Mechano-adaptable materials and structures for customizable electrochemical energy storage devices

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**NANYANG
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SINGAPORE

**MECHANO-ADAPTABLE MATERIALS AND STRUCTURES
FOR CUSTOMIZABLE ELECTROCHEMICAL ENERGY
STORAGE DEVICES**

LV ZHISHENG

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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STORAGE DEVICES**

LV ZHISHENG

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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

2019

Statement of Originality

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

11/01/2019

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Supervisor Declaration Statement

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

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Chen Xiaolong
.....

Authorship Attribution Statement

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

Chapter 4 is published as Z. Lv, Y. Luo, Y. Tang, J. Wei, Z. Zhu, X. Zhou, W. Li, Y. Zeng, W. Zhang, Y. Zhang, D. Qi, S. Pan, X. J. Loh, and X. Chen. Editable supercapacitors with customizable stretchability based on mechanically strengthened ultralong MnO₂ nanowire composite. *Advanced Materials* **30**, 1704531 (2018). DOI: 10.1021/adma.201704531.

The contributions of the co-authors are as follows:

- Prof Chen and Prof. Loh provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by Mr. Luo, Dr Tang, Mr. Wei and Dr. Zhu.
- All microscopy, including sample preparation, was conducted by me in the Facility for Analysis, Characterization, Testing and Simulation.
- Mr. Zhou and Mr. Li assisted in the drawing the schematics.
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The contributions of the co-authors are as follows:

- Prof. Chen and Prof. Loh suggested the project direction and edited the manuscript drafts.

- I wrote the drafts of the manuscript. The manuscript was revised together with Dr. Tang, Dr. Zhu, Mr. Wei, Mr. Li and Mr. Luo.
- I performed all the materials synthesis and device fabrication, collected X-ray diffraction patterns, carried atomic force microscope and Fourier-transform infrared spectroscopy spectrum, and analysis the data.
- Dr. Xia assisted in the simulation of the electrochemical and mechanical performance in the two-dimensional and three-dimensional supercapacitors with different thickness.
- Dr. Jiang, Dr. Liu and Dr. Ge assisted in the simulation and analysis the strain distribution on the two-dimensional and three-dimensional supercapacitors.
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- Prof. Chen and Prof. Loh suggested the project direction and edited the manuscript drafts.
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Abstract

The ever-advancing electronic industry is reshaping our daily life with various flexible and customizable electronics, requiring electrochemical energy storage (EES) device with concreted flexibility and customizability to finish the entire packaging system. In this thesis, based on the mechano-adaptive electrode materials and device structures, three new kind of mechano-adaptive composite materials for strain enhancement, device editability and effective stress relief of material expansion during charging/discharging process are coupled with two kind of mechano-adaptable structures to achieved flexible EES devices with customizable structures, shapes and enhanced energy density.

An “editable strategy” was firstly proposed to make supercapacitors with customizable shapes and structures for versatile plug-and-play applications while maintain the electrochemical performance to power various flexible and wearable electronics. Supercapacitor units were made up of flexible materials assembled from freestanding interwoven ultralong MnO₂ nanowire/CNT composites, the flexible units were then edited into a desirable structure. The stretchability of this editable structure (up to 500%) is much superior to conventional stretchable structure (usually less than 200%).

Along with the customizable two-dimensional (2D) supercapacitor, stretchable supercapacitors with customizable three-dimensional (3D) shapes and enhanced areal capacitance is also developed, which is inspired by the traditional artifact-honeycomb lantern. With a honeycomb pop-up structure, the customizable 3D supercapacitors can overcome the limited device thickness of traditional 2D supercapacitors. Notably, a honeycomb-lantern-inspired 3D supercapacitor with a 1.0-cm-thick rectangular shape exhibited improved specific areal capacitance of 7.34 F cm⁻², which is 61 times that of the conventional 2D planar supercapacitors (120 mF cm⁻²). The supercapacitor comprises flexible polypyrrole (PPy)/black phosphorous oxide (BPO)-carbon nanotube electrode configured in expandable honeycomb structures for maintaining the stable electrochemical performance (capacitance retention of 95%) under the reversible 2000% tensile strain after 10,000 stretch-and-release cycles.

Furthermore, to achieve flexible and customizable EES device with higher energy storage performance, a biomass-based and elastic NC binder is employed to fabricate flexible high-voltage lithium ion battery cathode. The elastic nanocellulose (NC) binder was used to function as the porous freestanding framework to protect the intergranular of the $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ (NCM523) secondary particles from cracking. The NC-binder based electrode owns improved rate performance and more stable long-term capacity (145.8 mAh g^{-1} after 300 cycles at 1 C) at 4.6 V compared to that of conventional PVDF binder-based electrode (113.2 mAh g^{-1}).

The above results show that mechano-adaptive electrodes and device structures provide a new design platform for customizable EES devices. Following it and cooperating with functional materials, many other new methods and flexible and customizable harvesting and integrated electronics could be further developed.

Lay Summary

The power sources that can be bent and stretchable are vital to power wearable electronics. This thesis employs new methods to fabricate flexible and stretchable power sources. The achievement of the flexible and stretchable power sources is through improvements in both electrode materials and device structures.

Firstly, to adapt to wearable electronics with arbitrary configurations, it is highly desirable to develop editable power sources that can be directly transferred into customizable shapes and stretchable structure according to application scenarios. In this regard, an editable fabric-like power sources with customizable shapes and structures was developed, which can retain its ability to power electronics after being folded, cut and stretched.

Secondly, the stretchable power sources with customizable three-dimensional (3D) shapes is designed. This work tackled the problem of traditional stretchable power sources which is restricted to a two-dimensional (2D) plane, and their areal energy storage capability are limited by device thickness. With this unique expandable honeycomb structure inspired by honeycomb-lantern, the power sources based on a flexible porous polymer-based electrode can be stretched to 2000% without performance decay. The areal energy storage capacity can be linearly enhanced by increasing its device thickness.

Finally, flexible lithium ion battery with high-voltage cathode material is prepared by using and the nanocellulose binder. The nanocellulose binders can cover the electrode materials to protect electrodes and electrode materials from rupture after long-term cycling. The nanocellulose binder endows the electrodes with anti-fracture properties and makes it possible for the flexible higher voltage lithium ion batteries with higher energy density to power wearable electronics.

The flexible and stretchable power sources with customizable shapes and enhanced energy storage performance provides a new design platform for customizable power sources.

Based on these, many other new methods and customizable electronics could be further developed.

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of stretchable supercapacitors with predesigned stretchability. The mismatch between predesigned structures of electrodes and the substrates or gel electrolytes may result in severe stress concentrations at interfaces that initiate microcracks and facilitate the crack propagation during stretching. While the editable strategy (b) only need to cut the supercapacitors into desirable shapes and structures. The customizable structures, such as honeycomb-like structures, pyramid pop-up structure, living-hinge structure and so on, make the as-prepared supercapacitors stretchable in an arbitrary direction. The red arrows indicate the stretchable direction of the as-prepared supercapacitors with customizable structures.

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Figure 4.4 (a) XRD patterns of MnO_2 materials obtained from tradition hydrothermal and stirring hydrothermal method (24 h). (b) XRD patterns of MnO_2 samples obtained from stirring hydrothermal (500 rpm) under different reaction time.

Figure 4.5 TEM images of synthesized MnO_2 nanomaterials with different reaction conditions: (a) 0.5 h under 500 rpm, (b) 1 h under 500 rpm, (c) high resolution image for 1 h under 500 rpm, (d) 3 h under 500 rpm, (e) 6 h under 500 rpm, (f) 24 h under 500 rpm. (g) high resolution image of 0 rpm for 24h and (h) the SAED pattern of MnO_2 nanoflowers.

Figure 4.6 Characterization of mechanically reinforced MnO_2 nanowires materials towards editable supercapacitor: (a) SEM image of ultralong MnO_2 nanowires. (b) TEM image, (c) HRTEM of MnO_2 nanowires, and (d) the corresponding SAED image. (e) The high resolution XPS spectrum of Mn 3p for MnO_2 nanowires. (f) top-view of CNT film, the inset is magnified top-view of CNT film. (g) The top-view and (h) magnified top-view of MnO_2 nanowires/CNT composite film comprising 30% CNT. The insert in (g) is the digital photograph of the composite film being bended.

(i) SEM image of gold coated nanocellulose fiber film on MNW/CNT electrode, the inset is the digital photograph of porous and transparent nanocellulose film. (j) MNW70-NCF films are stable in water after agitation, bend and ultrasound for 5 mins in water. (k) Stress-strain curves of MnO_2 -based composite electrodes and MNW70-NCF-PVA-based supercapacitors.

Figure 4.7 (a) Photograph of MNW/CNT and MNF/CNT composite with different weigh ration of CNT. The number suffixed to MNW and MNF represents weight percent of MNW or MNF in the composite film, respectively. MNF100, MNF90, and MNF80 cannot be peeled off from the filter paper due to poor mechanical integrity. MNF70 is barely able to form freestanding film, as illustrated by the incomplete film. Other films are easily detached from the filter paper. (b) The break of MNW100 film under a slight bending. Stress-strain curves of (c) MNW/CNT and (d) MNF/CNT composite films. (e) Comparison of ductility of MNW/CNT and MNF/CNT composite films with varying CNT content.

Figure 4.8 Electrical conductivity of MNW/CNT and MNF/CNT composite films with the increasing CNT weight ratio.

Figure 4.9 (a) Cyclic voltammograms of MNW/CNT composite films with different CNT content. The scanning rate of CV is 50 mV s^{-1} . (b) Specific capacitance measured from cyclic voltammetry curves at increasing scanning rate for MNW/CNT films (0.6 mg cm^{-2}) with different content of CNT.

Figure 4.10 (a) Dependence of specific area capacitance and film thickness on the mass loading of MNW/CNT film. The scanning rate of CV is 50 mV s^{-1} . (b) Nyquist plot of symmetric supercapacitors based on MNW/CNT films with different mass loading.

Figure 4.11 (a) CV curves of MNW70 composite film tested at different scan rates. (b) Galvanostatic charging-discharging (GCD) curves of MNW70 composite film tested at different charging-discharging current.

Figure 4.12 Electrochemical and mechanical performance of MNW/CNT electrode. (a) CV curves of MNW70 film electrodes at a scan rate of 50 mV s^{-1} in 1 M LiCl aqueous solution. (b) GCD curves of MNW70 film electrodes at a charging-discharging current of

6.4 mA cm⁻² in 1 M LiCl aqueous solution. (c) Specific capacitance of CNT, MNF70, and MNW70 films calculated from GCD curves at increasing current density.

Figure 4.13 (a) SEM and (b) magnified SEM top views of MNF70 composite film.

Figure 4.14 The contact angel of a water droplet on the surface of (a) CNT, (b) MNF 70, (c) MNW 70 and (d) MNW70-NCF films.

Figure 4.15 Nyquist plot of supercapacitors based on MNW70-NCF films with different thickness of nanocellulose fiber films.

Figure 4.16 Electrochemical and mechanical performance of editable supercapacitors based on MnO₂-based composite electrodes under different mechanical deformation. (a) Schematic illustration of supercapacitor construction (side view). (b) Galvanostatic charging-discharging and (c) cyclic voltammetry (CV) curves of flexible supercapacitors based on MNW70-NCF film electrodes at different scanning rates. (d) Electrochemical performance comparison between flexible symmetric supercapacitors based on MNW70-NCF and MNF70-NCF electrode when cycling under various mechanical deformations, at a current density of 1.6 mA cm⁻². The insets are the flexible supercapacitors under various mechanical deformations. (e) Digital images of honeycomb-like supercapacitors under different strain tests. The upper image is the schematic diagram showing linear cutting strategy of the editable supercapacitor, the L_c is the cut length, x and y is the space length in transverse and axial direction. (f) The normalized specific capacitance of polyurethane threads interlocked honeycomb-like supercapacitors tested at 1.6 mA cm⁻² based on MNW70-NCF and/or MNF70-NCF electrodes under different strains. (g) Capacitance retention ratio of honeycomb-like supercapacitors at a current density of 1.6 mA cm⁻² under the recycling tensile strain of 400%. C corresponds to specific capacitances after stretch and C_0 is the initial specific capacitance of first cycle after stretch to 400%. (h) Specific areal capacitance versus reversible stretchability of editable supercapacitor (this work) as compared with previous reported stretchable supercapacitors.

Figure 4.17 CV curves of flexible supercapacitors based on (a) MNW70-NCF and (b) MNF70-NCF film electrodes (at a scan rate of 50 mV s^{-1}) under different bending state. (c) The normalized specific capacitance of flexible supercapacitors between MNW70-NCF and MNF70-NCF as a function of bending angle at a scan rate of 50 mV s^{-1} .

Figure 4.18 Dependence of strain on L_c with thickness of 1 mm (inserted, the schematic of a basic unit of the kirigami pattern on stretchable supercapacitor, where the L_c is the cut length, x and y is the space length in transverse and axial direction). (b) Stress-strains curve for the paper-cut supercapacitors with linear patterns.

Figure 4.19 SEM images of MnO_2 nanowires with the length of (a) $1\sim 2 \mu\text{m}$ and (b) $20\sim 30 \mu\text{m}$ respectively synthesized at the stirring speed of 300 rpm and 400 rpm by the stirring hydrothermal method, the inset figures are the magnified SEM images. (c) The normalized specific capacitance of polyurethane threads interlocked honeycomb-like supercapacitors tested at 1.6 mA cm^{-2} based on MNF, MNW (2, with the length up to $2 \mu\text{m}$), MNW (30, with the length up to $30 \mu\text{m}$) and MNW (50, with the length up to $50 \mu\text{m}$) composite electrodes under different strains. (d) The GV curves of stretchable honeycomb-like supercapacitors tested at 1.6 mA cm^{-2} under different strain.

Figure 4.20 In-situ motion-charging/discharging curves of honeycomb-like supercapacitors with the maximum stretchability up to 400% under different strain rates. The charging/discharging current density is 1.6 mA cm^{-2} .

Figure 4.21 Specific volume capacitance versus stretchability of shape-tailorable supercapacitors with honeycomb-like structure as compared with previous reported stretchable supercapacitors.

Figure 4.22 (a) CV curves (at a scan rate of 50 mV/s) of symmetric supercapacitors based on MNW70 and MNW70/PPy. For MNW70/PPy electrode, the total charge passing the MNW70 electrode is 4 C cm^{-2} . In comparison with the symmetric supercapacitors based on MNW70 electrode, the areal capacitance of supercapacitors based on MNW/PPy

increase by about 2 times to 435 mF cm^{-2} . (b) The increase of the specific areal capacitance of editable supercapacitors by vertical stacking in parallel. The resulted editable supercapacitor with five stacking units can increase the specific areal capacitance to 1090 mF cm^{-2} under tensile strain of 400% at a charging-discharging current density of 1.6 mA cm^{-2} .

Figure 4.23 (a) Strain distribution on the honeycomb-like supercapacitors under different strains obtained by the finite element analysis. (b) The maximum strain on the electrode versus stretchability of supercapacitors for the stretchable honeycomb-like supercapacitors.

Figure 4.24 (a) CV curves of five honeycomb-like supercapacitors in series under different scan potential windows at 50 mV s^{-1} . The insets show the schematic of the corresponding connection type. (b) Galvanostatic charging-discharging curves of (i) single (1×1), (ii) three honeycomb-like supercapacitors in series (3×1), (iii) in parallel (1×3), and (iv) nine supercapacitors in series-parallel (3×3). All the test current densities were 1.6 mA cm^{-2} . The insets show the schematic illustrations of the corresponding connection types. (c) Five honeycomb-like supercapacitors in series powering a white LED watch under dynamic stretch. (d) 3×3 honeycomb-like supercapacitor array powering LED panel at the strain of 100%. (e) Supercapacitor basket (1, supercapacitor pyramid conformal to three-dimensional objects), four pyramid-like supercapacitors (2) connected in series, forming a stretchable pop-up spring structure. (f) Four symmetric supercapacitors connected in series and tailored into more complicated and delicate paper-cutting.

Figure 4.25 Digital images of shape-tailorable supercapacitors tailed into (a) honeycomb-like structure, (b) supercapacitor pyramid and (c) stereoscopic Chinese word ‘spring’ under unfold and fold condition. (d) The pop-up spring-like supercapacitor strips pasted on two sides of arms to power a red LED.

Figure 4.26 (a) The current response in a strain sensor powered by a stretchable honeycomb-like supercapacitor under two conditions: 1) non-integrated sensors experience deformation; 2) integrated sensors and supercapacitors simultaneously

experience deformation during test. (b) The output currents of the non-integrated and integrated devices under different arm swing frequency test. (c) Relationship between maximum output current and arm swing frequency.

Figure 5.1 Schematic illustration of the enhancement of specific areal capacitance in stretchable supercapacitors through (a & b) 2D stretchable strategy (e.g., wave-like structure), and (c & d) 3D stretchable strategy. (a) The 2D stretchable supercapacitor with a limited device thickness (T) relies on the design of stretchable planar electrodes, which depends on increasing the electrode thickness (t) for higher specific areal capacitance. (b) The simulation data of electrochemical and mechanical properties (the inset figure shows the representative strain distribution by the finite element modeling analysis) for the 2D stretchable supercapacitors under different electrode thicknesses. In 2D stretchable supercapacitors, the increase in the electrode thickness would lead to increased internal resistance, further compromising the improvement of areal specific capacitance. The peak strain of wave-shaped electrodes with the same microstructure is also increased when increasing the electrode thickness, which limits the stretchability of supercapacitors. (c) Inspired by the structure of honeycomb lantern, supercapacitors are assembled into 3D expandable honeycomb structures with unlimited device thickness for enhanced specific areal capacitance. (d) The simulation data of electrochemical and mechanical properties for the 3D stretchable supercapacitors under different device thicknesses. A device-thickness-independent ion transport path enables an unlimited increase in the specific area capacitance. Additionally, the device thickness has no influence on the peak strain of the expandable honeycomb structure, which provides a device-thickness-independent stretchability.

Figure 5.2 The internal resistance for 2D stretchable supercapacitors under different electrode thicknesses. The simulation data and method are shown in 5.2.7.

Figure 5.3 A representative strain distribution on the expandable honeycomb structures with a hexagonal unit ($x=194\text{ }\mu\text{m}$, $y=1.5\text{ cm}$, $m=0.2\text{ cm}$, $T=1.0\text{ cm}$) under strains of 0%, 500%, 2000%, 5000% obtained by the finite element analysis (y is the space length

between the adjacent adhesives in the transverse direction, m is the width of the adhesives, x is the space length between the adjacent supercapacitors in the axial direction, and T is the device thickness of expandable honeycomb structure). The simulation of the expandable honeycomb structure under different strains from 0% to 5000%.

Figure 5.4 (a-c) AFM and height profile of few-layer (black phosphorus) BP nanosheets measured at different positions. The adjacent puckered layers of BPS is 5.3 Å.

Figure 5.5 Schematics of preparation steps for PPy nanocomposite with different additions of dopants through one-step electrosynthesis method (CE: counter electrode, RE: reference electrode, WE: working electrode). (a) One-step electrosynthesis of closely packed PPy/SO₄²⁻ composites via electropolymerization of pyrrole while using SO₄²⁻ as the anionic dopant. (b) One-step electrosynthesis of laminated PPy/GO composites via electropolymerization of pyrrole while using GO as the anionic dopant. (c) One-step electrosynthesis of porous PPy/BPO composites via electropolymerization of pyrrole while using black phosphorus (BP) as the additives and the partially oxidized BPs as the anionic dopant: (I) BPs in the aqueous suspension were gradually oxidized by oxygens into BPOs with some oxygen-phosphorus moieties (P-O⁻ and O=P-O⁻) on the surface of BPs upon exposure to air; (II) the oxidized functional groups act as the anion dopant of PPy during galvanostatic electrodeposition process (2 mA) while the unoxidized surface BPs on BPOs cannot be wrapped by PPy and produce the open channels in the 3D PPy/BPO composites during the electrodeposition process.

Figure 5.6 Schematic illustration of the formation of PPy/BPO composite. (a) The addition of over-oxidized BPOs (exposure of the BP aqueous to air for 2 days before mixed with pyrrole) to form dense PPy/BPO: (I) the electropolymerization of pyrrole into PPy with the over-oxidized BPOs as the dopants; (II) formation of dense PPy/BPO composites after a continuous electrodeposition process. (b) The addition BPs in the electroplating electrolyte to form porous PPy/BPO: (I) the electropolymerization of pyrrole into PPy with the partially oxidized BPOs as the dopants; (II) formation of porous PPy/BPO composites after a continuous electrodeposition process. (c) The top-view SEM image of the dense

PPy/BPO composite. (d) The top-view SEM image of the porous PPy/BPO composite.

Figure 5.7 Material characterizations of PPy/BPO composites on CNT film towards 3D stretchable supercapacitors: (a) SEM image of reticulated CNT film. The inset shows magnified top-view of CNT film. (b) SEM cross-section image of PPy/BPO-CNT film at electrodeposition charge density of 7 C cm^{-2} . The inset shows the optical images of the flexible PPy/BPO-CNT film (scale bar = 1 cm). (c) SEM top-view image of porous PPy/BPO-CNT film and the magnified top-view. (d) FTIR spectra of CNT and PPy/BPO-CNT film. (e) The high-resolution XPS spectrum of P2p for PPy/BPO-CNT electrode. (f) Stress-strain curves of CNT and PPy-based electrodes.

Figure 5.8 SEM images of PPy/BPO-CNT electrodes prepared under different charging densities: (a) 0 C cm^{-2} , (b) 1 C cm^{-2} , (c) 3 C cm^{-2} , (d) 5 C cm^{-2} , (e) 7 C cm^{-2} , and (f) 10 C cm^{-2} . The inset is the magnified top view of these electrodes.

Figure 5.9 (a) FTIR spectra of CNT film, BP coated CNT film and PPy/BPO-CNT electrode at 3 C cm^{-2} . (b) FTIR spectra of PPy/BPO-CNT electrodes obtained from electrodeposition under different charging densities.

Figure 5.10 XPS spectra of (a) C 1s, (b) P 2p without etching, (c) P 2p with argon gas etching and (d) N1s of 3D porous PPy/BPO-CNT electrode (7 C cm^{-2}).

Figure 5.11 Electrochemical performance of PPy/BPO-CNT film electrodes under different charge density: (a) Cyclic voltammetry (CV) and (b) galvanostatic curves of PPy/BPO-CNT film electrode grown for 7 C cm^{-2} . The specific areal capacitance of PPy/BPO-CNT film electrodes with different charge densities based on (c) CV test at different scan rates and (d) galvanostatic charging-discharging test at different charging-discharging current density.

Figure 5.12 Specific areal capacitances (a) and (b) specific volumetric capacitances of flexible PPy/BPO-based supercapacitors with increasing charge density at different

discharging current density.

Figure 5.13 (a) The thickness of the PPy electrodes with different dopants under different charge densities, and (b) the electrical conductivity of PPy electrodes with different dopants under different charge densities.

Figure 5.14 The SEM images of cross section of different PPy composite electrodes at a charge density of 7 C cm^{-2} : (a-c) PPy/ SO_4^{2-} -CNT electrode, (b-f) PPy/GO-CNT electrode, (g-i) PPy/BPO-CNT electrode.

Figure 5.15 (a and b) The optical images of PPy/ SO_4^{2-} -CNT electrode before and after being bent at an angle of 150° for ten times. (c and d) The optical image of PPy/GO-CNT electrode before and after being bent at an angle of 150° for ten times. The inset is the SEM image of PPy/GO-CNT electrode after being bent. (e and f) The optical image of PPy/BPO-CNT electrode before and after being bent at an angle of 150° for ten times. The inset is the SEM image of PPy/BPO-CNT electrode after being bent.

Figure 5.16 Stress-strain curves of symmetric supercapacitors based on different PPy-based composite electrodes.

Figure 5.17 Electrochemical performance of flexible supercapacitors with PPy-based electrodes. (a) Cyclic voltammetry (CV) and (b) galvanostatic charging/discharging (GCD) curves of flexible supercapacitors based on PPy/BPO-CNT electrodes at different scanning rates. (c) Specific areal capacitances of PPy/BPO-CNT, PPy/GO-CNT and PPy/ SO_4^{2-} -CNT electrodes calculated from GCD curves at increasing current density. (d) Capacitance retention ratio of PPy-based supercapacitors cycling at a charging/discharging rate of 2 mA cm^{-2} . C_0 corresponds to the initial specific areal capacitance before cycling and C is the specific areal capacitance after cycling. (e) CV curves of flexible supercapacitors based on PPy/BPO-CNT electrodes (at a scan rate of 20 mV s^{-1}) under different bending conditions. (f) The normalized specific capacitance of PPy-based flexible supercapacitors as a function of bending angle at a scan rate of 20 mV s^{-1} .

Figure 5.18 Comparison of (a) CV curves at 20 mV s^{-1} and (b) GCD curves at 2 mA cm^{-2} of symmetric supercapacitors based on PPy/BPO-CNT, PPy/GO-CNT, PPy/SO₄²⁻-CNT electrodes with the charge density of 7 C cm^{-2} .

Figure 5.19 The gravimetric capacitances of PPy-based electrodes at the charge densities of (a) 1 C cm^{-2} and (b) 7 C cm^{-2} calculated from cyclic voltammetry curves at increasing scan rate.

Figure 5.20 (a) and (b) SEM images of 7 C cm^{-2} PPy/GO-CNT electrode before and after 10000 charging/discharging cycles in a three-electrode electrochemical cell tested at a current density of 2 mA cm^{-2} . (c) and (d) SEM images of 7 C cm^{-2} PPy/BPO-CNT electrode before and after 10000 cycles.

Figure 5.21 CV curves of flexible supercapacitors based on (a) PPy/GO-CNT and (b) PPy/SO₄²⁻-CNT film electrodes (at a scan rate of 20 mV s^{-1}) under different bending states.

Figure 5.22 (a) Schematic drawing of the fabrication process for 3D stretchable supercapacitors: (I) The PPy-based electrodes were first to shaped into identical electrode strips with predefined shapes; (II) the electrode strips were adhered by adhesives (PVA/H₃PO₄ gel electrolyte) and connected into two electrode arrays (array A and array B); (III) the edge of the array A and B were coated with silver paste to ensure conductive connections, and then the array A were intersected with array B; (IV) two arrays were separated by a thin nanocellulose separator (about $20 \text{ }\mu\text{m}$). (V) The array A and B were coated with PVA/H₃PO₄ gel electrolyte to form a 3D stretchable supercapacitor with expandable honeycomb structures. (VI) The 3D stretchable supercapacitor was stretched to form a honeycomb structure and packaged with a thin-layer PDMS. (b) Digital images of stretchable rectangular-shaped supercapacitors (with geometric parameters of $y=0.7 \text{ cm}$, $m=0.2 \text{ cm}$, $x=194 \text{ }\mu\text{m}$, $T=0.5 \text{ cm}$) under different strain test. The inset images (upper left) are the scheme showing the expandable honeycomb structure and the hexagonal unit cell before and after being stretched. (c) Dependence of rupture strain on different device

thicknesses in the 3D stretchable supercapacitors (with geometric parameters of $y=0.7$ cm, $m=0.2$ cm, $x=194$ μm). T is the device thickness. (d) The performance comparison of 3D stretchable supercapacitors with different device thicknesses tested at a current density of 7.8 mA cm^{-2} . (e) The normalized capacitance of rectangular-shaped stretchable supercapacitors with different PPy-based electrodes tested at 7.8 mA cm^{-2} under different strains. (f) Capacitance retention ratio of 3D stretchable supercapacitor (with geometric parameters of $y=0.7$ cm, $m=0.2$ cm, $x=194$ μm , $T=1.0$ cm) based on PPy/BPO-CNT electrodes tested at 7.8 mA cm^{-2} under the cycling tensile strain of 2000%. (g) Specific areal capacitance as a function of reversible stretchability of 3D stretchable supercapacitor (this work) as compared with previously reported 2D stretchable supercapacitors.^{[1-14][1-14]}

Figure 5.23 (a) Dependence of rupture strain on y with different device thickness. The image (left up) is a schematic diagram showing the expandable honeycomb structure after being stretched, and the T is the device thickness in the 3D stretchable supercapacitors. The inset image (right down) is schematic diagrams showing hexagonal unit cell before and after being stretched (y is the space length between the adjacent adhesives in the transverse direction, m is the width of the adhesives and x is the space length between the adjacent supercapacitors in the axial direction). (b) A representative stress-strain for the expandable rectangular-shaped supercapacitors (with geometric parameters of $x=194$ μm , $y=0.7$ cm, $m=0.2$ cm, $T=0.5$ cm).

Figure 5.24 SEM images of (a) the PPy/BPO-CNT electrode, (b) PPy/GO-CNT electrode in the stretchable 3D supercapacitors after cycling test. (c) The SEM image of the orientations of CNT in PPy/BPO-CNT electrode after the PPy/BPO is scraped off the tested PPy/BPO-CNT electrode. (d) SEM images of the PPy/BPO-CNT electrode coated with PVA gel electrolyte. The insets are the magnified SEM images.

Figure 5.25 Nyquist plot of 3D stretchable supercapacitors based on PPy/BPO-CNT electrode before and after cycling test. The inset shows the magnified Nyquist plot and the equivalent electrical circuit^[15]. The simulation results of the R_s and R_{ct} before and after cycling test are (7.08 Ω and 0.77 Ω) and (9.48 Ω and 1.71 Ω), respectively. The 3D

supercapacitor experienced a slight increase of the internal resistance ($R_s + R_{ct}$) from 7.85 Ω to 11.19 Ω before and after cycling test.

Figure 5.26 The Ragone plot of the 1-cm-thick 3D stretchable supercapacitors.

Figure 5.27 (a) Galvanostatic charging/discharging curves of i) single supercapacitor unit, ii-iv) supercapacitor units connected in series (3×1), in parallel (1×3), and in-series/in parallel combination (3×3) at a current density of 7.8 mA cm^{-2} . The red line in the inset image is the conductive connection and the blue line is the insulated connection. (b) Rectangle-shaped stretchable supercapacitors with 48 supercapacitor units (4×12) powering red LED under different bending and stretching conditions. (c) 3D stretchable supercapacitors with chair shape: (c1) the optical images of the shape of the supercapacitor unit; (c2) the optical images of chair-shaped stretchable supercapacitors which can be expanded like an accordion under bending and stretching conditions; (c3) the chair-shaped supercapacitors connected with an inverter to power an electroluminescent panel ($10 \text{ cm} \times 10 \text{ cm}$) under bending condition. (d) Arched bridge-shaped supercapacitors: (d1) the optical image of the shape of the supercapacitor unit; (d2) supercapacitors connected into a ball-like structure (upper left) which can deform into a bowl-like structure (upper right), the volcano-like structure (down left) and conform to the surface of 3D balloon (down right); (d3) the as-prepared arched bridge-shaped supercapacitors acted as a 3D helmet worn on the head of an owl toy model to power a 3.0 V flexible LED strip (right). The scale bar for Figure 5.27 is 1 cm.

Figure 5.28. (a) The digit photo of the stretchable rectangular-shaped supercapacitors with a small size ($y=0.7 \text{ cm}$, $m=0.2 \text{ cm}$, $x=194 \mu\text{m}$, $T=0.5 \text{ cm}$) and a large size ($y=1.5 \text{ cm}$, $m=0.2 \text{ cm}$, $x=194 \mu\text{m}$, $m=0.5 \text{ cm}$). (b) The rectangular-shaped supercapacitors bent like a hollow cylinder shape. (c) The rectangular-shaped supercapacitors adapted to the shape of forearm to power a 3V white flexible LED strip.

Figure 5.29 (a) 3D pipe-shaped supercapacitors: (a1) the optical images of the shape of the supercapacitor unit (the diameter for the outer circle is 6 cm); (a2) the flexible pipe-

shape 3D supercapacitor bent on plane surface like the ‘slinky’; (a3) the flexible pipe-shape supercapacitor worn on the elastic Ecoflex pillar under bending and stretching conditions. (b) Flexible pipe-like 3D supercapacitors with shrunk size (the diameter for the outer circle is 1.8 cm): (b1) the digital photo of a hand model; (b2) the respond of the 3D pipe-shaped supercapacitor when it is loaded with external force; (b3) the finger in an artificial hand equipped with the 3D pipe-like supercapacitor to power a red LED under various bending and stretching conditions.

Figure 6.1 (a) Schematic illustration of the fabrication process of flexible nanocellulose (NC) binder-based NCM523 electrode and (b) the flexible NC-based electrode.

Figure 6.2 Mechanical flexibility of a conventionally produced electrode versus an electrode produced using NC-based electrode: (a,b) SEM images of fresh NCM523 electrode using PVDF binder-based electrode, (c) stresses originating from a conventional PVDF binder-based electrode under bending induce formation of cracks and partial electrode delamination, and (d,e) SEM images of flexible NCM523 electrode using NC binder, (f) the flexible NC binder-based NCM523 electrode under bending condition. (g, h) SEM cross-sectional morphology of cathode film with NC binder-based electrode.

Figure 6.3 Photo images of (a) mechanical tester MTS C42 and (b) sample gripped by the holder. Tensile test diagrams of (c) pure NC and (d) NCM523 electrode with NC as binder.

Figure 6.4 (a) Charging/discharging curves at the first, second and third cycle; (b) Discharge capacity and coulombic efficiency of NCM523/Li cells at the first and third cycle; (c) Cycling performance and coulombic efficiency of NCM523/ Li half-cells cycled at 1 C under 3.0-4.6 V conditions. (d,e) Rate performance and (f,g) charge/discharge curves of NCM523/Li cells cycled under 3.0-4.6 V conditions under different C rates from 0.1 C to 10 C.

Figure 6.5 Self-discharge curves of NCM523/Li cells with PVDF binder and NC binder after shelved at the fully charged state after 10 cycles for 10 days.

Figure 6.6 Optical images of (a) a NC binder-based flexible cathode electrode, a flexible NC binder-based NCM523/graphite full cell lighting a red LED under flat (b), being bended (c) and being folded (d).

Figure 6.7 CV curves of NCM523/Li cell with (a) PVDF binder and (b) NC binder at a scan rate of 0.1 mV s^{-1} .

Figure 6.8 CV curves of NCM523/Li cell with PVDF (a) and NC (b) at different sweep rate. (c) The peak current (I_p) as function of the square root of scan rate ($v^{1/2}$). Nyquist plot of charge NCM523/Li cell with PVDF binder and NC binder: (d) after 3 cycles at 0.1 C (e) after 300 cycles at 1 C. The inset scheme is the equivalent circuit. (f) Plots of Z' versus $\omega^{-1/2}$ of two binder-based electrodes. (g) Characterization of wetting properties. Comparison of the contact angles of an electrolyte droplet on a PVDF binder-based film electrode and a NC binder-based film electrode.

Figure 6.9 Photographs of the NCM523 electrode after (a) 0 cycle and (b) 300 cycles at 1 C under 3.0-4.6 V conditions. SEM images of NCM523 electrodes: (c,d,e) PVDF binder-based and (f,g,h) NC binder-based electrode after 300 cycles under 3.0-4.6 V conditions. The process illustration of enhancing the performance of NCM523 electrode with (i) PVDF binder and (j) NC binder after 300 cycles under 3.0-4.6 V conditions.

Figure 6.10 Photographs of the NCM523 electrode with PVDF and NC binders and separator of the cells after (a) 0 cycle and (b,c) 300 cycles when cycled at 1 C under 3.0-4.6 V conditions, and (d) Ni, Co, Mn dissolution amount in NCM523 electrode at 1 C after 300 cycles.

Figure 6.11 TEM images of NCM523: (a) fresh particles, NCM523 electrodes with PVDF (b) and NC (c) after 300 cycles under 3.0-4.6 V conditions. HRTEM Images of NCM523: (d) fresh particles, NCM523 electrodes with PVDF (e) and NC (f) after 300 cycles under 3.0-4.6 V conditions. Correspond to the FFTs and IFFT of NCM523: (g) fresh particles,

NCM523 electrodes with PVDF (h) and NC (i) after 300 cycles under 3.0-4.6 V conditions. XRD of NCM523: (j) 10-70° (k) 18-19.5°. (l) Illustration of the ordered and disordered phase in NCM523 and the structural transformation (TM-transition metal, blue boll-Li ion, yellow boll-Oxygen, red boll-transition metal).

Figure 6.12 XPS of NCM523 electrodes with PVDF and NC binders after 300 cycles.

Figure 6.13 A schematic illustrating the formation process of intergranular crack in a secondary NCM particle with (a) PVDF binder and (b) NC binder. The green arrows indicate the aggregation of primary particles with different crystal orientations into secondary particles. The first three cycles initiate intergranular crack and expose the surface of intergranular to the electrolyte. Long-term cycles aggravate the spread of intergranular cracks and pulverize the secondary NCM523 particles.

Figure 7.1 The drive of the emerging customizable electronics for customizable electrochemical energy storage devices.

Figure 7.2 (a and b) The digital photo of expandable honeycomb structure with a positive Poisson's ratio and (c and d) the reentrant honeycomb structure with a negative Poisson's ratio.

Figure 7.3 (a) Laser-printing of the hydrophobic ink into filtration films to leave uncovered space with desirable shapes for vacuum filtration; (b) The deposited active materials transfer into a PDMS substrate.

Figure 7.4 The technology building blocks for future advances in customizable electrochemical energy storage devices.

Abbreviations

EES	Electrochemical Energy Storage
PDMS	Poly(dimethyl siloxane)
CNT	Carbon Nanotube
NCM523	$\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$
LIB	Lithium Ion Battery
EDL	Electrical Double Layer
GO	Graphene oxide
CVD	Chemical Vacuum Deposition
PP	Polypropylene
PE	Polyethylene
PVDF	Poly(vinylidene fluoride)
PPy	Polypyrrole
PEDOT	Poly(3,4-ethylenedioxythiophene)
PSS	Polystyrene Sulfonate
PANI	Polyaniline
LCO	LiCoO_2
LMO	LiMn_2O_4
LFP	LiFePO_4
LTO	$\text{Li}_4\text{Ti}_5\text{O}_{12}$
SWCNT	Single Walled Carbon Nanotube
OCP	Open Circuit Potential
XRD	X-ray Diffraction
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
SAD	Select Area Diffraction
XPS	X-ray Photoelectron Spectroscopy
FTIR	Fourier-transform infrared spectroscopy
CV	Cyclic Voltammetry
EIS	Electrochemical Impedance Spectroscopy

AC	Alternating Current
DC	Direct Current
MNF	MnO ₂ Nanoflower
MNW	MnO ₂ Nanowire
NCF	Nanocellulose Fiber
DI	Deionized Water
SDBS	Sodium Dodecyl Benzene Sulfonate
AQS	9,10-anthraquinone-2-sulfonic acid
BPO	Black Phosphorous Oxide
2D	Two Dimensional
3D	Three Dimensional
GCD	Galvanostatic Charging-discharging
LED	Light-emitting Diode
NC	Nanocellulose

Chapter 1

Introduction

The ever-advancing electronic industry is reshaping our daily life with various flexible electronics, such as strain sensors, electronic textile, and electronic skins, that enable intimately integration of electronics with the human body for fitness, communication and health monitoring applications. These emerging flexible electronics require electrochemical energy storage (EES) devices with concerted flexibility to finish the entire packaging system. Considering the mismatch in the interface between the conventional electrode materials and electrode structures, there is a need to redesign electrode materials and deformation-tolerant structures for fabricating high-performance and highly flexible EES devices. In this thesis, flexible and stretchable EES devices were fabricated through the innovations in both electrode materials and device structures. The innovations in the mechano-adaptive composite electrode materials enhance the tensile strain of the electrodes, while the innovations in the reconfigured device structures regulate the strain distribution on the device and reduce the peak strains on the composite electrode. The combination strategies make the flexible and stretchable EES devices with high customizability, high energy density and sturdy integration.

1.1 Hypothesis

The ever-advancing electronic industry is reshaping our daily life with various flexible and stretchable electronics, such as strain sensors, electronic textile, and electronic skins, that enable intimately integration of electronics with the human body for fitness, communication and health monitoring applications. To seamlessly wiring up these emerging flexible and stretchable electronics, there is an urgent need for fabricating electrochemical energy storage (EES) devices with concerted flexibility and stretchability (much greater than 100%) to complete the entire package. Traditional configurations of EES devices are typically composed of two electrodes, electrolyte, separators and packaging. Since the electrical and mechanical performance of EES devices are greatly influenced by the electrochemical and mechanical compatibility among the individual components mentioned above, the prerequisite of turning conventional rigid devices into flexible devices is the development of components with high stretchability, i.e. stretchable electrodes, electrolytes, separators and packaging.

In terms of electrolytes, separator and packaging, the inextensible materials in these components can be directly replaced by their organic counterparts. Using a simple replacement method, polymeric elastomers such as poly(dimethyl siloxane) (PDMS) are frequently the packaging material for stretchable EES devices, and gel electrolytes with elastomeric-like properties are employed and meanwhile eliminate the necessity of poorly elastic separator and danger from liquid electrolyte leakage. However, for electrodes, the active materials are usually fragile and crackly inorganics, while the maximum elastic strains of these materials are usually less than 0.1%, which makes conventional electrodes inextensible for stretchable EES devices. Besides, the nonconductive properties of active materials require the intimate contact with current collectors during bend and stretch to allow the electron transfer between electrodes, but the deformation of the current collector during stretch often results in the detachment of the active materials from the current collector. The resulted loss of contact between active materials and current collectors breaks the continuous electronic pathway in EES devices and makes the capacity loss and

inflexible as a unit for flexible devices. Therefore, preparing highly flexible and stretchable electrodes remains the most challenging part of achieving highly flexible and stretchable EES devices.

To finish the entire package of stretchable EES devices, we need to develop correspondingly stretchable electrodes. Since there are not elastic alternatives for active materials in electrodes, building composite architectures with one component serving as an elastic mechanical backbone and the other components providing intended charge storage function is a way out. However, even using novel materials, the maximum elastic strains possessed by the key active materials (e.g., <10% for CNT and graphene) in electrodes of SCs are still far from accommodating the substantial deformation (much greater than 100%) experienced by stretchable EES devices.^[1, 2] As a result, composite electrodes cannot be made highly stretchable by simply replacing conventional active materials with stretchable composites.

To bridge this gap, instead of developing a new chemical system, recent research has intensified in the field of the innovation of structure-dependent strategies for highly stretchable electrodes. In this respect, three kinds of typical structure configurations comprise pre-stretch “wave”-like structure,^[3] bridge-island structure,^[4-6] and textile fiber structure^[7-9] have been designed to impart stretchability to the established brittle electrodes. Normally, these methods require depositing active materials with designed structures on the elastic substrates. However, the required structures are merely compatible to active materials that are robust enough, mainly CNTs and graphene materials, to form required structure.^[10-13] The limitation of materials selection and material loading hinders the further increase of performance of the as-prepared EES devices. Furthermore, the mismatch in terms of resiliency between active materials and elastic substrate often results in stress concentration in the interface, which causes a decrease in the long term stability of EES devices during the stretch-and-release process.^[12] The above-mentioned problems show the established structure methods are incompatible with the current electrode material systems.

Considering the drawback of the conventional electrode materials and electrode structures, there is a need to redesign electrode materials and stretch-tolerant structures for fabricating high-performance and highly flexible and stretchable EES devices. Therefore, the hypothesis is obtaining flexible and stretchable EES devices through the rational design of both electrode materials and device structures. The redesign of mechano-adaptable electrode materials can make the device structure reconfigurable, enhance the tensile strain of the electrodes and suppress the electrode material pulverization from material expansion during charging/discharging process for stable performance stability. The reconfigured device structures can further regulate strain distributions on the electrode and reduce the peak strains on the electrode for customizable needs in different wearable scenarios. The combinations strategies make as-prepared flexible and stretchable EES devices with high energy density, high mechanical robustness and sturdy integration.

1.2 Objectives and Scope

The objective of this thesis is to fabricate long-life flexible and stretchable EES devices with high customizability, high flexibility and high energy density through developing new mechano-adaptive electrode materials and device structures. To fulfill the objective, the scope of this thesis is listed below:

1. Developing a mechanically reinforced electrode for editable supercapacitors with customizable stretchability and shapes for real-life needs in wearable systems.
2. Developing a highly bendable electrode and a method for stretchable supercapacitors with customizable 3D shapes and enhanced areal energy storage performance.
3. Develop an elastic binder to form a protective layer to minimize the secondary particles fatigue in high voltage cathode of lithium ion batteries. This is to ensure flexible EES devices with higher energy density.

1.3 Dissertation Overview

The thesis addresses how to obtain flexible and stretchable EES devices with customizable

properties and high energy density based on the rational design of mechano-adaptive electrode materials and device structures. The framework of the thesis is illustrated as follows:

Chapter 1 underlines the importance of achieving flexible and stretchable EES devices and provides a rationale for the project. The hypothesis of mechano-adaptive materials and devices is analyzed and proposed. The goals, scope and implications of this thesis are also elucidated.

Chapter 2 reviews the literature concerning the current status of flexible and stretchable EES devices. The state-of-the-art method from both materials and structures to stretchable electrodes for stretchable EES devices is also summarized. The features and drawbacks of current strategies are compared and stated.

Chapter 3 discusses the methods to synthesize materials, characterize the morphology of the electrode materials and devices, and test the electrochemical performance of the flexible EES devices. Principles underlying the characterization methods are also included in this chapter.

Chapter 4 elaborates an editable strategy to fabricate stretchable supercapacitors for regulation of the strain on the electrodes. The editable supercapacitors with customizable structures can regulate the peak strain of the electrodes below the fracture of the electrode materials, which enables a wider range of electrode materials for stretchable supercapacitors. The mechanically reinforced ultralong MnO₂ composite electrode materials for the editable supercapacitors further guarantee the editable process and improve the mechanical stability of EES devices with customizable stretchability and shapes. The editable strategy provides a new design platform for the electrode materials in the customizable and stretchable electrochemical energy storage devices.

Chapter 5 elaborates the combination of flexible porous polypyrrole composite electrodes with expandable honeycomb structures for fabrications of three-dimensional (3D)

stretchable supercapacitors. The supercapacitors comprise flexible polypyrrole/black phosphorous oxide-carbon nanotube electrode configured in expandable honeycomb structures for maintaining the stable electrochemical performance of supercapacitors under deformation. The unique expandable honeycomb structure with flexible PPy composite electrodes further provides the supercapacitors with a device-thickness-independent ion transport path and stretchability. These two features enable thicker supercapacitors to be customized into various 3D shapes for enhanced specific areal capacitance while maintaining stable stretchability.

Chapter 6 elaborates the high energy lithium ion batteries based on $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ (NCM523) could be obtained by employing elastic nanocellulose binders. The elastic nanocellulose binder was used to serve as the freestanding architecture to fabricate flexible cathode and the protective layer to minimize the NCM523 secondary particles fatigue. The flexible and high voltage cathode paves the way for flexible lithium ion batteries with higher energy density to power flexible and wearable electronics.

Chapter 7 concludes the whole thesis by linking each section, and provides some preliminary data not included in the main chapter to show some challenges that need to be addressed and the future work that can be further extended.

1.4 Findings and Outcomes/Originality

This research led to several novel outcomes by:

1. Developing three kinds of mechano-adaptive composite materials for strain enhancement, device editability and effective stress relief of material expansion during charging/discharging process, which can help maintain the capacity stability of the flexible and stretchable EES devices with higher energy density and customizability.
2. Developing an editable strategy for the fabrication of the customizable and stretchable EES devices. The idea of transforming stretchable EES devices to highly customizable

devices would see great applications in today's emerging everywhere-able electronics. It would also motivate the research community to devote efforts on other electronics with customizability.

3. Developing an expandable honeycomb structure for fabricating stretchable EES devices with customizable 3D shapes and improved areal energy storage capacity. The 3D strategy provides a new design platform of electrode materials and 3D structures for the customizable 3D EES devices and electronics.

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Chapter 2

Literature Review

In this chapter, the most recent and significant advances in the field of flexible and stretchable EES devices are covered. The article initially reviews the materials and design strategies for flexible and stretchable EES devices. The following section involves the electrode structure strategies for obtaining stretchable electrodes, with a brief summary of the design ideas, mechanical properties and the analysis models that promote mechanical optimization. The latest advances in the exploration of the stretchable EES devices with the help of novel materials and unique structure are then described and compared. Although some progress has been made on the stretchable EES devices, there are still some critical issues, such as the mismatch between electrode and substrate, the lack of customizability, the limited energy storage capability, and so on. To address these issues, the combination of mechano-adaptive electrode materials and device structures is proposed.

2.1 Introduction

The ever-advancing electronic industry is shaping our future with various portable electronics that enable users to hands-free access information in real time.^[1-6] Especially in recent years, several wearable electronics, like Jawbone UP, Apple Watch, T-ShirtOS and Hololens, are constantly emerging as the new generation technology and the trend towards flexible, wearable and implantable electronics enable users on the device side to hands-free collect and exchange information in real time (Figure 2.1).^[7]

Despite great progress in modern electronics, the current achieved portability and flexibility are still far from the requirement of future wearable and biomedical application where electronics are required to intimately integrate with the human body. Since the arbitrarily curved surfaces in human body and the randomly moving body parts require the electronics to be able to withstand the repeated and prolonged strain ($> 100\%$) of stretch, one more recent direction of modern electronics is to fabricate stretchable electronics, which is capable of maintaining stable performance under the conditions of being bended, twisted, stretched and even deformed into arbitrary shapes.^[8, 9] The superior mechanical characteristics of stretchable electronics endow them with excellent conformity to complex surfaces and further offer exciting possibilities for an array of attractive yet technically challenging applications, such as ‘epidermal’ wellness monitors,^[10-13] electronic eyeball-like cameras, smart surgical and athletic equipment.^[14-17] Given the better envisioned practical application, the stretchable devices are projected to flourish in less than twenty years and have profound impacts on accelerating developments of future lifestyle and industries, e.g., consumer electronics, telecommunications and healthcare, as shown in Figure 2.1.^[18-20]

As a dispensable component of portable electronics, the current electrochemical energy storage (EES) devices, mainly supercapacitors and batteries, have become the bottleneck of the development of stretchable electronics, because the rigid nature of common EES devices cannot match the recent stretchable trend for integrated systems. To seamlessly wiring up stretchable electronics, there is an urgent need for fabricating corresponding EES devices with high deformability and stretchability (much greater than 100%) to complete

the entire package.^[20] Figure 2.1 shows the projected applications of stretchable EES devices for various wearable/stretchable electronics.

Figure 2.1 An overview of some potential applications of stretchable electrochemical energy storage EES devices for wearable and stretchable electronics (electric eyeball-like cameras, stretchable LEDs, stretchable strain sensor, stretchable solar cell and healthcare monitoring and therapy device). Reproduced with permission.^[21] Copyright 2013, American Chemical Society. Reproduced with permission.^[22] Copyright 2014, American Chemical Society. Reproduced with permission.^[23] Copyright 2015, American Chemical Society. Reproduced with permission.^[24] Copyright 2011, Royal Society of Chemistry. Reproduced with permission.^[12] Copyright 2016, Springer Nature Publishing AG.

2.2 Methods to achieve flexible and stretchable EES devices

2.2.1 EES device classification and configurations

Supercapacitors and lithium-ion batteries (LIBs) are the two leading EES devices for portable electronics, wherein supercapacitors are used to power devices that require high power in short time while LIBs are deployed for long-term operation of devices.^[25-31] Traditional configurations of both these two devices are typically composed of two electrodes, electrolyte, separators and packaging (Figure 2.2a). Since the electrical and mechanical performance of supercapacitors and LIBs are greatly influenced by the electrochemical and mechanical compatibility among the individual components

mentioned above, the prerequisite of turning traditional supercapacitors and LIBs into stretchable electronic device is the development of components with high stretchability, i.e. stretchable electrodes, electrolytes, separators and packaging.

Figure 2.2 (a) and (b) Schematic illustrations of the design evolution from traditional EES devices to stretchable EES devices. (c) Materials used in conventional and stretchable supercapacitors and lithium-ion batteries (LIBs) and their maximum elastic strain.^[32] The green background indicates the components of electrodes and the blue background corresponds to other components in supercapacitors and LIBs. Abbreviations: PP: Polypropylene; PE: Polyethylene; PVDF: Poly(vinylidene fluoride); PPy: polypyrrole; PEDOT: PSS: poly(3,4-ethylenedioxythiophene) polystyrene sulfonate; PVA: Polyvinyl alcohol; PEO: Poly(ethylene oxide); PDMS: Polydimethyl siloxane.

2.2.2 Enabling stretchability for energy storage materials

From the mechanics point of view, objects under tensile stress undergo either elastic deformation or plastic deformation.^[33] In the elastic deformation region, deformation is

reversible, which means the material is capable of returning to its original state upon the removal of the applied force. While in the plastic deformation region, the internal intermolecular forces in materials cannot resist the increased load, which results in malposition of molecules in objects and leads to permanent deformation. To maintain the stable performance of the stretchable EES devices, it is necessary to control the elongation of all components in EES devices within the range of elastic deformation so that electrochemical degradation due to atomic displacement is minimized.

Figure 2.2c summarizes the maximum elastic strain ranges for commonly used materials in supercapacitors and LIBs.^[34-38] As can be seen from Figure 2.2c, materials used in various components of energy storage devices span from most brittle inorganics to most resilient elastomers, not to mention the infinitely deformable liquid electrolyte. This wide range of mechanical properties enables intrinsic material modification to enhance elastic deformation limits, which can be generalized into replacement strategy and composite strategy. The replacement strategy is to replace inorganic materials with organic counterparts, since polymers are generally more elastic than metals and ceramics. Adopting this method, conductive polymers are widely used for electrode active materials, polymeric elastomers such as poly(dimethyl siloxane) (PDMS) and Ecoflex® are frequently the packaging material for stretchable EES devices, and PVA- or PEO-based gel electrolytes or hydrogel electrolytes with elastomeric-like properties are employed and meanwhile eliminate the necessity of poorly elastic separator and danger from liquid electrolyte leakage.^[35-38]

Where more elastic alternatives are not available or not electrochemically competent, building composite architectures, with one component serving as elastic mechanical backbone and the other components providing intended charge storage function, is also a powerful strategy. For example, CNT and graphene are at the higher end of maximum elastic strain range among currently available active materials, yet they are very limited in charge storage capability as compared to many other materials like metal oxides. Therefore, they are frequently used as the mechanical scaffolds for brittle active materials (Figure 2.2b). The high conductivity of CNT and graphene also eliminates the usage of conductive

additives that are also not as elastic. Moreover, binder-free construction can be achieved by direct chemical or physical bonding in these CNT and graphene composite electrodes, which excludes another source of inelasticity and eliminates the instabilities at inter-phase during mechanical deformation. Another component where this compositing strategy is commonly seen in a current collector, wherein low-dimensional mobilizable conductive materials, such as metal nanowires^[39-42], carbon nanotubes (CNTs),^[43-45] and conducting polymers,^[46-48] form composites with elastic polymer substrates. While compositing architecture varies from work to work (homogeneous mixing, surface coating, etc.), the essence to realize stretchability is the high elastic tolerance of polymeric matrix with structure modification of conductive fillers.

2.2.3 Enabling stretchability for stretchable electrodes

As a complementary approach for employing highly elastic materials in stretchable EES devices, the strategy of redesigning structure layout has drawn much attention in both academia and industry due to its enormous potential for mass producing stretchable EES devices based on traditional manufacturing techniques. As shown in Figure 2.2, it is obvious that even using novel materials, the maximum elastic strains possessed by the key active materials (e.g., <10% for CNT, <5% for graphene) in electrodes of supercapacitors and LIBs are still far from enough to accommodate the substantial deformation (much greater than 100%) experienced by stretchable EES devices.^[49, 50] As a result, electrodes cannot be made highly stretchable by simply replacing conventional active materials with stretchable alternatives. Instead, innovations of structure-dependent strategies rely on the rearrangement of electrode components with fewer or even without new chemicals. This strategy may be a quicker winner for stretchable EES devices in the short term since minor materials research and development is involved and the fabrication is more compatible with current technology.

In general, two progressive steps constitute the cornerstone of the structure-based strategy: achieving high material bendability and utilizing bendability in stretchable structures. The first consideration roots in a simple mechanics theory:

$$\varepsilon = \frac{h}{2r} \times 100\% \quad 2-1$$

where the peak tensile strain (ε) is linearly proportional to the thickness (h) of the electrode when the radius of curvature (r) remains constant.^[51] Therefore, a brittle material in bulk phase can be made flexible when the thickness is reduced such that the peak strain does not exceed intrinsic failure strain. This concept was widely adopted in stretchable electronics (not limited to EES devices) involving inorganic semiconductors and metals. Taking silicon for example, where the tensile fracture occurs at a strain of $\sim 0.7\%$.^[51] Ribbons with a thickness of 100 nm only experience a peak strain of 0.0005% when bent to a radius of 1 cm, and nanoribbons can achieve bendability with a bending radius as low as $\sim 150 \mu\text{m}$.^[9] Other bendable forms include nanowires,^[40, 42] nanomembranes,^[9, 52, 53] nanomeshes,^[54] etc.

By further combining such lamellar structure with proper structure layout, active electrodes become not only bendable but also stretchable. In this regard, a wide range of sophisticated structure layouts for stretchable electrodes have been proposed including but not limited to wave-like structure, bridge-island structure, origami and kirigami structure, and textile fiber structure:

1) In wave-like structures, the wavy thin film electrodes attached on elastic substrates are stretched to flat and return to buckled shape when stress is released, resembling an accordion bellows (Figure 2b). It is not difficult to visualize that the enabler of stretchability in such structure lies in bendability of the wavy films. If the bending radius of thin film electrodes can be reduced, a more tortuous wave shape results, which corresponds to a higher tensile strain when the film is stretched from relaxed to flat.

2) The second structure, bridge-island structure, where ‘islands’ of miniature devices/electrodes are electrically connected by specially patterned ‘bridges’, realises stretchability through shielding the islands from mechanical strain. Large extent of stretching is borne by the interconnections and the layout of interconnections usually adopts wave-like shapes, which again essentially depends on the bendability of interconnect materials.

3) Origami and kirigami designs involve folding-unfolding and cutting into patterns that transfer tensile strain on the whole device to bending of finer structural elements.

4) Lastly, the textile fibre structure deals with wrapping and twisting of electrode materials, which fundamentally relies on their bendability.

The intrinsic properties of materials determine their maximum elastic strains and the electrode structure could help achieve higher stretchability while maintaining operation within an elastic deformation range. Therefore, material selection and development, as well as rational electrode structure design, is important to developing highly stretchable EES devices.

2.3 Material selection for stretchable energy storage devices

Fundamentally, the intrinsic charge storage capacity of active materials caps the energy density of a supercapacitor and LIB. Hence, material selection is the core issue in constructing stretchable energy devices.

2.3.1 Active materials for stretchable supercapacitors

Active materials for supercapacitors can be categorized according to their charge storage mechanism into two types: electrical double layer (EDL) capacitive materials and pseudo-capacitive materials. EDL capacitive materials store charges in an electrical double layer formed on the surface of electrodes through adsorption of ions in the electrolyte, whereas in pseudo-capacitive materials, electrolyte ions permeate into the electrode and undergo redox reactions with active materials, storing charges by chemical processes.^[27]

Currently available active materials for supercapacitors consist of three types: carbon materials (EDL capacitance), metal oxides/hydroxides, and conducting polymers (pseudo-

capacitance). Among carbon allotropes, CNTs and graphene offer tremendous opportunities in stretchable supercapacitor electrodes, because of high electrical conductivity, mechanical flexibility and strength. Many approaches have been proposed to produce freestanding electrodes with large stretchability, yet low capacitance ($8\text{--}60\text{ F g}^{-1}$ for stretchable supercapacitor prototypes) is the major restricting factor.^[35, 47, 55-63] On the contrary, high-capacitance pseudo-capacitive materials (metal oxides/hydroxides and conducting polymers) are hardly freestanding or highly conductive, hence difficult to realize stretchability on their own. Nanostructuring and compositing with stretchable conducting materials turned out to be a powerful tool to utilize electrically insulative and mechanically brittle metal oxides/hydroxides as well as mechanically weak conducting polymers, producing stretchable supercapacitors with higher energy and power densities (specific capacitance in the range of $100\text{--}300\text{ F g}^{-1}$).^[47, 48, 56, 64-70]

2.3.2 Carbon-based active materials

Carbon allotropes including activated carbon, carbon nanotubes (CNTs), graphene, etc. are widely studied for supercapacitor application. Carbon-based EDL capacitive materials are advantageous for high power and cycling stability due to the physical nature of charge storage mechanism, and are attractive in view of their abundance in nature, chemical and thermal stability, non-toxicity and lightweight.^[71-74] Activated carbons are the active materials used in commercial EDLCs (Electrical Double Layer Capacitors),^[71] well known for ultrahigh specific surface area (up to $3000\text{ m}^2\text{ g}^{-1}$);^[73-75] their specific capacitance ($40\text{--}400\text{ F g}^{-1}$);^[71] can be among the highest for carbon materials. Despite the desirable electrochemical performance and low cost, activated carbons are hardly found in stretchable supercapacitors, probably because of their fabrication method and physical form.

Figure 2.3 Summary of strategies used for fabricating stretchable CNT electrodes. (a) Wrapping and twisting method to produce fiber-shaped electrodes. Reproduced with permission.^[59] Copyright 2013, John Wiley & Sons, Inc. Reproduced with permission.^[63] Copyright 2014, John Wiley & Sons, Inc. (b) Prestrain-and-release method to produce buckled CNT films. Reproduced with permission.^[35] Copyright 2013, John Wiley & Sons, Inc. (c) Spray-coating method to fabricate micro-supercapacitor arrays. Reproduced with permission.^[76] Copyright 2013, American Chemical Society. (d) Dip-coating to produce CNT-coated textiles. Reproduced with permission.^[56] Copyright 2010, American Chemical Society.

In contrast to activated carbons, CNTs are the most frequently studied active material for stretchable supercapacitors. Many properties of CNTs are not only favorable to capacitive charge storage, but also beneficial to stretchable electrode construction: 1) CNTs are mechanically flexible, especially pliable along the long axis. This enables many approaches to manipulate CNT morphology, resulting in final structures that can be stretched to high strain values while maintaining high electric conductivity. For example, wire-shaped

electrodes are frequently prepared by wrapping aligned CNTs on elastic fibers^[59, 60, 62, 77] and then overtwisting CNT microfibers into a spring shape.^[63] Either wrapping or twisting would only be possible if CNTs are highly compliant. Another well-developed strategy, ‘prestrain-and-release’ to produce buckled film electrodes,^[35, 55] also relies on the mechanical flexibility of CNTs to prevent cracking in deformed films. 2) Surfaces of CNTs are easily modified with functional groups, which help bonding with elastic materials (such as PDMS^[35, 55] and cotton^[56]) and stabilize CNT colloids. The interfacial bonding among CNTs and elastic materials in above mentioned wire-shaped electrodes and buckled film electrodes prevent delamination during repeated stretching.^[35, 55, 56] In addition, CNT ink is readily available from functionalized CNTs, which can be used to soak and coat^[56] or to print defined patterns on elastic substrates.^[57] 3) The one-dimensional structure of CNTs on the one hand offers continuous electronic pathways even under mechanical deformation, which cannot be achieved by powdery activated carbons,^[71] and on the other hand helps maintain electrode integrity under stress. These intrinsic material properties combined with special structure design (e.g. textile structure,^[56] spring-like CNT rope,^[50] align CNT forest^[44] and aligned CNT sheets^[78, 79]) enable many ways to fabricate stretchable CNT electrodes, as summarized in Figure 2.3.

The outstanding properties of CNTs make them an ideal choice for stretchable supercapacitors. However, how to utilize all surface area in a CNT bundle, and how to reduce production cost without compromising quality, are two decisive problems. Specific capacitance of CNT-based electrodes ($30\text{-}200\text{ F g}^{-1}$)^[73] does not surpass activated carbon-based electrodes, which is believed restricted by small specific surface area ($120\text{-}500\text{ m}^2\text{ g}^{-1}$).^[74, 75] Debundling and opening formation on tube surface are two common countermeasures but results are not very satisfying.^[71, 80] Furthermore, current market price of CNTs is more than 10^3 times higher than activated carbons. Since superior performance requires highly pure and debundled CNTs,^[71, 81] fabrication cost of CNT supercapacitors is almost impossible to compete with activated carbons in the short term. An adoptable method alleviating these issues might be to use CNTs as stretchable current collector/conductive mechanical support for other cheaper and higher-capacitance active materials.

As the building block of CNTs, graphene offers many attractive features similar to CNTs: high electric conductivity, mechanical strength and flexibility,^[82, 83] compatibility with additive-free construction,^[84-86] plus an additional advantage of high specific surface area (theoretical specific surface area is projected to be $2630 \text{ m}^2 \text{ g}^{-1}$).^[74] It was predicted that ideal single-layer graphene can provide a specific capacitance of $\sim 550 \text{ F g}^{-1}$ if all surface area was utilized,^[74] showing the great potential of graphene as supercapacitor electrodes. Because of these attributes, graphene is also explored for stretchable supercapacitors.^[47, 58, 61, 66] Reported strategies to impart stretchability are summarized in Figure 2.4.

(a) Graphene fiber (Physically constrained synthesis)

(b) Wavy-shape graphene (CVD)

(c) Graphene textile (Dip coating method)

Figure 2.4 Summary of strategies used for fabricating stretchable graphene electrodes. (a) Fabrication of graphene springs by hydrothermal treatment of graphene oxide (GO) suspension in high-aspect ratio glass tubes. Reproduced with permission.^[87] Copyright 2012, John Wiley & Sons, Inc. Reproduced with permission.^[88] Copyright 2013, John Wiley & Sons, Inc. (b) Fabrication of buckled graphene sheets through CVD on wavy metal substrates. Reproduced with permission.^[61] Copyright 2014, American Chemical Society (c) Dip-coating method to produce reduced graphene

oxide (rGO)-coated textiles. Reproduced with permission.^[47] Copyright 2015, Elsevier B.V.

Wrapping and twisting, which are often employed for CNTs, should ideally also apply to graphene with a 2D nanostructure. However, this is in fact not the case, because the production of large-scale flat graphene sheets remains unsolved. Instead, CVD on wavy metal substrates is used more frequently (Figure 2.4b). For example, buckled graphene sheet grown on wavy Cu foil realized electrode stretchability up to 40%,^[61] and wavy graphene foam (GF) coated with conducting polymer could withstand 180° bending and 30% stretching.^[66] However, stretchability of this configuration is limited to the wavy structure of metal substrates and preparation processes require the use of metal substrates and corresponding removal steps, in addition to the high cost of CVD.^[89] Besides this buckled film strategy, dip-coating of graphene oxide (GO) followed by reduction on flexible^[90] or stretchable^[47] textiles is also a viable approach (Figure 2.4c). This method relies on surface functionalities of GO flakes to bind firmly on textile fibers, which is similar to functionalized CNTs. Graphene film electrodes prepared by the above methods demonstrated comparable performance (electrochemical and mechanical) to CNT counterparts. More encouragingly, attempts to fabricate fiber-shaped graphene to mimic CNT morphology were successful (Figure 2.4a). Highly pliable and conductive graphene fiber was prepared through hydrothermal treatment of GO in high aspect-ratio glass tubes;^[88] when coated with 3D porous graphene and coiled in spring shape, it delivered stable capacitive behaviour under severe bending, compression, and stretching.^[58] The success fabrication of graphene fiber presages highly stretchable wire-shaped supercapacitors adopting analogous strategies to wire-shaped CNT electrodes.

On the other hand, prevention of restacking of graphene nanosheets due to strong π - π interactions and van der Waals forces^[89] is a major technical hurdle to produce high-capacitance graphene, which is believed the main reason why commonly measured specific capacitance of graphene supercapacitors ($100\text{--}220\text{ F g}^{-1}$)^[74] is not as high (even lower than activated carbons) as expected from its outstanding properties.^[82] Furthermore, a cost-effective fabrication method is ultimately necessary to make use of this wondering material, which is exactly one of the current research focuses of graphene. With the progressively

deepening insights into the knowledge of its properties and fabrication process, graphene, as a newly emerging material, forecasts an exciting solution to stretchable EES devices.

2.3.3 Pseudo-capacitive and composite active materials

Transition metal oxides/hydroxides and conductive polymers are two common types of pseudo-capacitive materials. The motivation behind developing pseudo-capacitive materials is the higher energy density compared to EDL carbon materials,^[72, 82, 91] but their power density and cycling stability are penalized accordingly. Usually, a highly electrically conductive and mechanically sturdy substrate/scaffold is utilized, because pseudo-capacitive materials are rarely sufficiently conductive and hardly made in freestanding forms. The abovementioned stretchable carbon materials turned out to be an ideal candidate that provides good electronic contact and mechanical backbone.^[56] From the other perspective, pseudo-capacitive materials are somewhat regarded as capacitance enhancing agents for EDLCs.

Transition metal oxides/hydroxides possess more than one oxidation states that allow storage of charge by switching between different oxidation states. Theoretical specific capacitances of metal oxides/hydroxides are generally higher than 1000 F g^{-1} up to more than 3000 F g^{-1} .^[72, 82, 91, 92] RuO_2 is the most extensively studied metal oxides for supercapacitor electrodes but its prohibitive cost restricts practical application.^[72] MnO_2 turned out to be a promising alternative delivering comparable energy storage capability, which is abundant, cheap, and environmentally friendly.^[77] It, in fact, dominates stretchable supercapacitors involving inorganic pseudo-capacitive materials. However, the low electronic conductivity and rigid structure of MnO_2 are not suitable for stretchable applications.^[93] On the other hand, two kinds of structural strain are expected in pseudo-capacitive materials under stretching: one from external mechanical stress and the other from the volume expansion of materials.

To circumvent these issues, nanostructuring and compositing are two powerful approaches.

Nano-sized microstructure reduces diffusion length for ions and electrons, thus improving reaction kinetics,^[82] while the space present in a nanostructure can accommodate structural strains.^[72] As for compositing, stretchable carbon electrodes are often the substrates to be composited with, because carbon backbones not only enhance electrochemical performance of MnO₂ through increased conductivity and surface area,^[82, 91, 94, 95] but also provide reliable mechanical support under severe deformations; *in-situ* electrochemical deposition of MnO₂ on carbon scaffolds eliminates the usage of binders and conducting additives, which further improves energy and power densities and reduces interphase instabilities. Hu et al. first improved areal capacitance of a sheet capacitor composed of single walled carbon nanotube (SWCNT)-coated nylon fabric by 24 times via electrodeposition of MnO₂ nanoparticles.^[56] Later on, MnO₂ nanofiber-decorated MWCNT-wrapped nylon fiber^[69] and MnO₂ nanoarray-coated CNT reticulate film^[70] demonstrated outstanding stretchability up to 150%. Besides poor conductivity and flexibility, electrode dissolution is another problem for MnO₂, which results in cycling degradation.^[72, 82, 91] Polymeric coating is an effective strategy to hinder such unfavorable side reactions,^[82] and the flexible nature of polymer coating also prevents cracking and disintegration during repeated stretching, as revealed by Huang et al. in PPy-MnO₂ nanocomposite.^[96] The polymeric coating is usually conducting polymers, contributing to charge storage as well.

Conducting polymers store charges through reversible oxidation and reduction of polymer backbones with concurrent insertion of ions to maintain charge neutrality. Commonly studied conducting polymers for supercapacitor electrodes include polypyrrole (PPy), polythiophene (PTh), polyaniline (PANI), poly(3,4-ethylenedioxythiophene) (PEDOT), etc. Conducting polymers are favorable for stretchable supercapacitors because of intrinsic mechanical flexibility, conductivity, and facile fabrication that is compatible with binder-free configuration (*in situ* deposition).^[66, 97] In fact, the majority of stretchable pseudocapacitive supercapacitor prototypes are based on conductive polymer.^[47, 48, 60, 64-68] Nevertheless, they are hardly strong enough to form freestanding electrodes, so conductive polymer composites are very often the solution, where conductive polymers are either chemically or electrochemically coated on mechanically robust and electrically conductive

substrates. Some examples of such substrates are reduced graphene oxide (rGO) coated nylon lycra fabric,^[47] buckled elastic substrates coated with Au film,^[48] 3D graphene network (GF),^[66] and buckled SWCNT reticulate film.^[68] Compared with metal oxides/hydroxides, conductive polymers might be a cost-effective solution to stretchable supercapacitors. However, they usually degrade easily with cycling (within ~1000 cycles) due to swelling/deswelling caused by ion insertion/extraction.^[72, 95]

2.3.4 Active materials for stretchable LIBs

Active materials for LIBs are broadly classified based on lithium storage mechanism as intercalation/insertion materials, conversion materials, and alloying materials, in the sequence of increasing volume changes during lithiation/delithiation and higher energy density.^[98] Intercalation materials dominate the playgrounds for both cathode (e.g., LiCoO₂ (LCO), LiMn₂O₄ (LMO), LiFePO₄ (LFP)) and anode (e.g., graphite and Li₄Ti₅O₁₂ (LTO)).^[99] LCO is till now the most successful and widely commercialized cathode material, yet it suffers from low thermal stability which poses great safety hazards to the usage of LIBs, and the high cost of Co is not desirable.^[99, 100] LMO as a low-cost and environmentally friendly alternative, however, is inferior in specific capacity^[100] and chemical stability.^[99] Polyanionic LFP has good thermal stability and extraordinary high rate performance yet its energy density is limited by low operating voltage.^[99, 100] On the opposite side to cathode, carbon (graphitic carbon and hard carbon^[99]) has remained popular for more than 20 years since the first carbon anode LIB came into the market,^[100] but the intensifying safety concerns may lead to more advantageous competitive edge for LTO, where higher intercalation potential prevents Li dendritic growth. Moreover, LTO experiences minimal volume alterations from lithium insertion/extraction, which helps provide high rate capability and long cycle life. Nevertheless, reduced energy density due to higher intercalation potential is a main drawback.^[99, 100]

Figure 2.5 Common types of scaffolds for active material deposition in stretchable LIB electrodes, i.e. CNT fibers/springs, buckled CNT sheets, and polymeric sponges. (a) SEM image of aligned CNT sheet. Reproduced with permission.^[101] Copyright 2015, John Wiley & Sons, Inc. (b) SEM images of a CNT/LTO anode spring twisted from CNT/LTO hybrid fibers at different magnifications. Reproduced with permission.^[63] Copyright 2014, John Wiley & Sons, Inc. (c) SEM images of CNT/LTO-CNT composites in relaxed state with 450% prestrain (left) and enlarged view of the arched structure (right). Reproduced with permission.^[101] Copyright 2015, John Wiley & Sons, Inc. (d) Comparison between conventional electrode based on metal foil and the PDMS sponge-based stretchable electrode. Reproduced with permission.^[102] Copyright 2016, John Wiley & Sons, Inc.

Since readily available active materials for LIBs are all inorganic solids, with the characteristics of rigidity, brittleness, poor electrical conductivity, and sometimes large

volume alterations, the strategies applied for metal oxides/hydroxides in supercapacitors should also provide a viable path to construct stretchable LIBs, i.e. forming nanocomposites with stretchable carbon electrodes as mechanical support and conductive network. For example, Zhang et al. coated CNT fiber with LTO and LMO nanoparticle slurry, achieving 85% capacity retention while stretched to 100% strain (Figure 2.5a).^[63] Weng et al. constructed a buckled sandwich structure where a blend of CNT and LTO (or LMO) nanoparticles was well contained in between two CNT sheets.^[103] (Figure 2.5b) More recently, Zhang et al. achieved a record stretchability of 600% (with 88% capacity retention) by dispersing LTO nanoparticles and LMO microparticles in CNT fibers.^[104] In contrast, a recent study reported stretchable electrodes with PDMS sponge as the substrate for LTO and LFP nanoparticles, without using stretchable carbon backbone. Resistivity was found to increase 6~8 times when the electrodes were stretched to ~50%, due to loss of electrical contact between active particles.^[105] Such difference suggests the indispensable role of carbon backbone. In terms of nanostructuring, interpenetrating nanostructured active materials usually showed improved rate capability, cycle stability, and reversible capacity, as a result of enhanced electronic and ionic conductivity and more allowance for volume alterations,^[99, 100, 106] which should be more deformation-friendly as well. Durability of bonding between active materials and substrates is another critical factor. In situ synthesis such as electrodeposition^[107, 108] and hydrothermal deposition,^[85] which allows for additive-free configuration, is expected to give stronger adhesion, while post-synthesis coating such as slurry pasting,^[109-111] dip-coating^[107] and drop-casting,^[84, 105, 109] where polymeric binders are employed, may also results in reliable bonding. In the example of PDMS sponge-based electrodes, plasma treatment was conducted on PDMS before drop-casting electrode slurry for better bond strength, possibly due to which ~90% capacity was retained at relaxed state after being stretched for 500 cycles (Figure 2.5c).^[105]

2.4 Stretchable structures for stretchable electrodes

Even though the stretchability of various components in EES devices can be effectively improved by employing more elastic materials, the final mechanical capability depends

largely on the electrode structure, through which highly stretchable EES devices can be produced using conventional materials. Stemming from the bendability of structural components with small thickness, some examples of novel structure designs that will be discussed in this section are wave-like structure, bridge-island structure, origami and kirigami structure, and textile fiber structure.

2.4.1 Wave-like structure

The wave-shaped strategy for elastic electrode begins with the research on the formation of controlled and ordered wave-like geometrics in thin metal films modified polymer substrates through a thermal-induced expansion or pre-stretch method.^[112, 113] Khang and colleagues^[114] subsequently produce the stretchable electronics with practical functionalities that consists of wavelike single-crystal silicon onto rubber substrates and this work ignites the rapid popularization of this strategy for stretchable supercapacitors and LIBs, forming stretchable electrodes made of thin-film system such as single wall carbon nanotube,^[55, 115] polypyrrole,^[116] graphene.^[117, 118] In the case of the initial fabrication procedure of wave Si ribbons on a PDMS substrate as illustrated in Figure 2.6a, the thin single-crystal Si ribbons without bonding with the underlying Si wafer were firstly prepared by traditional photolithographic method. Upon the coating with pre-stretched poly(dimethylsiloxane) (PDMS) under the UV/ozone activation, the intimate contact between PDMS and Si ribbons will form the covalent -Si-O-Si- bonding along the Si-PDMS interface and result in the transfer of Si ribbons on PDMS substrate.^[114, 119] Upon relaxation, the pre-strain, highly periodic “wavy”-like configuration of Si ribbons instantly form at the surface of PDMS substrate with 15% external deformations tolerance (Figure 2.6b&c). The mechanical models of the thin-film Si buckling on PDMS substrate, which can be referred to several reviews,^[120-122] have been developed to quantitatively analyse and predict the wavelength and amplitude of the buckling system under different tensile test. When the applied strain is smaller than 5%, through the minimization of the total energy system,^[123, 124] the wavelength (λ_0) and amplitude (A_0) follows the Equation 2-2 and 2-3:

$$\lambda_0 = 2\pi h_f \left(\frac{\overline{E}_f}{3\overline{E}_s} \right)^{1/3} \quad 2-2$$

$$A_0 = h_f \sqrt{\frac{\varepsilon_{pre}}{\varepsilon_c} - 1} \quad 2-3$$

where thin film and substrate are respectively represented by f and s in the subscript; h_f is the thickness of thin film; $\overline{E}_s$ and $\overline{E}_f$ separately correspond to the plain-strain moduli of Si ribbons and PDMS substrate, which can be calculated according to the equation $\overline{E} = E/(1-\nu^2)$ with E and ν denoting Young's modulus and the Poisson ratio, individually; and $\varepsilon_c = 0.25/(3\overline{E}_s/\overline{E}_f)$ is the critical strain that induces buckling. As for a larger prestrain (ε_{pre}), ranging from 5% to 30%, the wavelength and amplitude of the buckling system become dependent on the prestrain, as given by Equation 2-4 and 2-5:

$$\lambda = \frac{\lambda_0}{(1+\varepsilon_{pre})(1+\xi)^{1/3}} \quad 2-4$$

$$A = \frac{A_0}{\sqrt{1+\varepsilon_{pre}}(1+\xi)^{1/3}} \quad 2-5$$

where λ_0 and A_0 respectively represent the wavelength and amplitude acquired from Equation 2-2 and 2-3 in the small-strain case, while the $\lambda_0/(1+\varepsilon_{pre})$ and $A_0/\sqrt{(1+\varepsilon_{pre})}$ individually stand for the variation of wavelength and amplitude based on the mechanics of a simple accordion bellow. Note that the ξ only relies on pre-strain and conforms to $\xi = \frac{5}{32} \varepsilon_{pre} (1+\varepsilon_{pre})$ and the coefficient $(1/(1+\xi)^{1/3})$ appears in the Equation 2-4 and 2-5 stems from the geometric nonlinear constitutive model.^[119, 125, 126]

Figure 2.6 (a) Schematic illustration of the fabrication procedure of wave Si ribbons on an elastomeric PDMS substrate. Reproduced with permission.^[114] Copyright 2005, American Association for the Advancement of Science. (b) Optical (with PDMS prestrained to $\approx 28\%$) and (c) SEM images of wavy, single-crystal Si ribbons (with PDMS prestrain of $\approx 15\%$). Reproduced with permission.^[119] Copyright 2007, National Academy of Science, US. (d) SEM image of Si nanomembrane with 2D herringbone structures. Reproduced with permission.^[127] Copyright 2007, American Chemical Society. (e) SEM image of the crumpled graphene film obtained through biaxially stretch and relax method. Reproduced with permission.^[118] Copyright 2007, American Chemical Society.

Apart from the uniaxial wave-like configurations, the biaxial “wave” structure has also been utilized to generate a two dimensional (2D) stretchability along with all the in-plane directions.^[126-129] Similar to the fabrication procedures of 1D structural design, the 2D herringbone structure was spontaneously formed through depositing nanomembranes in a biaxial pre-stretched compliant PDMS, followed by the release of the biaxial pre-strain. Figure 2.6d shows the as-formed Si nanomembranes with 2D herringbone structures on PDMS substrate. The theoretical models for analysing the buckling Si nanomembrane under biaxial pre-strain have been carried out and summarized in previously reported papers.^[123, 124, 130, 131] In such system, the buckling membranes are capable of escaping from

fracture during 2D stretch, because the biaxial strains that come from external stretch and other nonplanar deformations can be accommodated by the adjustable wavelengths and amplitudes in horizontal and longitudinal orientations of the buckling structure. Hence, by carefully modulating the “wave” geometry, the buckling system integrated into electronic devices can exhibit a reversible stretchability or compressibility with a nearly unchanged performance. It is worth noting that the wave-like bulking approach is also applicable in designing stretchable membrane with other inorganic materials besides the above-mentioned semiconductor materials. Lee et al.^[40] introduced this design strategy in Ag nanowire thin-film electrodes on a pre-stretching polymer substrate to form a superelastic conductor, in which the electrical conductivity, as well as transparency, remains nearly unchanged even when the thin-film is stretched to 460%. As for stretchable EES devices, Zang and colleagues^[118, 132] adopted 2D “wave” structure to form a stretchable graphene paper electrode (Figure 2.6e) for supercapacitor through bonding and then releasing the graphene films (with 3-10 layers) on the biaxial prestretched elastomeric substrates (up to 400%). The crumpled graphene electrode exhibits high stretchability up to 800% areal strain and a reliable stretchability with about 5% degradation in capacity after being uniaxial stretched to strains of 200% over 1000 stretch/relax cycles.

2.4.2 Bridge-island structure

The bridge-island structure represents another efficient strategy to obtain stretchable ESDs. This configuration is evolved from the interconnect-island mesh configuration, in which the whole active electrode is divided into several smaller islands and each pair of neighboring islands is connected by an elastic metal bridge that offers the stretchability, as shown in Figure 2.7a.^[133] Lacour et al. initially applied this strategy to fabricate a stretchable inverter of thin film transistors that can be repeatedly stretched and released up to 12% strain while maintaining functionality.^[134] Along this line, a non-coplanar mesh structure designed by Kim et al. has been implemented to achieve a higher level of elastic and tensile property as compared with the previous coplanar mesh configuration.^[135] Figure 2.7b illustrates the circuit-fabrication process of manufacturing an arc-shaped network for

a non-coplanar configuration. The silicon islands with Au interconnects on a silicon wafer coated with a layer of poly(methylmethacrylate) (PMMA) are firstly produced through photolithographic method. The immersion of Si wafer in acetone results in remove of the PMMA layer and then the released circuit mesh is transferred onto a piece of PDMS. After depositing a thin film of Cr/SiO₂ at the underside of the islands, the circuit mesh is delivered to a biaxial pre-stretched PDMS substrate. With the surface of PDMS being activated by ozone, there is a formation of -O-Si-O- linkage between the SiO₂ and PDMS. The following release procedure of the pre-stain witnesses the bonded Si islands approach towards each other while the non-bonded Au bridges are subject to compressive force and rise sheer from the plane to form arc-shaped structures. The maximum strains in the bridges ($\varepsilon_{bridge}^{max}$) and islands ($\varepsilon_{island}^{max}$) under a pre-strain (ε_{pre}) can be obtained as^[136, 137]

$$\varepsilon_{bridge}^{max} = 2\pi \frac{h_{bridge}}{L_{bridge}^0} \sqrt{\frac{\varepsilon_{pre}}{1 + \varepsilon_{pre}}} \quad 2-6$$

and

$$\varepsilon_{island}^{max} = \frac{\varepsilon_{bridge}^{max} E_{bridge} h_{bridge}^2}{(\bar{E}_{island} h_{island}^2)} \quad 2-7$$

where h_{bridge} and h_{island} respectively represent the thickness of interconnected bridges and islands. L_{bridge}^0 is the original length of interconnects; E_{bridge} is the Young's modulus of bridges and $\bar{E}_{island}$ is the plane-strain modulus of islands. According to Equation 2-7, the maximum strain in the island ($\varepsilon_{island}^{max}$) is usually negligible, considering the thickness of bridge (h_{bridge}) is much smaller than that of the island (h_{island}). Therefore, because of the poor adhesion of Au bridges, accompanied with the narrow geometrics and low bending stiffness of device bridges compared with that of islands, the out-of-plane mechanical forces are mostly focused on the interconnected metal bridges while the fragile islands with

active materials avoiding stress concentration.

Figure 2.7 (a) Bridge-island structure with a Si island and Ti interconnects attached on a pre-stretch PDMS substrate (top). Cross-sectional diagram of the elastic electronic circuit on the released substrate (bottom). (b) Schematic illustration of the circuit-fabrication process of manufacturing an arc-shaped network for a non-coplanar configuration with mesh networks. Reproduced with permission.^[135] Copyright 2008, National Academy of Science, USA. (c) Schematic illustration of typical configuration of a representative serpentine interconnect with m unit cells (top). SEM images of island-bridge design with straight (bottom left) and (b) serpentine interconnects (bottom right). Reproduced with permission.^[121] Copyright 2009, American Vacuum Society. (d) Bright-field reflected light microscopy images of tortuous gold nanowires attached on PDMS substrate with different amplitude–wavelength ratios before (top) and after (middle) being stretched. The scale bars are 100 μm . Images (bottom) of the original structure of serpentine gold nanowires bonded to the elastomer (left) and the elongated structure (right). Reproduced with permission.^[138] Copyright 2004, John Wiley & Sons, Inc. (e) Schematic diagram of island-bridge design with fractal interconnects. The inset shows the geometric construction of fractal inspired serpentine interconnects from order 1 to 4. Reproduced with permission.^[139] Copyright 2013, Elsevier B.V.

For non-coplanar bridge-island mesh configuration under stretch, the overall stretchability ($\epsilon_{\text{stretchability}}$) of such device is given by^[121]

$$\mathcal{E}_{stretchability} = \frac{\mathcal{E}_{pre}}{1 + \left(1 + \mathcal{E}_{pre}\right) \frac{L_{island}^0}{L_{bridge}^0}} \quad 2-8$$

where L_{island}^0 is the length of islands. From Equation 2-8, the design rules for obtaining the higher stretchability based on this strategy is to enlarge the pre-strain, increase the length of bridges, and reduce the length of islands. However, the increase in ratio between the length of bridges and islands for the linear interconnects means smaller islands with a larger distance between them, thereby curtailing the effective surface area and leading to a drop in total specific capacity. In view of this, the bridge-island design with serpentine spring-like connects is proposed to alleviate this problem.^[20, 137] Figure 2.7c schematically illustrates the typical configuration of serpentine bridge with a specific amplitude-wavelength ratio, in which the individual unit comprises two semicircles that are linked by straight lines. Different from the wave-like structure which accommodates the strains through the movement of the non-coplanar waves of the substrate, the modulation of the applied strain in serpentine structure mainly relies on the changes in amplitude and wavelength of the tortuous metal wires. In principle, the stretchability of device is positively associated with the amplitude-wavelength ratio, i.e., the stretchability of such device increase with the increasing amplitude-wavelength ratio.^[138] For example, the straight Au wires (Figure 2.7d, left) attached on PDMS substrate fracture when the strain is simply 2.4 ± 0.5 %. The serpentine Au wires with an amplitude-wavelength ratio of 0.5, however, increases the strain at the electronic failure up to 14.2 ± 0.5 % (Figure 10d, middle). Further doubling amplitude-wavelength ratio (i.e. 1) sees the tortuous wires produce a higher stretchability of 27.2 ± 0.9 % (Figure 2.7d, right). By selecting appropriate amplitude-wavelength ratio and thickness of interconnects, the serpentine metal interconnections are desirable to prevent electronics from slowdowns in performance under remarkable strains.

Fractal-inspired interconnects developed from serpentine bridges is another kind of bridge-island strategy to make the restricted area more utilized.^[20, 139] Figure 2.7e shows an example of the serpentine configuration in fractal design up to 4 times of iteration. The 1st order has a serpentine structure, and the fractal configuration with higher order ($n > 1$) is

created by the accumulation of the original serpentine layout in the previous interconnects with (n-1)th order. The fractal configuration achieves higher tensile properties by conforming to the larger strain in a mechanism of unraveling the fractal interconnects from the higher order to the lower order and reversing the process back to the original fractal pattern in the region of elastic deformation. For every unit increase in order, there is approximately 3 times increase in the length and stretchability of fractal interconnects. This leads to a huge improvement (about 200 times) in the system-level stretchability from 10.7% in the first order interconnects to ~2140% in fourth order interconnects.^[139] Except the serpentine pattern, Peano, Greek cross, Hilbert and other curves have already been demonstrated as fractal layouts.^[140] The associated mechanical analyses about these fractal interconnects have been provided for interested readers which will not be explored more here.^[122, 125]

2.4.3 Origami and kirigami structure

Inspired by the art of shaping a piece of paper into various beautiful and intricate structures, the concepts of origami ('ori' = folding; 'kami' = paper) and kirigami ('kiri' = to cut) have been recently introduced into stretchable supercapacitors and batteries.

Miura folding is a form of origami method, which was firstly employed by Cheng et al.^[141] and Song et al.^[142] to obtain highly deformable batteries with higher areal energy density. During a continuous Miura-origami process, only the creases experience large strain from refolding process, while the formed parallelogram faces remain completely flat and do not undergo large deformation.^[143, 144] Therefore, the key point to accomplish foldability of the overall system is to determine the critical curvature radius of the crease that induces plastic yielding. The improved method for this strategy can thus be the selection of highly bendable materials to increase critical curvature radius of the creases or the reduction of the strain level below critical stress by virtue of the formation of reasonably distributing creases. In the origami LIBs as shown in Figure 2.8a,^[142] CNT-coated paper was adopted to serve as current collector to increase the foldability of electrodes and two crease patterns was applied, with the left part of Figure 2.8a referring to '45° Miura folding' which can be

compressed in linear direction and the right one of Figure 2.8a referring to ‘90° Miura folding’ which can be collapsed in biaxial direction. The neighbouring ‘mountain’ and ‘valley’ crease with different angles (45° and 90°) divides the paper-based LIBs into identical parallelogram faces in a form of tessellation. Once the three parameters of parallelograms were determined (the length of short and long sides, and the acute angle $\beta \in [0^\circ, 90^\circ]$ where the two lines meet), the only variable left is the projection angle $\varphi \in [0^\circ, 2\beta^\circ]$ between two ridges, wherein $\varphi = 0^\circ$ and $\varphi = 2\beta$ respectively represent the flat state and the fully compressed state. Figure 2.8b shows the detailed strain distribution of 45° Miura patterns under the conditions of twisting and bending by means of finite element analyses (FEA), where the maximum principal strain is less than 0.9%, demonstrating the significant mechanical advantage of origami strategy.^[142]

Figure 2.8 (a) Schematic illustration Miura folding with two representative origami patterns. (b) FEA simulation of a lithium ion batteries with 45° Miura pattern under twisting (top panel), and bending (bottom panel). Reproduced with permission.^[142] Copyright 2014, Macmillan Publishers Limited. (c) Illustration of a cut-N-shear pattern. Reproduced with permission.^[145] Copyright 2015, Macmillan Publishers Limited. (d) SEM images of two kinds of kirigami GO-PVA electrodes. The inset indicates the corresponding micro-cut patterns. (e) Stress-strain curves for kirigami sheet

(green), pristine sheet (grey curve), and a sheet with a single cut in the middle (dashed blue). I, II and III respectively represent the initial elastic deformation (purple region), secondary elastic deformation (green region) and the pattern collapse (white region). The top inset show SEM images (i–iv) of the elongated kirigami pattern electrode under different strains and the bottom inset is the unit cell of the kirigami pattern. Reproduced with permission.^[146] Copyright 2015, Macmillan Publishers Limited. (f) Electrical properties of kirigami graphene spring in approximately 10 mM KCl before stretching (blue) and when stretched by 240% (orange). Reproduced with permission.^[147] Copyright 2015, Macmillan Publishers Limited.

Through a combination of folding and cutting process, Song and his colleagues further developed a kirigami-based LIBs.^[145] In the process of creating kirigami batteries, a cut-N-shear pattern is utilized, where the creases of the folded foil are symmetrically cut and subsequently the shear of the folded structure makes the kirigami finished (Figure 2.8c). As a result, the larger batteries are transferred into various smaller units connected by cut current collectors. By rotating the connection part, the neighboring units are capable of accommodating the stretch and inducing no out-plane deformation when separating from each other, which endows great stretchability (over 150%) to the fabricated LIBs that can even power a Samsung Gear smartwatch. More recently, instead of using the above-mentioned origami variant kirigami method, studies shift to direct kirigami method to achieve resilience of membrane electrodes by constructing specific kirigami patterns in membrane electrodes from a micro angel (Figure 2.8d).^[147-149] Figure 2.8e shows GO-PVA nanocomposite with a network of incisions made through the photolithography process. The resulted composite sheets prevent the unpredictable local fracture and can withstand the strain up to 370% from an original 4%.^[148] Using optical lithography, a microscopic sheet of graphene paper as an electrode for transistor is carefully cut and developed into in-plane kirigami springs and out-of-plane kirigami pyramid.^[147] Although the stretchable graphene electrode is only one-atom thick, the kirigami graphene spring can be stretched to 240% (Figure 2.8f) and the kirigami graphene pyramid survives after 10,000 times of open-and-close cycles. Both studies show the membrane kirigami strategy as a simple yet powerful approach for the development of stretchable EES devices. Just as a piece of paper can be folded and cut into cranes, snowflake or airplanes, origami and kirigami designs for

membrane electrodes can be applied to take on many different configurations of stretchable EES devices and may open up many new applications.

2.4.4 Textile fiber structure

Along with the human history, textiles or clothes consist of interlaced fibers (whether synthetic or natural) have been worn on human body to protect humankind against the alteration of the external environment.^[150] In fact, several synthetic polymer fibers have superior tensile properties than natural rubber. Spandex, as an example, is capable of being elongated to 500% of its original length and completely returns back to its initial shape after release of the fibers.^[151] Because of the nonintrusive properties, the smaller and lighter textile fiber structures have become one of the desired configurations for fabrication of future electronics or EES devices that require omnidirectional flexibility.^[152-156] Generally, there are four levels (i.e., fibers, yarns, fabrics and textile products) in hierarchical structures of textiles (Figure 2.9a-d). Despite the electric capabilities and highly elastic properties can be introduced into textiles, the most effective and unobtrusive method remains engineering electronic functionalities into textiles at fiber level without losing the accompanying desired attributes such as texture and comfort.^[133, 157]

Figure 2.9 The hierarchical structure of textiles. (a) Fibrils: polymer chains organized in dispersed crystalline and amorphous domains. (b) Fibers: high aspect ratio fibers made from natural and

synthetic polymers in many cross-sectional shapes. (c) Yarns: assembled from fibers through twisting or wrapping processes. (d) Fabrics: woven from yarns with an enormous variety of patterns. (e) Textile products. (f) Elastomer-CNT sheath-core fibers. Reproduced with permission.^[157] Copyright 2015, American Association for the Advancement of Science. (g) Stretch ratio of helically coiled structure.

As a basic element of textile, polymer fibers are usually electric insulation. But a recent development in material science and engineering technology entitles such fibers with excellent electrical performance, which paves the way for the inconspicuous introduction of electrical characteristics into the textile to produce textile electronics (e-textile).^[56, 158] From this, many efforts have been made to wrap such elongated fibers with a conductive thin film, where highly stretchable conductors and EES devices were obtained.^[151, 159-163] Liu et al.^[160] introduced this design method in carbon nanotube films on a pre-stretching rubber fiber cores, in which large pre-strain up to 1400% can be employed to prepare hierarchically buckled sheath-core fibers (Figure 2.9e) for superelastic conductors. Impressively, the resistance change is less than 5% even when the fiber is stretched to 1000%.

Additionally, the inherently stretchable properties of the fiber material, the stretchability of textiles can also come from the diverse stretchable structures which are fabricated by various assembling methods (e.g., twisting or interlacing) at the fiber level.^[87, 164, 165] Figure 2.9c shows yarns fabricated by coaxially twisting fiber bundles into helical spring structures, which have the ability to resist tensile deformation and completely recover when unloading due to resilience. The maximum stretch ratio ($\nu_{sr}^{\max}$) of the fibers is expressed as:

$$\nu_{sr}^{\max} = \frac{1}{\sin \theta} \quad 2-9$$

where θ is the pitch angle (Figure 2.9f).^[133, 164] The equation states that the maximum stretch ratio for helical spring structure is in inverse proportion to $\sin \theta$ and the helical spring structure with a smaller pitch angle is expected to have a higher stretchability. For instance, when $\theta = 30^\circ$, the yarn with such a structure can be stretched to 200% without plastic

cracking. Further decreasing the pitch angle will enlarge the maximum stretch ratio above 200%. Also, it is worth noting that the fiber can still undertake an elastic deformation deriving from the inherent properties of materials provided that the applied force is beyond the elastic range of spring structure.^[166]

Besides the choice of material and structure at a fiber level, design factors at another hierarchical level including the size and number of fibers inside a yarn, fabric structure (Figure 2.9d) and interlaced layers may also affect the tensile properties in the final products. This from another side also means an enormous variety of structures are possible in a textile structural configuration for highly stretchable EES devices. Many related theoretical and experimental studies have been performed to assess the mechanical properties of textiles from micro-scale to macro-scale, wherein the detail design-related dynamic analyses at each level are comprehensively described in some excellent work.^[164, 167-169] Owing to the diversiform arrangement and controllable fabrication process, it is not difficult to foresee the stretchable EES devices with the textile structure is worn on a human body while powering various wearable electronics.

2.4.5 Other stretchable structures

Apart from the aforementioned structures, other stretchable configurations, although not specifically mentioned, are also possible to find niches in offering an effective stretchability to ESDs. One such approach is randomly distributing elongated conductive nanowires (NWs) beneath the surface of the elastic substrate to construct a percolating network (Figure 2.10a).^[170-173] In a percolating network, the entangled nanowire in the structure is competent to prevent the loss of connection in the junction of nanowires by reconstructing themselves in a manner by increasing its length and shrinking its width to adapt to the externally applied strain, thereby retaining the highly conductive pathway for electron transfer during the stretch. Owing to the unique fishnet-like structure as shown in Figure 2.10b, the electrode based on AgNW percolating networks with a stretchability of 20% was achieved and further increment in the nanowire length can lead to an enhancement of the tensile properties in such electrode.^[22, 41]

Figure 2.10 (a) SEM images of Ag nanowires grown by the successive multistep growth (SMG) method after one- and seven-times growth (left) and the COMSOL numerical simulation of a longer NW network structure undergoes the larger deformation under the same stress (right). Reproduced with permission.^[40] Copyright 2012, John Wiley & Sons, Inc. (b) Schematic illustration of the deformation of an ideal nanowire network wherein the nanowire junctions are intact during uniaxial stretching. Reproduced with permission.^[22] Copyright 2014, American Chemical Society. (c) Images of open mesh using paper to present the stretchability of nanomesh structure (upper) and SEM images of Au nanomesh/PDMS electrode under strains of 50%, 100% and 150% (bottom). Reproduced with permission. Copyright 2014, Macmillan Publishers Limited. (d) The fabrication process of multifunctional nano-accordion structures using interference lithography. (e) SEM images of the 30 nm thick ZnO nano-accordion structure before and after being stretched to 51% strain. Reproduced with permission.^[174] Copyright 2015, Royal Society of Chemistry.

Designing a nanomesh structure into electrodes is another useful approach to acquire highly stretchability.^[54] The mechanism of the stretchable nanomesh structure relies on two aspects, as illustrated in Figure 2.10c. When a low strain is applied, the open nanomesh structure undertakes an in-plane motion of the mesh similar to the process of the percolating network. Whilst for a large strain, the mesh performs an out-of-plane elastic buckling behavior until rupturing into patches, enabling the nanomesh structure more stretchable (withstand a maximum strain up to 160%) than that of the percolating network (lower than 100%).^[18, 54]

Other than percolating network and nanomesh strategies, the design of “nano-accordion” at device level have been recently employed to develop stretchable electrodes, as shown in Figure 2.10d.^[53] In the fabrication process of nano-accordion structure, a photoresist template with a comb-like pattern is firstly prepared using interference lithography (Figure 2.10d). Through atomic layer deposition, a conductive ZnO thin film is subsequently deposited on the surface of the photoresist template to create accordion-fold geometry. After dissolving the template, the ZnO accordion-like electrode is finally transferred and bonded to a PDMS substrate. The as-fabricated electrode is capable of repetitive expansion and contract without systematic failure (up to 51% strain), like the bellows of an accordion. In the illustration above, it is obvious that the new emerging structural designs at both material and device levels will offer a simple and versatile route to accelerate the development of the stretchable EES devices.

2.5 Prototypes of stretchable energy storage devices

Up to now, the development of stretchable EES devices is still at an early and exploratory stage, and many works on this field only acquire elasticity in a certain part of the EES devices, i.e., stretchable electrolyte,^[175-177] stretchable current collectors^[39, 178, 179] and stretchable electrodes,^[47, 64, 116] etc. To fully assess the mechanical and electronic performance of EES devices, it is necessary to integrate all these stretchable components into a device for practical application. Along this direction, based on previously described electrode materials and structural design, some novel prototypes of stretchable supercapacitors and LIBs that can absorb large strain without substantial deterioration in electrochemical performances have been successfully demonstrated in recent years.

2.5.1 Stretchable supercapacitors

Since the invention of supercapacitors in 1966 by General Electric and their commercialization for a kind of important ESD by Nippon Electric Company in 1978, conventional bulky supercapacitors witness great progress in terms of energy density,

power density and cycle life.^[180] However, stretchable supercapacitors for powering stretchable electronics are just beginning to take off and the development of stretchable supercapacitors are far behind that of the conventional supercapacitors.

Figure 2.11 (a) Fabrication steps for buckled CNT macrofilms, comprising (i) pretraining PDMS substrate, (ii) exposure to UV light, (iii) transferring CNT macrofilm to PDMS substrate, and (iv) under release condition. Reproduced with permission.^[55] Copyright 2009, John Wiley & Sons, Inc. (b) Schematic illustration of assembling procedures for stretchable supercapacitors based on wave-shape SWCNT film on PDMS substrate. (c) Top: SEM images of buckled SWCNT film without strain (top left) and with 140% strain (top right). Middle: Illustration of electron transport pathways in continuous reticulate network structure different strains. Bottom: Galvanostatic charging/discharging curves of the stretchable supercapacitor at a constant current of 10 A g⁻¹ with and without strains. Reproduced with permission.^[35] Copyright 2013, John Wiley & Sons, Inc. (d) Left: Photographs of the Na₂SO₄-aPUA(4)/PAAM hydrogel electrolyte elongated two-directionally (insert is the photo of initial hydrogel). Middle: Photo of six red LED powered by three series

connected supercapacitors. Right: constant charge-discharge curves of the CNT@MnO₂/Na₂SO₄-aPUA(4)/PAAM/CNT@MnO₂ stretchable supercapacitors under varying tensile strains. The charge-discharge current density is 0.5 mA cm⁻². Reproduced with permission.^[70] Copyright 2015, Elsevier B.V.

The first stretchable supercapacitor was pioneered by Yu et al. in 2009, wherein the stretchable electrodes is made of two wave-shape single-walled carbon nanotube (SWCNT) macrofilms and the PVA gel electrolyte functions as both electrolyte and separator.^[55] The key of realization of stretchability in this supercapacitor is the utilization of wave-like structure strategy to construct the stretchable electrode by bonding SWCNT macrofilm onto the PDMS substrate with pre-stretch of 30% followed by a releasing process (Figure 2.11a). The specific capacitances of the as-prepared supercapacitor remain nearly unchanged with 0% and 30% applied force after 1000 charging-discharging cycles at a current density of 1 A g⁻¹, indicating its good mechanical and electronic stability. Despite this, there is one drawback in the design of this supercapacitor. The employment of liquid-based organic electrolyte requires a polymer separator to prevent internal electrical shorts, but the relatively inextensible separator suppresses the total stretchability of this stretchable supercapacitor.

To make full use of the bulking structure and achieve the desired stretchability of over 100%, our group firstly utilize H₂SO₄-PVA gel electrolyte as both the stretchable electrolyte and separator to constructing highly stretchable and integrated supercapacitors.^[35] Further study by Zhao et al. also verify that PVA-based gel electrolytes with a proper molecular weight of PVA and mole ratio of electrolyte in PVA possess a high fracture strain at 410% and display a small plastic deformation (5%) after 1000 stretch-release cycle at 100% strain.^[48] By using H₂SO₄-PVA gel electrolyte accompanying with bulking SWCNT film electrode with a particularly continuous reticulate architecture, the as-prepared supercapacitors sustain the stable specific capacitances in the range of 48-54 F g⁻¹ with or without 120% applied strain (Figure 2.11b&c). Following our groups' work, Zhang and coworkers optimize the electrodes by *in-situ* electrochemical polymerization of PANI (pseudocapacitor) on the SWCNT films and nearly double the specific capacitance

of stretchable supercapacitors up to 106 F g^{-1} .^[68] For common H_3PO_4 (or H_2SO_4)-PVA hydrogel electrolytes, it is essential for them to absorb enough aqueous electrolyte to guarantee the good ionic conductivity, but too much aqueous electrolyte in PVA polymeric matrix dramatically decrease their mechanical strength. In this respect, a novel Na_2SO_4 -anionic polyurethane acrylates/polyacrylamide (Na_2SO_4 -aPUA/PMMA) hydrogel electrolyte, which exhibits ultrahigh conductivity (36 mS cm^{-1}), extensibility ($>1000\%$) and even after absorbing 500% water (36 mS cm^{-1}) even after adsorbing 500 wt% water (Figure 2.11d), was developed to replace PVA gel electrolyte for stretchable supercapacitor device.^[70] Owing to the high ionic conductivity and mechanical strength of Na_2SO_4 -aPUA/PMMA hydrogel electrolyte as well as the higher reversible capacitance of CNT@ MnO_2 films than that of CNT films, the bulking supercapacitor adopting wave-like strategies achieves excellent specific capacitance of 201.1 F g^{-1} and maintain capacitance of 91.5% after 3000 cycles at a tensile strain of 150%, which represents a high value ever reported for stretchable supercapacitors.

Another widely employed approach to construct stretchable supercapacitors is to use the textile fiber structure to enhance the stretchability of supercapacitors. By dyeing stretchable fabric sheets with SWCNT ink through a simple dip-and-dry process, highly conductive textiles as a platform for stretchable supercapacitor were firstly demonstrated by Hu et al.^[56] Figure 2.12a shows negligible change appears in the specific capacitance ($\sim 0.48 \text{ F cm}^{-2}$) of the textile supercapacitor before and after being stretched under 120% strains for 1000 times. Also, it is found that further incorporation of the pseudocapacitor materials into these stretchable textiles could result in 24 times increase in the areal capacitance of the device. Besides CNT, other capacitive materials like polypyrrole (PPy),^[64] active carbon^[182] and reduced graphene oxide^[47] have been also implanted into the textile to fabricate the stretchable electrodes of supercapacitors. Via a chemical polymerization or facile dyeing followed by electropolymerization process, the nylon Lycra® fabric electrodes coated with PPy or PPy/reduced graphene oxide composites exhibit enhanced cycling stability as well as a higher capacitance at respective strains of 60% and 50% when compared with the performance without applied force.^[47, 64] The study from Yu et al. also validates the pre-straining of textiles decorated by CNT and MnO_2 nanoparticles can significantly enhance

the specific capacitance of the stretchable supercapacitor due to the reduction in resistance deriving from the alignment of the CNT and textile fibers in the direction of tensile force, indicating the textile-based supercapacitors are well-suited for wearable ESDs that will experience mechanical tensile force during operation.^[183]

Figure 2.12 (a) Top: Schematic of the 3D porous microstructure of SWCNTs dip-coated on cotton textiles. Bottom: Specific capacitance of a stretchable supercapacitor made from SWCNT coated fabric, before and after experiencing 100 cycles of 120% tensile strain, at a current density of 1 mA cm^{-2} . The left inset shows the SEM image of the SWCNTs coated fabric sheet. The right inset shows a sketch map of the stretchable supercapacitor with SWCNT coated fabric electrodes and stretchable fabric separator (top), and a photo of the supercapacitor under 120% strain (bottom). Reproduced with permission.^[56] Copyright 2010, John Wiley & Sons, Inc. (b) Top: Optical microscope image of a coiled CNT/nylon electrode fiber. Bottom left: Capacitance retention as a function of the applied strain (maximum up to 150%) in a stretch-release cycle. The inset optical

image is the stretch-release process of the coil fiber supercapacitor. Capacitances obtained from cyclic voltammetry (CV) curves at a scan rate of 50 mV s^{-1} . Bottom right: CV curves measured at the scan rate of 50 mV s^{-1} during a stretch-release cycle up 120% strain in comparison with the CV curve obtained without strain. The stretch rate is $17.1\% \text{ s}^{-1}$. Reproduced with permission.^[181] Copyright 2015, John Wiley & Sons, Inc. (c) Schematic illustration of the preparation process for a coaxial fiber-shaped supercapacitor with high stretchability. Reproduced with permission.^[181] Copyright 2013, John Wiley & Sons, Inc. (d) Top: SEM images of buckled CNTs-surrounded elastic wire with 30%, 60% and 100% pre-strains. Bottom: Digital photos of a twisted CNT-wrapped wire-shaped supercapacitor before and after being elongated to 370%. Reproduced with permission.^[163] Copyright 2015, John Wiley & Sons, Inc.

Instead of endowing supercapacitor with resilience at the fabric level, designing stretchable fibriform supercapacitors is a bottom-up approach towards more elastic textile-based supercapacitors. One of the most common methods is managing the wire-shaped supercapacitor into a coiled spiral structure as shown in Figure 2.12b.^[58, 184, 185] In 2013, a hierarchical all-graphene hybrid core-sheath fiber was prepared and the wire-shaped supercapacitors twined into a spring-like structure show well compressible (ca. 50%) and stretchable (ca. 200%) properties while presenting similar charge-discharge features to that of the initial one.^[87] Other stretchable fiber-shaped supercapacitors were also devised by combining CNT sheets or fibers with elastic polymers.^[59, 159, 163] Using textile fiber structure accompanying with a prestraining-then-releasing approach, the CNT fibers in a sinusoidal wavy shape enable the corresponding stretchable fiber supercapacitor without sacrificing specific capacitance after stretching by 100% for 20 cycles (Figure 2.12c).^[159] Fiber-shaped supercapacitor fabricated by wrapping elastic fiber with aligned CNT sheets maintains high capacitance of $\sim 18 \text{ F g}^{-1}$ after 100 mechanical stretch-release cycles with the maximum strain up to 75%.^[59] Subsequently applying a pre-stretched elastic wire, a buckling structure of highly overlapped CNT sheets appears in the coating layer (Figure 2.12d) and the resultant stretchable wire-shaped supercapacitors exhibit an enhancement in both the elasticity (up to 350%) and device capacitance (30.7 F g^{-1}).^[163]

Apart from above-mentioned ideas, stretchable-tolerant strategies including bridge-island design,^[57] stretchable stainless steel mesh,^[96, 186] water surface assisted method,^[67] and

modified wave-like structure^[61, 66, 78, 187] have been recently fused into stretchable supercapacitors for specific requirements. Figure 2.13a shows the bridge-island design of stretchable micro-supercapacitor arrays with planar SWCNT electrodes connected by the long and narrow serpentine Au interconnections. After being encapsulated with an ion-gel-type electrolyte, the formed micro-supercapacitor array show stable energy density and power density even at the current density of 50 A g^{-1} when being stretched up to 30% without any noticeable degradation.^[57] Using an intrinsic stretchable stainless steel mesh, the fabricated solid-state supercapacitors achieve remarkable capacitance retentions of 87% under 20% strains at a very high charge-discharge current of 10 A g^{-1} after 10000 cycles mainly due to the high conductivity of the stainless steel mesh.^[186]

Figure 2.13 (a) Top left: Photograph of stretchable serpentine-based micro-supercapacitor arrays. The inset is the transferred micro-supercapacitor arrays. Top right: A magnified image of a single micro-supercapacitor with serpentine interconnections. Bottom: Photographs of a complete 3×3 micro-supercapacitor array at relaxed state (left) and 30% strained state (right). Reproduced with permission.^[76] Copyright 2013, American Chemical Society. (b) Schematic drawings of the cross-sectional electrode structure and corresponding strain distribution by finite element modeling analysis for planar (top), wrinkled (middle) and suspended wavy-like structure (bottom). (c) Peak strain distribution among planar, wrinkled, and suspended wavy-like structure at various strain levels. Reproduced with permission.^[187] Copyright 2013, John Wiley & Sons, Inc.

Traditional prestretching-then-releasing method usually leads to a randomly distributed wrinkled structure in the elastic substrate, inducing stress concentration in the area of interface between electrode materials and stretchable substrate. To alleviate this problem, suspended wavy graphene microribbons have been designed to fabricate highly stretchable microsupercapacitors (Figure 2.13b). The stress in the electrode material can be obviously

reduced in a suspended structure as compared with wrinkled and in-planar structure (Figure 2.13c). When stretch by 100%, the performance of the as-prepared microsupercapacitor remains virtually unaffected.^[187] Other modified wave-like structures use a predetermined wavy-shaped Cu and Ni-foam as a temple to fabricate wavy-shaped graphene electrodes for stretchable supercapacitor and the as-fabricated wavy shaped graphene supercapacitors can be stretched 40% and 30%, respectively. As an additional property, the transparent (50-60% at 550 nm) has also been integrated into the wavy-shaped supercapacitor with 40% stretchability, which is a very valuable characteristic for various power-integrated optoelectronic systems.^[61]

2.5.2 Stretchable Batteries

Figure 2.14 (a) Top: Overview of the structures in the serpentine battery. Bottom left: A battery to power a red LED while relaxed and being biaxially stretched to 300%. Bottom right: Illustration of interconnects with serpentine geometries (black line is the first level serpentine and yellow line is the second level serpentine). Reproduced with permission.^[20] Copyright 2013, Macmillan Publishers Limited. (b) Schematic illustration of the multilayered structure of a super-stretchy LIB.

Reproduced with permission.^[101] Copyright 2015, John Wiley & Sons, Inc. (c) Photograph of stretching a kirigami LIB. Reproduced with permission.^[145] Copyright 2015, Macmillan Publishers Limited.

Researches on stretchable LIBs are relatively limited as compared to stretchable supercapacitors. This could perhaps be the result of the more stringent requirements for device packaging. The emergence of stretchable LIBs is landmarked by Liu et al.'s work. In their study, electrode material (active materials, carbon black, and binder) was mixed in poly(ethylene oxide) (PEO) solution; the liquid mixture was drop-casted into film electrodes that were then pressed together with PEO-based solid electrolyte film. PEO as a binder took up a considerable portion of electrode mass, serving as the stretchable mechanical backbone, which was the essence of realizing stretchability.^[188]

Rapid advancement started in 2013, after which various forms of stretchable LIBs were demonstrated, mainly film-shaped and wire-shaped. Amongst film LIBs, Xu et al.'s pioneering work based on the bridge-island structure using conventional electrode materials proved the power of interconnecting geometry engineering. The full battery consisted of an array of 10*10 cell disks connected electrically in parallel, encapsulated in highly stretchable silicone substrates. Each disk was packed in the conventional configuration: LCO and LTO slurries on Al and Cu thin films as cathode and anode respectively, with PEO-based gel electrolyte sandwiched in between (Figure 2.14a). The metallic interconnects between each disk adopted a novel 'self-similar serpentine' structure, where the primary serpentine shape was made up of finer secondary serpentine shape (Figure 2.14a). This special geometry substantially reduced strain experienced by metal wires, enabling stretchability up to 300%. The battery delivered an area-specific capacity of $\sim 1.1 \text{ mAh cm}^{-2}$ in the first cycle and $\sim 0.8 \text{ mAh cm}^{-2}$ after 20 charge/discharge cycles. This stretchable LIB was also coupled with a wireless charging component, employing electromagnetic induction from a charging coil to a receiving coil. The intricate wire patterns and small sizes of electronic components enabled seamless assembly in the stretchable system without sacrificing either electrochemical or mechanical performance of the battery. Such an integrated charging and delivering system is highly favorable for

biomedical devices and wearable electronics in view of minimal interruption of surrounding tissues during charging.^[20] In fact, a complete wearable electronic system was recently demonstrated, powered by stretchable LIBs. This wearable, self-powering system was designed to monitor body movements and transmit signals wirelessly. Wrist-worn triboelectric generator harvested mechanical energy from arm motion and converted to electricity, which charged nearby LIB and constantly powered the entire system. The stretchable LIB was constructed from two flexible sheet LIBs based on flexible current collectors (carbon fabrics) interconnected by elastic, conductive nylon (C-Nylon) fabric. In other words, stretchability was realized from the interconnecting material instead of the battery itself. C-Nylon could be stretched up to 100% without significant reduction in conductivity, rendering a 100% stretchability to the assembled LIB wrist band.^[189]

The former two examples rely on interconnect engineering towards stretchability. Tackling electrode stretchability, prestretch-and-release was successfully employed in Weng et al.'s work, where sheet electrodes were adhered to pre-stretched PDMS substrates to give a buckled structure upon release of prestrain (Figure 2.14b). A novel sandwich structure was adopted for sheet electrodes, consisting of active materials (CNT/LTO as anode and CNT/LMO as the cathode) between two CNT sheets, infiltrated with uncured PDMS fluid that could bond strongly to a pre-strained PDMS film (Figure 2.14b). The sandwich structure was believed a core reason for stable electrochemical performance under severe stretching. The two CNT sheets restricted migration of active material nanoparticles, thus the electrode deformed as a whole during stretching/releasing. In addition, capacity retention of sandwich electrode significantly surpassed that of electrodes made of active material blends on single CNT sheet, showing a clear superiority of sandwich electrodes. With a prestrain of 450%, the output energy of the full battery showed minor decay at a strain of 400%, and 97% was maintained after 200 stretching cycles.^[103] While this prestretch-and-release approach is frequently used to construct stretchable devices, the active material and current collector (or a composite of them) must be flexible/bendable in the first place in order to conform to a buckled shape. This requires material innovation with accompanying cost increment and slow commercialization. In contrast, a more versatile approach would be the kirigami method. As demonstrated in Song et al.'s work,

conventional materials (graphite on Cu foil, LCO on Al foil, liquid electrolyte) and laminated cell structure can be borrowed from conventional LIB configuration, except that all layers need to be cut in a predefined shape according to kirigami patterns. After sealing of side edges and injection of liquid electrolyte, the originally flat battery was folded to impart stretchability. Three kirigami patterns were tested and cut-N-twist was taken as an example (Figure 2.14c). Figure 2.14c displays photos of the battery at different stress levels. The battery showed virtually no difference in charging/discharging behaviour at most compact state and most stretched state (more than 100% elongation), with a stable capacity of 30 mAh (specific capacity of $\sim 316 \text{ mAh g}^{-1}$ based on graphite mass and 20 mAh g^{-1} based on total cell mass) at C/3 cycling rate. Impressively, the maximum output power remained unvaried (2.75 W g^{-1}) over 3000 cycles of repeated stretching with a maximum strain of 90%. The kirigami method effectively circumvented strain developed in materials, attributing to which no cracks were observed on current collectors after 100 cycles of stretching.^[145]

Figure 2.15 (a) Schematic illustration of the preparation for stretchable LIBs based on MWCNT/LiMn₂O₄ composite fiber cathode and MWCNT/Li₄Ti₅O₁₂ composite fiber anode. Reproduced with permission.^[104] Copyright 2014, Royal Society of Chemistry. (b) Top left: charging and discharging curves before and after being stretched to 600% at a current density of 0.1 mA cm^{-1} . Bottom left: photograph of stretchable fiber-shaped LIBs woven into a bracelet textile. Right: photographs of super-stretchy fiber-shaped LIBs woven into a knitted sweater under folding and stretching. Reproduced with permission.^[104] Copyright 2014, Royal Society of Chemistry. (c)

A long wire-shaped LIB with a length of 200 cm. Reproduced with permission.^[63] Copyright 2014, John Wiley & Sons, Inc.

The other panel of stretchable LIB prototypes is wire-shaped battery, primarily developed by Peng's group. The group firstly fabricated a fiber-shaped LIB by wrapping wire electrodes around an elastic fiber substrate. Figure 2.15a summarizes the fabrication process and final cell structure. In brief, MWCNT sheets were drawn from vertically aligned CNT forest, soaked with MWCNT/LMO and LTO nanoparticle suspensions, and then rolled into composite yarns. The cathode and anode yarns were kept parallel at a small distance and wrapped around an elastic heat-shrinkable tube. A full battery was finally produced through coating with gel electrolyte and sealing in another heat-shrinkable tube. Such wire-shaped LIB could deliver a high specific capacity of 0.28 mAh m^{-1} (138 mAh g^{-1} with respect to anode mass) at 0.01 mA , a volumetric energy density of 17.7 mWh cm^{-3} and a power density of 0.56 W cm^{-3} based on the total volume of electrodes. When the battery was stretched to 100%, more than 90% of capacity remained, and capacity decayed gradually to 80% over 200 cycles of repeated stretching.^[190] In a later work, heat-shrinkable tube was substituted with more elastic PDMS fibre and encasing membrane, which greatly boosted mechanical stretchability. By increasing the radius of PDMS fibre or reducing the separation between two fibre electrodes, the maximum strain of such fibre-shaped battery could be further enhanced up to 600% (with 88% capacity retention) (Figure 2.15b).^[104] Following on, the group modified wrapping strategy and produced a bare CNT electrode with stretchability up to 300%. In this prototype, several composite yarns were directly twisted together to give a spring-like electrode without the aid of elastic substrates (Figure 2.15b). The resultant battery delivered a high length-specific capacity of 2.2 mAh m^{-1} (92.4 mAh g^{-1}) at 0.1 mA cm^{-1} .^[63] The main advantage of this twisting strategy is the elimination of non-electrochemically active substrate, which gave rise to around 10 times improvement of length specific energy and power densities. In comparison, the use of elastic substrates renders more freedom in device diameter, loading density, and stretchability; higher stretchability is also attained with the aid of elastic substrates. For all the three prototypes, the use of composite yarns/fibers was believed to benefit stable charging/discharging behaviours under mechanical stretching, where CNTs acted as both mechanical skeleton

and current collector maintaining electrode morphology as well as ensuring fast electronic transport, respectively.^[104] An additional merit of wire-shaped construction is scalability (200 cm length was achieved),^[190] which would be beneficial for weaving wearable textiles, as demonstrated in Figure 2.15c.

2.6 PhD in Context of Literature

Although some progress has been made on the flexible and stretchable EES devices, there are still some critical issues, such as the mismatch between electrode and electrolyte/substrate, the lack of customizability, and the limited energy storage capability compared with conventional devices. Normally, current methods for fabricating flexible EES devices require depositing active materials with designed structures on the elastic substrates. However, the required structures are merely compatible with active materials that are robust enough, mainly CNTs and graphene materials, to form required structure. The limitation of materials selection and material loading hinders the further increase of performance of the as-prepared EES devices. Furthermore, the mismatch in terms of resiliency between active materials and elastic substrate often results in stress concentration in the interface, which causes a decrease in the long-term stability of EES devices during the stretch-and-release process. Moreover, the simultaneous expansion of the active materials in the charging/discharging process will also aggravate the interface mismatch and the performance decay of EES devices during mechanical deformation. Besides, currently developed flexible and stretchable EES devices are mainly based on a predesigned configuration, which cannot satisfy the customizable needs (e.g., arbitrarily shaped demand and omnidirectionally stretchable design) in different wearable and bio-integrated scenarios. To address these issues, there is a need to redesign mechano-adaptive electrode materials and device structures for fabricating highly flexible and customizable EES devices.

This work is to develop a new strategy to fabricate mechano-adaptive electrode and flexible EES devices with high performance including high stretchability, customizability, stability and high energy storage capacity. The proposed new strategy is through the innovations in

both electrode materials and device structures. The innovations in the electrode materials enhance the tensile strain and mechanical stability of the mechano-adaptive electrodes, while the innovations in the editable and customizable device structures accompanying with the electrode materials and reduce the peak strains on the electrode. The combination strategies make the stretchable EES devices with high energy density, high mechanical robustness and sturdy integration. The mechano-adaptive electrodes with customizable EES devices provide a new platform for flexible and customizable EES devices. Based on it, three kinds of composite electrode were developed: one for stretchable supercapacitors with editability, the other for the stretchable supercapacitors with enhanced energy storage performance, and the rest is for flexible high-voltage LIBs with enhanced stability.

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Chapter 3

Experimental Methodology

In this chapter, the content in the experimental methods and the principle of test instruments are discussed. The EES material and device characterizations are divided into three parts: the material characterization, mechanical characterization and electrochemical characterization. The material characterization is mainly focused on the morphology and chemical composition of the materials and electrodes. The mechanical characterization and electrochemical characterization are used to analyses the strain and the electrochemical performance of the electrodes and EES devices. The mechanisms and the principle behind these surface detection, mechanical and electrochemical testing are also present here.

3.1 Material characterization

Crystal structures of materials were investigated using thin film XRD (LabX XRD-6000, Shimadzu) with Cu K α radiation. The theta-2theta configuration was taken for thin film measurements, with a tilt angle of 0.5° for better signals. Thin film samples were prepared by spreading ethanol dispersion of nanoparticles dropwise on glass slides with concurrent evaporation of ethanol. Surface elemental analysis was obtained by X-ray photoelectron spectroscopy (XPS) on a VG ESCALAB 220I-XL system equipped with a monochromatic Al K α (1486.6 eV) source and a concentric hemispherical energy analyzer. All samples were subjected to drying at 100°C for 2h to evaporate trace water before measurement. Microscopic morphologies of various nanoparticles and nanocomposite electrodes were measured by using SEM (JEOL JSM-6340F or 7600) and TEM (JEOL 2010 HR or 2010 UHR). Surface area and pore size was characterized through N₂ adsorption-desorption in ASAP TriStar II 3020 (micromeritics). Before analysis, powder samples were dried in oven overnight at 80°C, and degassed at 100 °C for 12-20 h. Three to four tests were conducted for each synthesizing condition, and the average was taken for trend analysis. Electrical conductivity of vacuum-filtered films was tested by a four-probe resistivity measurement system. Three points were measured for each film of a specific composition.

3.2 Mechanical characterization

Tensile tests of bare electrode films were conducted using Mechanical Tester MTS Model C42. Freestanding film electrodes were cut into rectangles of dimensions 5-15 mm $\times$ 30-40 mm. The films were then pasted on homemade paper frames with 40 mm $\times$ 40 mm outer edges and 20 mm $\times$ 20 mm inner edges (shown in Figure 3.1a). Width and thickness of each sample were measured before testing. After the paper frame attached with vacuum-filtered film was clamped on the tensile tester, side edges of the frame were cut with scissors (Figure 3.1b). The tensile tester used a 250 N load cell and a 100 N screw action grip. Extension rate was set at 0.001 mm s⁻¹, corresponding to a strain rate of 5 $\times$ 10⁻⁵ s⁻¹ (for 20 mm gage length). Tests were manually stopped when load dropped to (below) zero. Mechanical tests of EES devices were conducted in a similar manner.

Figure 3.1 Experimental setup for mechanical tests. Images of samples clamped on mechanical tester with indication of paper frame dimensions (a), and scission location before testing (b).

3.3 Electrochemical characterization

The CHI 660d (Shanghai Chenhua) and Solartron (Ametek Scientific Instruments) potentiostat were used to measure the electrochemical performance of the as-prepared electrodes and the full EES devices. Electrochemical performance of as-prepared electrodes was characterized in aqueous electrolyte using electrochemical workstation in a three-electrode system, where Pt serves as counter electrode, Ag/AgCl serves as reference electrode and vacuum-filtered film as working electrode. Cyclic voltammetry (CV) and galvanostatic (GV) charge-discharge tests were conducted at varying scanning speed and scanning current in a potential window between 0 and 0.8 V. For the electrochemical characterization of symmetric EES devices, the same equipment was used. The two electrodes in an EES device were connected as working electrode and counter/reference electrode, respectively. The electrochemical impedance spectroscopy (EIS) was used as a nonintrusive technique to test the resistance changes in full cell SCs during mechanical test. By applying a sinusoidal excitation signal of 10 mV, the impedance spectroscopy was recorded in the open circuit potential (OCP) and operated in a range between 10,000 and 0.01 Hz. The obtained results were fit with an equivalent electric circuit using Zview

software (Scribner Associates, Inc.)

3.4 Principles behind Characterization Techniques

3.4.1 X-ray Diffraction

Figure 3.2 Schematics showing the Bragg's diffraction model in the crystal plane.

X-rays are classified as electromagnetic waves with wavelength from 0.1 nm to 10 nm, which fall in the similar range as that of the interatomic spacing in materials. Therefore, X-ray diffraction (XRD) technique is widely used to determine the crystal structure and lattice information of the materials. As shown in Figure 3.2, in materials with crystallinity, periodical regular arrangement of atoms with a constant spacing will cause the diffraction of the incident beams and the reflected beams with constructive patterns are described by Bragg's law:

$$2d \sin \theta = n\lambda \quad 3-1$$

where d is the distance between crystal planes and λ is the wavelength of incident X-ray source. Using this equation, any constructive patterns at certain diffraction angle θ are reflected as diffraction peaks and can be used to calculate the crystal lattice plane distance.

Figure 3.3 Powder XRD setup: (a) schematics showing the setup of different components inside the apparatus; (b) the actual components inside the system.

In the thin film XRD setup, θ - 2θ configuration is adopted. Figure 3.3 shows the operation scheme. Briefly, the incident X-rays from X-ray tube will pass through the primary optics to minimize the divergence. After interaction with the specimen, the reflected X-rays pass through secondary optics to reduce air scattering and divergence and finally collected by

the detector. In real measurement, the X-ray tube is fixed, while the samples are rotated by an angle θ , the detector needs to move simultaneously with an angle of 2θ to collect the diffracted beams. Therefore, in the thin film XRD patterns obtained, the x-axis is usually 2θ .

3.4.2 Scanning Electron Microscopy (SEM)

The SEM is used to probe surface topography of materials with resolution beyond the limit of conventional microscope. Resolution is defined as the smallest distance to distinguish two objects as individual ones, according to Abbes's equation, the minimum resolvable distance d is calculated by:

$$d = \frac{0.61\lambda}{NA} \quad 3-2$$

where λ is the wavelength of energy source and NA refers to numerical aperture, which is a constant given the setup of the microscope. The large wavelength of visible light (~ 400 nm) hinders the resolution of optical microscope. For the electrons under certain accelerating voltage, the wavelength is given by:

$$\lambda = \frac{h}{\sqrt{2meV}} \quad 3-3$$

where h is the Planck's constant, e refers to electron charge, m represents electron mass, under accelerating of 5 kV, and the wavelength of the electron is around $0.173 \text{ \AA}$, yielding much smaller d value than conventional optical microscope, therefore providing resolution in nanometer range for imaging of nanomaterials.

When the electron beams interact with the specimen, there will be elastic scattering events and inelastic scattering events (Figure 3.3). In elastic interactions, only the trajectory of the electron beam is affected by the atom while the kinetic energy remains the same, if such

electrons deflected back out of the specimen, then it is termed as backscattered electrons. As for the inelastic scattering event, the energy from the incident electrons will be transferred to the atoms of specimen, which will lead to potential secondary electrons from from that atom. The topography of the surface features affects the number of secondary electrons reaching the detector; therefore, the local variation of the electron density can be used to reveal the surface morphology. In current study, the topography information of the electrode materials can be obtained by collecting the secondary electrons using the detector.

Figure 3.4 Interaction of electron beam with specimen: (a) the general interaction scheme, (b) production of secondary electrons (c) production of back scattered electrons.

3.4.3 Transmission Electron Microscopy (TEM)

Similar to SEM, TEM uses even higher accelerating voltages to produce even smaller electron wavelength to get higher resolution. There are different modes in terms of operation, such as the imaging mode and the diffraction mode (Figure 3.5). In the imaging mode, bright field images are generated by the transmitted beam with small objective aperture; while dark field image is formed when the aperture is placed around diffracted beam. The diffraction mode is obtained by removing the objective aperture and inserts the selected area diffraction (SAD) aperture, giving the diffraction pattern of the materials with diffracted beams.

Figure 3.5 Schematics on the diffraction and imaging modes of transmission electron microscope.

High resolution images (HRTEM) is obtained by using a large objective aperture to select many beams, inducing both transmitted and diffracted beams and reconstructed to yield contrast related to atomic structure of materials. In the HRTEM mode, both the images and diffraction patterns can be obtained in order to determine the crystal lattice spaces and phases. In current study, the morphology of materials is confirmed by TEM images and the

HRTEM images are collected to study lattice distance and crystal phases.

3.4.4 X-ray Photoelectron Spectroscopy (XPS)

Figure 3.6 Schematic illustration of XPS.^[1] Reproduced with permission. Copyright © 2016 Elsevier Inc.

XPS is a quantifiable spectroscopic technique to analyze the atomic structure, obtain the information about ionization energies and electron structure. After a sample is irradiated by an x-ray beam, the ejected numbers and the kinetic energy of the electrons can be quantified. This technique can help to probe the chemical composite of materials. It reveals which chemical elements and the chemical bonds between these elements are present at the surface. The advantage is that it is a non-destructive and surface-sensitive method, which is helpful to do an elemental mapping. Another advantage is that it provides quantitative

measurements and it gives us information about chemical bonding and chemical composition of a molecule. XPS can detect all elements with an atomic number of 3 and above.

The physical principle of XPS relies on the photoelectric effect. An x-ray is firstly emitted onto the surface of the samples. If the energy of x-ray is high enough, an atom will absorb it, and these photons eject electrons from the inner shells. The ejected electrons have certain kinetic energies, which are collected to analyze the chemical composition and the electronic structure (Figure 3.6). Following the law of conservation of energy, the sum of binding energy (BE) and kinetic energy of photoelectron ($KE_{electron}$) should equal to the energy of ionizing photon, which can be mathematically expressed as:

$$E_{photon} = BE + KE_{electron} \quad 3-4$$

Meanwhile, the energy of a photon is given by:

$$E_{photon} = h\nu \quad 3-5$$

where ν is the photon's frequency, and h is Planck's constant. From equations 3-4 and 3-5, the equation 3-5 can be rearranged as:

$$h\nu = BE + KE_{electron} \quad 3-6$$

Because h , ν , and $KE_{electron}$ are already, the binding energy BE is as follow:

$$BE = h\nu - KE_{electron} \quad 3-7$$

3.4.5 Fourier-transform infrared spectroscopy (FTIR)

FTIR is an established tool to obtain the infrared spectrum for characterization of structural

materials. The IR spectrum like a fingerprint of a molecule can be used to identify chemical substance. The covalent bond between two atoms is an average value because the bond behaves like two atoms connected by a vibrating spring. There are two conditions for infrared absorbance to occur: 1) the vibration of diatomic molecular leads to a change in the molecular dipole moment. This change in the molecular dipole moment can interact with the alternating IR radiation waves; 2) If the natural vibration frequency matches well with the radiation frequency, the IR photon will be absorbed. The vibration amplitude will increase, and the peak is observed (Figure 3.7).

Figure 3.7 Schematics on the occurrence of infrared absorbance.

3.4.6 Cyclic Voltammetry (CV)

Figure 3.8 The excitation signal for CV test.

CV is an electrochemical tool to measure the dynamic changes in the current by cycling the potential applied to the electrode. Figure 3.8 shows the typical reduction and oxidization voltage for CV test. The slope of the curves refers to the scan rate applied to the electrode.

A CV curve is to measure the resulting current generated by oxidation and reduction of the analyte. For a reversible reaction as follow:

The reaction rate v is given by:

$$v = \frac{dN}{Adt} \quad 3-9$$

$$Q = nNF \quad 3-10$$

Rearranged,

$$N = \frac{Q}{nF} \quad 3-11$$

Combining the equation 3-9 with 3-11, the reaction rate can be given by:

$$v = \frac{dQ}{nAFdt} = \frac{i}{nAF} = \frac{J}{nF} \quad 3-12$$

where N is the mol number occurs the reaction, F is the Faraday constant (96458 C mol^{-1}), Q is the total electric charge, n is the electron number, i is current through the electrode, A is the projected surface area of the electrode and J is the current density.

Figure 3.9 Pathway of a general electrode reaction. Ox is short for oxidant, and Red is short for reductant.

Figure 3.9 shows a general reaction occurs on the electrode. The reaction is affected by the thermodynamics, kinetics and mass transfer. The reversible reaction process is governed by the Nernst equation:

$$E = E^{\theta} - \frac{RT}{nF} \ln \frac{C_{ox}}{C_{Red}} \quad 3-13$$

Rearranged the equation 3-13, the equation can be given by:

$$\ln \frac{C_{ox}}{C_{Red}} = \frac{RT}{nF} (E^{\theta} - E) \quad 3-14$$

where E^{θ} is the standard potential of this redox couple, E is the potential at the working electrode. When $E < E^{\theta}$, the reduction occurs. This means that the reduction won't occur

until potential is sufficiently reducing.

The driving force for mass transfer is the difference in electrochemical potential. Such differences can be due to a gradient of electrical field, concentration and fluid density, which respectively corresponds to the modes of migration, diffusion and convection. The mass transfer for an electrode follows the Nernst-Planck equation:

$$J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i v(x) \quad 3-15$$

where D_i is the diffusion coefficient, $J_i(x)$ is the flux of species, $\partial C_i(x)/\partial x$ is the concentration gradient, z_i is the charge of species, F is Faraday constant, C_i is the concentration of the species, $\partial \phi(x)/\partial x$ is the potential gradient, R is the ideal gas constant, T is absolute temperature, $v(x)$ is the velocity of a volume element along the x-axis. All these values are at the distance x from the electrode surface.

Figure 3.10 A typical voltammogram of one cycle CV curves.

After reduction, the current decreases with time as analyte near electrode is depleted. Therefore, as shown in Figure 3.10, there is an oxidation peak when the electrode is undergoing an oxidation reaction (loss electrons). The current is proportional to the concentration of reactants. Once oxidized potential is reversed, a reduction peak is observed when the electrode is undertaking a reduction process (get electrons).

The Randles-Sevcik equation can be applied when the current is limited by diffusion and not by the rate of reduction/oxidation at the electrode surface:

$$i_{pa} = i_{pc} = (2.69 \times 10^5) n^{3/2} A D^{1/2} C v^{1/2} \quad 3-16$$

3.4.7 Electrochemical Impedance Spectroscopy (EIS)

EIS is a technique to probe the dynamic electrochemical processes of the electrode through applying small perturbative alternating current (AC) circuit. Based on Ohm's law in direct current (DC) circuit, the relationship between voltage (V) and current (i) is the ratio of those being the resistance (R).

$$V = iR \quad 3-17$$

Figure 3.11 AC waveform for an applied potential and the resulting current.

For AC methods, the resistance value is turned into the more generic term of impedance (Z), which includes resistance, capacitance, inductance, diffusion as a more general concept of defining the ‘impedance’ of the reaction and current flow.

$$V = iZ \quad 3-18$$

The AC voltage (E) and current (I) are given by:

$$E = dE \sin(\omega t) \quad 3-19$$

$$I = dI \sin(\omega t + \phi) \quad 3-20$$

$$\omega = 2\pi f (f = \text{frequency}) \quad 3-21$$

where E is the instantaneous value of the voltage at time t , dE is the maximum amplitude of perturbative voltage, ω is the radial frequency, f is the frequency. The respond current I lag the voltage (separated by phase ϕ , Figure 3.11), dI is the maximum amplitude of the resulting current. It is worth noting that both E and I are a function of frequency.

The resulting expression of the impedance can be calculated by:

$$Z = \frac{E_t}{I_t} = \frac{E_0 \sin(\omega t)}{I_0 \sin(\omega t + \phi)} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t + \phi)} \quad 3-22$$

The impedance is then a function of a phase shift ϕ and magnitude Z_0 .

The Butler Volmer equation is used to determine electrode kinetics:

$$I = I_0 \left[-e^{\frac{-\alpha n F \eta}{RT}} + e^{\frac{(1-\alpha) n F \eta}{RT}} \right] \quad 3-23$$

where I is the electrode current density, I_0 is the exchange current density, α is the charge transfer coefficient, η is the activation overpotential, n is the electron numbers, R is the universal gas constant, F is Faraday constant, T is absolute temperature.

Figure 3.12 The schematic of Lissajous Figure

When overpotential is small, using expansion of e^x and ignoring quadratic and higher order terms:

$$e^x \approx 1 + x \quad 3-24$$

Such that Butler-Volmer equation simplifies to

$$I = \frac{I_0 \alpha n F \eta}{RT} \quad 3-25$$

Hence, as shown in Figure 3.12, if a small voltage is applied, a small current is obtained. Under this circumstance, the current varies linearly with potential from equation 3-25. If a large voltage is applied, the relationship will become non-linear.

With Euler's relation,

$$\exp(j\phi) = \cos \phi + j \sin \phi \quad 3-26$$

The impedance can be expressed as a complex function. The voltage is given as,

$$E = dE \exp(j\omega t) \quad 3-27$$

and the resulting current is as,

$$I = I_0 \exp(j\omega t - \phi) \quad 3-28$$

The impedance can then be presented as a complex value,

$$Z(\omega) = \frac{E}{I} = Z_0 \exp(j\phi) = Z_0 (\cos \phi + j \sin \phi) \quad 3-29$$

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Chapter 4*

Editable supercapacitors with customizable stretchability based on mechanically strengthened ultralong MnO₂ nanowire composite

Stretchable supercapacitors are one of the most promising EES devices for wearable electronics. Although some progress has been made on stretchable supercapacitors, traditional stretchable supercapacitors fabricated by predesigning structured electrodes for device assembling still lack the device-level editability and programmability. To adapt to wearable electronics with arbitrary configurations, it is highly desirable to develop editable supercapacitors that can be directly transferred into desirable shapes and stretchability. In this work, editable supercapacitors are developed for customizable shapes and stretchability using electrodes based on mechanically strengthened ultralong MnO₂ nanowire composites. The editable supercapacitor with customizable structure and stretchability showed good energy performance covering the requirement of stretchability, programmability, and long-term stability, which is superior to most of the state-of-the-art stretchable supercapacitors.

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4.1 Introduction

The ever-growing demands for stretchable electronics in applications of electronic textiles,^[1, 2] electronic skins^[3, 4] and wearable health monitors,^[5, 6] require concerted stretchability in energy storage devices.^[7-11] As one of the main energy supplies for stretchable and wearable electronics, stretchable supercapacitors are drawing increasing attention in recent years owing to their superior power density and long calendar life.^[12-17] To date, many stretchable supercapacitors have been made by a predesigned strategy, which configures electrodes with predefined stretchable structures, such as wave-like structure,^[18-20] bridge-island structure,^[21] and textile fiber structure,^[22, 23] followed by assembling these structured electrodes into supercapacitors (Figure 4.1a).^[24]

(a) Predesigned strategy

(b) Editable strategy

Figure 4.1 Schematics for the assembling process of stretchable supercapacitors through (a) predesigned strategy and (b) our editable strategy. The predesigned strategy (a) can only apply an unchangeable structure, and requires three steps to prepare stretchable supercapacitors: (I) predesigning electrodes into stretchable architectures (e.g., upper: wave-like structure, bottom left: spring-like fiber structures, bottom right: serpentine bridge-island structure), (II) coating the structured electrodes with gel electrolyte, and (III) overlapping structured electrodes for assembling of stretchable supercapacitors with predesigned stretchability. The mismatch between predesigned structures of electrodes and the substrates or gel electrolytes may result in severe stress

concentrations at interfaces that initiate microcracks and facilitate the crack propagation during stretching. While the editable strategy (b) only need to cut the supercapacitors into desirable shapes and structures. The customizable structures, such as honeycomb-like structures, pyramid pop-up structure, living-hinge structure and so on, make the as-prepared supercapacitors stretchable in an arbitrary direction. The red arrows indicate the stretchable direction of the as-prepared supercapacitors with customizable structures.

However, the mechanical mismatches between structured electrodes and substrates/gel electrolytes may result in severe stress concentrations at the contact interfaces, which deteriorates the electrochemical performance of supercapacitors during stretching.^[20, 25] Furthermore, the requirement of structured electrodes and the unchangeable structure after fabrication not only complicates fabrication process, but also limits editability on the device level, which further confines the plug-and-play function of supercapacitors for arbitrarily shaped demand and omni-directionally stretchable design. Therefore, to address the issues of conventional predesigned strategy, such as interface mismatch, fabrication complexity and incompatibility with arbitrary configurations, an editable supercapacitor, which can be directly edited into any shape and stretchable structure according to application scenarios, is highly desirable (Figure 4.1b).

From materials perspective, there are two obstacles hindering the successful fabrication of editable supercapacitors. The primary issue stems from the intrinsic rigidity of electrode materials. Because of the lower specific capacitance of carbon-based materials, they are required to be combined with high-capacitance pseudocapacitive materials.^[10, 23, 26, 27] However, most of electrodes with pseudocapacitive materials cannot withstand stress without losing electrochemical performance during editing (folding, cutting and stretching) supercapacitors into stretchable structures. The other issue arises from the instability of interfaces among electrode, separator and electrolyte. Conventional assembly method for stretchable supercapacitors mostly involves the coating of gel electrolyte on electrodes, where the gel electrolyte also serves as a separator.^[9, 10, 20] However, because of the weak intermolecular interaction within gel electrolytes, they cannot effectively serve as a separator to prevent dislocation of electrodes and short circuit of supercapacitors during

editing process.^[28] Therefore, a mechanically reinforced and separator-integrated electrode is crucial for the fabrication of editable supercapacitors.

Herein, we developed a new type of supercapacitors, which can be directly edited into desirable shapes and structures. The electrodes of so-called editable supercapacitors compose of ultralong MnO₂ nanowires (MNWs) and carbon nanotubes (CNTs) sandwiched by nanocellulose fibers (NCFs). Such electrodes behave high mechanical robustness, high energy density, and sturdy integration. Two electrodes were further coated with poly(vinyl alcohol)-based (PVA) gel electrolyte to produce a paper-like editable supercapacitor that can be directly transferred into various customizable shapes and structures (Figure 4.1b). The customizable structures (such as honeycomb-like structure, pyramid pop-up structure, and living-hinge structure) can provide the supercapacitor with programmable stretchability in any arbitrary direction. For example, the supercapacitor edited with honeycomb-like structure showed a specific capacitance of 227.2 mF cm⁻² and can be stretched up to 500% without degradation of electrochemical performance, which is superior to most of the state-of-the-art stretchable supercapacitors. In addition, it maintained nearly 98% of the initial capacitance after 10000 stretch-and-release cycles under 400% tensile strain. As a representative of concept for system integration, an integrated device composed of the honeycomb-like supercapacitors and a strain sensor exhibited a stable sensing performance even under dynamic arm swing. This work suggests the promise of editable supercapacitor as a generalized and customizable approach to develop arbitrarily shaped and highly stretchable supercapacitors for wearable and stretchable electronics.

4.2 Experimental Methods

4.2.1 Preparation of MnO₂ Nanomaterials

MnO₂ nanoflowers (MNFs) and nanowires (MNWs) are respectively synthesized through hydrothermal method without or with magnetic stirring, as shown in Figure 4.2. In a typical synthesis process, a 15 ml aqueous mixture solution containing 0.4 mM KMnO₄ and 0.4

mM NH_4Cl was firstly added into a 20 ml Teflon reactor, and then the reaction was performed in an oil bath at $150\text{ }^\circ\text{C}$ for 24 h for MNF synthesis (without magnetic stirring) or with magnetic stirring at 500 rpm for MNW synthesis. MNFs with the length of $1\sim 2\text{ }\mu\text{m}$ and $20\sim 30\text{ }\mu\text{m}$ respectively synthesized at the stirring speed of 300 rpm and 400 rpm by the stirring hydrothermal method. The as-synthesized MnO_2 materials were collected, washed by deionized water (DI water), and dried at $100\text{ }^\circ\text{C}$ for 12 h.

Figure 4.2 Schematics of preparation steps for MnO_2 nanoflowers and nanowires under normal and stirring hydrothermal method at $150\text{ }^\circ\text{C}$ for 24 h respectively. (a) NH_4Cl and KMnO_4 dissolved in DI water in Teflon-lined autoclave. (b-c) Route 1 for the synthesis of the MnO_2 nanoflowers under static hydrothermal process. (d-e) Route 2 for the formation of ultralong MnO_2 nanowires through stirring hydrothermal process.

4.2.2 Fabrication of Flexible MnO_2 Composite Films

MnO_2 nanomaterials/single-walled carbon nanotube (CNT) composite electrodes were produced via vacuum filtration for later test. In brief, CNT powders (Bu-202, BuckyUSA) was firstly treated with 1M HNO_3 aqueous solution to remove the metallic impurities,

followed by filtration with DI water for five times. Then, weighed amount of MNFs or MNWs and aqueous mixture solution with 1 mg mL^{-1} CNT and 2 mg mL^{-1} sodium dodecyl benzene sulfonate (SDBS) mixtures were transferred into ethanol to form 40 mL mixture solutions. The mixture solutions were then operated under stirred magnetic stirring at 1000 rpm for 12 h. After 1 h bath sonication, the other 1 h probe-type sonication was used to obtain a homogenous mixture solution. The mixture solutions were further vacuum-filtrated on a polyvinylidene fluoride (PVDF) filter membranes ($0.2 \text{ }\mu\text{m}$) and was then thoroughly rinsed with DI water to remove the residual SDBS. The as-prepared composite film electrodes were finally peeled off from the PVDF filter membrane and vacuum-dried at $80 \text{ }^{\circ}\text{C}$ for 12 h. For PPy(polypyrrole)-modified MNW/CNT composite electrode, a constant potential of 0.8 V was applied for the anodic electropolymerization of PPy on the MnO_2/CNT composite electrode in a non-stirred N_2 -saturated aqueous solution that contained 10 mM 9,10-anthraquinone-2-sulfonic acid (AQS) and 0.12 M pyrrole. The deposition of PPy was controlled by varying the total charge passing through these working electrodes. The as-received PPy-modified MNW/CNT electrode was washed by DI water for several times and vacuum-dried at $80 \text{ }^{\circ}\text{C}$ for 12 h.

4.2.3 Preparation of Gel Electrolyte

For PVA/LiCl gel electrolyte, 1 g of PVA powder (99% hydrolyzed, $M_w = 86000\sim 98000$, Aldrich[®]) and 1 g of LiCl ($\geq 99.0\%$, Sigma-Aldrich) was dispersed in 10 ml of DI water under vigorously magnetic stirring at $90 \text{ }^{\circ}\text{C}$ for 2 h for the homogeneous mixing.

4.2.4 Assembly of Flexible and Stretchable Supercapacitors

The as-obtained reinforced electrode was noted as MNF/CNT-NCF or MNW/CNT-NCF electrode, and the part to connect current collector was well-protected by a designed double-sided conductive tap to avoid the coverage of nanocellulose fibers in this area. After that, the part of electrode in the nanocellulose films was soaked into the PVA gel electrolyte. Then two electrodes were overlapped with each other to prepare a symmetric supercapacitor and the PVA gel electrolyte was pasted one more time on the overlapped

area. The as-prepared symmetric supercapacitors were left on a vacuum chamber to release the gas in the electrolyte. Finally, the as-fabricated supercapacitors were left on the fume hood overnight (about 12h) to wait for the solidification of the gel electrolyte. For stretchable supercapacitor, a flexible supercapacitor was firstly fabricated. After drying flexible supercapacitors in oven at 40 °C for 1 h, a scissor was directly used to cut the as-prepared flexible supercapacitor in the overlapped part, creating the various shapes and structures.

4.2.5 Material and Mechanical Characterization

Crystal structures of MNWs and MNFs were investigated using thin film XRD (LabX XRD-6000, Shimadzu) with Cu K α radiation. Thin film samples were prepared by spreading ethanol dispersion of nanoparticles dropwise on glass slides with concurrent evaporation of ethanol. Surface elemental and oxidation state of Mn species analysis was obtained by X-ray photoelectron spectroscopy (XPS) on a VG ESCALAB 220I-XL system equipped with a monochromatic Al K α (1486.6 eV) source and a concentric hemispherical energy analyzer. All samples were subjected to drying at 120°C for 2 h to evaporate trace water before measurement. Microscopic morphologies of various nanoparticles and composites were recorded using SEM (JEOL JSM-6340F or 7600) and TEM (JEOL 2010 HR or 2010 UHR). Tensile tests of bare MnO₂/CNT films were conducted using Mechanical Tester MTS Model C42. Electrical conductivity of vacuum-filtered films was tested using a four-probe resistivity measurement equipment. Three points were measured for each film of a specific composition.

4.2.6 Electrochemical Characterization

Cyclic Voltammetry (CV), Galvanostatic charging-discharging (GCD) and electrochemical impedance spectroscopy (EIS) tests were conducted to test the electrochemical performance of composite electrodes and the supercapacitors. The CHI 660d potentiostat (Shanghai Chenhua) were used to measure the electrochemical performance of the as-prepared single MnO₂ composite electrodes and the corresponding

symmetric supercapacitors. Electrochemical performance of MnO₂/CNT electrode was characterized in aqueous electrolyte of 5 M LiCl using electrochemical workstation in a three-electrode system, where Pt is counter electrode, Ag/AgCl is reference electrode and vacuum-filtered film as working electrode. For the electrochemical characterization of symmetric supercapacitors, the same equipment was used. The two electrodes in a supercapacitor were connected as working electrode and counter/reference electrode, respectively. The current outputs of the integrated devices with or without integrated stretching were recorded by Keithley 4200A-SCS.

Specific mass capacitances of composite electrodes were calculated based on CV (C_{A-CV} , mF g⁻¹) and GV (C_{A-GV} , mF g⁻¹) curves according to Equation S1-1 and S1-2, respectively. Specific mass capacitances of symmetric supercapacitors were calculated based on GV curves according to Equation 4-(1-3).

$$C_{m-CV} = \frac{\oint IdU}{2vm\Delta U} \quad 4-1$$

$$C_{m-GV} = \frac{i\Delta t}{m\Delta U} \quad 4-2$$

$$C_{m-device} = \frac{it}{m_{total}\Delta U} = \frac{it}{m_{total}\Delta U} \quad 4-3$$

In the above equations, I is response current (A), U is potential (V), v is scanning rate (V s⁻¹), m is electrode mass (mg), m_{total} is the total mass of two electrodes in symmetric supercapacitor (mg), ΔU is potential window (V), i is discharging current (A), and Δt is discharging time (s).

Specific area capacitances (C_{A-GV} , mF cm⁻²) of composite electrodes and devices were calculated based on GV curves according to Equation 4-4. Specific volumetric capacitances (C_{V-GV} , mF cm⁻³) of composite electrodes and devices were calculated based

on GV curves according to Equation 4-4 and 4-5.

$$C_{A-GV} = \frac{i\Delta t}{A\Delta U} \quad 4-4$$

$$C_{V-GV} = \frac{i\Delta t}{V\Delta U} \quad 4-5$$

In the above equation, I is response current (A), v is scanning rate ($V\ s^{-1}$), A is projected area of the electrodes or project area of the overlapped part (cm^2) for supercapacitors, V (cm^3) is the volume of the supercapacitors, ΔU is potential window (V), Δt is discharging time (s), and i is discharging current (A).

The energy density (E_A) and power density (P_A) of editable supercapacitors can be calculated according to Equation 4-6 and 4-7.

$$E_A = \frac{C_{A-GV} \times \Delta U^2}{2} \quad 4-6$$

$$P_A = \frac{E_A}{\Delta t} \quad 4-7$$

In the above equation, ΔU is potential window (V), Δt is discharging time (s), i is discharging current (A).

4.3 Principal Outcomes

4.3.1 Synthesis and characterization of ultralong MnO_2 electrode

Firstly, the ultralong MnO_2 nanowires used for electrodes of editable supercapacitors were synthesized by a stirring hydrothermal method (Figure 4.2).^[29-31] The selection of MnO_2 as a representative pseudocapacitive material is due to the high theoretical capacitance of

1370 F g⁻¹.^[23] As shown in the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images (Figure 4.3f, 4.5f and 4.6a), nanowires with diameter of 30-100 nm and length up to 50 μ m were produced.

Figure 4.3 SEM images of synthesized MnO₂ nanomaterials under different reaction conditions: (a) 24 h under 0 rpm, (b) 3 h under 500 rpm, (c) 6 h under 500 rpm, (d) 12 h under 500 rpm, (e) 18 h under 500 rpm, and (f) 24 h under 500 rpm.

XRD patterns of the reaction products (Figure 4.4) confirm the formation of tetragonal α -MnO₂ phase as all peaks match well with the standard X-ray diffractogram (JCPDS 44-0141). Planes (112), (420), (211), (220), and (110) can be founded among all MnO₂ nanoparticles synthesized through different reaction conditions. However, (541), (521), (600), (411), (510), (310), and (200), can only observed after 12 h of stirring hydrothermal process. Figure 4.4b shows the nanowires dominate the nanostructure after reaction for 12 h. Hence, the new peaks emerging in X-ray diffractograms stemmed from unidirectional growth of nanowires.^[32]

Figure 4.4 (a) XRD patterns of MnO₂ materials obtained from tradition hydrothermal and stirring hydrothermal method (24 h). (b) XRD patterns of MnO₂ samples obtained from stirring hydrothermal (500 rpm) under different reaction time.

Transmission Electron Microscopy (TEM) is further used to investigate the crystal structure as well as the formation process of the MnO₂ nanowires (MNWs) prepared by stirring hydrothermal method, as shown in Figure 4.5. At the early stage under 0.5 h reaction time, the petal-like moieties with MnO₂ nuclei can be found (Figure 4.5a), and further prolong the reaction time to 1 h, some short nanowires randomly formed in the petal-like moieties (Figure 4.5b,c), similar to the morphology of MNFs formed in conventional hydrothermal process with 24 h reaction time (Figure 4.5g). When increasing the reaction time to 3 h, the elongated nanowire bundles appeared (Figure 4.5d). After 6 h reaction, the nanowire bundles become longer in length and shrink in diameter under 6 h and the MnO₂ nanowires with a high aspect ratio (Figure 4.5e) were finally formed under 24 h reaction (Figure 4.5f). These results indicate that the stirring did not change the morphology of early MnO₂ seeds and nuclei, but mechanical intervention may promote mass transport of reactant.^[29] After the formation of nanoflowers, the shear force results in different mass transport condition around MnO₂ nanomaterials to accelerate disassembling of nanoflowers into nanosheets. The nanosheets can then be reassembled into nanowires. After enough time for growth, the shearing force of magnetic stirring helps nanowires elongated along a preferred direction to form ultralong nanowires. Figure 4.5(g, h) and 4.6(c, d) show the high-resolution TEM images and the selected area electron diffraction

(SAED) pattern of MNFs and MNWs prepared by hydrothermal method without or with stirring under 24 h, respectively.

Figure 4.5 TEM images of synthesized MnO_2 nanomaterials with different reaction conditions: (a) 0.5 h under 500 rpm, (b) 1 h under 500 rpm, (c) high resolution image for 1 h under 500 rpm, (d) 3 h under 500 rpm, (e) 6 h under 500 rpm, (f) 24 h under 500 rpm. (g) high-resolution image of 0 rpm for 24h and (h) the SAED pattern of MnO_2 nanoflowers.

The inset image of Figure 4.5h is the SAED pattern of the as-synthesized MNFs. The SAED pattern demonstrates the polycrystalline structure of MNFs which derives from the random exposure of crystal face in the MNFs. While for the MNWs, the SAED pattern in Figure 4.6c index the tetragonal MnO_2 and the nanowires are single crystallines with the growth axis in the $[001]$ direction. The exclusive presence of the $(hk0)$ peaks in XRD test also verifies the most, if not all, nanowires grow along the $[001]$ direction. The high-resolution TEM image (Figure 4.6c) and the selected area electron diffraction (SAED) pattern (Figure 4.6d) prove that the MnO_2 nanowires are single crystalline growing along the $[001]$ direction. Moreover, the spin energy separation of 11.8 eV between $\text{Mn } 2p_{3/2}$ and $\text{Mn } 2p_{1/2}$ peaks (Figure 4.6e) agrees well with the values of MnO_2 in the previous reports.^[33-35] All of the above results suggest the successful synthesis of ultralong α - MnO_2 nanowires with high purity from the stirring hydrothermal process.

Figure 4.6 Characterization of mechanically reinforced MnO_2 nanowires materials towards editable supercapacitor: (a) SEM image of ultralong MnO_2 nanowires. (b) TEM image, (c) HRTEM of MnO_2 nanowires, and (d) the corresponding SAED image. (e) The high-resolution XPS spectrum of Mn 3p for MnO_2 nanowires. (f) top-view of CNT film, the inset is magnified top-view of CNT film. (g) The top-view and (h) magnified top-view of MnO_2 nanowires/CNT composite film comprising 30% CNT. The insert in (g) is the digital photograph of the composite film being bent. (i) SEM image of gold coated nanocellulose fiber film on MNW/CNT electrode, the inset is the digital photograph of porous and transparent nanocellulose film. (j) MNW70-NCF films are stable in water after agitation, bend and ultrasound for 5 mins in water. (k) Stress-strain curves of MnO_2 -based composite electrodes and MNW70-NCF-PVA-based supercapacitors.

4.3.2 Optimization of the mechanically reinforced ultralong MnO_2 nanocomposite electrode

To withstand the associated strains during editing supercapacitors into stretchable

structures, the electrodes need to be mechanically flexible and electrochemically stable. However, mere MNW film cannot meet these criteria due to their fragility (Figure 4.7) and poor electronic conductivity (Figure 4.8).

Figure 4.7 (a) Photograph of MNW/CNT and MNF/CNT composite with different weigh ratio of CNT. The suffixed number for MNW and MNF represents weight percent of MNW or MNF in the composite film, respectively. MNF100, MNF90, and MNF80 cannot be peeled off from the filter paper due to poor mechanical integrity. MNF70 is barely able to form freestanding film, as illustrated by the incomplete film. Other films are easily detached from the filter paper. (b) The break of MNW100 film under a slight bending. Stress-strain curves of (c) MNW/CNT and (d) MNF/CNT composite films. (e) Stretchability of MNW/CNT and MNF/CNT composite films with different CNT content.

Figure 4.8 Electrical conductivity of MNW/CNT and MNF/CNT composite films with an increasing CNT weight ratio.

In this regard, CNTs were mixed with MNWs, forming MNW/CNT composite films with a percolating network structure. The strong van der Waals forces among CNTs enhance the fracture strains of MNW-based electrodes from less than 0.5% (10 wt% CNTs) to of 4.7% (50 wt% CNTs) (Figure 4.7e). The inset of Figure 4.6g shows the excellent flexibility of a freestanding MNW/CNT film. In addition, the highly conductive CNTs also provide long-range electron-transport pathways, increasing conductivity of composite electrodes (Figure 4.8). The top-view SEM image of MNW/CNT composite film (Figure 4.6h) reveals the interweaving of MNWs and CNTs, which helps to maintain intimate contact between MNWs and CNTs during mechanical deformation. Apart from mechanical reinforcement and conductivity enhancement, the hierarchically porous structure in the percolating network exposes large area to electrolytes, ensuring fast ion transport.

To testify indispensable role of interwoven MNW/CNT network in enhancing electrochemical performance, we characterized the charging-discharging behavior of the MNW/CNT electrodes in a three-electrode electrochemical cell at different scanning rates, and compared their capacitance with that of MnO₂ nanoflowers (MNFs)/CNT electrodes. The fabrication process and the morphology of MNFs (Figure 4.2a).

To optimize the electrochemical performance of nanocomposite electrode, the optimal CNT content in MNW/CNT nanocomposite film (0.6 mg cm^{-2}) was investigated. Figure 4.9 displays the specific capacitances of MNW/CNT films with CNT content in the range from 10 wt% to 50 wt% measured from cyclic voltammetry (CV) at increasing scanning rates. The optimal CNT content is 30 wt% for moderate electrical conductivity (150 S cm^{-1} , Figure 4.8) and high mass loading of high pseudo-capacitance of MnO_2 . Therefore, MNW/CNT composite films with 70 wt% MnO_2 nanowires and 30 wt% CNTs (noted as MNW70, the number suffix behind ‘MNW’ and ‘MNF’ represents the weight percent of MnO_2 nanoparticles in the composite film) were chosen as the representative electrodes to investigate the electrochemical performance of composite films with increased mass loading.

Figure 4.9 (a) Cyclic voltammograms of MNW/CNT composite films with different CNT content. The scanning rate of CV is 50 mV s^{-1} . (b) Specific capacitance measured from cyclic voltammetry curves at increasing scanning rate for MNW/CNT films (0.6 mg cm^{-2}) with different content of CNT.

To make full use of symmetric supercapacitors for further in-series or in-parallel connection, it is necessary to reduce the resistance of the symmetric supercapacitors to the least. As shown in Figure 4.10a, specific areal capacitances of symmetric supercapacitors increase from 117.6 to 401.4 mF cm^{-2} with the increasing mass loading from 0.6 to 8.0 mg cm^{-2} at a large scanning rate of 50 mV s^{-1} . Although the composite films with higher mass

loading exhibits higher specific areal capacitance (Figure 4.10a), the distance of ion-conduction pathway increased at the same time with the increase in the film thickness. The corresponding Nyquist plots of symmetric supercapacitors based on these composite films with the increasing thickness (Figure 4.10b) show that the lowest equivalent resistance of 4.1Ω appeared at the mass loading of 1.6 mg cm^{-2} . Thus, further electrochemical tests were carried out on 1.6 mg cm^{-2} MNW70, MNF70, and CNT films.

Figure 4.10 (a) Dependence of specific area capacitance and film thickness on the mass loading of MNW/CNT film. The scanning rate of CV is 50 mV s^{-1} . (b) Nyquist plot of symmetric supercapacitors based on MNW/CNT films with different mass loading.

The optimal weight percentage of CNTs in both composite electrodes is 30% (denoted as MNW70 and MNF70 electrodes) and the optimal mass loading is 1.6 mg cm^{-2} (Figure 4.9 and 4.10). Therefore, following tests were all conducted based on such optimized conditions.

As shown in Figure 4.11a and 4.12a, cyclic voltammetry (CV) curves of MNW70 electrode have a nearly rectangular shape, indicating a reversible capacitive behaviour, and such behaviour is well maintained at a high scan rate of 100 mV s^{-1} . Galvanostatic charging-discharging curves (Figure 4.12b) suggest that MNW70 experienced less potential drop (due to lower internal resistance) than MNF70, which is consistent with the conductivity measurements (Figure 4.8). The maximum specific areal capacitance of 508.8 mF cm^{-2} was obtained at a current density of 1.6 mA cm^{-2} and 238.4 mF cm^{-2} was retained at a high rate

of 25.6 mA cm^{-2} . In contrast, MNF70 showed a specific capacitance of 134.2 mF cm^{-2} at 25.6 mA cm^{-2} , which is only half of that of MNW70 (Figure S12c).

Figure 4.11 (a) CV curves of MNW70 composite film tested at different scan rates. (b) Galvanostatic charging-discharging (GCD) curves of MNW70 composite film tested at different charging-discharging current.

Figure 4.12 Electrochemical and mechanical performance of MNW/CNT electrode. (a) CV curves of MNW70 film electrodes at a scan rate of 50 mV s^{-1} in 1 M LiCl aqueous solution. (b) GCD curves of MNW70 film electrodes at a charging-discharging current of 6.4 mA cm^{-2} in 1 M LiCl aqueous solution. (c) Specific capacitance of CNT, MNF70, and MNW70 films calculated from GV curves at increasing current density.

Furthermore, at all charging-discharging current densities, MNW70 film exhibits higher specific capacitances than those of MNF70, indicating its superior rate performance and charge storage capacity (Figure 4.12c, Supporting Information). The better electrochemical performance of MNW/CNT electrodes should stem from their interwoven and porous

structure.

Figure 4.13 (a) SEM and (b) magnified SEM top views of MNF70 composite film.

Figure 4.14 The contact angle of a water droplet on the surface of (a) CNT, (b) MNF 70, (c) MNW 70 and (d) MNW70-NCF films.

As shown in Figure 4.6h, MNWs with high aspect ratio disperse and interweave uniformly with CNTs without appreciable agglomeration, resulting in fast electronic conduction.^[29-31] However, MNF film shows agglomeration of nanosheets in the flower structure and MNF have thus less contact with the network of CNTs (Figure 4.13). The more uniformly

distribution of MnO₂ NWs (Figure 4.6g) as compared with the random distribution of NFs (Figure 4.13) throughout the films allows more chance for the electrolyte to contact with active materials, which will be favorable for better wettability of electrodes. In addition, the hierarchically porous network in MNW70 electrode also promotes hydrophilic wetting of electrolyte more effectively than MNF70 electrode, confirmed by the contact angle measurements (Figure 4.14a-c). This hydrophilic property of the electrode further promotes faster ionic conduction.

Besides mechanical flexibility, it is essential to protect the electrodes from short circuit in an editable supercapacitor. Although PVA gel electrolyte is sufficient to act as a separator between electrodes, the weak intermolecular force in the gel electrolyte is not competent to prevent two electrodes from contact under intense mechanical cutting during the editing process.^[28, 36] To address this problem, we deposited a thin layer of nanocellulose fiber film (about 5 μm thick) on each side of MNW70 electrode via vacuum filtration (denoted as MNW70-NCF). The nanocellulose fiber films serve both as the separator for the symmetric supercapacitors and the mechanical reinforcement for composite electrodes.

When the thickness of the electrode is too thick, the function of nanocellulose film as the separator is not strong enough to avoid short circuit during editing process. Only after the thickness of nanocellulose fiber film is larger than 5 μm , the as-prepared supercapacitor can remain operative after editing process. However, increasing the thickness of nanocellulose films on the electrode will lead to the larger distance between two electrodes, which increases the infiltration resistance and the charge transfer resistance of the electrode-electrolyte interfaces. As shown the Figure 4.15, a supercapacitor with thicker nanocellulose film results in higher impedance that will decay the electrochemical performance of the editable supercapacitors.

Figure 4.15 Nyquist plot of supercapacitors based on MNW70-NCF films with different thickness of nanocellulose fiber films.

Of particular note is that nanocellulose fibers entangle with each other to form a fishnet-like structure that tightly wraps the interwoven MNW/CNT composite film (Figure 4.6i). Agitating and ultrasonicing (5 mins) MNW70-NCF electrode in water did not cause any detachment or disintegration of the components, demonstrating the robust microstructure of the MNW70-NCF electrode (Figure 4.6j). After sandwiching MNW70 electrode with nanocellulose fibers, the electrode witnessed an improvement in the mechanical properties: elongation at break increased from 3.2% to 5.4% and tensile strength increased from 2.0 MPa to 4.7 MPa (Figure 4.6k). The resulted robustness should be attributed to the network of nanowires and the strong van der Waals forces between CNTs and nanocellulose fibers.^[37] Moreover, the high hydrophilicity (Figure 4.14d, Supporting Information) and the high porosity (Figure 4.6i) of nanocellulose fiber films facilitate penetration of gel electrolyte into micro-structured electrodes. Such effective water absorption is verified by the reduced Young's Modulus of MNW-NCF after coated with PVA gel electrolyte (Figure 4.6k).

4.3.3 Editable supercapacitors with customizable stretchability

To fully examine the capability of MNW70-NCF film electrodes as a candidate for editable

supercapacitor, the electrochemical performance of symmetric sheet supercapacitors before editing (Figure 4.16a) was tested at different scan rates and under various forms of mechanical deformation. In the absence of deformation, nearly symmetric and triangle galvanostatic charging-discharging curves were observed (Figure 4.16b), indicating reversible capacitive behaviour. Specific areal capacitance of 230.5 mF cm^{-2} was obtained at a current density of 1.6 mA cm^{-2} and 109.1 mF cm^{-2} was maintained at a high rate of 12.8 mA cm^{-2} . CV curves and corresponding capacitance calculation shown in Figure 4.16c also indicate stable performance at high rates. During mechanical bending, MNW-based sheet supercapacitors experienced a minor change in CV curves even at complete folding (180° bending angle), better than MNF-based supercapacitors (Figure 4.17). Figure 4.16d further illustrates the cycling stability of the sheet supercapacitor based on MNW70-NCF electrodes under various mechanical deformations with comparison to MNF70-NCF-based sheet supercapacitor. Both supercapacitors underwent gradual capacitance reduction during the first 1000 cycles but rapidly returned to or exceeded the initial value afterwards. This is likely due to the self-activation process previously observed for MnO_2 -based supercapacitors.^[38, 39] After 2000 cycles, the supercapacitors were subject to various forms of mechanical deformation. MNW-based supercapacitor experienced minor capacitance fluctuation and 95% of the initial capacitance was preserved after 10000 cycles with concurrent bending, folding, and twisting, exhibiting excellent stability. In contrast, MNF-based supercapacitor showed large capacity decay (around 85% of the initial capacitance maintaining) and obvious capacity fluctuations. With superior electrochemical performance and mechanical endurance, MNW/CNT-NCF electrode is promising for editable supercapacitor application.

Figure 4.16 Electrochemical and mechanical performance of editable supercapacitors based on MnO₂-based composite electrodes under different mechanical deformation. (a) Schematic illustration of supercapacitor construction (side view). (b) Galvanostatic charging-discharging and (c) cyclic voltammetry (CV) curves of flexible supercapacitors based on MNW70-NCF film electrodes at different scanning rates. (d) Electrochemical performance comparison between flexible symmetric supercapacitors based on MNW70-NCF and MNF70-NCF electrode when cycling under various mechanical deformations, at a current density of 1.6 mA cm⁻². The insets are the flexible supercapacitors under various mechanical deformations. (e) Digital images of honeycomb-like supercapacitors under different strain tests. The upper image is the schematic diagram showing linear cutting strategy of the editable supercapacitor, the L_c is the cut length, x and y is the space length in transverse and axial direction. (f) The normalized specific capacitance of polyurethane threads interlocked honeycomb-like supercapacitors tested at 1.6 mA cm⁻² based on MNW70-NCF and/or MNF70-NCF electrodes under different strains. (g) Capacitance retention ratio of honeycomb-like supercapacitors at a current density of 1.6 mA cm⁻² under the recycling tensile strain of 400%. C corresponds to specific capacitances after stretch and C_0 is the initial

specific capacitance of first cycle after stretch to 400%. (h) Specific areal capacitance versus reversible stretchability of editable supercapacitor (this work) as compared with previous reported stretchable supercapacitors. (Ref. 1^[21], 2^[40], 3^[25], 4^[41], 5^[42], 6^[43], 7^[44])

Figure 4.17 CV curves of flexible supercapacitors based on (a) MNW70-NCF and (b) MNF70-NCF film electrodes (at a scan rate of 50 mV s⁻¹) under different bending state. (c) The normalized specific capacitance of flexible supercapacitors between MNW70-NCF and MNF70-NCF as a function of bending angle at a scan rate of 50 mV s⁻¹.

Following the fabrication and optimization of flexible supercapacitor, the editing process is implemented to render supercapacitors stretchability. As shown in Figure 4.16e, a linear pattern cutting process transforms the supercapacitor sheet into a honeycomb-like structure when tensile strain perpendicular to the cutting lines is applied. Such linear pattern has theoretical maximum stretchability (in % strain) calculated by: ^[45]

$$\% strain = \frac{\Delta L}{L_i} \times 100\% = \frac{(L_c - x)}{2y} \times 100\% \quad 4-8$$

where ΔL is the length increment after stretch, L_i is the initial length before stretch, L_c is the cut length, x and y are the distances between adjacent cutting lines in transverse and axial directions, respectively (Figure 4.16e). Equation 4-8 suggests that the final stretchability is highly tunable by changing parameters L_c , x , and y , which essentially represent the cutting pattern. To examine the applicability of this model to our editable supercapacitors, we varied the cutting length L_c and measured the corresponding stretchability. Experiment results in Figure 4.18 suggest good consistency with theoretical prediction. The slight decrease from theoretical values is due to the uncounted out-of-plane

buckling in the ideal model. Overall, the stretchability of editable supercapacitors is highly programmable through pattern design and theoretical calculation.

Figure 4.18 Dependence of strain on L_c with thickness of 1 mm (inserted, the schematic of a basic unit of the kirigami pattern on stretchable supercapacitor, where the L_c is the cut length, x and y is the space length in transverse and axial direction). (b) Stress-strains curve for the paper-cut supercapacitors with linear patterns

When the honeycomb-like supercapacitors (with parameters of $L_c = 1.5 \text{ cm}$, $x = 0.2 \text{ cm}$, $y = 0.1 \text{ cm}$) is under stretching test, the resulted supercapacitor avoid the undesirable local fracture and are capable of withstanding the strain up to 630% (Figure 4.16e and 4.18). Moreover, the specific capacitances (normalized to 1) at different strains were measured and compared between MNF70-NCF and MNW70-NCF electrodes, as shown in Figure 4.16f. The honeycomb-like supercapacitors based on MNW70-NCF electrodes were capable of being stretched to 500% without electrochemical performance decay, but the performance degradation was observed for the MNF70-based supercapacitors (decreased by 28.8% at the strain of 500%). The honeycomb-like supercapacitors made of MNW70-NCF electrodes exhibited better mechanical stability in comparison to MNF70-based supercapacitors. This can be explained by the fact that the incorporated ultralong MNWs remained contact with the CNT networks during stretch test, but MNF particles may detach from the conductive CNT networks. Furthermore, compared with of MNWs with low and middle length (1-2 μm and 20-30 μm), the ultralong MNW-based the supercapacitors show the most stable performance under different strains (Figure 4.19). These results provide

evidence that ultralong MNW/CNT composite plays a crucial role in stabilizing the electrochemical performance of the honeycomb-like supercapacitors.

Figure 4.19 SEM images of MnO₂ nanowires with the length of (a) 1~2 μm and (b) 20~30 μm respectively synthesized at the stirring speed of 300 rpm and 400 rpm by the stirring hydrothermal method, the inset figures are the magnified SEM images. (c) The normalized specific capacitance of polyurethane threads interlocked honeycomb-like supercapacitors tested at 1.6 mA cm⁻² based on MNF, MNW (2, with the length up to 2 μm), MNW (30, with the length up to 30 μm) and MNW (50, with the length up to 50 μm) composite electrodes under different strains. (d) The GV curves of stretchable honeycomb-like supercapacitors tested at 1.6 mA cm⁻² under different strain.

Because of the non-elasticity of supercapacitor sheets, these honeycomb-like supercapacitors can only achieve one-time stretching. To overcome this issue, polyurethane (PU) threads with high elasticity were inserted to help the structure to achieve reversible stretchability. Figure 4.16g illustrates the cycling stability of honeycomb-like supercapacitors interlocked by PU threads under repeated 400% strain deformation. As seen from the result, the honeycomb-like supercapacitors underwent slight capacitance

reduction during the initial 1000 cycles but rapidly returned and remained nearly 98% of initial capacitance even after 10000 stretch-and-release cycles. Besides, the in-situ charging/discharging curve of supercapacitors edited with honeycomb-like structures remained nearly constant even under a high strain rate of 5 cm s^{-1} , indicating their excellent stability Figure 4.20.

Figure 4.20 In-situ motion-charging/discharging curves of honeycomb-like supercapacitors with the maximum stretchability up to 400% under different strain rates. The charging/discharging current density is 1.6 mA cm^{-2} .

The honeycomb-like supercapacitor exhibited a specific volumetric capacitance of 16.2 F cm^{-3} based on the total volume of the device and a specific areal capacitance of 227.2 mF cm^{-2} (corresponding to the energy density of $21.07 \text{ } \mu\text{Wh cm}^{-2}$ at a power density of 0.51 mW cm^{-2}). To our best knowledge, the specific areal and volumetric capacitance, as well as the reversible stretchability (400%) of our newly developed supercapacitors, are higher than most of the stretchable supercapacitors reported to date (Figure 4.16h and 4.21).^[21, 25, 40-44]

Figure 4.21 Specific volume capacitance versus stretchability of shape-tailorable supercapacitors with honeycomb-like structure as compared with previous reported stretchable supercapacitors (Ref. 1^[46], 2^[47], 3^[27], 4^[10]).

Moreover, some other methods can be used to improve the electrochemical performance of our editable supercapacitors, such as increasing the mass loading of MNW/CNT composites, electrodeposing electrodes with a conductive polymer like polypyrrole and stacking the editable supercapacitors (Figure 4.22).

Figure 4.22 (a) CV curves (at a scan rate of 50 mV/s) of symmetric supercapacitors based on MNW70 and MNW70/PPy. For MNW70/PPy electrode, the total charge passing the MNW70 electrode is 4 C cm⁻². In comparison with the symmetric supercapacitors based on MNW70 electrode, the areal capacitance of supercapacitors based on MNW/PPy increase by about 2 times

to 435 mF cm^{-2} . (b) The increase of the specific areal capacitance of editable supercapacitors by vertical stacking in parallel. The resulted editable supercapacitor with five stacking units can increase the specific areal capacitance to 1090 mF cm^{-2} under the tensile strain of 400% at a charging-discharging current density of 1.6 mA cm^{-2} .

The relatively low specific capacitance of traditional stretchable supercapacitor is mainly due to the limitation of predesigned stretchable structures. In general, the stretchability of structure-based strategy (prestretched wave-like structure or textile fibre structures) relies on the high bendability of electrodes. According to the mechanics theory $\varepsilon = h/2r$ (where ε is the peak tensile strain, h is the thickness of the electrode and r is the radius of curvature), an electrode with a thinner film corresponds to a smaller radius of curvature. Therefore, in order to achieve a micro-sized curvature in the wave-shape structures and thus the high stretchability, a thin-film electrode (usually less than $1 \mu\text{m}$) are often required. The demand of these thin-film electrodes with low areal mass loading limits the improvement of electrochemical performance in current stretchable supercapacitors.

Figure 4.23 (a) Strain distribution on the honeycomb-like supercapacitors under different strains obtained by the finite element analysis. (b) The maximum strain on the electrode versus stretchability of supercapacitors for the stretchable honeycomb-like supercapacitors.

In contrast, the editable supercapacitors for fabricating stretchable supercapacitors do not need to predesign the electrode with confined microstructures. The supercapacitors edited with honeycomb-like structure enable a centimeter-sized curve to accommodate the deformation. As can be seen in the Figure 4.23, the improved mechanical property of 2%

in the electrode of our honeycomb-like supercapacitor will increase the stretchability of the final stretchable supercapacitor by $\sim 150\%$, while a stretchable supercapacitor based on suspended wavy structure (graphene film about $0.5\mu\text{m}$) experience a 2% normalized peak strain in the electrode when maximum 25% tensile strain is applied on the supercapacitors.^[25]

Another merit of the editable supercapacitors lies in the tuneable voltage and discharging time after interconnection in parallel and/or series to match the requirement of connected electronics. As a proof of concept, five units of honeycomb-like supercapacitors were connected in series, which enlarged the total voltage to 4 V (Figure 4.24a), while three units connected in parallel increased the discharging time by a factor of about three under the same testing current (Figure 4.24b). More interestingly, the output voltage and discharging time can be simultaneously improved by combining series and parallel connections (Figure 4.24b). As a demonstration, five supercapacitor units were connected in series to light up a light emitting diode (LED) watch (Figure 4.24c) and 3×3 honeycomb supercapacitor array can power an LED panel (Figure 4.24d). Because of the high stretchability of the as-prepared supercapacitors, such supercapacitor watchband and arrays can be stretched as a whole and adapted to different size and shape at different parts of our body.

Besides, the editable construction and facile assembly procedure promise much freedom in device construction. Apart from the honeycomb-like structure shown in Figure 4.25a, other 2D and 3D architectures can also be easily constructed from this editable supercapacitor. For example, a pyramid structure (Figure 4.24e and Figure 4.25b), cut from a circular arrangement of alternate cutting lines, enables conformal contact with 3D elastic objects (Figure 4.24e). Connecting four pyramid-like supercapacitors in series further produces a pop-up spring-like supercapacitor that can be pressed into a single sheet and stretched reversibly (Figure 4.24e). When pasted across the elbow, this spring-like supercapacitor remained in operation to power a red LED when the arm was moving randomly (Figure 4.25d). Furthermore, the editing process can be operated after the connection of supercapacitors, realizing more complicated, delicate, and artistic patterns

while maintaining its electrochemical function (Figure 4.24f). The versatility and customizability in shape and 3D architecture of editable supercapacitors promise a wide range of applications in wearable and portable electronics.

Figure 4.24 (a) CV curves of five honeycomb-like supercapacitors in series under different scan potential windows at 50 mV s^{-1} . The insets show the schematic of the corresponding connection type. (b) Galvanostatic charging-discharging curves of (i) single (1×1), (ii) three honeycomb-like supercapacitors in series (3×1), (iii) in parallel (1×3), and (iv) nine supercapacitors in series-parallel (3×3). All the test current densities were 1.6 mA cm^{-2} . The insets show the schematic illustrations of the corresponding connection types. (c) Five honeycomb-like supercapacitors in series powering

a white LED watch under dynamic stretch. (d) 3×3 honeycomb-like supercapacitor array powering LED panel at the strain of 100%. (e) Supercapacitor basket (1, supercapacitor pyramid conformal to three-dimensional objects), four pyramid-like supercapacitors (2) connected in series, forming a stretchable pop-up spring structure. (f) Four symmetric supercapacitors connected in series and tailored into more complicated and delicate paper-cutting.

Figure 4.25 Digital images of shape-tailorable supercapacitors tailed into (a) honeycomb-like structure, (b) supercapacitor pyramid and (c) stereoscopic Chinese word ‘spring’ under unfold and fold condition. (d) The pop-up spring-like supercapacitor strips pasted on two sides of arms to power a red LED.

To further verify system stability of the editable supercapacitors on integration level, two honeycomb-like supercapacitors connected in series were fixed on an elastic Ecoflex[®] substrate and integrated with a stretchable strain sensor^[48]. When the integrated device was worn on an arm, the honeycomb-like supercapacitors successfully powered the strain sensor after the supercapacitors were charged to 0.8 V. Under the non-integrated or integrated stretching, it is shown that the larger the arm swing frequency was, the greater the maximum output current was observed when releasing the arm (Figure 4.26a and b). A linear relationship between swing frequency and maximum output current was observed as indicated by $R^2 = 0.9774$ for regression of all detected signals (Figure 4.26c), which suggests the stable sensing performance of the integrated device under dynamic strains in the frequency range from 0.33 to 0.76 Hz. In the future study, more functionalities, such as energy conversion^[49, 50] and other physical monitoring capabilities^[51], can be further

brought to the editable supercapacitors through layering functional materials on the electrodes.

Figure 4.26 (a) The current response in a strain sensor powered by a stretchable honeycomb-like supercapacitor under two conditions: 1) non-integrated sensors experience deformation; 2) integrated sensors and supercapacitors simultaneously experience deformation during test. (b) The output currents of the non-integrated and integrated devices under different arm swing frequency test. (c) Relationship between maximum output current and arm swing frequency.

4.4 Conclusion

In summary, editable supercapacitors have been demonstrated for developing supercapacitors with customizable stretchability through: (1) assembling the freestanding interwoven ultralong MnO_2

nanowire/CNT composite electrodes with high conductivity and high flexibility; (2) reinforcing the mechanical properties of electrodes and preventing short circuit by depositing porous nanocellulose films on the flexible electrodes; and (3) implementing editing process to obtain stretchable structures. Benefiting from the interconnected fabric-like microstructure and hierarchical porous structure, the supercapacitors based on MNW70-NCF electrodes not only possessed good specific capacitance, but also demonstrated superior cycling stability and deformation tolerance, with 95% capacitance retention at the 10000th cycle with concurrent bending, folding and twisting. Additionally, supercapacitors can be tailored into various shapes and structures for versatile plug-and-play function without noticeably impairing their performance. The supercapacitors with honeycomb-like structure interlocked by PU fibers maintained nearly 98% of initial capacitance even after 10000 stretch-and-release cycles under reversible 400% tensile strain. Furthermore, such editable supercapacitors integrated with a strain sensor also showed stable sensing of arm swing under simultaneous deformation, demonstrating the systematic stability of the integrated devices. Being highly stretchable, easily programmable as well as connectable in series and parallel, the editable supercapacitor is promising to produce stylish energy storage devices with programmable stretchability for various portable, stretchable and wearable electronics.

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Chapter 5***3D Stretchable Supercapacitors with Enhanced Specific Areal Capacitance Based on Porous Polypyrrole Composite Electrode**

Traditional stretchable supercapacitors, possessing a thin electrode and a two-dimensional (2D) shape, have limited areal specific areal capacitance and are incompatible with three-dimensional (3D) wearables. To overcome the limitations of 2D stretchable supercapacitors, it is highly desirable to develop 3D stretchable supercapacitors with higher mass loading and customizable shapes. In this work, we report a new 3D stretchable supercapacitor inspired by honeycomb lantern based on expandable honeycomb composite electrode composing of polypyrrole/black phosphorous oxide electrodeposited on carbon nanotube film. The 3D stretchable supercapacitors possessing device-thickness-independent ion-transport path and stretchability can be crafted into customizable device thickness for enhancing the specific areal energy storage and integrability with wearables.

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5.1 Introduction

The demand for energy storage systems for powering wearable and medical devices has motivated the development of functional supercapacitors.^[1-6] Specifically, stretchable supercapacitors are regarded as a promising energy storage device to power wearable and stretchable electronics for communication, fitness and healthcare applications.^[7-15] Currently, the reported stretchable supercapacitors are mainly based on 2D shapes, which rely on the design of planar stretchable electrodes, such as pre-stretched wave- or wrinkle-like electrode,^[16-20] bridge-island electrode,^[21] and textile electrode^[22, 23] (Figure 5.1a). However, these 2D stretchable supercapacitors usually require thin electrode ($<100\text{ }\mu\text{m}$) for high stretchability ($>100\%$), which restricts active material loading in the vertical direction (z-axis), leading to low specific areal capacitance.^[3, 16, 17, 19, 24-33] Moreover, the 2D stretchable supercapacitors are limited to the 2D surface, leading to poor utilization of the entire 3D space of the wearable device. To overcome the above-mentioned limitations of 2D stretchable supercapacitors, 3D stretchable supercapacitors with higher mass loading and enhanced specific areal capacitance are highly desired. In conventional 2D stretchable supercapacitors, extended device thickness with higher mass loading corresponding to thicker electrode would suffer from longer ionic transport path, which increases the internal resistance and deteriorates the enhancement of the specific areal capacitance (Figure 5.1b and Figure 5.2). Additionally, the peak strains of stretchable electrodes are increased with increasing electrode thickness, which restricts the stretchability of the supercapacitors (Scheme 5.1b).^[8, 34] Therefore, in order to achieve 3D stretchable supercapacitors with simultaneous improved specific areal specific capacity and stretchability, the critical challenge is to design thicker supercapacitors with device-thickness-independent ion transport path and good stretchability.

Honeycomb lantern is made by attaching pieces of paper with adhesives into a 3D stretchable artefact, with an internally expandable honeycomb structure (Scheme 5.1c).^[35] Instead of stretching a flat piece of paper, the enhanced stretchability of the 3D artefact is achieved by morphing of the interconnected honeycomb units. Alluding from this design, when supercapacitors are assembled into an expandable honeycomb structure, the

vertically aligned supercapacitor units with an unchanged electrode thickness in the expandable honeycomb structures can provide a device-thickness-independent ionic transfer path for the unlimited enhancement of specific areal capacitance (Scheme 5.1c). The supercapacitor units in the expandable honeycomb structure experience an out-of-plane bending, and the strain distribution in the vertical direction (z -axis) are identical during the stretching process (Scheme 5.1c and 5.1d, and Figure 5.3), which means the stretchability of the 3D supercapacitors is independent of device thickness. Therefore, fabricating 3D stretchable supercapacitors with expandable honeycomb structure is a viable strategy to circumvent the intrinsic limitations of 2D stretchable supercapacitors.

Figure 5.1 Schematic illustration of the enhancement of specific areal capacitance in stretchable supercapacitors through (a & b) 2D stretchable strategy (e.g., wave-like structure), and (c & d) 3D stretchable strategy. (a) The 2D stretchable supercapacitor with a limited device thickness (T) relies

on the design of stretchable planar electrodes, which depends on increasing the electrode thickness (t) for higher specific areal capacitance. (b) The simulation data of electrochemical and mechanical properties (the inset figure shows the representative strain distribution by the finite element modeling analysis) for the 2D stretchable supercapacitors under different electrode thicknesses. In 2D stretchable supercapacitors, the increase in the electrode thickness would lead to increased internal resistance, further compromising the improvement of areal specific capacitance. The peak strain of wave-shaped electrodes with the same microstructure is also increased when increasing the electrode thickness, which limits the stretchability of supercapacitors. (c) Inspired by the structure of honeycomb lantern, supercapacitors are assembled into 3D expandable honeycomb structures with unlimited device thickness for enhanced specific areal capacitance. (d) The simulation data of electrochemical and mechanical properties for the 3D stretchable supercapacitors under different device thicknesses. A device-thickness-independent ion transport path enables an unlimited increase in the specific area capacitance. Additionally, the device thickness has no influence on the peak strain of the expandable honeycomb structure, which provides a device-thickness-independent stretchability.

From the perspective of electrode design, to maintain the stable performance of the 3D stretchable supercapacitors during stretching, the electrodes in the supercapacitor units need to be highly flexible to withstand the stress from the out-of-plane bending (Figure 5.1c). On account of its intrinsic flexibility and high capacitance, doped polypyrrole (PPy) is a promising pseudocapacitive material for fabricating such flexible electrodes.^[36-39] However, the reported doped PPy composites usually present a dense structure, mainly including close-packed structures and laminated structures.^[39-43] The mechanical stress developed in these dense-packing PPy composites due to ion exchange in charging/discharging process would aggravate the cracking of PPy electrodes, leading to degradation of electrochemical and mechanical performance under extended periods of physical stress.^[44, 45] Moreover, the dense structure greatly impedes electrolyte penetration and ion transport, which deteriorates the electrochemical performance at high charging/discharging rates.^[46-48] Therefore, designing flexible PPy composite electrodes with porous structure for effective stress relief and ion transfer is crucial for fabrication of 3D stretchable supercapacitors.

Herein, inspired by the structure of honeycomb lantern, for the first time, a 3D stretchable supercapacitor with an expandable honeycomb structure is developed, which delivers outstanding specific areal capacitance. The electrodes in 3D stretchable supercapacitors are composed of porous PPy/black phosphorus oxide (BPO) composites electrodeposited on carbon nanotube (CNT) films. Such electrodes exhibit high flexibility and high porosity for effective stress relief and ion transport. The electrodes were further connected to form 3D supercapacitors with expandable honeycomb structures. The unique expandable honeycomb structure with flexible PPy composite electrodes provides the supercapacitors with a device-thickness-independent ion transport path and stretchability. These two features enable thicker supercapacitors to be customized into various 3D shapes for enhanced specific areal capacitance while maintaining stable stretchability. As a proof of concept, 1.0-cm-thick rectangular-shaped stretchable supercapacitors showed an ultrahigh specific areal capacitance of 7.35 F cm^{-2} and a 95% capacitance retention even under 2000% tensile strain after 10000 stretch-and-release cycles, which is superior to state-of-the-art stretchable supercapacitors. The 3D stretchable supercapacitors open an avenue for the fabrication of highly stretchable and customizable 3D energy storage devices with enhanced energy storage performance for a wide spectrum of applications in metamaterials, robotics, wearable, and stretchable electronics.

Figure 5.2 The internal resistance for 2D stretchable supercapacitors under different electrode thicknesses. The simulation data and method are shown in 5.2.7.

Figure 5.3 A representative strain distribution on the expandable honeycomb structures with a hexagonal unit ($x=194\ \mu\text{m}$, $y=1.5\ \text{cm}$, $m=0.2\ \text{cm}$, $T=1.0\ \text{cm}$) under strains of 0%, 500%, 2000%, 5000% obtained by the finite element analysis (y is the space length between the adjacent adhesives in the transverse direction, m is the width of the adhesives, x is the space length between the adjacent supercapacitors in the axial direction, and T is the device thickness of expandable honeycomb structure). The simulation of the expandable honeycomb structure under different strains from 0% to 5000%.

5.2 Experimental Methods

5.2.1 Preparation of Graphene oxide (GO) and Black Phosphorus (BP) Flakes

Figure 5.4 (a-c) AFM and height profile of few-layer (black phosphorus) BP nanosheets measured at different positions. The adjacent puckered layers of BPS is 5.3 Å.^[39]

The GO was synthesized from graphite flakes (Sigma-Aldrich) by a modified Hummer's method.^[49, 50] The exfoliation of bulk BP powder (Nanjing MKNANO Tech. Co., Ltd. China) into BP nanosheets were synthesized by the liquid exfoliation method.^[51] Typically, 500 mg BP powder was added into 100 mL isopropyl alcohol (IPA). Argon gas was then bubbled into the mixture to eliminate the dissolved oxygen. The dispersion was then treated by tip sonication in an ice bath for 12 h. After that, the obtained brown suspension was settled for 1 h and then centrifuged at 3000 rpm for 30 min. Finally, the stable supernatant was collected for further characterization and electrode preparation. The size of the few-

layer black phosphorus flakes (most are around 1-10 layers) is around 0.1 to 1 μm measured from the AFM (Figure 5.4).

5.2.2 Fabrication of Flexible Polypyrrole (PPy) Composite Films

The substrate is the CNT film ($\sim 15 \mu\text{m}$) purchased from Chengdu Organic Chemicals Co. Ltd. Prior to electropolymerization, the CNT film was treated with 1 mol L^{-1} HNO_3 (aq) and then 1 mol L^{-1} HCl (aq) for 12 hours, followed by a thorough rinse with deionized water and dry at 50 $^\circ\text{C}$. The CNT film was then cut into required size for further electrodeposition. Electropolymerization of pyrrole on CNT film was performed in the aqueous solutions which contain pyrrole monomers (0.1 M) and corresponding solution (0.2 mg mL^{-1} Na_2SO_4 , graphene oxide or black phosphorus nanosheet aqueous solution). The room-temperature electropolymerization was performed in a three-electrode electrochemical cell including a reference electrode (Ag/AgCl), a carbon felt counter electrode and a working electrode (CNT film). A constant current of 0.002 A was applied for the electrodeposition. The deposition of PPy was controlled by varying the total charge (projected surface area of the CNT film) passed to the working electrodes. The as-received PPy/ SO_4^{2-} -CNT, PPy/GO-CNT and PPy/black phosphorus oxides (BPO)-CNT electrodes were washed by DI water for several times and vacuum-dried at 80 $^\circ\text{C}$ for later use.

5.2.3 Preparation of Gel Electrolyte

The PVA/ H_3PO_4 gel electrolyte was chosen as the gel electrolyte for our solid-state supercapacitors. Typically, 3 g H_3PO_4 was mixed with 30 mL deionized water, and 3 g PVA powder (85% hydrolyzed, $M_w = 86000 \sim 98000$, Aldrich[®]) was subsequently added into the H_3PO_4 aqueous solution. The mixture was stirred vigorously at $\sim 90^\circ\text{C}$ for 2 h for complete solvation and homogeneous mixing.

5.2.4 Assembly of Flexible Supercapacitors and 3D Stretchable Supercapacitors

Two PPy-based electrodes were firstly soaked into the PVA gel electrolyte. The two PPy-based electrodes further sandwiched a thin-layer nanocellulose fibre separator ($\sim 20\ \mu\text{m}$) to prepare a symmetric supercapacitor. After the solidification of the gel electrolyte, the as-prepared supercapacitors were used to measure the electrochemical performance. For stretchable 3D supercapacitors, the standard fabrication process is shown in Figure 5.21. In brief, The PPy-based composite film electrodes were first cut into identical planar electrode strips with desirable shapes. Adhesives (PVA/ H_3PO_4 gel electrolyte) are then applied on alternating sides of the strips, creating 2 different planar electrode arrays (array A and array B), with each adhesive having a gap apart from each other. Once prepared, array A and array B were stacked on top of each other in alternating order. Two electrode arrays with customizable shapes were coated with poly(vinyl alcohol)-based (PVA) gel electrolyte and intersected in an alternating order. After the fabrication of the supercapacitors, a thin layer of PDMS is coating on the surface of the honeycomb pop-up supercapacitors to prevent the contact between each electrode and avoid the evaporation of the water from the gel electrolyte in the ambient conditions. The whole structure can then be extended apart, opening to present a honeycomb structure.

5.2.5 Material and Mechanical Characterization

All samples were subjected to vacuum drying at $120\ ^\circ\text{C}$ for 2 h to evaporate trace water before measurement. Microscopic morphologies of various nanosheets and composites were recorded using SEM (JEOL JSM-6340F or 7600), AFM (Cypher S, Asylum Research) and TEM (JEOL 2010 HR & UHR). The composition and structure of PPy composites were analyzed by Fourier-transform infrared spectroscopy (FTIR) using FT-Raman Spectrometer & IR Microscope (Thermo Scientific). The XPS measurements were performed using PHI-5400 equipment with Al Ka beam source (250 W) and position-sensitive detector (PSD). The binding energy resolution is 0.8 eV, angle resolution is 45° and the detection limit is 80 K CPS. Base pressure of the measurement chamber is 3.0×10^{-7} Pa. The Ar ion (voltage 12 kV, current 4.2 mA) sputtering speed is 0.28 nm/s over an area of $300 \times 300\ \mu\text{m}^2$. For the PPy composite sample treated with Ar ion etching, the

etching time is 20 s and the etching depth is 5 nm. Tensile tests of PPy composite films and the honeycomb pop-up supercapacitors were conducted using Mechanical Tester MTS Model C42. Electrical conductivity of PPy composite films was measured using a four-probe resistivity measurement system. Three points were measured for each film of a specific composition.

5.2.6 Electrochemical Characterization

Cyclic Voltammetry (CV) and Galvanostatic charging-discharging (GCD) were conducted using the CHI 660d potentiostat (Shanghai Chenhua) and Solartron (AMETEK, Inc.). Electrochemical performance of PPy composite electrode was characterized in the aqueous electrolyte of 1 M H_3PO_4 using electrochemical workstation in a three-electrode configuration, where Pt is a counter electrode, Ag/AgCl is reference electrode and composite electrode is the working electrode. For the electrochemical characterization of flexible supercapacitors and honeycomb pop-up supercapacitors, the Solartron (AMETEK, Inc.) was used. Specific areal and volumetric capacitances were determined using the CV and CP curves according to equation mentioned in the previous reference.^[3] Specific volumetric capacitances (C_{V-GV} , mF cm^{-3}) is based on the total volume of the supercapacitors. The impedance spectra were recorded in the frequency range from 10,000 to 0.01 Hz with a sinusoidal excitation signal of 10 mV at the open circuit potential.

5.2.7 Simulation of the electrochemical and mechanical properties for 2D stretchable supercapacitors under different electrode thicknesses

In 2D stretchable supercapacitors, the increase in the device thickness for high mass loading corresponds to increasing the electrode thickness.^[52] To explore the effects of the electrode thickness on the specific areal capacitance of supercapacitors, the mathematical model developed by Srinivasan and Weidner is used. According to the model, the specific areal capacitance $C(t)$ can be expressed as:

$$C(t) = \frac{\kappa\sigma}{Im^* \omega (\kappa + \sigma) t} \quad 5-1$$

where t is thickness of the electrode, κ corresponds to the effective conductivity of the electrolyte in the electrode, σ is matrix phase conductivity, Im^* is the dimensionless imaginary impedance, and ω is the angular frequency. Im^* can be calculated by the following formula:

$$Im^* = \frac{1 + \gamma^2}{(1 + \gamma^2)^2 \omega^*} \left\{ \frac{\sinh(\omega^*) \cosh(\omega^*) + \sin(\omega^*) \cos(\omega^*)}{\cosh^2(\omega^*) - \cos^2(\omega^*)} \right\} + \frac{2\gamma}{(1 + \gamma^2)^2 \omega^*} \left\{ \frac{\sinh(\omega^*) \cos(\omega^*) + \cosh(\omega^*) \sin(\omega^*)}{\cosh^2(\omega^*) - \cos^2(\omega^*)} \right\} \quad 5-2$$

where γ is the ratio of solution to matrix phase conductivity (κ/σ), and ω^* is the dimensionless angular frequency that can be calculated by the formula:

$$\omega^* = \sqrt{\frac{\omega a C t^2 (\kappa + \sigma)}{2\kappa\sigma}} \quad 5-3$$

where a is the interfacial area per unit volume, and C is the capacitance per interfacial area. The effective conductivity of the electrolyte in the electrode is estimated using the correlation^[53]:

$$\kappa = \kappa_0 \zeta^{1.5} \quad 5-4$$

where ζ is the porosity of the electrode.

According to the model, the dependence of specific arear capacitance on electrode thickness can be calculated with parameters in Table 5.1. The corresponding result is shown in Figure 5.1b. As shown in Figure 1b, by increasing the thickness, the specific areal

capacitances of 2D supercapacitors increase firstly and then decrease. This is because the twofold effect of electrode thickness on the cell behavior: first, as the volume of the electrode is increased, the capacitance grows proportionally, and second, by increasing the thickness, the internal resistance of the supercapacitors increases.

The internal resistance of the supercapacitor mainly contains the three parts: ionic resistance of electrolyte between electrodes ($R_{separator}$), ionic resistance of electrolyte in electrodes (R_{ionic}) and electronic resistance of electrodes ($R_{electronic}$). For 2D supercapacitor, the effects of electrode thickness (t) on resistance can be calculated by:

$$\begin{aligned} R(t) &= R_{separator} + 2(R_{ionic} + R_{electronic}) \\ &= \frac{1}{\kappa} \frac{t_s}{S} + 2\left(\frac{1}{\kappa} \frac{t}{S} + \frac{1}{\sigma} \frac{t}{S}\right) = \frac{t_s}{\kappa S} + 2\left(\frac{1}{\kappa S} + \frac{1}{\sigma S}\right)t \end{aligned} \quad 5-5$$

where t_s is the distance between two electrodes, t is the thickness of electrode and S is the overlapping area of two electrodes in supercapacitors. According to equation 5-5, the internal resistance increases with the increasing electrode thickness. If S is 2.7 cm^2 and t_s is $10 \text{ }\mu\text{m}$, the results are as shown in Figure 5.2.

According to the mechanics theory^[54]:

$$\varepsilon = \frac{t}{2r} \times 100\% \quad 5-6$$

where ε is the peak tensile strain, t is the thickness of the electrode and r is the radius of curvature. If a 2D wave-shape electrode forms a minimum curvature with a radius of $500 \text{ }\mu\text{m}$, the peak strains of the electrodes are increased with the increasing electrode thickness (Figure 5.1b). Considering the strains of active materials is usually less than 10% ^[9], the stretchable wave-shaped electrode is rupture when the peak strain excess 10% .

Table 5.1 Parameters used in the simulation to generate Figure 1b and 1d

Parameter	Value	Reference
a	$3 \times 10^6 \text{ cm}^2/\text{cm}^3$	[55]
C	$30 \text{ } \mu\text{F cm}^{-2}$	[55]
ζ	0.25	[55]
κ_0	$1.47 \times 10^{-3} \text{ } \Omega^{-1} \text{ cm}^{-1}$	[56]
σ	$100 \text{ } \Omega^{-1} \text{ cm}^{-1}$	Tested
ω	$1 \times 10^{-1} \text{ s}^{-1}$	Assumed
t	1-1000 μm	Variable

5.2.8 Simulation of the electrochemical and mechanical properties for 3D stretchable supercapacitors under different device thicknesses

In 3D stretchable supercapacitors with an expandable honeycomb structure, the electrode thickness is fixed and is independent on the device thickness. Assuming the electrode thickness is 70 μm , the simulated specific areal capacitance of the supercapacitor unit is 280.9 mF cm^{-2} (Figure 5.1b). Given that the thickness of supercapacitor units equals to 150 μm (two electrodes + one separator), the corresponding specific volumetric capacitance (C_{Vol}) is 18.73 F cm^{-3} . Theoretically, the specific areal capacitance of the 3D supercapacitor ($C(T)$) grows proportionally as the thickness of the device is increased (Figure 5.1d), which can be expressed as:

$$C(T) = \frac{C_{\text{vol}} AT}{A} = C_{\text{vol}} T \quad 5-7$$

where the A is the cross-sectional areal of supercapacitor units in a 3D stretchable supercapacitor, T is the device thickness of the 3D supercapacitor.

For 3D stretchable supercapacitors, the supercapacitor units in the expandable honeycomb structure experience an out-of-plane bending. The thickness of supercapacitor units is fixed. According to the mechanics theory:

$$\varepsilon = \frac{t_l}{2r} \times 100\% \quad 5-8$$

where ε is the peak tensile strain, t_l is the thickness of the supercapacitor units and r is the radius of curvature, the peak strain is constant at a given radius of curvature and is independent on the thickness of the 3D device. If the t_l is 150 μm and r is 2 cm, the simulation result is shown in Figure 5.1d.

5.3 Principal Outcomes

5.3.1 The formation process of porous PPy/BPO composites on CNT films through one-step electrodeposition

The flexible and porous PPy/BPO-CNT electrodes of 3D stretchable supercapacitors were prepared by one-step electropolymerization process (Figure 5.5c and Figure 5.6). Pyrrole monomers were mixed with BP nanoflake to form aqueous suspension as the electroplating solution. During the electrochemical polymerization process, pyrrole monomers were polymerized into polypyrrole chains, while some phosphorus moieties (P-P) on the surface of BPs were gradually oxidized by oxygens into the oxygen-phosphorus moieties (O-P=O and P-O-P).^[57] The surface oxygen-phosphorus moieties further reacted with water to form anionic functional groups, such as O=P-O⁻ and P-O⁻, which allows the BPOs to serve as the anion dopants of PPy.^[58, 59] The doping of BPOs in PPy matrix led to the formation of PPy/BPO composites, which were further driven onto CNT film by constant current electrodeposition. It is noted that under electrodeposition condition, not all surface moieties of BPs were oxidized into oxygen-phosphorus moieties. The unoxidized BPs cannot act as dopants for electropolymerization of PPy, and the unoxidized surface of BPOs were not covered by PPy, which results in the formation of pores in the PPy/BPO composites (Figure 5.6b and 5.6d).

Figure 5.5 Schematics of preparation steps for PPy nanocomposite with different additions of dopants through one-step electrosynthesis method (CE: counter electrode, RE: reference electrode, WE: working electrode). (a) One-step electrosynthesis of closely packed PPy/ SO_4^{2-} composites via electropolymerization of pyrrole while using SO_4^{2-} as the anionic dopant. (b) One-step electrosynthesis of laminated PPy/GO composites via electropolymerization of pyrrole while using GO as the anionic dopant. (c) One-step electrosynthesis of porous PPy/BPO composites via electropolymerization of pyrrole while using black phosphorus (BP) as the additives and the partially oxidized BPs as the anionic dopant: (I) BPs in the aqueous suspension were gradually oxidized by oxygens into BPOs with some oxygen-phosphorus moieties ($\text{P}-\text{O}^-$ and $\text{O}=\text{P}-\text{O}^-$) on the surface of BPs upon exposure to air; (II) the oxidized functional groups act as the anion dopant of PPy during galvanostatic electrodeposition process (2 mA) while the unoxidized surface BPs on BPOs cannot be wrapped by PPy and produce the open channels in the 3D PPy/BPO composites during the electrodeposition process.

During the electrodeposition process, the partial oxidization of BP into BPO plays a key role in the anisotropic stacking of PPy/BPO composites for the porous structure. When over-oxidized BPOs (exposure of the BP aqueous suspension in the air for two days) were used as the dopant for electropolymerization of PPy, a dense PPy/BPO composite was synthesized (Figure 5.6c). Because the surface of the over-oxidized BPOs is fully covered by the oxygen-phosphorus functional group, the over-oxidized BPOs can be fully wrapped by the PPy matrix, and then the PPy/BPO composites laminate with other BPOs/PPy

composites to form the dense structure (Figure 5.6a and 5.6c). In contrast, starting from the BPs as the additive for electroplating electrolyte, only partial surface moieties of BPs were oxidized into oxygen-phosphorus moieties. The unoxidized BPs cannot act as dopants for electropolymerization of PPy, and only the oxidized surface can be wrapped by PPy matrix. The partially wrapped PPy/BPOs results in an anisotropic stacking among PPy/BPOs composites during the electrodeposition process. The uncovered surface of PPy/BPOs and the anisotropic stacking of PPy/BPOs composites contribute to the formation of porous PPy/BPO composites (Figure 5.6b and 5.6d).

Figure 5.6 Schematic illustration of the formation of PPy/BPO composite. (a) The addition of over-oxidized BPOs (exposure of the BP aqueous to air for 2 days before mixed with pyrrole) to form dense PPy/BPO: (I) the electropolymerization of pyrrole into PPy with the over-oxidized BPOs as the dopants; (II) formation of dense PPy/BPO composites after a continuous electrodeposition

process. (b) The addition BPs in the electroplating electrolyte to form porous PPy/BPO: (I) the electropolymerization of pyrrole into PPy with the partially oxidized BPOs as the dopants; (II) formation of porous PPy/BPO composites after a continuous electrodeposition process. (c) The top-view SEM image of the dense PPy/BPO composite. (d) The top-view SEM image of the porous PPy/BPO composite.

Figure 5.7 Material characterizations of PPy/BPO composites on CNT film towards 3D stretchable supercapacitors: (a) SEM image of reticulated CNT film. The inset shows magnified top-view of CNT film. (b) SEM cross-section image of PPy/BPO-CNT film at electrodeposition charge density of 7 C cm^{-2} . The inset shows the optical images of the flexible PPy/BPO-CNT film (scale bar = 1 cm). (c) SEM top-view image of porous PPy/BPO-CNT film and the magnified top-view. (d) FTIR spectra of CNT and PPy/BPO-CNT film. (e) The high-resolution XPS spectrum of P2p for PPy/BPO-CNT electrode. (f) Stress-strain curves of CNT and PPy-based electrodes.

CNT films with reticulated network (Figure 5.7a) were used as the highly conductive and flexible current collector for the deposition of the composite electrodes. As shown in scanning electron microscopy (SEM) images (Figure 5.7b and 5.7c), the PPy/BPO composites with submicron/nano-sized pores were formed on CNT film. The Fourier-transform infrared spectroscopy (FTIR) spectrum of PPy/BPO-CNT electrode feature the characteristic peaks of PPy, indicating that PPy chains were electrodeposited on the composites (Figure 5.7d).^[40, 60] Moreover, the high-resolution X-ray photoelectron

spectroscopy (XPS) spectrum for the P 2p of PPy/BPO-CNT electrode (Figure 5.7f) can be decomposed into two peaks, representing P-C (132.9 eV) and P-O_x (133.8 eV), respectively.^[61, 62] The P-O_x bonding confirms the formation of some oxygen-phosphorus moieties on the surface of BPOs; while P-C bonding is ascribed to the strong interaction between P atom on the surface of BPOs and C atoms in PPy chains, indicating the intimate wrapping of PPy matrix around BPOs. These results suggest the successful electrodeposition of porous PPy wrapping BPO on CNT films.

5.3.2 Characterization of PPy/BPO composite under different charge densities

The SEM image of CNT film shows a reticulated structure (Figure 5.8). Electropolymerization at 1 C cm⁻² (Figure 5.8b) appears to have minimal difference and resembles pure CNT. Nanoplates of BPOs is an indication of the initial growth and deposition of the PPy/BPOs on CNT films. Electropolymerization at 3 C cm⁻² shows slight coverage of the PPy/BPO composite on CNT films with anisotropic stacking PPy/BPO composites. When the charging density is more than or equal to 5 C cm⁻², the PPy/BPO films form a porous structure and show good coverage of porous PPy/BPO on CNT films.

Figure 5.8 SEM images of PPy/BPO-CNT electrodes prepared under different charging densities: (a) 0 C cm⁻², (b) 1 C cm⁻², (c) 3 C cm⁻², (d) 5 C cm⁻², (e) 7 C cm⁻², and (f) 10 C cm⁻². The inset is the magnified top view of these electrodes.

Figure 5.9 (a) FTIR spectra of CNT film, BP coated CNT film and PPy/BPO-CNT electrode at 3 C cm⁻². (b) FTIR spectra of PPy/BPO-CNT electrodes obtained from electrodeposition under different charging densities.

FTIR spectra of PPy/BPO-CNT film electrodes feature the characteristic peaks of PPy, indicating that PPy chains were electrodeposited on the composites.^[40, 60] As shown in the Figure 5.9, the band at about 784 cm⁻¹ belongs to the pyrrole ring vibrations. The bands at 911 cm⁻¹ and 1219 cm⁻¹ can be assigned to the stretching vibration of doped PPy, demonstrating the PPy chains on the composites. The bands at 964 cm⁻¹ and 1045 cm⁻¹ can be assigned to the C-H out-of-plane vibration and C-H in-plane vibration, respectively. The band of the C-N stretching vibration appears at about 1474 cm⁻¹. The band near 1554 cm⁻¹ corresponds to C=C and C-C stretching vibrations. Besides, XPS test was further used to reveal the chemical bonding in the PPy/BPO-CNT film electrode. Table 5.2 shows an increase in the atomic percent of N and P in composites with a higher charge density, indicating the increase deposition amount of PPy/BPO composite on the CNT film. As for C 1s and N 1s spectra of PPy/BPO-CNT film at 7 C cm⁻², the C-N bonding of pyrrole

corresponds to the peak located at 285.2 eV and the bonding of benzenoid amine (-NH-) corresponds to the peak located at 399.6 eV (Figure 5.10a and 5.10d).^[63-65] P2p spectrum of PPy/BPO-CNT electrode (Figure 5.10b) can be decomposed into two peaks, representing P-C (132.9 eV) and P-O_x (133.8 eV), respectively.^[61, 62] The P-O_x bonding confirms the formation of some oxygen-phosphorus moieties on the surface of BPOs; while P-C bonding is ascribed to the strong interaction between P atom on the surface of BPOs and C atoms in PPy chains, indicating the intact wrapping of PPy matrix around BPOs. The additional characteristic peak of pure P-P located at 132.9 eV was observed after the PPy/BPO-CNT electrode was etched by argon gas for 20 s, indicating the existence of unoxidized BPs in the PPy/BPO composites (Figure 5.10c). All these results suggest the successful electrodeposition of porous PPy wrapped BPO composites on CNT films.

Figure 5.10 XPS spectra of (a) C 1s, (b) P 2p without etching, (c) P 2p with argon gas etching and (d) N 1s of 3D porous PPy/BPO-CNT electrode (7 C cm⁻²).

Table 5.2 Surface elemental composition of PPy/BPO-CNT electrodes at different charging density. Results expressed as atomic percent %.

Specimens	C	N	O	P
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CNT film	94.81	0.56	4.26	0.37
1 C cm ⁻² PPy/BPO-CNT	91.9	2	5.68	0.41
3 C cm ⁻² PPy/BPO-CNT	79.18	10.85	8.17	1.8
5 C cm ⁻² PPy/BPO-CNT	71.3	10.76	13.84	2.10
7 C cm ⁻² PPy/BPO-CNT	72.73	10.86	13.05	3.46
10 C cm ⁻² PPy/BPO-CNT	72.83	11.04	12.98	3.15

5.3.3 Electrochemical performance of PPy composite electrodes for 3D stretchable supercapacitors

Figure 5.11 Electrochemical performance of PPy/BPO-CNT film electrodes under different charge density: (a) Cyclic voltammetry (CV) and (b) galvanostatic curves of PPy/BPO-CNT film electrode grown for 7 C cm⁻². The specific areal capacitance of PPy/BPO-CNT film electrodes with different charge densities based on (c) CV test at different scan rates and (d) galvanostatic charging-discharging test at different charging-discharging current density.

Figure 5.12 Specific areal capacitances (a) and (b) specific volumetric capacitances of flexible PPy/BPO-based supercapacitors with increasing charge density at different discharging current density.

Figure 5.13 (a) The thickness of the PPy electrodes with different dopants under different charge densities, and (b) the electrical conductivity of PPy electrodes with different dopants under different charge densities.

To testify the indispensable role of PPy/BPO-CNT electrodes in enhancing the mechanical and electrochemical stability of supercapacitor units for 3D stretchable supercapacitors, the mechanical and electrochemical performance of the PPy/BPO-CNT electrodes were characterized in symmetric supercapacitors. To optimize the electrochemical performance of nanocomposite electrode, the optimal deposition of PPy/BPO nanocomposite on CNT film was investigated. Figure 5.11 displays the specific areal capacitances of PPy/BPO

composite deposited on CNT film with increased charge densities from 0 C cm^{-2} to 10 C cm^{-2} at different scanning rates. Although the specific areal capacitances of electrodes increase with the higher electrodeposition charge density, the charge density at 7 C cm^{-2} provides PPy/BPO-CNT-based supercapacitors with the highest specific areal and volumetric capacitance at high charging/discharging rate when total volume of the device (including electrode, the separator, the gel electrolyte and the packaging) were considered (Figure 5.12). Therefore, 7 C cm^{-2} (with a thickness of $72 \text{ }\mu\text{m}$ and a conductivity of 180 S cm^{-1} , Figure 5.13) is the optimal charge density for assembling of stretchable 3D supercapacitors. The PPy-based composite electrodes used for the following tests were all obtained at 7 C cm^{-2} .

Figure 5.14 The SEM images of cross section of different PPy composite electrodes at a charge density of 7 C cm^{-2} : (a-c) PPy/ SO_4^{2-} -CNT electrode, (b-f) PPy/GO-CNT electrode, (g-i) PPy/BPO-CNT electrode.

Figure 5.15 (a and b) The optical images of PPy/SO₄²⁻-CNT electrode before and after being bent at an angle of 150° for ten times. (c and d) The optical image of PPy/GO-CNT electrode before and after being bent at an angle of 150° for ten times. The inset is the SEM image of PPy/GO-CNT electrode after being bent. (e and f) The optical image of PPy/BPO-CNT electrode before and after being bent at an angle of 150° for ten times. The inset is the SEM image of PPy/BPO-CNT electrode after being bent.

The performances of PPy/BPO-CNT electrodes were further compared with those of two other typical PPy-based electrodes: PPy/SO₄²⁻-CNT electrodes^[42] and PPy/graphene oxide (GO)-CNT electrodes^[41] (Figure 5.5 and 5.14). As shown in Figure 5.15, PPy/SO₄²⁻-CNT with close-packed structure and PPy/GO-CNT electrodes with laminated structure are fragile and easily cracked after being bent at an angle of 150° for ten times. By contrast, the PPy/BPO-CNT electrode exhibited exceptional flexibility without noticeable crack

during the bending process. Cross-sectional SEM images of the PPy/BPO-CNT film clearly display hierarchically porous structures (Figure 5.7c and 5.14g-i). The unique sponge-like porous structure is beneficial for relieving stress on the electrodes and enhancing the fracture strains of the PPy/BPO-CNT composite electrode to 11.2% in comparison with that of PPy/SO₄²⁻-CNT electrode at 4.9% and PPy/GO-CNT electrode at 7.1% (Figure 5.7g). Likewise, the maximum elongation at break of different PPy-based symmetric supercapacitors followed the same trend, with 35.9% for PPy/BPO-CNT, 25.1% for PPy/GO-CNT and 16.5% for PPy/SO₄²⁻-CNT (Figure 5.16). These results indicate the critical role of porous structures in enhancing the mechanical properties of the supercapacitors.

Figure 5.16 Stress-strain curves of symmetric supercapacitors based on different PPy-based composite electrodes.

Apart from the enhanced mechanical flexibility, the porous structure of PPy/BPO-CNT film electrodes also ensures sufficient ion transport kinetics for high rate performance and the essential buffer for stresses during charging/discharging process. The cyclic voltammetry (CV) curves of PPy/BPO-CNT-based symmetric supercapacitors (Figure 5.17a) have a quasi-rectangular shape and such behaviour is well maintained even at a high rate of 100 mV s⁻¹, indicating efficient charge transfer kinetics. Besides, nearly mirror-like

and linear galvanostatic charge/discharge curves were observed (Figure 5.17b), suggesting reversible capacitive behaviour.

Figure 5.17 Electrochemical performance of flexible supercapacitors with PPy-based electrodes. (a) Cyclic voltammetry (CV) and (b) galvanostatic charging/discharging (GCD) curves of flexible supercapacitors based on PPy/BPO-CNT electrodes at different scanning rates. (c) Specific areal capacitances of PPy/BPO-CNT, PPy/GO-CNT and PPy/ SO_4^{2-} -CNT electrodes calculated from GCD curves at increasing current density. (d) Capacitance retention ratio of PPy-based supercapacitors cycling at a charging/discharging rate of 2 mA cm^{-2} . C_0 corresponds to the initial

specific areal capacitance before cycling and C is the specific areal capacitance after cycling. (e) CV curves of flexible supercapacitors based on PPy/BPO-CNT electrodes (at a scan rate of 20 mV s^{-1}) under different bending conditions. (f) The normalized specific capacitance of PPy-based flexible supercapacitors as a function of bending angle at a scan rate of 20 mV s^{-1} .

As expected, the PPy/BPO-CNT supercapacitors (Figure 5.17c and 5.18) exhibits high specific areal capacitance of 165.6 mF cm^{-2} at a current density of 0.2 mA cm^{-2} , and high rate performance of 87.8 mF cm^{-2} at 10 mA cm^{-2} , much higher than those of supercapacitors based on PPy/GO-CNT electrode (148.6 mF cm^{-2} at 0.2 mA cm^{-2} and 54.2 mF cm^{-2} at 10 mA cm^{-2}) and PPy/ SO_4^{2-} -CNT electrode (75 mF cm^{-2} at 0.2 mA cm^{-2} and 10.3 mF cm^{-2} at 10 mA cm^{-2}), implying fast kinetics for charge-storage process in PPy/BPO-CNT electrode.

Figure 5.18 Comparison of (a) CV curves at 20 mV s^{-1} and (b) GCD curves at 2 mA cm^{-2} of symmetric supercapacitors based on PPy/BPO-CNT, PPy/GO-CNT, PPy/ SO_4^{2-} -CNT electrodes with the charge density of 7 C cm^{-2} .

Previous report has shown the addition of oxygen group in BPs as the dopants for electrodeposition of PPy can promote the capacitance of the PPy composites.^[39] In this work, the role of BPO is used to produce the porous structure of PPy/BPO-CNT electrode. Indeed, the BPO can contribute to the capacitance improvement when compared with the dopant of SO_4^{2-} , but the effect of BPO as a larger size anion to boost the capacitance of PPy-based electrode is similar to that of GO. As shown in Figure 5.19, the gravimetric capacitance of PPy/BPO-CNT (1 C cm^{-2}) is close to that of PPy/GO-CNT electrode (1 C

cm^{-2}) at a low mass loading ($\sim 0.9 \text{ mg cm}^{-2}$), demonstrating the identical electrochemical performance of these two electrodes. At higher mass loading ($\sim 3 \text{ mg cm}^{-2}$) at the charge density of 7 C cm^{-2} , the PPy/BPO-CNT electrode exhibits higher gravimetric capacitance than that of PPy/GO-CNT electrode. The difference of gravimetric capacitance in these two electrodes under different mass loadings indicates that the enhanced capacitance performance mainly comes from the difference in the porous structure rather than the difference in the dopants.

Figure 5.19 The gravimetric capacitances of PPy-based electrodes at the charge densities of (a) 1 C cm^{-2} and (b) 7 C cm^{-2} calculated from cyclic voltammetry curves at increasing scan rate.

Furthermore, after 10000 charging/discharging cycles (Figure 5.17d), the PPy/BPO-CNT-based supercapacitors also demonstrated excellent cycling stability without noticeable performance degradation (around 4% capacitance decay), while performance degradations were observed for PPy/GO-CNT-based supercapacitors (decreased by 11%) and PPy/ SO_4^{2-} -CNT-based supercapacitors (28%). The better cycling performance of PPy/BPO-CNT supercapacitor should stem from the stress relieving functions of the porous structure. As shown in Figure 5.20c and d, although there was an expansion in PPy/BPO composites after cycling, the porous structure helped to maintain the overall structure over 10000 charging/discharging cycles. Moreover, the SEM images of PPy/GO-CNT show that the stress from charging/discharging process results in cracking and stripping of PPy/GO from the underlying CNT films (Figure 5.20a and b), leading to degradation of electrochemical performance during long-term cycling.

Figure 5.20 (a) and (b) SEM images of 7 C cm^{-2} PPy/GO-CNT electrode before and after 10000 charging/discharging cycles in a three-electrode electrochemical cell tested at a current density of 2 mA cm^{-2} . (c) and (d) SEM images of 7 C cm^{-2} PPy/BPO-CNT electrode before and after 10000 cycles.

To evaluate the capability of PPy/BPO-CNT film electrode for flexible supercapacitors, the supercapacitors were further subjected to bending conditions. The PPy/BPO-CNT-based supercapacitors exhibited a minor change in CV curves even at complete folding, better than the supercapacitors made of PPy/SO₄²⁻-CNT and PPy/GO-CNT electrodes (Figure 5.17e, 5.17f and 5.21). The slight increase in capacitance of PPy-based electrode at an initial bending state is likely due to the closer distance between two electrodes, which stems from the compression of supercapacitors during initial bending. The porous PPy/BPO-CNT electrode with high flexibility, fast ion transport and stress relieving functions makes it a preferable electrode for 3D stretchable supercapacitors.

Figure 5.21 CV curves of flexible supercapacitors based on (a) PPy/GO-CNT and (b) PPy/SO₄²⁻-CNT film electrodes (at a scan rate of 20 mV s⁻¹) under different bending states.

5.3.4 Customizable 3D stretchable supercapacitors

Following the verification of the essential role of porous structure in maintaining the mechanical and electrochemical properties of flexible supercapacitors, the PPy/BPO-CNT electrode was assembled into 3D stretchable supercapacitors (Figure 5.22a). As shown in Figure 5.22a, the 3D stretchable supercapacitor has a rectangular shape and is composed of multi-layer supercapacitor units. A honeycomb structure with hexagonal units is formed after the rectangular-shaped supercapacitor is fully expanded. The maximum stretchability of the expandable honeycomb structure can be geometrically formulated by^[66]

$$\% strain = \frac{\Delta l}{l_0} \times 100\% = \frac{(y-m)}{x} \times 100\% \quad 5-9$$

where Δl is the length of extension after stretch, l_0 is the original length of the specimen before stretch, y is half the width of a single hexagonal units, m is the width of the adhesives (polyvinyl alcohol (PVA)-H₃PO₄ gel electrolyte) and x is the distance between the centrelines of adjacent supercapacitors in the axial direction (Figure 5.22b). From equation 5-9, the final stretchability of expandable honeycomb structure is highly programmable by tuning the geometric parameters of y , m and x , and is independent on the device thickness

(T). To verify the applicability of this model, the rupture strains of the rectangular-shaped supercapacitors were measured by varying the distance between adjacent adhesive distances (y) and the device thickness (T) in the rectangular-shaped supercapacitors. As shown in the Figure 5.23a and Figure 5.22c, the experiment results are consistent with theoretical prediction and a further increase of the device thickness (T) from 0.1 cm to 3.0 cm did not alter the rupture strain, revealing the device-thickness/shape-independent stretchability.

Figure 5.22 (a) Schematic drawing of the fabrication process for 3D stretchable supercapacitors: (I) The PPy-based electrodes were first to shaped into identical electrode strips with predefined shapes; (II) the electrode strips were adhered by adhesives (PVA/H₃PO₄ gel electrolyte) and connected into two electrode arrays (array A and array B); (III) the edge of the array A and B were

coated with silver paste to ensure conductive connections, and then the array A were intersected with array B; (IV) two arrays were separated by a thin nanocellulose separator (about 20 μm). (V) The array A and B were coated with PVA/ H_3PO_4 gel electrolyte to form a 3D stretchable supercapacitor with expandable honeycomb structures. (VI) The 3D stretchable supercapacitor was stretched to form a honeycomb structure and packaged with a thin-layer PDMS. (b) Digital images of stretchable rectangular-shaped supercapacitors (with geometric parameters of $y=0.7$ cm, $m=0.2$ cm, $x=194$ μm , $T=0.5$ cm) under different strain test. The inset images (upper left) are the scheme showing the expandable honeycomb structure and the hexagonal unit cell before and after being stretched. (c) Dependence of rupture strain on different device thicknesses in the 3D stretchable supercapacitors (with geometric parameters of $y=0.7$ cm, $m=0.2$ cm, $x=194$ μm). T is the device thickness. (d) The performance comparison of 3D stretchable supercapacitors with different device thicknesses tested at a current density of 7.8 mA cm^{-2} . (e) The normalized capacitance of rectangular-shaped stretchable supercapacitors with different PPy-based electrodes tested at 7.8 mA cm^{-2} under different strains. (f) Capacitance retention ratio of 3D stretchable supercapacitor (with geometric parameters of $y=0.7$ cm, $m=0.2$ cm, $x=194$ μm , $T=1.0$ cm) based on PPy/BPO-CNT electrodes tested at 7.8 mA cm^{-2} under the cycling tensile strain of 2000%. (g) Specific areal capacitance as a function of reversible stretchability of 3D stretchable supercapacitor (this work) as compared with previously reported 2D stretchable supercapacitors.^[3, 17, 19, 24-33, 67]

Figure 5.23 (a) Dependence of rupture strain on y with different device thickness. The image (left up) is a schematic diagram showing the expandable honeycomb structure after being stretched, and the T is the device thickness in the 3D stretchable supercapacitors. The inset image (right down) is schematic diagrams showing hexagonal unit cell before and after being stretched (y is the space length between the adjacent adhesives in the transverse direction, m is the width of the adhesives

and x is the space length between the adjacent supercapacitors in the axial direction). (b) A representative stress-strain for the expandable rectangular-shaped supercapacitors (with geometric parameters of $x=194\text{ }\mu\text{m}$, $y=0.7\text{ cm}$, $m=0.2\text{ cm}$, $T=0.5\text{ cm}$).

Aside from the device-thickness-independent stretchability, the 3D stretchable supercapacitors also possess a device-thickness-independent specific volumetric capacitance due to the unchanged ion transport path between adjacent electrodes in the vertically aligned supercapacitor units (5.1c). The device-thickness-independent specific volumetric capacitance corresponds to the specific areal capacitance of 3D stretchable supercapacitors proportional to the device thickness. The maximum mass loading of a composite electrode in the 3-cm-thick rectangle-shaped supercapacitor can reach $453\pm36\text{ mg cm}^{-2}$. A linear relationship between the specific areal capacitance and the device thickness in the rectangular-shaped supercapacitors was observed in Figure 5.21d ($R^2=0.9994$) for all the experimental results, which suggests the viable 3D strategy for enhancing the specific areal capacitances of stretchable supercapacitors.

When a rectangular-shaped supercapacitor (with geometric parameters of $y=0.7\text{ cm}$, $m=0.2\text{ cm}$, $x=194\text{ }\mu\text{m}$, $T=0.5\text{ cm}$) is subjected to a stretching test, it expands to form a honeycomb structure and shows a stretchability up to 2540% (Figure 5.23b, Supporting Information). Moreover, the specific capacitances (normalized to 1) of rectangular-shaped supercapacitors based on PPy/BPO-CNT electrodes were measured at different strains and compared with the other two PPy-based composite electrodes (Figure 5.22b and 5.22e). The supercapacitors based on PPy/BPO-CNT electrodes were capable of being stretched to 2400% without electrochemical performance degradation, but the supercapacitors based on PPy/GO-CNT and PPy/SO₄²⁻-CNT witnessed large capacitance decays (decreased by 13% and 21% at the strain of 2400%, respectively). The significant drop in the electrochemical performance of densely packed PPy-based supercapacitors reflects the indispensable role of porous PPy/BPO-CNT electrodes in enhancing the flexibility of supercapacitor units, thus accounting for the improvement in the mechanical and electrochemical performance. Figure 5.22f further illustrates the cycling stability of the thicker rectangular-shaped supercapacitors (with geometric parameters of $y=0.7\text{ cm}$, $m=0.2$

cm, $x=194\text{ }\mu\text{m}$, $T=1.0\text{ cm}$) under repeated 2000% strain cycling test. It was noted that the 1.0-cm-thick rectangular supercapacitors had 95% capacitance retention even after 10000 cycles of continuous stretching test. After 10000 cycles, the capacitance remained very close to that of unstretched supercapacitors (97%), indicating the well-maintained CNT orientations and nanostructures of the PPy/BPO-CNT electrode (Figure 5.24) is favorable for their excellent mechanical and electrochemical stability.

Figure 5.24 SEM images of (a) the PPy/BPO-CNT electrode, (b) PPy/GO-CNT electrode in the stretchable 3D supercapacitors after the cycling test. (c) The SEM image of the orientations of CNT in PPy/BPO-CNT electrode after the PPy/BPO is scraped off the tested PPy/BPO-CNT electrode. (d) SEM images of the PPy/BPO-CNT electrode coated with PVA gel electrolyte. The insets are the magnified SEM images.

The slight increase in the internal resistance of the supercapacitor from to $7.85\text{ }\Omega$ to $11.19\text{ }\Omega$ before and after cycling test further demonstrates the stable performance of the 3D stretchable supercapacitors (Figure 5.25).

Figure 5.25 Nyquist plot of 3D stretchable supercapacitors based on PPy/BPO-CNT electrode before and after cycling test. The inset shows the magnified Nyquist plot and the equivalent electrical circuit^[68]. The simulation results of the R_s and R_{ct} before and after cycling test are (7.08 Ω and 0.77 Ω) and (9.48 Ω and 1.71 Ω), respectively. The 3D supercapacitor experienced a slight increase of the internal resistance ($R_s + R_{ct}$) from 7.85 Ω to 11.19 Ω before and after cycling test.

The 1.0-cm-thick rectangular-shaped supercapacitors exhibited a specific areal capacitance of 7.35 F cm⁻² at the current density of 7.8 mA cm⁻², corresponding to the energy density of 653 μ Wh cm⁻² at a power density of 5.27 mW cm⁻² (Figure 5.26). The specific areal capacitance of such 3D supercapacitors is 61 times as high as that of its original 2D supercapacitor (120 mF cm⁻² at the current density of 5 mA cm⁻²). To the best of our knowledge, the specific areal capacitance (7.35 F cm⁻²) in conjunction with the reversible stretchability (2000%) of our newly developed 3D stretchable supercapacitors were significantly higher than those stretchable supercapacitors (< 2.9 F cm⁻² and < 800%) reported to date (Figure 5.22g and Table 5.3).^[3, 17, 19, 24-33, 67] Moreover, the stretchability and the specific areal capacitance are highly programmable by tuning the distance between adjacent adhesives in the hexagonal units (y) and the device thickness (T) (Figure 5.23a and Figure 5.22d).

Figure 5.26 The Ragone plot of the 1-cm-thick 3D stretchable supercapacitors.

Table 5.3 Performance comparison with other PVA gel electrolyte-based stretchable supercapacitors

Materials (electrode thickness)	Specific areal capacitance (scan rate/charging current density)	Maximum reversible stretchability	Methods to enhance stretchability
PPy/black phosphorus oxide nanocomposite on CNT film (72 μm)	7.35 F cm^{-2} (7.8 mA cm^{-2})	2000%	3D expandable honeycomb structure (This work)
Ultralong MnO_2 nanowires/CNT composites (100 μm)	227.2 mF cm^{-2} (1.6 mA cm^{-2})	400%	Editable structures ^[3]
Graphene film (2 nm)	5.8 $\mu\text{F cm}^{-2}$ (0.1 V s^{-1})	40%	Wrinkle (wave-shaped) structure ^[19]
CNT film (19 nm)	47.5 $\mu\text{F cm}^{-2}$ (200 mV s^{-1})	70%	Pre-stretched waved-shaped structure ^[24]
Suspended wavy graphene microribbons on Au film (440 nm)	0.58 mF cm^{-2} (0.08 mA cm^{-2})	50%	Pre-stretched waved-shaped structure ^[17]
Buckled acid treated CNT@PANI film (not mention)	1147.12 mF cm^{-2} (10 mV s^{-1})	200%	Pre-stretched wrinkled-like structure ^[16]
Graphene/carbon nanotube/cross-linked PH1000 film ($\sim 8 \mu\text{m}$)	107.5 mF cm^{-2} (5 mV s^{-1})	200%	Pre-stretched waved-shaped structure ^[25]
CNT@ MnO_2 films ($\sim 8 \mu\text{m}/\sim 50 \mu\text{m}$ under wrinkle structure)	478.6 mF cm^{-2} (0.5 mA cm^{-2})	150%	Pre-stretched waved-shaped structure ^[26]
Graphene core-sheath microfibers (diameter $\sim 80 \mu\text{m}$)	1.2 mF cm^{-2} (50 mV s^{-1})	100%	Textile (Spring-like microfibers) ^[27]
MnO_2 /CNT/nylon fiber (not mention for active materials)	40.9 mF cm^{-2} (50 mV s^{-1})	50%	Textile (Coiled nylon fiber) ^[28]

CNT film electrode (54.4 μm)	61.4 mF cm^{-2} (1 mA cm^{-2})	116%	Pyramid-shaped CNT film ^[67]
Laser-induced graphene electrode/PDMS ($\sim 80 \mu\text{m}$)	650 $\mu\text{F cm}^{-2}$ (50 mV s^{-1})	50%	Laser-induced graphene electrode ^[29]
PANI on CNT/graphene fiber ($\sim 200 \text{ nm}$)	273.7 mF cm^{-2} (10 mV s^{-1})	800%	Coiled and buckled fibre ^[30]
Ag–Au core–shell NW electrodes (not mention)	209.9 $\mu\text{F cm}^{-2}$ (50 mV s^{-1})	60%	Nanowire electrodes (NW) ^[31]
Graphene/CNT electrodes (1 mm)	2.9 F cm^{-2} (0.5 A g^{-1})	100%	2D Re-entrant structure ^[32]
$\text{V}_2\text{O}_5/\text{PEDOT}$ (19.5 μm)	135 mF cm^{-2} (0.5 mA cm^{-2})	50%	Intrinsic stretchability of PEDOT ^[33]

Figure 5.27 (a) Galvanostatic charging/discharging curves of i) single supercapacitor unit, ii-iv) supercapacitor units connected in series (3 $\times$ 1), in parallel (1 $\times$ 3), and in-series/in parallel combination (3 $\times$ 3) at a current density of 7.8 mA cm^{-2} . The red line in the inset image is the

conductive connection and the blue line is the insulated connection. (b) Rectangle-shaped stretchable supercapacitors with 48 supercapacitor units (4×12) powering red LED under different bending and stretching conditions. (c) 3D stretchable supercapacitors with chair shape: (c1) the optical images of the shape of the supercapacitor unit; (c2) the optical images of chair-shaped stretchable supercapacitors which can be expanded like an accordion under bending and stretching conditions; (c3) the chair-shaped supercapacitors connected with an inverter to power an electroluminescent panel ($10 \text{ cm} \times 10 \text{ cm}$) under bending condition. (d) Arched bridge-shaped supercapacitors: (d1) the optical image of the shape of the supercapacitor unit; (d2) supercapacitors connected into a ball-like structure (upper left) which can deform into a bowl-like structure (upper right), the volcano-like structure (down left) and conform to the surface of 3D balloon (down right); (d3) the as-prepared arched bridge-shaped supercapacitors acted as a 3D helmet worn on the head of an owl toy model to power a 3.0 V flexible LED strip (right). The scale bar for Figure 5.27 is 1 cm.

Another noteworthy advantage of the expandable honeycomb structure for 3D stretchable supercapacitors is the unlimited connections of supercapacitor units in series and parallel combinations to tune the output voltage and discharging time to meet the requirement of connected electronics. It is noted that a respective threefold increase in voltage to 2.4 V (three supercapacitor units connected in series) and capacitance (three supercapacitor units connected in parallel) was observed under the same charging/discharging current, as shown in Figure 5.27a. Additionally, the combination of in series and parallel connections increased output voltage and discharging time simultaneously by a factor of about three (Figure 5.27a). As a demonstration, four rectangular-shaped supercapacitors (with geometric parameters of $y=1.5 \text{ cm}$, $m=0.2 \text{ cm}$, $x=194 \text{ }\mu\text{m}$, $T=0.5 \text{ cm}$) were connected to turn on a red light-emitting diode (LED). Because of their high stretchability, the rectangular-shaped supercapacitors remained in operation to drive the LED with concurrent double bending, fanning and stretching (Figure 5.27b). Moreover, the stretchable rectangular-shaped supercapacitors can adapt to the shape of the forearm and power a 3.0 V white flexible LED strip (Figure 5.28). These results demonstrate on-demand control of voltage and current in the 3D stretchable supercapacitors for wearable electronics.

Figure 5.28. (a) The digit photo of the stretchable rectangular-shaped supercapacitors with a small size ($y=0.7$ cm, $m=0.2$ cm, $x=194$ μm , $T=0.5$ cm) and a large size ($y=1.5$ cm, $m=0.2$ cm, $x=194$ μm , $m=0.5$ cm). (b) The rectangular-shaped supercapacitors bent like a hollow cylinder shape. (c) The rectangular-shaped supercapacitors adapted to the shape of forearm to power a 3V white flexible LED strip.

The intriguing point of the 3D stretchable supercapacitors is their malleable 3D shapes. Different from conventional stretchable supercapacitors limited to 2D planes, the newly developed supercapacitors can be shaped into customizable 3D shapes without losing their stretchability. Apart from the rectangular-shaped, other 3D shapes were also developed by utilizing the expandable honeycomb structures (Figure 5.27c and 5.27d). As shown in Figure 5.27c, five chair-shaped stretchable supercapacitors connected in series can be bent and outstretched like an accordion. The chair-shaped supercapacitors with an inverter can power a flexible electroluminescent panel ($10\text{ cm} \times 10\text{ cm}$) under a bending condition (Figure 5.27c). Besides, the 3D stretchable supercapacitor is developed into an arched bridge shape (Figure 5.27d). When the arched bridge-like supercapacitors are connected into a ball-like structure (four units in series), the supercapacitor can deform in the 3D space into a bowl-like structure, a volcano-like structure as well as being conformed to the surface of a balloon (Figure 5.27d). Moreover, the arched bridge-like supercapacitors can expand to serve as a helmet worn on the head of a toy model to power a 3V flexible blue LED strip (Figure 5.27d).

To further verify 3D systematic integration and stability of the 3D stretchable

supercapacitors for 3D space utilization, flexible 3D pipe-shaped supercapacitors integrated with 3D objects were prepared (Figure 5.29). The outer and inner radius of the pipe shape are 3 cm and 2 cm, respectively. Figure 5.29a shows that the flexible pipe-like supercapacitors could be bent on two planes like a ‘slinky’ and worn on elastic Ecoflex pillar to bend and stretch according to the movement of the elastic pillar. Furthermore, the size of the flexible pipe-shaped supercapacitors can be shrunk to the outer and inner radius of 0.9 cm and 0.7 cm. The shrunk flexible pipe-shaped supercapacitors (three units in series) is integrated with an elastic artificial hand and served as a part of the finger to power a red LED (Figure 5.29). Under the integrated status as a knuckle of a finger, the 3D soft-pipe like supercapacitors with good capability to bending could remain functioning to drive the red LED under bending and stretching conditions towards arbitrary directions, which suggests the stable performance of the 3D integrated device under dynamic mechanical deformation. In the future study, the established strategy could potentially be used in the fabrication of other stretchable 3D energy storage device (e.g., lithium-ion batteries^[69-75]), and could also be integrated with other stretchable devices, such as energy harvesting devices^[66, 76, 77] and wearable sensors^[78-81]. Functions, including self-healing, electrochromic, shape memory and photo/thermo-responsive, could be further incorporated in the 3D stretchable supercapacitors to build smarter 3D energy storage systems.^[1, 4, 5, 82, 83]

Figure 5.29 (a) 3D pipe-shaped supercapacitors: (a1) the optical images of the shape of the supercapacitor unit (the diameter for the outer circle is 6 cm); (a2) the flexible pipe-shape 3D supercapacitor bent on plane surface like the ‘slinky’; (a3) the flexible pipe-shape supercapacitor worn on the elastic Ecoflex pillar under bending and stretching conditions. (b) Flexible pipe-like supercapacitors integrated with an elastic artificial hand to power a red LED.

3D supercapacitors with shrunk size (the diameter for the outer circle is 1.8 cm): (b1) the digital photo of a hand model; (b2) the respond of the 3D pipe-shaped supercapacitor when it is loaded with external force; (b3) the finger in an artificial hand equipped with the 3D pipe-like supercapacitor to power a red LED under various bending and stretching conditions.

5.4 Conclusion

In summary, a 3D stretchable supercapacitor with enhanced specific areal capacitance has been demonstrated. The expandable honeycomb structure combined with the highly flexible PPy/BPO-CNT electrodes creates a powerful integration of electrochemical and mechanical reliability for the 3D stretchable supercapacitors. The hierarchical porous structure of PPy/BPO-CNT composite electrode contributes to maintaining the electrochemical performance during deformation, while the device-thickness-independent ion-transport path and stretchability of expandable honeycomb structure enable the thicker stretchable supercapacitors to be customized into desired 3D shapes for higher areal energy storage. A 3D stretchable supercapacitor with rectangular shape exhibited an ultrahigh specific areal capacitance of 7.35 F cm^{-2} and maintained nearly 95% of the initial capacitance even after 10000 stretch-and-release cycles under a repeated 2000% tensile strain, superior to the traditional 2D stretchable supercapacitors. Such supercapacitors integrated with 3D objects also show stable function to power wearable electronics under simultaneous deformation, demonstrating the stable 3D systematic integration. The versatility and customizability in size, stretchability, and shapes of the 3D stretchable supercapacitors with enhanced specific areal energy storage promise a wide range of applications in deployable structures, robotics, stretchable and wearable electronic devices.

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Chapter 6

Flexible High Voltage Lithium-ion Battery Cathode Based on Elastic Nanocellulose Binder

In this chapter, a flexible high voltage lithium-ion battery cathode was fabricated. The elastic nanocellulose (NC) binder was used to serve as the freestanding architecture to fabricate flexible cathode and the protective layer to minimize the $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ (NCM523) secondary particles fatigue. The minimized intergranular fracture of secondary particles prevents the excessive oxidation of the electrolyte. The as-prepared nanocellulose-based NCM523 electrodes exhibit excellent rate and cycling performances for long-term cycling at 4.6 V. The discharge capacity of the NCM523/Li cell with NC binder-based electrode was 145.8 mAh g^{-1} after 300 cycles at 1 C, while the polyvinylidene fluoride (PVDF) binder-based cell only obtains 113.2 mAh g^{-1} . Even after 300 cycles, the capacity retention of NC binder-based cell is 78.9%, higher than that of 59.9% in PVDF binder-based cell, indicating the excellent performance of the NC-based NCM523 electrode. This flexible and high voltage cathode paves the way for flexible high energy lithium ion batteries, and may find emerging application to power flexible and wearable electronics.

6.1 Introduction

$\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ (NCM523) is a promising cathode material for lithium ion batteries owing to its high specific capacity ($\geq 250 \text{ mAh g}^{-1}$ at 4.8 V). However, the use of high voltage NCM523 electrode for lithium ion batteries is limited by its intergranular cracks during long-term cycling, especially when the operation voltage is higher than 4.3 V.^[1, 2] The intergranular cracking of the NCM electrode would lead to the loss of continuity in both ionic and electronic conductivity of cathode electrode, which increase the internal resistance of lithium ion batteries and causes the performance degradation after long-term cycling.^[3-5] More importantly, the fracture of the electrode may expose more surface of the active materials to the carbonate based electrolytes. This exposure will accelerate the oxidation of electrolyte and the parasitic reactions at the cathode/electrolyte interface during entire cell life-span, resulting in low coulombic efficiency and poor cycling performance.

To meet the growing demands and improve the energy density of flexible EES devices for powering flexible electronics, it is important to fabricate flexible high voltage cathode with improved rate performance and extended long-term life.^[6] According to the aforementioned secondary particle fatigue, suppressing the crack of secondary particles is vital to avoiding the extensive electrolyte decomposition and maintaining the interfacial compatibility for the flexible electrode. Commercial cathodes typically utilize polyvinylidene fluoride (PVDF) binder to fabricate the electrode. However, PVDF binder with weak intermolecular force exhibits poor coverage of the active materials, resulting in exposure of active materials to the electrolyte and the degradation of electrode performance. Besides, PVDF binder becomes soft in the electrolyte and often fails to construct flexible support for the flexible electrodes, which leads to microcrack in the electrode, the delamination of active materials from current collectors and the performance degradation.^[7] To obtain flexible high-voltage lithium ion batteries, an ideal binder should enable mechanical robust framework and fast lithium ion diffusion, possess the ability to restrain the intergranular cracking, and prevent electrolyte oxidation. In this regard, nanocellulose (NC) with rich hydroxyl groups to form strong hydrogen bonding and the porous reticulate

structure is presented as a great platform for flexible high-voltage electrode.^[8-11] The NCM523 particles covered by the porous reticulate structure of NC enables the facile lithium ion diffusion and buffer the expansion of active materials to avoid the crack of secondary particles during charging/discharging process. The strong hydrogen bonding and reticulate structure endow the cathode with enhanced tensile strength and make the electrode flexible.

Figure 6.1 (a) Schematic illustration of the fabrication process of flexible nanocellulose (NC)

binder-based NCM523 electrode and (b) the flexible NC-based electrode.

Herein, a biomass-based and elastic NC binder is employed to fabricate flexible high-voltage NCM523 cathode (Figure 6.1). The elastic nanocellulose (NC) binder was used to serve as the porous freestanding framework to protect the intergranular of the NCM523 secondary particles from cracking. The NC-binder based electrode owns improved rate performance and more stable long-term capacity (145.8 mAh g^{-1} after 300 cycles at 1 C) at 4.6 V compared to that of PVDF binder-based electrode (113.2 mAh g^{-1}). Furthermore, the NC binder-based full cell lithium ion battery functions well to power red LED under bending and folding conditions. This flexible and high voltage cathode paves the way for customizable high energy lithium ion batteries, and may find emerging application to power flexible and wearable electronics.

6.2 Experimental Methods

6.2.1 Dispersion and Preprocessing of Nanocellulose

Nanocellulose (NC) was purchased from NingBo ATMK Lithium Ion Technologies, Inc. and stored in a powder form. For the application in the battery field, the 10% NC suspension was obtained from the repeated high-pressure homogenization of wood cellulose pulp in 5 wt% NaOH aqueous solution. The as-prepared colloid was sealed in the container.

6.2.2 Preparation of the Electrode Composites and the Electrode Films

In this experiment, the fabrication process of the facile approach to prepare the $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ (NCM523) electrodes with NC-based electrode were prepared for the following steps as follows. Initially, NC colloid and 95% ethanol was added into a juice extractor, and was divided to the NC suspension. The NC slurry was first diluted to a 3% suspension by adding 95% ethyl and 1 h magnetic stirring. The mass of NCM523 powder was set as 0.25 g. The NCM powder was further mixed with NC and further as the ratio of

NCM523-NC- acetylene black (AB) (80-10-10, wt%) in the test tube. Added 15 ml ethanol, the solution went through magnetic stirring at 1000 rpm for 24 h to get an even distribution solution.

The procedure for preparing the free-standing NCM523 electrode films is summarized as follows. A homogenous dispersion of the active material (NCM523) and NC was obtained after the magnetic stirring. Vacuum filtration with a filter membrane was then conducted to get the film. When the filter film was almost dry, the electrode film was peeled off from the membrane. The electrode films were then dried in the vacuum box at 110 °C for 12 h. Then films were cut into 10 mm circular pieces and were weighed for further fabrication.

6.2.3 Electrochemical Characterization

NCM523/Li 2032-type coin cells were prepared with 1 M ($M = \text{mol L}^{-1}$) LiPF_6 (Sigma-Aldrich) dissolved in ethylene carbonate: ethyl methyl carbonate: dimethyl carbonate (1:1:1, wt.%) as an electrolyte and Celgard 2400 as a separator. Cyclic voltammetry (CV) and electrochemical impedance spectroscopies (EIS) were tested by an electrochemical workstation (CHI660d, Chenghua, Shanghai) in a three-electrode system. In the three-electrode system, NCM523 electrode is the working electrode, and two lithium metal foils separately function as counter and reference electrodes. EIS was further operated over a frequency range from 100 kHz to 0.01 Hz.

6.2.4 Material characterization of the electrode

NCM523 electrodes were firstly washed by high purity DMC. The washed electrodes were then moved into a vacuum oven for 4 h at 45 °C. The X-ray powder diffraction (XRD, Rint-2000, Rigaku) using Cu-K α radiation is employed to identify the crystal structure of the prepared samples. Data were collected in the 2-theta range of 10-90° at 2° min⁻¹. The microstructures of the samples were observed by SEM (JEOL/JSM-7600F) and TEM (JEOL, JEM-2100). The chemical composition of the sample surface was identified by using XPS (PHI 5700 ESCA System, U.S.).

6.2.4 Calculation methods for lithium-ion diffusion coefficient

The lithium-ion diffusion coefficient can be calculated by Randles-Sevcik equation:^[1]

$$I_p = 2.69 \times 10^5 \cdot A(\sqrt{n})^3 C \sqrt{\nu D} \quad 6-1$$

Where I_p is the angular frequency region; A is the surface area of the electrode; C is the molar concentration of lithium ions; D is the diffusion coefficients of the lithium ions; ν is the scan rate. Linear fitting coefficient of both peak of NCM523 with PVDF and NC are around 0.99 (Figure 6.8c), indicating a linear relationship between the square root of scan rates and peak currents. The Li^+ diffusion coefficients of oxidation peak and reduction peak of NCM523 electrode with NC-based electrode are 18.88×10^{-11} and $3.58 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$, respectively, while those of NCM523 electrode with PVDF are 5.79×10^{-11} and $2.18 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$, respectively.

EIS of two samples are compared (Figure 6.8d-f), and these obtained plots consist of two semicircles arc and a straight line. The impedance in the semicircle at high frequency for lithium ion migration from the electrolyte to the electrode corresponds to the interfacial layer resistance (R_f). The charge transfer resistance (R_{ct}) is related to the semicircle at a medium frequency, which comes from the impedance of charge transfer. The straight line at the low frequency is assigned to the Warburg impedance (W_0).^[2, 3] Additionally, these exchange current densities (i^0) are calculated by the formula 6-2. The plots of the real axis Z_{re} as a function of the reciprocal square root of the lower angular frequencies $\omega^{-1/2}$ are illustrated in Figure 6.8f.^[5] This relation is governed by equation 6-3.

$$i^0 = \frac{RT}{nFR_{ct}} \quad 6-2$$

$$Z_{re} = R_f + R_{ct} + \sigma_w \sqrt{\omega} \quad 6-3$$

$$D = 0.5 \left(\frac{RT}{AF^2 \sigma_w C} \right)^2 \quad 6-4$$

where R is the gas constant; T is the absolute temperature; n is the number of transferred electrons; F is Faraday's constant; ω is the angular frequency; A is the electrode surface; and C is the molar concentration of lithium ions. According to equation 6-3, the slope of the straight lines represents the values of the Warburg impedance coefficient (σ_w). The diffusion coefficients (D) of the lithium ions in the bulk electrode materials are calculated using equation 6-4.

6.3 Principal Outcomes

6.3.1 Morphology and Mechanical Properties

The thickness of deposited NCM523 cathode film can reach $\sim 256.6 \mu\text{m}$ ($\sim 10 \text{ mg cm}^{-2}$, Figure 6.2g), which is ready for commercial use. Notably, the as-prepared integrated structure exhibits a flexible feature, as illustrated in Figure 6.2. The flexibility was mainly attributed to the toughness of the NC structure, suggesting potential applications for flexible electrodes. A conventional PVDF binder-based electrodes easily form cracks and delaminate from the current collector foils under bending condition, as shown in Figure 6.2c, while the proposed electrode with NC binder maintains the electrode without forming cracks (Figure 6.2f). This integrated cathode film is expected to achieve a high mechanical characterization due to the reticulated NC structure with high mechanical strength. Moreover, the porous feature of the 3D porous structure is beneficial to provide fast ion-conducting channels and accommodate the volume expansion during the charging/discharging process (Figure 6.2h). This structure can also improve the wetting due to its hydrophilic properties and large surface area.

Figure 6.2 Mechanical flexibility of a conventionally produced electrode versus an electrode produced using NC-based electrode: (a,b) SEM images of fresh NCM523 electrode using PVDF binder-based electrode, (c) stresses originating from a conventional PVDF binder-based electrode under bending induce formation of cracks and partial electrode delamination, and (d,e) SEM images of flexible NCM523 electrode using NC binder, (f) the flexible NC binder-based NCM523 electrode under bending condition. (g, h) SEM cross-sectional morphology of cathode film with NC binder-based electrode.

In addition, the mechanical performance of NC binder-based electrodes was tested by the tensile test. The mechanical behaviors of electrode films were tested with Mechanical Tester MTS C42 (Figure 6.3 a and b). In Figure 6.3c, a 15.9% elongation of the NC film can be achieved before rupture. The tensile strength of the NC film is 23.87 MPa, which is higher than that of Celgard 2400 (10.7 MPa). This is because the linear chain of ringed

glucose molecules of NC fiber contains rich hydroxyl groups. It enables facile formation of hydrogen bonds. The strong hydrogen bonding stabilizes the linkage among reticulate NC fibers and enhances the mechanical properties. During the fabrication of the electrode film, it was found that the traditional battery electrode using PVDF binder could not form a free-standing film. It is worth mentioning that the tensile strain of NC-based electrode is 21% (Figure 6.3d), indicating the NC binder-based cathode is a promising electrode for flexible lithium ion batteries.

Figure 6.3 Photo images of (a) mechanical tester MTS C42 and (b) sample gripped by the holder. Tensile test diagrams of (c) pure NC and (d) NCM523 electrode with NC as the binder.

6.3.2 Electrochemical Performance Analyses

The electrochemical performance was measured using a two-electrode coin-type cell (CR2032) of $\text{Li} \mid \text{LiPF}_6 (\text{EC: EMC: DMC}=1:1:1 \text{ in weight}) \mid \text{NCM523}$. The discharge capacity of the NCM523/Li cell with PVDF binder-based electrode (NCM523: PVDF: acetylene black (AB)=8:1:1 in weight) was 194.2 mAh g^{-1} at first cycle (coulombic efficiency, 83.2%) and 186.5 mAh g^{-1} at the third cycle (coulombic efficiency, 96.8%) at

0.1 C in Figure 6.4a and b. However, the discharge capacity of the NCM523/Li cell with NC binder-based electrode (NCM523: NC: acetylene black (AB)=8:1:1 in weight) was 191.5 mAh g⁻¹ at first cycle (coulombic efficiency, 85.0%) and 191.0 mAh g⁻¹ at the third cycle. The discharge capacity of the NCM523/Li cell with NC binder-based electrode was 145.8 mAh g⁻¹ after 300 cycles at 1 C, while 113.2 mAh g⁻¹ was acquired from the NCM/Li cell with PVDF binder-based electrode. The capacity retentions are 78.9% and 59.9% of NCM523/Li cells with NC binder and PVDF binder after 300 cycles, respectively. Thus, the NCM523/Li cell using NC binder-based electrode exhibited superior long-term cycling performance (Figure 6.4c).

Figure 6.4d shows typical galvanostatic charge/discharge curves at different C rates from 0.1 to 10 C with a potential window between 3.0 and 4.6 V. The NCM523/Li cell with NC binder-based electrode exhibited improved rate performance than that of PVDF-based cell, indicating that the NC binder can enhance the kinetics of cathode. To further understand the electrochemical performance of electrodes, the first charge/discharge curves under different discharge rates from 0.1 to 10 C are shown in Figure 6.4e-g. It is clearly seen that the NCM523/Li cell with NC binder-based electrode exhibits high discharge capacity of 191.8 mAh g⁻¹ at 0.1 C, and a 72.9% capacity retention of 139.9 mAh g⁻¹ at 10 C. For the PVDF binder-based cell, the specific discharge capacities are respectively 192.7 at 0.1 C and 122.9 mAh g⁻¹ at 10 C. The capacity retention at 10 C is 63.7% of that at 0.1 C, suggesting NC binder-based electrode displays significantly better rate performance.

Figure 6.4 (a) Charging/discharging curves at the first, second and third cycle; (b) Discharge capacity and coulombic efficiency of NCM523/Li cells at the first and third cycle; (c) Cycling performance and coulombic efficiency of NCM523/ Li half-cells cycled at 1 C under 3.0-4.6 V conditions. (d,e) Rate performance and (f,g) charge/discharge curves of NCM523/Li cells cycled under 3.0-4.6 V conditions under different C rates from 0.1 C to 10 C.

Moreover, NCM523/Li cells in two kinds of electrodes show much different rate performance under different C rates (Figure 6.2e-g). The drop in the lithiation/delithiation potential of the NCM523/Li cell with PVDF binder-based electrode from 0.1 C to 10 C is 0.88 V, which is lower than that of the NCM523/Li cell with NC binder-based electrode (0.38 V). The smaller electrode polarization supports the fact that NCM523 electrode with NC binder-based electrode shows improved kinetics, which stems from the reduced activation barriers for lithium ion transfer.

Figure 6.5 Self-discharge curves of NCM523/Li cells with PVDF binder and NC binder after shelved at the fully charged state after 10 cycles for 10 days.

To address the key role of binder coating on NCM523 microparticles, the voltage decay of the cells as a function of time was monitored. The NCM523/Li cells were firstly cycled 5 cycles and then charged to 4.6 V, followed by storing for 10 days (Figure 6.5). The cell with PVDF binder-based electrode showed the rapid variation of open circuit voltage (OCV) drop ($\Delta V=0.45$ V), which indicated its fast relithiation via self-discharge compared with NC binder-based electrode ($\Delta V=0.35$ V). The discharge capacity with NC binder-based electrode retains 149.3 mAh g⁻¹ for shelving 10 days. Corresponding to the discharge capacity with PVDF-based electrode it is retained at 132.8 mAh g⁻¹. PVDF binder has

linear long-chain structure, the interaction with other electrode components is mainly via weak van der Waals forces. Therefore, the surface coverage of NCM523 by PVDF binder is poor, and a high fraction of the electrode surface is exposed to the electrolyte. In contrast, NC binder, with abundant hydroxyl groups to form reticulate fishnet structure to surround NCM523 materials, has better coverage on the NCM523 microparticles (Figure 6.2e).

Furthermore, to verify the feasibility of this NC binder-based electrode for flexible lithium ion batteries, it was directly applied as the cathode in a pouch cell. The obtained lithium ion battery shows excellent flexibility when being bent and folded to power a red LED light (Figure 6.6), confirming the sustainable operation of the NC binder-base cathode for flexible lithium ion batteries.

Figure 6.6 Optical images of (a) a NC binder-based flexible cathode electrode, a flexible NC binder-based NCM523/graphite full cell lighting a red LED under flat (b), being bent (c) and being folded (d).

6.3.3 Kinetic Diffusion Analysis

There is a pair of peaks reflecting the typical oxidation process and reduction process, which corresponds to $\text{Ni}^{2+/3+}$ and Ni^{4+} redox reaction^[12] (Figure 6.7). Compared with

NCM523/Li cell with PVDF-based electrode ($\Delta E = 0.195$ V), NCM523/Li cell with NC-based electrode ($\Delta E = 0.129$ V) exhibits a smaller electrochemical polarization. It shows that NC can enhance the ionic conductivity of the material and reduce electrode polarization.

Figure 6.7 CV curves of NCM523/Li cell with (a) PVDF binder and (b) NC binder at a scan rate of 0.1 mV s^{-1} .

To further confirm a positive effect of nanocellulose binders on the transfer of lithium ions to the surface of NCM523 electrodes, NCM523 electrode with NC binder and NCM523 electrode with PVDF binder were investigated via CV test under different scan rates (Figure 6.8). It can be indicated that NCM523 with NC binder-based electrode has higher lithium ions diffusion coefficient. When the scan rate increases, the height and area of redox peak increases. The potential differences of NCM523 with NC are smaller than those of NCM523 with PVDF at the same scan rate. The Li^+ diffusion coefficient at the oxidation stage is a little higher than that at the reduction stage, indicating that it is easier for lithium ions in NCM523 to release than to insert. The higher Li^+ diffusion coefficients may result from the porous network structure of NCM523 with NC binder, which promotes the improvement of the diffusion rate of lithium ions and further results in excellent electrochemical performance.

To gain insight into the reason that the particle with NC binder exhibits such excellent electrochemical properties, EIS of two kinds of electrodes are compared (Figure 6.8d-f). It

is worth noting that NCM523 electrode with NC binder has lower R_f and R_{ct} than NCM523 electrode with PVDF binder at the 3rd cycle. The interfacial layer resistance is $38.04\ \Omega$ for NCM523 electrode with PVDF binder after 3 cycles, and $34.44\ \Omega$ is obtained with NCM523 electrode with NC binder (Table 6.1). After 300 cycles, the interfacial impedance of NCM523 electrode with NC ($146.50\ \Omega$) is lower than that of PVDF-based electrode ($194.60\ \Omega$). As shown in Figure 6.8 (d and e) and Table 6.1, both the impedance of lithium ion immigration and charge transfer were improved. Therefore, compared to NCM523 electrode with PVDF binder, the radius of two semicircles in NCM523 electrode with NC binder are significantly decreased during long-term lithiation/delithiation process, confirming NC binder-based electrode with superior rate performance.

Figure 6.8 CV curves of NCM523/Li cell with PVDF (a) and NC (b) at different sweep rate. (c) The peak current (I_p) as a function of the square root of scan rate ($v^{1/2}$). Nyquist plot of charge NCM523/Li cell with PVDF binder and NC binder: (d) after 3 cycles at 0.1 C (e) after 300 cycles at 1 C. The inset scheme is the equivalent circuit. (f) Plots of Z' versus $\omega^{-1/2}$ of two binder-based electrodes. (g) Characterization of wetting properties.

Comparison of the contact angles of an electrolyte droplet on a PVDF binder-based film electrode and a NC binder-based film electrode.

Besides, the NCM523 with NC, as listed in Table 6.1, shows the smaller resistance for the lithium ion diffusion process owing to its fishnet-like structure which exhibits a higher diffusion coefficient than conventional small particles (8.60×10^{-11} vs. 7.57×10^{-11}). In addition, after 300 cycles at 1 C, the charge-transfer resistance of free-standing NCM523 electrode increases slightly to 154.40Ω and the lithium ion diffusion coefficient ($D_{\text{NC}} = 3.02 \times 10^{-11}$) is smaller than that of NCM523 electrode with PVDF ($D_{\text{PVDF}} = 1.96 \times 10^{-11}$), which matches with the analysis of cycling and rate performance above.

Table 6.1 The impedance parameters of NCM523 electrodes with PVDF and NC after 3 and 300 cycles.

Samples	$R_f (\Omega)$	$R_{ct} (\Omega)$	$\sigma_w (\Omega \text{ cm}^2 \text{ s}^{-1})$	$D (\text{cm}^2 \text{ s}^{-1})$	$i^0 (\text{mA cm}^{-2})$	Samples	$R_f (\Omega)$
PVDF (3 cycles)	38.04	103.20	4.15	7.57×10^{-11}	3.62×10^{-4}	PVDF (3 cycles)	38.04
NC (3 cycles)	34.44	70.80	3.64	8.60×10^{-11}	7.45×10^{-4}	NC (3 cycles)	34.44
PVDF (300 cycles)	194.60	252.00	16.01	1.96×10^{-11}	1.02×10^{-4}	PVDF (300 cycles)	194.60
NC (300 cycles)	146.50	154.40	10.40	3.02×10^{-11}	1.66×10^{-4}	NC (300 cycles)	146.50

The good wettability of electrodes with electrolytes has a pronounced impact on facilitating the diffusion of electrons/ions in the electrode. In contrast, the inferior wetting property is detrimental to electrolyte permeation and hence limits the reversible reaction kinetics, resulting in unsatisfactory reversible capacity.^[13] Their contact angles (CA) with liquid electrolyte were measured (Figure 6.8g). The PVDF electrode has a CA of 114.8° at 1 second and 41.4° at 3 seconds. In contrast, the CA of NC electrode with the electrolyte decreases from 68.2° to 10.4° , suggesting the improved wettability with electrolyte. Notably, the electrolyte droplet spreads out completely on NC electrode within 6 seconds, indicating its super wettability with the electrolyte. As described by Wenzel's equation,^[14]

$$\cos \theta' = r \cos \theta$$

6-5

where θ' is the apparent CA on a rough surface, θ is the intrinsic CA on the flat surface, and r is the surface roughness, the cooperation between the surface chemical compositions and topographic structures is crucial to construct special wettability.²³ Accordingly, the superior wettability of NC electrode can be attributed to the close polarity between hydroxyl groups and electrolyte as well as the properly horizontal arrangement of NC that enhance the surface roughness (r) of the electrode. The present results demonstrate that this smart surface engineering approach is very effective to create super-wettability for free-standing architecture.

6.3.4 Surface Analyses

Photographs of the NCM523 electrodes of the two sample cells after 300 cycles, when cycled at 1 C under 3.0-4.6 V, are shown in Figure 6.9a and 6.9b. There are some small bright spots on the surface of the electrode using PVDF. It can be ascribed to the loss of active material. The NCM523 electrode using NC relative to each other has no breaking electrical connectivity and no forming cracks. In fact, the capacity of the NCM523 electrode using PVDF decayed seriously than that using NC at around the 300th cycle. Further, the separator of PVDF-based NCM523 electrode and the separator of NC-based NCM523 electrode were then analyzed with ICP-MS (Figure 6.10). Indeed, the concentration of Ni, Co and Mn on the separator cycled with PVDF binder-based electrode are 6.978, 2.975 and 5.468 ppm, respectively. For the separator with NC binder-based electrode, the concentration of Ni, Co and Mn are 1.018, 0.487 and 0.723 ppm, respectively, which is lower than that with PVDF binder-based electrode. There are some cracks among the secondary particles and the surface of NCM523 electrode with PVDF (Figure 6.9c-e), which can lead to the parasite reaction. Such cracks and the loose structure were caused by stress concentration originated from the anisotropic changes in lattice dimension of secondary particles and weak mechanical properties of PVDF binder.^[1, 2, 15]

Figure 6.9 Photographs of the NCM523 electrode after (a) 0 cycle and (b) 300 cycles at 1 C under 3.0-4.6 V conditions. SEM images of NCM523 electrodes: (c,d,e) PVDF binder-based and (f,g,h) NC binder-based electrode after 300 cycles under 3.0-4.6 V conditions. The process illustration of enhancing the performance of NCM523 electrode with (i) PVDF binder and (j) NC binder after 300 cycles under 3.0-4.6 V conditions.

In comparison, the NCM523 electrode with NC binder shows a compact and flat surface as shown in Figure 6.9(f-h), which is ascribed to the multiple reasons, such as (i) the hydroxyl functional group of NC binders and (ii) the elastic and fishnet-like network coverage of the NCM523 particles. The NC-based electrode possesses abundant surface hydroxyl group, which can improve the wetting of the electrolyte and promote the electrolyte penetration properties (Figure 6.8g). Especially, because of NC with an elastic

and reticulate structure to interact with the NCM523 materials, it has better coverage on the NCM523 microparticles (Figure 6.2e) to avoid secondary particle crack, which restrains the capacity fading. The crack of the secondary particle will lead to discontinuous electronic and ionic transport. Figure 6.9(i and j) schematically illustrates the electrons and ions transfer between primary particles in secondary particles and the process causing crack in the secondary NCM523 particles with PVDF and NC binder.

Figure 6.10 Photographs of the NCM523 electrode with PVDF and NC binders and separator of the cells after (a) 0 cycle and (b,c) 300 cycles when cycled at 1 C under 3.0-4.6 V conditions, and (d) Ni, Co, Mn dissolution amount in NCM523 electrode at 1 C after 300 cycles.

Figure 6.11 TEM images of NCM523: (a) fresh particles, NCM523 electrodes with PVDF (b) and NC (c) after 300 cycles under 3.0–4.6 V conditions. HRTEM Images of NCM523: (d) fresh particles, NCM523 electrodes with PVDF (e) and NC (f) after 300 cycles under 3.0–4.6 V conditions. Correspond to the FFTs and IFFTs of NCM523: (g) fresh particles, NCM523 electrodes with PVDF (h) and NC (i) after 300 cycles under 3.0–4.6 V conditions. XRD of NCM523: (j) 10–70° (k) 18–19.5°. (l) Illustration of the ordered and disordered phase in NCM523 and the structural transformation (TM-transition metal, blue boll-Li ion, yellow boll-Oxygen, red boll-transition metal).

Furthermore, TEM images of fresh particles (Figure 6.11a), cycled NCM523 electrode with PVDF (Figure 6.11b), and NC (Figure 6.11c) electrolyte were obtained. The surface of fresh NCM523 particle is smooth. There are some large crystal grains at the edge of the

cycled NCM523 with PVDF binder, which leads to a loose structure at the electrode surface and causes the decomposition of solvents because of generating activate sites. In contrast, the NCM523 surface cycled with NC binder remains a flat surface, which prevents the extensive oxidation of electrolytes and the structure cracking of NCM523 particle surface, maintaining the fast ionic and electronic transport in the NCM523 electrode. This observation matches well with that of Figure 6.2. Moreover, Figure 6.11(e and f) show that these two electrodes have different solid electrolyte interface (SEI) films. The SEI film on the electrode with PVDF (~ 11 nm) is much thicker than that with NC (~ 5 nm), which clearly indicates an accelerated electrode erosion and oxidation of electrolyte in PVDF binder-based cells.

Figure 6.12 XPS of NCM523 electrodes with PVDF and NC binders after 300 cycles.

In addition, XPS spectra of two samples in F1s, O1s and C1s branches were carried out after the 300th cycled at 1 C (Figure 6.12). In the F1s branch, the spectra of the PVDF shows more pronounced peak corresponding to LiF (684.5 eV) after the 300th cycle, which are known to be formed near the surface of NCM523 active material.^[16] When the peak of LiF arise, the interface impedance increases as the poor conductivity of LiF impede the transmission of lithium ion in the solid electrolyte interface.^[17] In the O1s branch, the relative intensities of C=O bond (532.4 eV) and Li₂CO₃ (531.8 eV) from the NC binder-

based electrode after the 300th cycle are weaker than PVDF-based electrode, which corresponds to lithium alkyl carbonates (R-C-O-COOLi) (533.8 eV).^[18] This distinct result indicates the NCM523 electrode is protected by NC binders from PF_6^- to form HF which erodes the cathode materials, leading to less formation of organic components. SEI film derived from NC binder-based electrode is more stable than that derived from PVDF binder-based electrode. Moreover, four peaks in the C 1s spectra at 290.1 eV, 287.6 eV, 286.0 eV, 284.1 eV, are attributed to Li_2CO_3 (main reaction products of carbonate-based electrolyte), C=O bond (in lithium alkyl carbonates and polycarbonates), C-H bond (due to lithium alkyl carbonates and PVDF), and C-C bond (belonging to carbon black), respectively.^[19, 20] The lower intensity of Li_2CO_3 of NCM523 electrode with NC binder than that with PVDF suggests that carbonate-based electrolyte decomposition was reduced and the SEI film of the NC-based electrode is thinner than that of the PVDF-based electrode.

Fast Fourier transformation (FFT) and inverse fast Fourier transform (IFFT) studies were performed to estimate the range where the crystal structure occurred, as shown in Figure 6.11(g-i). The d-spacing of the primary particle, acquired from the lattice image and FFT, was ≈ 0.2727 nm. The lattice parameter of PVDF binder-based NCM523 electrode and NC binder-based electrode were ≈ 0.3262 and ≈ 0.2844 nm, respectively. To confirm the difference between PVDF-based electrode and NC-based electrode, XRD was analyzed; a diffraction pattern is revealed in Figure 6.11j. All peaks can be indexed as NCM523 (space group $R\bar{3}m$, ICSD No. 78687). Compared with pristine NCM, the intensities of all diffraction peaks for PVDF binder-based sample are more seriously declined after 300 cycles under 3.0-4.6 V conditions than those for NC binder-based counterpart, which implies the crystal structure of PVDF-binder electrode is suffered from varying degree of . The c-axis is normal to the set of planes that contribute to the (003). Compared with PVDF-binder electrode, the NC-architecture exhibits a smaller shift of (003) peak (Figure 6.11k), which is consistent with the mentioned before. Structural stability of layered materials is correlated to “cation mixing”, which comprises cations disordering between lithium sites (octahedral 3b site) and transition-metal sites (octahedral 3a site).^[21-24] Layered materials have $R\bar{3}m$ structure that is a repeating O_3 structure of oxygen-lithium-oxygen-TM(transient metal)-oxygen-lithium-oxygen-TM-oxygen along the rhombohedral direction.^[23]

Therefore, there are clearly separated transition metal sites (3a) and lithium sites (3b) in the perfect $R\bar{3}m$ structure (Figure 6.11l). In comparison with the well-ordered phase, the disordered phase has a higher activation energy barrier for lithium ion diffusion, which corresponds to a lower lithium diffusivity.^[24, 25] It is respectively ascribed to its smaller distance between the slabs and hindrance caused by the transition metal in the lithium layer. The disordering can give rise to a decrease in intensity of the (003) peak and a partial destructive interference of the (003) plane's constructive interference at a Bragg angle of $\theta_{d(003)}$, which was confirmed by XRD spectra from Figure 6.11(j and k). All the above experimental evidence confirmed that NC free-standing architecture maintains the structural integrity of layer materials under high voltage and ensuring it a superior electrochemical performance. As a result, significant cracks are formed on the PVDF-based electrode after cycling, while the NC-based electrode maintains the structural integrity due to the strong mechanical properties of NC.

6.3.4 Mechanism for Intergranular Crack Formation

Figure 6.13 schematically illustrate the formation process of cracks in the NCM523. The anisotropic changes in lattice constant due to lithium ion extraction and insertion during battery cycling, resulting in cracking at the grain boundaries. Intergranular crack forms and propagates progressively between neighboring primary particles after long-term cycles.^[1, 2] The intergranular cracks can form voids between primary particles and discontinuous electronic and ionic transport paths. The degradation in regeneration of the rock-salt type surface layer results in the increase in transfer resistance and electrolyte decomposition.^[21] Furthermore, the electrolyte seeps into the intergranular cracks of secondary particles, leading to the exposure of primary particles to the electrolyte, the oxidation of electrolytes and capacity fading. Finally, augment of such parasite reaction could in turns promote the intergranular cracks and expose more surface of the grain boundary to the electrolyte at extended cycles.^[1, 2, 25]

Figure 6.13 A schematic illustrating the formation process of intergranular crack in a secondary NCM particle with (a) PVDF binder and (b) NC binder. The green arrows indicate the aggregation of primary particles with different crystal orientations into secondary particles. The first three cycles initiate intergranular crack and expose the surface of intergranular to the electrolyte. Long-term cycles aggravate the spread of intergranular cracks and pulverize the secondary NCM523 particles.

NC binder-based film electrodes can improve tensile strength of flexible electrodes because of its high aspect ratio (diameter: ~ 30 nm, length: ~ 400 μm) and high mechanical strength (the ultimate tensile strength of the NC sheet is 23.87 MPa, Figure 6.3). In addition, the hydrogen bonding interacts among solvated nanofiber bundles, forming a three-dimensional network of cross-linked structure. NC binder endows the resulting electrodes highly flexible and stretchable, which prevents the pulverization of NCM523 secondary particles through maintaining the continuous connection of primary particle in secondary particles during repeated delithiation/lithiation process. The reticulate structure of NC binder coated on the pulverized NCM523 secondary particles plays a key role in preserving the electrode structure. Long-term capacity fading of NCM523 cathode is mitigated. By contrast, a PVDF binder cannot perform such functions, and the intergranular crack of secondary particles forms and propagates progressively during the life-span cycling.

6.4 Conclusion

In this work, an elastic and reticulated NC binder is employed to fabricate flexible and high voltage lithium ion battery cathode. The rich in hydrogen bonding among NC fibres enable the mechanical robust network to cover the secondary NCM523 particles. The NC binder functions as the freestanding support for the flexible electrode and the protective layer to prevent the formation of microcrack in the secondary particles and electrodes. This protection further suppresses the extensive oxidation of electrolyte and more stable SEI for a flexible electrode. As a result, NC binder-based electrodes exhibit a higher discharge capacity of 145.8 mAh g⁻¹ after 300 cycles at 1 C than that of 113.2 mAh g⁻¹ for PVDF binder-based electrode. Besides, the full cell can keep its function to light LED under bending and folding conditions, which shows excellent flexibility of NC-binder based electrodes. The biomass-based NC binder is a promising candidate for assembling of flexible, customizable and high voltage lithium ion batteries.

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Chapter 7 *

Discussion and Future Work

In this chapter, the implications of the thesis are concluded. Some preliminary results not included in the main chapter of miniature, stretchable and customizable EES devices are discussed. Also, the future directions of related field, including innovations in materials and structures of customizable devices, further extension of efficient fabrication methods and integrated multifunctional systems, artificial intelligence enabled programmable combinations of customizable properties, are discussed.

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7.1 General Discussion

This thesis aims at achieving the highly flexible and stretchable EES devices based on the new-developed mechano-adaptive electrodes and device structures: the mechano-adaptive electrodes behave enhanced tensile strains, mediate the stress concentration on the electrode and suppress the electrode material pulverization during charging and discharging. Such electrodes make the EES devices reconfigurable while maintaining the electrochemical performance of the devices stable during deformation. The reconfigured mechano-adaptable structures of the EES devices can further regulate and reduce the peak strain of the electrodes, which enables a wider range of electrode materials for flexible and stretchable EES devices.

Firstly, the current status of the flexible and stretchable EES devices is introduced, and the importance of the innovations in the electrode materials and structures is elucidated. The hypothesis of mechano-adaptive materials and devices for flexible and stretchable EES device is analyzed and proposed. Besides, the methods to synthesize materials, characterize the morphology of the electrode materials and devices, and test the electrochemical performance of the flexible EES devices are discussed.

Based on the mechano-adaptive electrode materials and device structures, three new kinds of mechano-adaptive composite materials for strain enhancement, device editability and effective stress relief of material expansion during charging/discharging process are coupled with two kinds of mechano-adaptable structures to achieved flexible EES devices with editable structures, customizable 3D shapes and enhanced energy density.

In detail, an “editable strategy” was proposed to make supercapacitors with customizable stretchability up to 500%. Supercapacitor units were first made up of flexible materials assembled from freestanding interwoven ultralong MnO₂ nanowire/CNT composites, the flexible units were then edited into a desirable structure, allowing the supercapacitor being stretched into customizable shapes. The stretchability of this editable structure (up to 500%) is much superior to conventional stretchable structure (up to 200%). Due to its editability,

supercapacitors can be customized into desirable shapes and structures for versatile plug-and-play applications while maintaining the electrochemical performance to power various flexible and wearable electronics.

Along with the customizable two-dimensional (2D) supercapacitor, stretchable supercapacitors with customizable three-dimensional (3D) shapes and enhanced areal capacitance is also developed, which is inspired by the traditional artifact-honeycomb lantern. With a honeycomb pop-up structure, the customizable 3D supercapacitors can overcome the limited device thickness of traditional 2D supercapacitors. Notably, a honeycomb-lantern-inspired 3D supercapacitor with a 1.0-cm-thick rectangular shape exhibited improved specific areal capacitance of 7.34 F cm^{-2} , which is 61 times than that of the conventional 2D planar supercapacitors (120 mF cm^{-2}). The supercapacitor comprises flexible polypyrrole (PPy)/black phosphorous oxide (BPO)-carbon nanotube electrode configured in expandable honeycomb structures for maintaining the stable electrochemical performance of supercapacitors under deformation (capacitance retention of 95% even under the reversible 2000% tensile strain after 10,000 stretch-and-release cycles).

Furthermore, to achieve flexible EES device with higher energy storage performance, a biomass-based and elastic NC binder is employed to fabricate flexible high-voltage NCM523 cathode. The elastic nanocellulose (NC) binder was used to function as the porous freestanding framework to protect the intergranular of the NCM523 secondary particles from cracking. The NC-binder based electrode owns improved rate performance and more stable long-term capacity (145.8 mAh g^{-1} after 300 cycles at 1 C) at 4.6 V compared to that of PVDF binder-based electrode (113.2 mAh g^{-1}). Furthermore, the NC binder-based full cell lithium ion battery functions well to power red LED under bending and folding conditions. This flexible and high voltage cathode paves the way for flexible high energy lithium ion batteries.

Based on mechanical adaptable electrodes and structures, the result shows that a series of flexible and stretchable EES devices with customizable 2D and 3D shapes can be

developed with superior properties. The idea of transforming EES devices to ultra-stretchable and highly customizable devices would see great applications in the emerging everywhere-able electronics. It provides a new design platform for stretchable EES devices. Following it and cooperating with functional materials, many other new methods and stretchable energy harvesting and integrated electronics could be further developed.

7.2 Future work: customizable EES device and smarter wearable and bio-integrated devices

With technological progress and increasingly human-oriented advancements, electronics have transformed from being immobile and bulky to being portable and compact, becoming user-friendly and easy to operate. It underlines the ongoing emergence of wearable and bio-integrated platforms, with an emphasis to guide the current electronics to a higher degree of customizability in terms of flexibility, shape, and bio-conformability (Figure 1). To intimately integrate with the human body, electronics are becoming flexible and stretchable to withstand the large strain of deformation during complex body motions, allowing users to bend, twist and stretch the electronics without compromising their functions. Apart from flexibility and stretchability to comply with body motion, the human-oriented electronics also gear towards having customizable shapes for optimized space-utilization for different needs, such as near-body, on-skin, and implantable applications. Moreover, the customizable bio-conformability guarantees the electronics the desired bio-interface with human body, where it needs to be comfortable, biocompatible, implantable or even ingestible in some applications. Success in such customizability of electronics offers exciting opportunities to fabricate wearable electronics, epidermal electronics, implantable electronics and ingestible electronics for personalized fitness and biomedical applications (e.g., activity tracking, health monitoring, and controlled drug delivery).¹⁻⁹

As more wearable and bio-integrated electronics are expected to be manufactured and used, there is an increased demand for complementary electrochemical energy storage (EES) devices, especially batteries and supercapacitors. As a result of the evolution of customizable electronics, the customizability in flexibility, shape, and bio-conformability

with human body has emerged as a new figure-of-merit for the future EES devices. The customizable EES devices are stretching the concept beyond capacity and rate capability, to an extent where they are adaptable with wearable and bio-integrated electronics. Such customizable EES devices should connect seamlessly with customizable electronics in order to obtain truly customizable integrated systems for human body application. They present a new alternative in how the electronics are charged and operated (Figure 1).¹⁰⁻¹²

Figure 7.1 The drive of the emerging customizable electronics for customizable electrochemical energy storage devices. Reprinted with permission from ref. 1. Copyright 2017 Wiley-VCH. Springer Nature Limited. Reprinted with permission from ref. 2. Copyright 2018 Wiley-VCH. Reprinted with permission from ref. 3. Copyright 2016 Springer Nature Limited. Reprinted with permission from ref. 10. Copyright 2013 Springer Nature Limited. Reprinted with permission from ref. 11. Copyright 2018 Wiley-VCH. Reprinted with permission from ref. 12. Copyright 2017 Springer Nature Limited.

In the future, allowing users to select, design and change its functions according to wearable and bio-integrated scenarios represents the inevitable direction towards next-generation customizable EES devices. Based on current research progress, some of the existing problems and future directions for customizable EES devices are discussed as follows.

7.2.1 Innovations in materials and structures of customizable devices

The primary function of EES devices is to store and supply energy. Intensive ongoing research aims to bring new materials with even higher specific capacity for next-generation customizable EES devices.¹³ However, in reality, the energy storage performance of customizable EES devices are usually much poorer than conventional counterparts due to the limited material selection available. Seeking novel materials with substantially higher energy density seems a promising avenue. The use of pseudo-capacitive materials and heteroatom-doped carbon materials in supercapacitors is an effective way to boost energy density, while alloy and conversion materials, such as silicon with much higher theoretical capacities (4200 mAh g^{-1}) compared with common insertion materials (372 mAh g^{-1} in graphite), are probably the solution for Li-ion batteries.¹⁴⁻¹⁶ Battery systems other than Li-ion batteries are being investigated extensively, specifically Li-S and Li-O₂ batteries, for promising next-generation high energy density EES devices.¹⁷ Nevertheless, batteries based on emerging systems are at still the embryonic stage; there is a long way to verify their practical role in customizable EES devices. Safety issues residing in current EES systems should not be overlooked when designing next-generation EES devices. Current corrosive or flammable electrolytes can result in health hazards due to potential electrolyte leakage during the device lifetime. Developing solid-state electrolytes is deemed as most critical to address the safety issue. Unfortunately, their ionic conductivity and adhesion with electrode materials are still lacking, losing out to conventional electrolytes for practical applications.¹⁸

Solely improving electrochemical properties is not enough; there are still many challenges in the current electrode and device structures, calling for more deformation-compatible structure designs. For wave-like and fiber-shaped structures, they are only compatible with active materials that are robust enough to form the desired structure. The limited materials selection, mainly CNT and graphene-based materials, restricts the use of active materials with higher capacity and hinders further increase in the performance of customizable EES devices. For the bridge-island structure, the balance between the high plane coverage of

active materials and high stretchability of electrodes is essential yet tricky. Moreover, the mismatch in terms of resiliency between active materials and elastic substrates often results in stress concentration at the interface, leading to performance degradation and long-term instability during the stretch-and-release process.¹⁹ Besides, newly developed flexible and stretchable structures are mostly focused on 2D surfaces with limited areal energy density, while the limited surface area of human body requires the development of customizable 3D EES devices with deformability and enhanced areal capacity.²⁰⁻²¹ The expandable honeycomb structure in chapter 5 can meet the requirement of EES devices with 3D shapes, but the positive Poisson's ratio in this structure cannot match well with ergonomic structure. In this regard, a modified expandable honeycomb structure with negative Poisson's ratio (Figure 7.2) is more suitable to improve the mismatch interfaces between 3D EES devices and curved human body surface.

Figure 7.2 (a and b) The digital photo of the expandable honeycomb structure with a positive Poisson's ratio and (c and d) the reentrant honeycomb structure with a negative Poisson's ratio.

Therefore, there is still a need to devise other ingenious electrode and device structures that

are compatible with current materials for fabricating high-performance and highly deformable EES devices. Furthermore, the lack of understanding the interactions in the electrolyte/electrode interface under deformation conditions results in uncontrolled performance in these devices. Studies through in-situ characterization and advanced simulation techniques will provide deep insights into the electrode interface behaviors in customizable EES devices, and will benefit the structure optimization and new structure design.^{19, 22-23}

7.2.2 Further extension of efficient fabrication methods and integrated multifunctional systems

As expected, the customizability of EES devices would require more complex fabrication processes than their conventional EES counterparts, which may potentially hinder the translation to industrial mass production. A slurry-coating process is usually used to fabricate planar electrodes in conventional supercapacitors and batteries. However, this process is not suitable for fabricating electrodes with different constituents and specially designed structures, which is usually the case in customizable EES devices.^{20, 24-27} Therefore, controllable, scalable and high-throughput manufacture of structured electrodes and devices will remain a research focus for customizable EES devices. As shown in Chapter 4, the editable supercapacitors are useful to produce customizable EES devices with desirable shapes and structures. However, the cutting process may be tedious for users. To enable facile preparation of the editable EES devices with customizable patterns, a laser-printing assisted vacuum filtration method has been developed to transfer customizable into desirable substrates as shown in Figure 7.3. Various printing technologies (screen, spray, jet, gravure and 3D printing), laser-writing and holographic patterning (photolithography) growing rapidly in recent years might be viable for the fabrication of customizable EES devices.²⁸⁻³⁰ Recently, 3D printers have successfully printed customizable Li-ion batteries with thick electrodes through extruding and then solidifying anode and cathode inks, coupled with the UV curable separator and packaging inks to form arbitrary geometries.³¹⁻³² It is feasible to apply these technologies to achieve customizable structural electrodes and devices with precise, highly-uniform structures.

Figure 7.3 (a) Laser-printing of the hydrophobic ink into filtration films to leave uncovered space with desirable shapes for vacuum filtration; (b) The deposited active materials transfer into a PDMS substrate.

The ultimate beneficiary of customizable EES devices would be wearable and bio-integrated electronics. The ability to integrate other electronics components or incorporate multi-functionalities into one device is an inevitable route for future customizable EES devices. Although abundant customizable EES device prototypes have been demonstrated, only a few functions have been integrated with the devices. Wireless power transmission presents a key feature to be integrated into customizable EES devices for wireless-charging electronics. Additionally, for self-powered electronics, customizable EES devices should further couple with energy conversion devices (e.g., solar cell, microbial fuel cell, piezoelectric nanogenerators) through harvesting energy from body heat, movement, and ambient light.³³⁻⁴⁰ Moreover, through functionalized electrode or electrolyte with advanced materials, functions such as optical transparency, self-healing, electrochromism can also be incorporated.⁴¹⁻⁴² Other functions including shape-memory, thermal responsiveness, and photodetection are believed to be essential in advanced applications of artificial intelligence and biomimetic technology, which will be explored for smarter and customizable four-dimensional (4D) electronics.⁴³

7.2.3 Artificial intelligence enabled programmable combinations of customizable properties

After the first decade of customizable EES devices, we are now entering a period where the combination of customizable properties is important. These customizable properties include but are not limited to energy storage capacity, mechanical flexibility, shape, and functionality, according to practical needs (Figure 3). However, the current research on customizable EES devices mainly focuses on improving each individual property, which unfortunately compromises the combination of these collective customizable properties. Recent years have witnessed explosive development of artificial intelligence and their broad-spectrum applications in various scientific areas. Artificial intelligence is becoming a powerful tool in predicting and analyzing complicated relationships, which may aid materials scientists to precisely link the relationship between the hierarchical structures (i.e., material, electrode, device and system) and customizable properties (i.e., energy storage, mechanical flexibility, shape, and functionality) of customizable EES device. Making full use of powerful computational capabilities, further studies could explore the following directions: (1) building multiparametric combinational database for computational simulation; (2) recruiting artificial intelligence in the discovery of new customizable EES devices; (3) merging computational simulations with experiments for database verification and analysis.

A multiparametric combinational database would provide us with higher versatility for the customizable combination of properties. Given the complex and interdependent physicochemical properties in the combinational process, an extensive interpretation of the key parameters for the customizable combination is necessary to optimize material-device interfaces and to deliver customizable combinational devices. The intrinsic energy storage capacity of a material is determined by its intrinsic thermodynamic properties of the material, while the real energy storage performance of an EES device is usually biased by some physical parameters (such as size, shape, and stacking structure). Based on these parameters of the electrode materials, the energy storage performance of an EES device can be affected by different pathways, such as the electrode conductivity, ion-transfer

pathways, and electrolyte penetration into the electrode. Furthermore, other physicochemical properties (e.g., mechanical, biocompatible, stimuli-responsive properties) of the materials can also influence the stability of the electrode structure, the feasibility of device fabrication and the expression of the functionality in the device systems. All these need to be factored as weighted parameters when modeling the performance of customizable EES devices. Building a multiparametric combinational database for the computer simulation will contribute to the systematic understanding of the combinational process.

Traditionally, experimental data are first collected, followed by prediction via extrapolation. However, this method is incompatible with a large amount of data for multiparametric prediction. Advances in artificial intelligence or machine learning enable the computers through learning empirical data to discover hidden relationships between inputs and outputs of a system without involving the explicit mechanisms. Considering the complex variables in customizable combination, machine learning can be a viable technique to increase the efficiency and accuracy of the design of a customizable EES device. Recently, artificial neural networks have been used in the prediction of electrochemical performance, including capacitance prediction for carbon-based supercapacitors⁴⁴, the design of Li-ion batteries⁴⁵ and the remaining battery life prediction⁴⁶. Deep learning can also be extended to predict and design the electrochemical and mechanical performance of the material, composite materials, combinational material and structure at multiscale structures of customizable EES devices.

It is noteworthy that through deep learning, the algorithms from machine learning models can permute the combinational properties to find new types of customizable EES devices and predict their physicochemical properties. The incorporation of multiparametric combinational database and artificial intelligence can profoundly accelerate the design and identification of optimal combination process, and effectively narrow down the permutations of the combinational properties for subsequent experimental verification and analysis. Merging computer simulation and experiments into holistic design tool will reciprocally benefit the translation of conceptual combinational properties of customizable

EES devices into controllable and programmable products.

Figure 7.4 The technology building blocks for future advances in customizable electrochemical energy storage devices. Reprinted with permission from ref. 7. Copyright 2017 American Chemical Society. Reprinted with permission from ref. 11. Copyright 2018 Wiley-VCH. Reprinted with permission from ref. 15. Copyright 2016 Springer Nature Limited. Reprinted with permission from ref. 18. Copyright 2016 Springer Nature Limited. Reprinted with permission from ref. 20. Copyright 2018 Wiley-VCH. Reprinted with permission from ref. 21. Copyright 2015 Springer Nature Limited. Reprinted with permission from ref. 22. Copyright 2018 Wiley-VCH. Reprinted with permission from ref. 23. Copyright 2018 Wiley-VCH. Reprinted with permission from ref. 27. Copyright 2014 Wiley-VCH. Reprinted with permission from ref. 29. Copyright 2011 Springer Nature Limited. Reprinted with permission from ref. 32. Copyright 2013 Wiley-VCH. Reprinted

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7.3 Outlook

The first-decade development of customizable EES devices has seen the fusion of customizable properties. Advances in the materials, electrode structures, device fabrications and system integrations each created the technological building blocks that provide the present EES devices with capacity, flexibility, shape, and functionality. The future of customizable EES devices should create the all-in-one platform, allowing manufacturers and users to program them to perform different functions for different needs in real life. Through novel materials engineering, innovative structure design, and robust computer simulation and artificial intelligence, we might expect the development of customizable EES devices to create a user-friendly and personalized interaction for future wearable and bio-integrated electronics.

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