)₂ nanofibers were prepared via single-spinneret electrospinning.

The as-spun hybrid nanofibers were then converted into carbon-SnO₂ core-shell nanofibers through carbonization, as discussed previously. The prepared carbon-SnO₂ nanofibers have a carbon-rich core of approximately 200 nm in diameter and SnO₂-rich shell of about 50 nm in thickness. After carbonization, an amorphous carbon layer was deposited onto HF50 surface via hydrothermal treatment using a glucose

Figure 20. Schematic illustration of the preparation of carbon-SnO₂-carbon sandwich-like hybrid nanofibers.

aqueous solution. The hydroxyl groups in the carbonaceous layer, which are detrimental to lithium storage, were completely removed via further calcination in argon at 550 °C. The thickness of the carbon skin can be tuned from a few nanometres to 30 nm (Figure 21) by adjusting the glucose concentration. As an example, a uniform carbon skin of 15 nm is deposited on the surface of HF50 at the glucose concentration of 5 mg/ml (Figure 22), forming a distinct carbon-SnO₂-carbon sandwich-like morphology (Figure 22a and 22b), and the sample is denoted as HF50/C15. A blank hydrothermal treated sample without adding glucose was also prepared as a reference and is denoted as HF50/C0. After the hydrothermal treatment, SnO₂ nanoparticles with size of less than 10 nm are observed in the interfacial region between the SnO₂ shell and the carbon skin in HF50/C15 (Figure 22c), whereas distinguishable nanoparticles are present in the surface region of HF50/C0 (Figure

22d). This might be caused by the high temperature and pressure applied during the hydrothermal treatment that drives water to penetrate into the SnO₂ layer, de-aggregating the relatively compact SnO₂ shell of HF50 into separated SnO₂ nanoparticles. The de-aggregation and outward displacement of the SnO₂ nanoparticles shorten the diffusion length of lithium ions, facilitating complete

Figure 21. TEM side views of carbon-SnO₂-carbon sandwich-like hybrid nanofibers with carbon skin in various thicknesses through adjusting the glucose concentration from (a) 1 mg/ml, (b) 2.5 mg/ml, (c) 5 mg/ml and (d) 10 mg/ml. Insets show the corresponding high magnification images.

alloying and de-alloying of lithium with SnO₂, especially at high charge current density.^[193, 194] Although the de-aggregation lessens the electrical contact between those surface-located SnO₂ nanoparticles in HF50/C0, all the nanoparticles are well embedded in the carbon in HF50/C15, ensuring much better electrical conduction.

Figure 22. (a), (b) and (c) cross-sectional views of HF50/C15 by TEM, showing the sandwich-like morphology with uniform deposition of carbon skin of about 15 nm by the hydrothermal treatment. (d) TEM image of HF50/C0, showing the distinguishable SnO₂ nanoparticles in the surface region.

The composition of the hybrid nanofibers was determined via TGA. As shown in Figure 23a, the SnO₂ content in both HF50 and HF50/C0 is 50 wt%, while that in HF50/C15 is 36 wt%. In order to check whether the Sn-component was lost from the hybrid nanofibers during the hydrothermal treatment, the by-product in the mother solution of HF50/C15 after hydrothermal treatment, denoted as BP-HF50/15, was collected and completely dried. A 100 % weight loss was observed from the TGA curve of BP-HF50/15 (Figure 23a), indicating that no Sn-compound escaped into the mother solution during the treatment. Therefore, the SnO₂-content reduction can be totally attributed to the deposition of the carbon skin. This is also confirmed by the XPS spectrum of BP-HF50/C15 (Figure 23b), where no Sn peak (binding energy of

Figure 23. (a) TGA curves of HF50, HF50/C0, HF50/C15 and BP-HF50/C15, (b) XPS result of BP-HF50/C15 collected from hydrothermal mother solution of HF50/C15, and (c) WAXD patterns of HF50, HF50/C0 and HF50/C15.

493.2 eV for Sn 3d^{3/2}) is detected. The WAXD results presented in Figure 23c show that rutile-type tetragonal phase of SnO₂ was formed in HF50.^[180] The oxide status is retained after the hydrothermal treatment and subsequent calcination.

5.3.2 Electrochemical properties of hybrid nanofibers

The electrochemical performances of HF50, HF50/C0 and HF50/C15 were demonstrated. The CV curves of the three samples in the first cycle are presented in Figure 24. For all the three samples, a broad reduction peak appears at 0.8~1.7 V (right graphe in Figure 24 for enlarged CV profile). This can be attributed to the formation of solid electrolyte interphase (SEI) and the irreversible conversion of SnO₂ to Sn.^[195, 196] The redox peaks at 0.1~0.8 V indicate the reversible alloying and de-alloying of Sn and Li as shown in equation (1):

Figure 24. Cyclic voltammograms of HF50, HF50/C0 and HF50/C15 at the 1st cycle. The voltage window and scanning rate are 3.0~0.0 V and 0.01 mV/s, respectively, and enlarged profiles between the voltage window of 2.1~0.8 V.

An oxidation peak at around 1.3 V is also observed, which could be due to the slight oxidation of Sn during discharge/charge.^[197, 198] To investigate the stability of the nanostructures, all samples were charged at 0.1C ($C = 522 \text{ mAh g}^{-1}$ in case of HF50/C15 by taking the theoretical capacity of carbon as that of graphite, which is 372 mAh g^{-1}) that ensures more complete lithium insertion/extraction. Here the graphite capacity is used for the calculation of the C-rate only, and the capacity of the amorphous carbon used in this work is actually higher, which will be discussed later. The initial discharge/charge capacities of HF50, HF50/C0 and HF50/C15 are shown in Figure 25a. Compared with HF50 and HF50/C0 which have initial charge capacity of 789 and 734 mAh g^{-1} , respectively, HF50/C15 exhibits a much higher value of 961 mAh g^{-1} , although they all exhibit the similar discharge capacity of around 1050 mAh g^{-1} . The corresponding initial columbic efficiency increases from 74.9 % for HF50 to 94.8 % for HF50/C15. In the following cycles at charging rate of 0.1C, the insertion/extraction of Li^+ in HF50/C15 becomes more reversible (Figure 25b). The charge capacities of HF50 and HF50/C0 drastically decrease to about 464 and 397 mAh g^{-1} , respectively, after 200 cycles, which corresponds to the average capacity decay of about 1.6~1.7 mAh g^{-1} per cycle. In contrast, the capacity of HF50/C15

Figure 25. (a) Initial discharge/charge profile at the current rate of 0.1C. (b) and (c) Cycle capacity at the current rate of 0.1C and 1C, respectively. (d) Rate capacity of HF50, HF50/C0 and HF50/C15. The voltage window is 3.0 ~ 0.005 V.

remains as high as 837 mAh g⁻¹ after 200 cycles, corresponding to a much smaller average capacity decay of only 0.62 mAh g⁻¹ per cycle. A similar trend can also be observed at a much higher charging rate of 1C (Figure 25c), and a high charge capacity of about 550 mAh g⁻¹ is still delivered after 200 cycles for HF50/C15. It is worth noting that the specific capacity of HF50/C15 obtained at 0.1C is higher than the value calculated based on the capacities of SnO₂ and graphite. Similar phenomena have been reported for other composite nanostructures.^[155, 164, 192] It may be partially caused by the amorphous nature of the carbon nanofibers and carbon skin. Although the capacity of amorphous carbon varies largely with microstructure, it is in general higher than that of graphite.^[1, 2] In this study, the capacity of the nanofibrous carbon mat hydrothermally coated with a carbon skin of 15-nm thickness was also measured and it is indeed higher than that of graphite (Figure 26). Therefore the great improvement is resulted from the synergetic effect of amorphous carbon and SnO₂

Figure 26. Discharge/charge profile (1st and 2nd cycle) of pure carbon nanofibers with hydrothermally coated carbon skin of 15-nm thickness.

layer, which will be discussed later. Furthermore, in addition to the reversible redox reaction, with relatively large surface and interfacial areas in this system, physical adsorption/desorption of Li⁺ might occur significantly during the discharge/charge process, which might also contribute to the high specific capacity values achieved. Compared with the electrochemical properties of other typical SnO₂-based anode composites, which are summarized in Table 6, the high charge capacity and excellent cyclability achieved firmly demonstrates the stability and effectiveness of our designed nanostructure for energy delivery/storage.

The rate capacities of the three samples are shown in Figure 25d. While the capacity decreases with increasing the current rate, the capacity of HF50/C15 is much higher than those of HF50 and HF50/C0 at each current rate. Even at very high current rate of 10C a high capacity value of 180 mAh g⁻¹ is achieved with HF50/C15 that is superior to that of HF50 and HF50/C0. This is a very impressive value especially considering that a wide cut-off voltage window of 3.0~0.005 V was used in this study. Wider window creates harsher environment for lithium ion insertion/extraction.^[161, 201]

Table 6. A brief comparison between the reported capacities of SnO₂-based anodes and the presented one in this work

Reference	Morphologies	Cyclability (mAh g ⁻¹)	Rate capacity (mAh g ⁻¹)
159	SnO ₂ nanorod array	580 after 100 cycles (0.1 C)	415 at 2C; 350 at 5C
161	SnO ₂ @C Hollow Nanospheres	460 after 100 cycles (0.8 C)	510 at 0.32C; 210 at 4.8C; 40 at 12C
164	SnO ₂ Nanoparticles on cross- stacked CNTs	1004 after 48 cycles (0.1 C)	---
169	Porous SnO ₂ Nanotubes	550 after 200 cycles (0.5 C)	---
173	Electrospun SnO ₂ /CNFs	470 after 40 cycles (50 mA g ⁻¹)	350 at 500 mA g ⁻¹
191	SnO ₂ Nanotubes	< 500 after 30 cycles (100 mA g ⁻¹)	---
193	SnO ₂ Nanosheets	559 after 20 cycles (0.1 C)	---
197	Dense core-shell SnO ₂ /C composites	630 after 50 cycles (100 mA g ⁻¹)	---
199	SnO ₂ /graphene	800 after 30 cycles (67 mA g ⁻¹)	270 at 1000 mA g ⁻¹
200	3D SnO ₂ @C core-shell	473 after 160 cycles (1104 mA g ⁻¹)	
Results in this work	C-SnO ₂ -C sandwich-like	837 after 200 cycles (0.1 C)	300 at 5C; 180 at 10C

To demonstrate the stability of our designed carbon-SnO₂-carbon nanofibers even under a harsh condition, the wide cut-off voltage was employed in this study. The rate capacity almost rebounds back to the original value when a low rate of 0.1C was applied again. This demonstrates the excellent stability and versatility of the designed morphology under various discharge/charge conditions. The good rate performance is due to the embedded SnO₂ nanoparticles and their extremely small size. On one hand, the SnO₂ nanoparticles are well embedded in the carbon phase, effectively preventing aggregation during discharge/charge. On the other hand, their small size (< 10 nm) ensures fast and complete lithium-Sn alloying/de-alloying at the high current rate as stated previously. The impressive results obtain under such harsh testing conditions

demonstrate that the designed nanostructure could be a good candidate for practical applications.

The EIS results of the samples before discharge/charge test (Figure 27a) show that HF50/C0 and HF50/C15 has much lower initial interfacial resistance (first semi-circle at high to middle frequency) and charge transfer resistance (second semi-circle or inclined line at middle to low frequency) than HF50.^[202] This is due to firstly the de-aggregation of the SnO₂ nanoparticles from the SnO₂ shell, which creates more pathways for the insertion/extraction of charges, and secondly the increased SSA of HF50/C15 than that of HF50 (Figure 28), which provides more surface adsorption sites for lithium alloying/de-alloying. As to HF50/C15, the deposition of a conductive carbon skin further reduces the resistances. It is believed that the carbon phase with high electrical conductivity plays a critical role to ensure fast charges transfer during discharge/charge, although the physical interconnections between nanofibers also have positive influence on the conduction. This is because that the electrolyte can penetrate into the nanofibrous

Figure 27. Nyquist plots obtained from the impedance spectroscopy of HF50, HF50/C0 and HF50/C15 (a) before and (b) after 50 charging cycles at the current rate of 0.1C. The insets show corresponding enlarged profiles.

Figure 28. N₂ adsorption/desorption isothermal profiles of pristine carbon-SnO₂ core-shell hybrid nanofibers (HF50) and carbon-SnO₂-carbon sandwich-like hybrid nanofibers (HF50/C15).

mat and reach all the nanofibers. Thus each nanofiber forms a “micro-battery” with lithium metal through the electrolyte. The lithium ions, which come from counter electrode, directly diffuse into and transfer within the long nanofiber via the conductive carbon phase for alloying/de-alloying, rather than “jumping” between the nanofibers due to the relatively large contact resistance encountered. Simultaneously, the interconnections between nanofibers would help to transfer electrons to those nanofibers which are not in direct contact with the current collector. After the cycling test, the interfacial and charge transfer resistances increase except that the interfacial resistance of HF50 is slightly reduced (Figure 27b). The increase in resistances is partially resulted from the formation of solid electrolyte interphase (SEI), whereas the collapse of the SnO₂ layer also plays an important role, as will be discussed below. However, HF50/C15 still has the lowest resistances, suggesting the easiest diffusion for lithium ions and electrons in this sample and hence justifying its higher initial and cycle capacity.

Morphology studies on HF50, HF50/C0 and HF50/C15 after 50 cycles at the charging rate of 0.1C show that the fibrous geometry is totally intact although all surfaces become rough, which is resulted from the repeated lithium insertion/extraction

Figure 29. SEM micrographs of (a) HF50, (b) HF50/C0 and (c) HF50/C15 after 50 charging cycles at the current rate of 0.1C, showing the intact fibrous geometry with appearance of rough surface in all cases after cycling test.

(Figure 29). In HF50, although the carbon core can act as a buffer to somewhat accommodate the volume change of the SnO₂ shell, the effect is limited as the outward expansion of the SnO₂ shell during the discharge/charge is fairly free, resulting in total detachment of the SnO₂ shell from the carbon core and therefore a wide gap in-between after the cycling (Figure 30a). Such outward expansion also occurs in HF50/C0, causing the looseness and detachment of the SnO₂ nanoparticles (Figure 30b). The severe structure collapse of HF50/C0 during the cycling test explains its similar fast capacity decay as that of HF50 although the former possesses lower interfacial and charge transfer resistance. The fast capacity decay is mainly

caused by the hampered electrical conduction resulted from the outward expansion of the SnO₂ shell. In contrast to HF50/C0 and HF50, the compact sandwich-like morphology is perfectly maintained in HF50/C15 after cycling (Figure 30c), indicating that the outward expansion is effectively buffered by the elastic carbon skin. The differences in morphology caused by the cycling are further confirmed by STEM-EDX Sn element mapping (Figure 31). The above results clearly show that a more

Figure 30. Side and cross sectional TEM images of (a₁ and a₂) HF50, (b₁ and b₂) HF50/C0 and (c₁ and c₂) HF50/C15 after 50 charging cycles at the current rate of 0.1C.

stable morphology and better electrical conduction can be provided to the SnO₂ phase via dual protection by the carbon core and carbon skin, benefiting the reversibility of lithium ion insertion/extraction.

Figure 31. STEM-EDX element mapping of (a) HF50, (b) HF50/C0 and (c) HF50/C15 after 50 charging cycles at current rate of 0.1C, showing the morphology change after discharge/charge.

5.4 Conclusions

In summary, carbon-SnO₂-carbon sandwich-like nanofibers have been successfully fabricated via single-spinneret electrospinning followed by carbonization and hydrothermal deposition. The tailored nanostructure exhibits excellent electrochemical profiles including high reversible capacity, high columbic efficiency and impressive rate capacity. The morphology stability and low diffusion resistances are effectively brought up by both the carbon core and deposited carbon skin. These two factors, coupled with the de-aggregation of SnO₂ nanoparticles of < 10 nm in size into the carbon skin during hydrothermal treatment, are responsible for the great improvements in electrochemical properties.

6 Silicon nanoparticles encapsulated in dopamine-derived hollow graphitized carbon nanofibers: electrical conductivity and electrochemical properties

6.1 Introduction

The carbon/inorganic material hybrid nanofibers obtained from electrospinning followed by carbonization have been widely studied for their use as anodes in LIBs. An example is carbon-SnO₂ hybrid nanofibers, in which the SnO₂ nanoparticles may locate either inside or on the surface of CNFs.^[172 - 174, 176] These hybrid nanofibers show better electrochemical properties than that of pure CNFs. However, the solid feature of the NFs may hinder the transport of lithium ions. Furthermore, the highly disordered carbon obtained in this way exhibits relatively low electrical conductivity. Therefore, the property improvements brought by the hybrid approach are limited.

Naturally-inspired materials have recently drawn great attention from researchers owing to their unique properties that mimic the processes of nature. One of such materials is polydopamine (PDA), which is a component found in mussel adhesive proteins (MAPs). Mimicking MAPs, synthetic dopamine can self-polymerize in alkaline aqueous solutions and the resultant PDA is also rich in catechol groups like MAPs. Owing to its excellent adhesion to a wide variety of materials offered by the catechol groups,^[203] PDA has strong tendency to form coatings on various bulk substrates and nanostructures, allowing facile functionalization of the host materials for many applications, such as creation of adhesive solid surfaces for immobilizing biomolecules and capturing nanoparticles,^[204 - 208] surface modification of nanoclay

platetes and simultaneously functionalization and reduction of graphene oxide sheets.^[209 - 211] The thickness of PDA coatings can be conveniently controlled in a range from that of nearly a monolayer to tens of nanometers. PDA can also be used as a carbon source.^[210, 212] Although the direct, real-space observation of atomic-scale structure of PDA has not yet been achieved, it was suggested that PDA may have similar structure to that of melanin, a biopolymer found abundantly in nature, which is composed of stacked oligomeric proto-molecules with indolequinone units.^[213, 214] The above features of PDA hint that it is a promising precursor for preparing carbon with layered structure, i.e., graphite-like materials.

The aforementioned limitations for the hybrid nanofibers may therefore be well addressed by utilizing PDA as the carbon source owing to its ease in preparation, controllable thickness, versatile adhesion properties and more importantly the possibility to achieve layered structures with high electrical conductivity. In this chapter, a further modification is applied to carbon-based hybrid nanofibers with uniform distribution morphology. Instead of SnO_2 , Si was used as active material since it is the one that possesses the highest theoretical specific capacity among all, about 4200 mAh g^{-1} . Although many efforts have been put to address the common issues associated with Si as LIB anodes, including low columbic efficiency and large volume change (400 %) during lithiation/de-lithiation,^[215 - 222] the practical use of Si is still a big challenge. Herein, a novel morphology, Si nanoparticles encapsulated in hollow graphitized CNFs derived from PDA, is designed to improve the electrochemical properties. The hypothesis is that Si is highly capable of alloying with lithium ions, while its large volume change will be effectively buffered by the carbon shell as well as accommodated by the hollow nature, leading to good cycling

performance. The layered structure of carbonized PDA will increase the electrical conductivity of the designed nanostructure therefore facilitate the charge diffusion during discharge/charge process.

6.2 Experimental

6.2.1 Chemicals

Silicon wafer was purchased from Dreihheit Technologies Pte Ltd (Singapore). Dopamine chloride (DOPA) and tris-(hydroxymethyl) aminomethan (Tris) were purchased from Sigma chemistry (USA). Si nanoparticles with average particle size of less than 50 nm were purchased from Alfa Aesar (USA). The other chemicals, including PAN, DMF, are the same as those used previously. All chemicals are used as received.

6.2.2 Preparation of polydopamine-derived carbon

To study the structure of PDA and carbonized PDA (C-PDA), PDA coating on various substrates, including oxidized silicon wafer, SnO₂ nanoparticle aggregates, and PDA powder were prepared and carbonized.

To obtain a silicon oxide layer of 500 nm in thickness on a p-type (100) silicon wafer, a wet oxidization process was carried out in oxygen at 1100 °C for 37 min using a Tystar three-zone atmosphere-pressure tube furnace. DOPA was then polymerized on the surface of the oxidized wafer (SiO₂/Si). In a typical experiment, the wafer (1 x 3 cm²) was vertically dipped into 80 mL 1.21 mg/mL tris-(hydroxymethyl) aminomethan (Tris) buffer aqueous solution, and 24 mg DOPA (0.3 mg/mL) was then added into the solution. The polymerization was conducted at room temperature for 2

hrs under continuous magnetic stirring. The deposited wafer was rinsed with deionized (DI) water for 3 times. Following the same procedure, the deposition was carried out for another 11 times using newly prepared solution with the same composition to increase the thickness of the coating. The PDA coating on the SiO₂/Si substrate was then dried in vacuum at 60 °C for 24 hrs. The PDA coating was carbonized in a Carbolite tube furnace with a temperature controller (Type 201) by heating from room temperature to 700 °C at a heating rate of 5 °C/min in Ar environment with an Ar flow rate of 100 sccm, and then annealed at 700 °C for 3 hrs to obtain C-PDA coating. To measure the electrical properties of the C-PDA coating in the direction perpendicular to the coating surface, PDA was deposited on a fluorine-doped tin oxide (FTO)-coated glass slide (1 x 3 cm²), and carbonized following the same procedure as described above. The sample is denoted as C-PDA coating-FTO. To directly observe layered structures of the PDA and C-PDA, coatings were also fabricated on inorganic nanoparticles. SnO₂ nanoparticle aggregations were dispersed in Tris buffer solution via vigorous ultrasonication. DOPA was added into the above suspension at the concentration of 0.3 mg/mL. The polymerization was conducted at room temperature for 2 hrs under continuous magnetic stirring. The washing, drying and carbonization were carried out under the same conditions as described above.

To characterize chemical structures of PDA and C-PDA, PDA and C-PDA particles were also prepared. DOPA was added into the Tri buffer solution directly under magnetic stirring at room temperature without the presence of substrate. The concentration of DOPA was 2 mg mL⁻¹ and the polymerization time was 24 hrs. The product was washed and dried under the same conditions as described above, and the

sample is denoted as PDA powder. The PDA powder was carbonized under the same condition as that for PDA coating, and the carbonized sample is denoted as C-PDA powder.

6.2.3 Preparation of Si-encapsulated hollow CNFs

PAN/Si nanofibrous mats were prepared via electrospinning with a specially designed liquid collector. Si nanoparticles were firstly dispersed in DMF via vigorous stirring and ultrasonication. PAN was then added into the mixture and stirred at 60 °C for 24 hrs to form homogeneous PAN/Si/DMF suspension. The concentration of PAN and Si in the suspension was 7.0 and 4.8 wt%, respectively. Electrospinning of the suspension was carried out for 20 min using a conventional electrospinning setup (MECC Nanon-01A, Japan) at the working voltage of 12 kV, working distance of 15cm and feeding rate of 0.4 mL h⁻¹. The spinneret used was 27G x 1/2 with inner diameter of 200 μm. The as-spun nanofibers were collected on the surface of deionized water (DI H₂O) and wetted by a few drops of DI H₂O. The nanofibers were then loosely suspended in DI H₂O for further treatment.

PDA was coated onto the electrospun P/Si NFs via multiple depositions. In a typical experiment, 120 mg DOPA was dissolved in 400 ml P/Si NFs-suspended DI H₂O. 0.484 g Tris was then added into the above solution to initialize the polymerization of DOPA under continuous air bubbling. The polymerization was conducted for 2 hrs at room temperature. The coated product was rinsed by DI H₂O. Following the same procedure, the coating was carried out for another 7 times using fresh solution with same composition. The coated sample is denoted as PDA-P/Si NFs. After that, PDA-P/Si NFs were treated in DMF at 60 °C for 6 hrs to leach out PAN. The treated hybrid is denoted as PDA/Si NFs. The dried PDA/Si NFs were then annealed at 700 °C for 3

hrs in pure argon atmosphere, and the final product is denoted as C-PDA/Si NFs. For comparison purpose, the P/Si NFs was directly carbonized under the same condition as that for PDA/Si NFs, and the carbonized sample is denoted as C-P/Si NFs.

Following the same procedure, hollow PDA nanofibers were also prepared via depositing PDA onto pure electrospun PAN nanofibers, leaching out PAN, drying and annealing.

6.2.4 Characterization

The morphologies and surface features of the materials were examined using FESEM, TEM, STEM-EDX and atomic force microscope (AFM, Weeco DI Dimension 3000). The diameter of the hybrid nanofibers was measured using a size measurement software ImageJ. The chemical composition and structure of the materials were characterized using TGA, XPS, WAXD, confocal Raman microscope and Fourier transform infrared spectroscopy (FTIR, Perkin-Elmer 2000 spectrometer). The SSA was measured using a Micromeritics ASAP 2020 system. The electrical conductivities of the C-PDA coating in the parallel and perpendicular directions to the surface were measured using a Hewlett Packard 4140B pA Meter/DC Voltage source. Gold contacting points was deposited onto the C-PDA coating using patterned masks for the measurement in the parallel direction. The related equipments information and operational conditions are the same as those used in previous chapter.

The electrochemical performance of the nanofibrous mat samples as anode of LIBs was characterized using the same procedure as in chapter 5. Cycle and rate capacity were measured in a voltage window of 1.5 to 0.005 V. Cyclic voltammetry test was

carried out between 1.0 and 0.01V at 0.1 mV s⁻¹. The EIS study was performed in a frequency range of 100 kHz to 0.01 Hz and at the a.c. amplitude of 0.2 V.

6.3 Results and discussion

6.3.1 Structures and electrical property of polydopamine-derived carbon

Carbon from PDA has been successfully used as Au-nanoparticle supporter for catalytic application very recently.^[213] However, many fundamental questions regarding the structures and properties of the C-PDA still remain unanswered. For example, how closely does the structure of the C-PDA resemble that of multilayer graphene? Is the C-PDA a semiconductor like PDA,^[223, 224] or a good electrical conductor like graphene? To clarify these issues, a systematic study is conducted to investigate the structures and electrical properties of the C-PDA.

To study the structures of the C-PDA coating and measure its in-plane electrical properties, oxidized silicon wafer was used as the insulating substrate for the coatings. PDA was firstly deposited onto the wafer. Upon the immersion of the wafer into the solution, DOPA prefers to self-polymerize on the surface of the wafer owing to the strong affinity of the catechol groups to silicon oxide.^[203] A multiple deposition process with low monomer concentration was used to prevent the formation of suspended PDA particles while ensuring sufficient coating thickness for structural characterization. The PDA coating was then carbonized at 700 °C in Ar environment. The thickness of the C-PDA coating obtained with 12 depositions is about 23 nm as determined by AFM (Figure 32).

The surface morphologies of the PDA (Figure 33a₁) and C-PDA (Figure 33a₂)

Figure 32. Thickness of the carbonized PDA coating on a SiO_2/Si wafer determined by AFM. It is shown that with 12 depositions the thickness of the carbonized PDA coating is 23 nm.

coatings were examined using FESEM. It is observed that the wafer is completely covered by the PDA and even after the carbonization, the C-PDA coating is still well adhered to the substrate, showing no cracks or peeling. The surface of the C-PDA coating is smoother than that of the PDA coating, which is probably due to the cross-linking reactions occurred during the carbonization; it will be discussed later. It is difficult to examine the cross-sectional structures of the PDA and C-DPA coatings on the SiO_2/Si wafer as the sectioning with Focused Ion Beam destroys the structures. It is believed that PDA would form similar layered structures on oxides. As the formation of the layered structure is mainly due to the planar conformation of the PDA oligomer,^[213, 214] it is unlikely that it would be significantly affected by the substrate surface. Thus, to observe the cross-sectional structures, dopamine was polymerized on the surface of SnO_2 nanoparticle aggregates and carbonized under the same condition. In order to achieve a thickness of a few nanometers to facilitate high-resolution transmission electron microscopic (HRTEM) examination, only one deposition of 2 hrs was carried out. Stacked layers with mean inter-layer spacing of about 0.40 nm, which is slightly larger than the reported value,^[214] are observed for the PDA coating (Figure 33b₁). The layered structure is well retained after the

Figure 33. FESEM images of (a₁) the PDA and (a₂) C-PDA coating on SiO₂/Si substrate, showing the surface morphology; TEM images of (b₁) the PDA and (b₂) the C-PDA coating on SnO₂ nanoparticle aggregates, showing the layered structure.

carbonization (Figure 33b₂), and the C-PDA coating has a slightly smaller mean inter-layer spacing of 0.37 nm. In both the PDA and C-PDA coatings, staggered layers can be observed.

The layered structures of the PDA and C-PDA coatings are further confirmed by WAXD studies. In the WAXD of the PDA coating (Figure 34a), a single peak appears at 2θ value of about 22° , which is in the region of (002) reflection for graphite, indicating some degree of ordered packing of PDA molecules.^[225, 226] After the carbonization, the diffraction peak of the C-PDA coating is slightly shifted towards the higher angle side. The corresponding d-spacings are about 0.43 nm and 0.41 nm for the PDA and C-PDA coatings, respectively, which are close to the inter-layer spacings measured from the HRTEM images. The preservation of the single diffraction peak in the WAXD pattern of the C-DPA coating indicates that there is no

Figure 34. (a) WAXD patterns, (b) Raman spectra, (c) XPS spectra and (d) FTIR spectra of the as-deposited and carbonized PDA.

major change in layered structure upon the carbonization. However, compared with the PDA coating, the C-PDA coating shows significantly increased structural order, as indicated by the sharpening of the diffraction peak that signifies an increase in crystal size from 2.0 nm for the PDA-coating to 5.3 nm for the C-PDA coating. Accompanied by the ordering, only a slight increase in the intensity ratio of G band (1580 cm^{-1}) to D band (1340 cm^{-1}) can be observed in the Raman spectra of the coatings (Figure 34b), implying that there are still considerable amount of structural defects in the C-PDA layers.

The XPS spectra shown in Figure 34c provide the information about the elemental compositions of the PDA and C-PDA coatings on SiO₂/Si wafer. As oxygen (O) could be detected from both the PDA coating and the oxidized silicon wafer, the compositions were calculated after subtracting the O in SiO₂, and the calculation results are given in the figure. After the carbonization, the contents of O and nitrogen (N) decrease from 10.7 % and 7.1% to 6.7% and 4.5%, respectively, implying the loss of some unstable O- and N-containing groups via pyrolysis in an inert atmosphere. The transformation of the chemical structure upon the carbonization was further investigated via FTIR spectroscopy (Figure 34d). For the FTIR studies, the power samples were prepared by self-polymerization of dopamine without the presence of any substrate. Although the polymerization mechanism of PDA is unclear to date, a possible molecular structure of PDA units has been proposed,^[211, 227] as shown in Figure 35a. All intensive bands in the FTIR spectrum of the PDA coating can be assigned to the functional groups of PDA,^[211, 228] including the strong, broad O-H, N-H and C-H bands in the region of 3680 to 2800 cm⁻¹, overlapped C=C and C=N stretching bands at 1594 cm⁻¹, and the benzene ring stretching band at 1510 cm⁻¹. After the carbonization, the drastic weakening of the broad bands in the region of 3680 to 2800 cm⁻¹, and the appearance of a strong band at 1189 cm⁻¹ (C-O-C stretching) and a weak band at 1787 cm⁻¹ (carbonyl group) suggest the dehydration of the catechol groups on neighbour PDA molecules to form C-O-C bonds and the formation of a small amount of C=O groups, as well as the extensive removal/conversion of C-H. The strong shoulder band at 1561 cm⁻¹ for the C-PDA coating can be attributed to C=C and probably also some C=N bonds. The broad, weak band at 3360 cm⁻¹ may be ascribed to a very small amount of residual N-H and O-H, while the weak band at 2360 cm⁻¹, which also appears in the PDA spectrum,^{[211,}

Figure 35. Proposed chemical structures of (a) a PDA unit ^[211, 221] and (b and c) the oxygen-containing components of the carbonized PDA.

^{222]} might be related to a stable N-containing bond. Based on our XPS and FTIR results, we propose that the PDA molecules are partially cross-linked via C-O-C bonds during carbonization (Figure 35b), while some catechol groups may be converted to conjugated C=O (Figure 35c) and some N atoms are also present in the cross-linked structure.

The above analysis shows that the C-PDA coating can be regarded as graphene multi-layers doped with heteroatoms.^[229 - 231] The I-V characteristic of the C-PDA coating in the basal plane was measured with the oxidized silicon wafer as the substrate, and the result is shown in Figure 36a. The electrical conductivity measurement through the basal plane was also carried out on the C-PDA coating deposited on a conductive substrate, fluorine-doped tin oxide (FTO)-coated glass slide (Figure 36b). Similar to that of multi-layer graphene, in both directions, linear I-V curves are obtained for the C-PDA coating. It is striking to see that although the C-PDA coating has more defects than the multi-layer graphene prepared using other procedures, the C-PDA has high electrical conductivity values of about 660 and 26600 S m⁻¹ in and through the basal planes, respectively, which are comparable to that of multi-layer graphene. The

high conductivities obtained may be attributed to the altered molecular charge-transfer behavior induced by the N-type doping by nitrogen,^[225] and effective π - π stacking. Such high conductivities greatly benefit capacity properties of the C-PDA in LIBs, as will be demonstrated in the next section.

Figure 36. The I-V curves and electrical conductivity of the carbonized PDA coating (a) in and (b) through the basal plane.

6.3.2 Structure and morphology of Si-encapsulated hollow CNFs

The preparation process and morphologies of the nanofibers achieved in each step are schematically illustrated in Figure 37. The P/Si NFs were prepared via conventional electrospinning. Instead of using a plate collector that will give compact mats with nanofibers touching each other, DI H₂O was used as a liquid collector to obtain loosely aggregated nanofibers (Figure 38). The P/Si NFs initially float on the surface of DI H₂O and after DI H₂O was dropped onto the floated nanofibers to wet them, the aggregate was suspended in the DI H₂O as a yellowish lump (Figure 37a). This loose morphology is essential for post-coating of PDA, which will be discussed later. Through FESEM characterization, it is verified that uniform PAN/Si NFs with average diameter of about 370 nm are formed (Figure 39a₁). Some beads are observed as slight aggregation of Si nanoparticles occurs during the electrospinning. The TEM image in Figure 39a₂ clearly shows the embedding of the Si nanoparticles and their

small agglomerates in nanofibrous PAN matrix. The homogeneous distribution of Si is confirmed by the STEM-EDX elemental mapping, as shown in Figure 40a.

Figure 37. A scheme showing nanofiber preparation process and corresponding morphologies formed in each step (cross-sectional view of a single hybrid nanofiber, and the schematics are not drawn to scale). The pictures show the loose aggregates of the nanofibers suspended in water before and after PDA coating.

Figure 38. An electrospinning setup with liquid collector.

Figure 39. Morphologies of (a) P/Si NFs, (b) PDA-P/Si NFs, (c) PDA/Si NFs and (d) C-PDA/Si NFs by FESEM (left) and TEM (right).

Figure 40. STEM-EDX elemental mapping (C, Si) of (a) P/Si NFs and (b) C-PDA/Si NFs.

The coating of PDA onto P/Si NFs was subsequently carried out. The PDA is directly deposited onto the surface of the hybrid nanofibers rather than the Si NPs, therefore no prior oxidation is required for the Si NPs. When the nanofibers were collected using a plate collector, it is difficult to coat PDA evenly on nanofiber surfaces as DOPA can hardly diffuse into the thick, compact nanofibrous mats. Consequently, upon the removal of PAN by DMF to create hollow nanofibers, a cracked morphology

Figure 41. The pictures of (a) electrospun PAN nanofibrous mat obtained from plate collector and (b) the one after 8-times PDA in-situ deposition under the same condition as that for loose pack of the PAN/Si nanofibers.

is observed (Figure 41). In contrast, the loose feature of the cotton-like nanofiber aggregate collected using the liquid collector facilitates even, thorough coverage of the nanofiber surface by PDA.

The FESEM and TEM images of PDA-P/Si NFs (Figure 39b₁ and b₂) confirm that PDA has been uniformly deposited onto the surface of P/Si NFs. With the PDA coating, the average diameter of the hybrid nanofibers is increased to 450 nm. After treated with DMF, the PAN in PDA-P/Si NFs is removed while the fibrous morphology is perfectly retained with most Si nanoparticles remaining inside (Figure 39c₁ and 1c₂). The average outer diameter of the hollow nanofibers is increased to about 560 nm owing to the relaxation of the PDA shell during leaching, whereas the wall thickness is around 40 nm. In order to further confirm the formation of the hollow structure, PDA was coated onto pure PAN nanofibers which were then leached out by DMF, and carbonized following the same procedure. The morphology was studied and shown in Figure 42. Hollow structure can be clearly observed, indicating that most of PAN has been removed by DMF.

Figure 42. (a) FESEM and (b) TEM images of a single C-PDA nanofiber, indicating the hollow structure.

An annealing process at 700 °C was carried out in argon environment to carbonize the PDA shell. After the carbonization, the average diameter of the nanofibers shrinks to

Figure 43. (a and b) WAXD patterns and (c and d) TGA profiles of as-spun PAN/Si hybrid nanofibers (P/Si NFs), carbonized PAN/Si hybrid nanofibers (C-P/Si NFs) and Si nanoparticles-encapsulated hollow C-PDA nanofibers (C-PDA/Si NFs).

about 440 nm due to the loss of H, N and O in pyrolysis (Figure 39d₁ and d₂). The encapsulation of Si in hollow C-PDA nanofibers is confirmed by the STEM-EDX elemental mapping (Figure 40b). The C-PDA formed has layered structure, as shown in Figure 39d₃, in most regions. This is consistent with our previous results that C-PDA coating has graphite-like structures. The WAXD patterns of the samples (Figure 43a and b) show that in the as-spun P/Si NFs, C-P/Si NFs, and C-PDA/Si NFs silicon is in face-centered cubic crystalline form.^[232] The content of Si in P/Si NFs and C-PDA/Si NFs determined via TGA (Figure 43c) are about 45.3 wt% and 47.9 wt%, respectively, while that in C-P/Si NFs is as high as 58.7 wt% (Figure 43d).

6.3.3 Electrochemical properties of Si-encapsulated hollow CNFs

The above results show that a hybrid nanostructure with the designed features, i.e. thin graphitized carbon shell as buffer phase and conducting agent; silicon nanoparticles in small size as main active material; hollow morphology as accommodating voids and charges diffusion channels, is successfully realized. To demonstrate the effectiveness of our approach, electrochemical properties of C-PDA/Si NFs as a LIB anode are characterized and compared with carbonized as-spun P/Si NFs (C-P/Si NFs). It is worth noting that the matrix in C-P/Si NFs is highly disordered graphitic carbon,^[233] while the shell in C-PDA/Si NFs has graphite-like structures. Typical Li-Si alloying/de-alloying behavior of C-P/Si NFs and C-PDA/Si NFs are shown by their cyclic voltammograms in Figure 44. The broad irreversible peak in the voltage range of above 0.5 V at the cathodic branch of 1st cycle is attributed to the formation of solid electrolyte interphase (SEI) on the surface of active materials.^[234] Two peak at about 0.01 and 0.16 V are attributed to the alloying of Li with Si during discharge, while another two at about 0.37 and 0.58 V correspond to the decomposition of Si-Li alloy during charge.^[235, 236] The increase of the

Figure 44. Cyclic voltammograms of (a) C-P/Si NFs and (b) C-PDA/Si NFs at the first 3 cycles.

intensities of peaks upon cycling indicates that the alloying of Li with Si is a gradual process; the activation of Si occurs at each cycle. This is also consistent with other reports.^[234, 237]

The cycling performance of the samples was investigated at a current density of 100 mA g⁻¹. It is striking to see that although C-PDA/Si NFs has lower Si content (47.9 wt%) than C-P/Si NFs (58.7 wt%), the initial discharge, charge capacity of C-P/Si NFs are 1930, 1274 mAh g⁻¹, respectively, with corresponding coulombic efficiency of about 66 % (Figure 45a), whereas that of C-PDA/Si NFs are 2265, 1698 mAh g⁻¹, respectively, with the initial coulombic efficiency of 75 % (Figure 45b). In the following cycles, the charging capacity of C-P/Si NFs dramatically falls down; it

Figure 45. (a) Discharge/charge curves of C-P/Si NFs at 100 mA g⁻¹, (b) discharge/charge curves of C-PDA/Si NFs at 100 mA g⁻¹, (c) cycling performance and corresponding coulombic efficiency at 100 mA g⁻¹, and (d) rate charging capacity of C-P/Si NFs and C-PDA/Si NFs.

drops to 327 mAh g^{-1} at 30th cycles. In contrast, the charging capacity of C-PDA/Si NFs is still as high as 960 mAh g^{-1} after 30th cycles, indicating much better cyclability of the latter (Figure 45c). The coulombic efficiency of C-PDA/Si NFs (around 95 %) is higher than that of C-P/Si NFs (90 %) at first few cycles while it is slightly lower thereafter. At higher discharge/charge current density, the capacity of C-PDA/Si NFs is still much higher than that of C-P/Si NFs (Figure 45d). For instance, relatively high charging capacity of around 280 mAh g^{-1} is achieved with C-PDA/Si NFs when the current density is 1000 mA g^{-1} , and it is only about 4 mAh g^{-1} for that of C-P/Si NFs under the same current density.

The above results indicate that the encapsulation of Si nanoparticles in hollow graphitized carbon nanofibers greatly benefits the release of the electrochemical potential of Si as well as provide structure stability. It is believed that the improved electrochemical properties of such morphology results from the following facts: (1) the large volume change of Si is effectively accommodated by the voids in hollow nanofibers and also buffered by the elastic C-PDA shell, leading to stable structure

Figure 46. Nyquist plots obtained from the impedance spectroscopy of C-P/Si NFs and C-PDA/Si NFs before and after cycling for 30 cycles.

Figure 47. N_2 adsorption/desorption isothermal profiles of C-P/Si NFs and C-PDA/Si NFs.

thus excellent cycling performance. (2) High electrical conductivity is achieved by the C-PDA shell as aforementioned. The EIS results, as shown in Figure 46, indicate that the charge transfer resistance (the semi-circle from high to middle frequency range) of C-PDA/Si NFs is much lower than that of C-P/Si NFs. Although the resistance is increased after cycling for both samples, which is probably due to the formation of SEI and iterative lithium insertion/extraction, the lower resistance of C-PDA/Si NFs facilitates charge diffusion. Relatively complete Li-Si alloying/de-alloying is thus achieved with resultant high columbic efficiency. (3) The small size of Si nanoparticles provides abundant reaction sites for lithium ions, while the hollow nature of nanofibers ensures enough space for lithium insertion, despite that the C-PDA/Si NFs possess slightly lower SSA than C-P/Si NFs, as shown in Figure 47. Most of silicon therefore can be activated for alloying with lithium. It is worth noting that although electrospinning-derived Si/CNFs with a much lower Si content of only 16.2 wt%^[148] could achieve better electrochemical performance than the electrospun ones with high Si content as demonstrated above, the capacity of Si/CNFs reported in

ref. 148 is rather limited ($< 800 \text{ mAh g}^{-1}$) due to the balanced requirements for high contents of both Si and carbon to ensure high electrochemical activity as well as effective buffering for the volume change.

6.4 Conclusions

In this work, layered C-PDA was successfully fabricated via a multi-deposition route followed by carbonization. The structure of the C-PDA is found to be similar to that of multilayer graphene doped with heteroatoms (O and N), but with a considerable amount of structural defects. Despite the presence of defects, the C-PDA exhibits excellent in-plane and through-plane electrical conductivities. On the basis of the above, Si nanoparticles were encapsulated in hollow C-PDA nanofibers to further improve their electrochemical properties. Electrospinning-derived PAN/Si NFs were used as the starting structure, and PDA was deposited onto the PAN/Si NFs followed by leaching out PAN and carbonization. Improved electrochemical properties, including higher cycled discharge/charge capacity, higher initial coulombic efficiency and rate capacity, were achieved with C-PDA/Si hollow nanofibers compared with C-P/Si NFs that were obtained by direct carbonization of PAN/Si NFs. The improvements can be attributed to the buffering effect of voids and elastic C-PDA shell on the volume change of Si, the high electrical conductivity achieved by graphitized C-PDA shell as well as the hollow nature of nanofibers and small size of Si nanoparticles.

7 Conclusions

1. Carbon-SnO₂ hybrid nanofibers with varied morphologies were prepared via single-spinneret electrospinning followed by carbonization. The formed morphology is critically dependent on the SnO₂ precursors used. When Sn(CH₃COO)₂ or SnCl₂ · 2H₂O was used as precursors, carbon-SnO₂ hybrid nanofibers with core-shell morphology were prepared, whereas when SnSO₄ or SnS was used as precursors, those with uniform distribution of SnO₂ in carbon phase were formed. Therefore the morphologies of carbon-metal oxide hybrid nanofibers can be controlled by this simple route. SnO₂ nanofibers, in either solid or hollow form, were also obtained through burning out the carbon from carbon-SnO₂ hybrid nanofibers. The structures of derived SnO₂ nanofibers, including grain size, facet structure, and surface area, also vary with different precursors.

2. Kirkendall effect is found to be responsible for the formation of core-shell morphology for Sn(CH₃COO)₂ and SnCl₂ · 2H₂O-derived carbon-SnO₂ hybrid nanofibers. The melting point and decomposition behavior of SnO₂ precursors are key properties influencing the morphology of the carbonized hybrid nanofibers. To form core/shell morphology, the following conditions must be met: 1) the precursors have much lower decomposition temperature in air (T_o) than that in oxygen-free environment (T_i) for building up concentration gradient, which acts as the driving force for outward diffusion of the tin compounds; 2) the precursors have a melting point between T_o and T_i , allowing fast diffusion for the formation of distinct core-shell morphology. The approach has been verified to be a generic one to prepare carbon-metal oxide and carbon-metal hybrid nanofibers with core-shell morphology.

3. The electrochemical properties of the carbon-SnO₂ core-shell hybrid nanofibers can be further improved by deposition of a thin carbon skin onto the surface of hybrid nanofibers via hydrothermal treatment, forming carbon-SnO₂-carbon sandwich-like hybrid nanofibers. Excellent electrochemical performance, including high reversible capacity, high columbic efficiency and impressive rate capacity, is achieved for the tailored sandwich-like nanostructure. The improvement is believed to result from the induced morphology stability and low diffusion resistances, as well as the embedded de-aggregated SnO₂ nanoparticles with size of less than 10 nm.

4. For the carbon-based hybrid nanofibers with uniform distribution morphology, a different modification can be applied to achieve improved electrochemical properties. Carbon-Si hybrid nanofibers, in which Si nanoparticles distribute uniformly in carbon matrix, were used as starting materials. Through multiple deposition of PDA onto the surface of hybrid nanofibers followed by post-treatment, Si nanoparticles were well encapsulated in hollow graphitized CNFs. The PDA-derived carbon has graphite-like structure with high electrical conductivity. The C-PDA/Si hollow NFs exhibit high capacity and good cyclability, which is due to the high theoretical capacity of Si, the hollow morphology, as well as the graphitized carbon shell, which acts as buffering layer and conducting agent.

8 Recommendations for Future Works

1. The route of single-spinneret electrospinning and carbonization is proven to be a generic route to prepare carbon-metal oxide hybrid NFs with core-shell morphology when the physical and chemical properties of SnO_2 precursors can meet the stated requirement and induce the Kirkendall effect. The extension of this concept to other material systems would be feasible, and moreover, necessary to widen the application areas of hybrid NFs with such core-shell morphology.

2. As stated in chapter 3, the obtained solid and hollow SnO_2 nanofibers possess long length, varied grain size and facet structure, high porosity and surface area. Therefore they have potential applications in many areas, such as LIBs, gas sensors, which have not been investigated yet. However, although the produced SnO_2 nanofibers are in free-standing mat form, the brittleness of the mat is an issue for device fabrication. Future work would be focusing on improving the mechanical strength of the SnO_2 nanofibers and designing proper device for certain application.

3. The large volume changes of SnO_2 and Si during discharge/charge process are effectively buffered by the carbon phase in the designed nanostructures. Exsitu studies on the morphologies and crystal structures of the anodes using FESEM, TEM and XRD are worthwhile to be explored in the future work to monitor the buffering effect and further confirm the mechanism for the enhanced anode performance.

4. The carbon-based hybrid nanofibers with either core-shell or uniform distribution morphology can be further modified, as elaborated in this thesis, for electrochemical

application as anodes in LIBs. The advantages of electrospinning and carbonization, such as achieving long length, controllable diameter, free-standing mat, and tunable morphology, make this approach attractive for many applications. Thus some future work may be conducted to create hybrid nanostructures with different morphologies from the hybrid NFs derived from electrospinning-assisted processes.

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