EDITORS
GUOZHEN SHEN | ZHENG LOU | DI CHEN

FLEXIBLE SUPERCAPACITORS

MATERIALS AND APPLICATIONS

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Flexible Supercapacitors

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Materials and Applications

Edited by

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WILEY

This edition first published 2022

Registered Office
John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, USA

Editorial Office
111 River Street, Hoboken, NJ 07030, USA

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Library of Congress Cataloging-in-Publication Data
Names: Shen, Guozhen (Electrical engineer), editor. | Lou, Zheng, editor. | Chen, Di, editor.
Title: Flexible supercapacitors : materials and applications / edited by Guozhen Shen, State Key Laboratory for Superlattices and Microstructures, Beijing, China, Zheng Lou, State Key Laboratory for Superlattices and Microstructures, Beijing, China, Di Chen, University of Science and Technology, Beijing, China.
Description: First edition. | Hoboken, NJ : John Wiley & Sons, Inc., 2022. | Includes bibliographical references and index.
Identifiers: LCCN 2021052431 (print) | LCCN 2021052432 (ebook) | ISBN 9781119506164 (hardback) | ISBN 9781119506188 (obook) | ISBN 9781119506171 (epdf) | ISBN 9781119506157 (epub)
Subjects: LCSH: Supercapacitors. | Flexible electronics.
Classification: LCC TK7872.C65 F555 2022 (print) | LCC TK7872.C65 (ebook) | DDC 621.31/5–dc23/eng/20211207
LC record available at https://lccn.loc.gov/2021052431
LC ebook record available at https://lccn.loc.gov/2021052432

Cover Design: Wiley
Cover Image: © draganab/Getty Images

Set in 9.5/12.5pt STIXTwoText by Straive, Pondicherry, India

10 9 8 7 6 5 4 3 2 1

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Preface

As an emerging and exciting research field, flexible electronics have attracted tremendous interests from both the academic and industrial communities. Till now, many kinds of flexible electronic devices and systems have been developed, such as flexible displays, electronic skins, health monitoring bioelectronics, chemical and biosensors, wearable smart textile, and intelligent soft robots, etc. This area develops very fast and some flexible products are already commercially available. For example, flexible organic light-emitting diode displays have been widely used in smart phones, smart watches, and tablet personal computers.

The booming development of flexible electronics has driven the demand for compatible flexible energy storage devices, ideally to make the whole electronic system flexible. Although conventional energy storage devices, such as lithium-ion batteries, lead acid batteries, supercapacitors, have been widely used in our modern society and affected our daily life, their rigid shape, heavy weight, and thickness make them not suitable for flexible electronics. Among different energy storage devices, supercapacitors have the advantages of simple device structure, high power density, short charge and discharge time, long cycle life and wide operating temperature range. When making supercapacitor flexible, it will also possesses the required features of excellent flexibility, portability, stretchability, miniaturized size, ultrathin thickness for flexible electronic devices. During the past several years, researches on flexible supercapacitors are very active and this field expanded very fast. Thus, it is considered timely to provide a survey of a number of important developments in this filed.

This book provides an up-to-date survey of the state of flexible supercapacitors. It contains a selection of 11 chapters contributed by a number of research teams. All the contributors are active researchers in the field of flexible supercapacitors. The most important topics related to flexible supercapacitors are included in this book, ranging from the selection and design of different active electrode materials, the design of different device structures, suitable fabrication techniques, and different functions. I hope this book will be a source of inspiration for graduate students, researchers, and industrial engineers, and will stimulate new developments in this challenging but exciting field.

Guozhen Shen, Professor
Beijing, China

1

Flexible Asymmetric Supercapacitors

Design, Progress, and Challenges

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1.1 Introduction

Recently, flexible electronic products, such as flexible microphones [1], elastic circuits [2–4], pressure and strain sensors [5–7], artificial skin sensors [8–10], intelligent garments [11], and wearable health monitoring devices have boomed as a new and important field of modern electronics (Figure 1.1). Therefore, the development of suitable energy storage devices, which can serve as an excellent power supply while sustaining high mechanical flexibility, are becoming increasingly necessary to power these electronics [13–21]. Supercapacitors (SCs), also known as electrochemical capacitors or ultracapacitors, have emerged as the bridge between batteries and traditional capacitors due to their promising merits of high power density (about 10 kW kg^{-1}), good reversibility, excellent cyclic stability (over 10^6 cycles), and safety [22, 23]. Meanwhile, accompanied with the advanced development of lightweight, foldable, and stretchable materials, substantial effort has been invested in the fabrication of flexible supercapacitors (FSCs) [24–28].

In order to satisfy the further demand for practical usage, the configuration of the two electrodes as well as the geometry of the devices are of vital importance and worth careful considerations [29]. The major obstacle of early designed FSCs is their relatively low energy density (E) to mismatch basic requirements of future applications. Thus, tremendous efforts have been denoted to optimize the overall performance of FSCs according to the Eq. (1.1), without sacrificing their power density and service life.

$$E = \frac{1}{2}CV^2 \tag{1.1}$$

In general, either enhanced capacitance (C) or enlarged operating voltage (V) of the device should make sense. Of which, the C of a FSC device can be equivalent to the negative electrode capacitance (C_n) and positive electrode capacitance (C_p) connected in series (Figure 1.2a), which can be calculated using Eq. (1.2)

$$\frac{1}{C} = \frac{1}{C_n} + \frac{1}{C_p} \tag{1.2}$$

Flexible Supercapacitors: Materials and Applications, First Edition. Edited by Guozhen Shen, Zheng Lou and Di Chen.

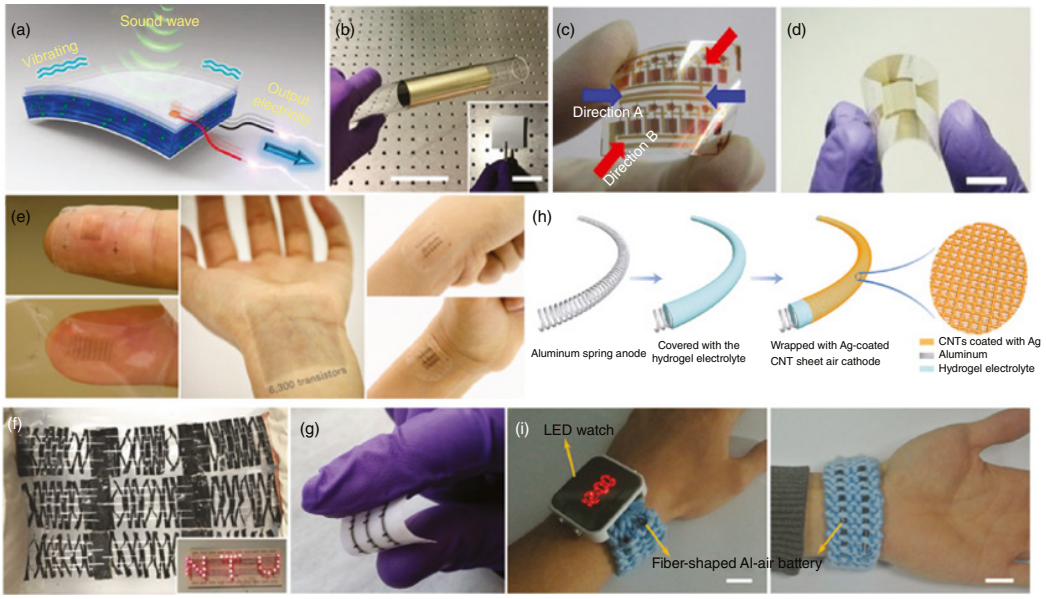

Figure 1.1 (a, b) Scheme and optical image of a flexible acoustic device. *Source:* Reproduced with permission from Ref. [121], © 2017, Springer Nature. Optical image of (c) a flexible circuit *Source:* Reproduced with permission from Ref. [2], © 2018, NPG, (d) multiplexed fingerprint sensor. Scale bar, 1 cm. *Source:* Reproduced with permission from Ref. [5], © 2018, NPG and (e) artificial skin electronics *Source:* Reproduced with permission from Ref. [8], © 2018, NPG. (f) 3 × 3 honeycomb-like supercapacitor array powering LED panel. *Source:* Reproduced with permission from Ref. [13], © 2017, Wiley. (g) Image of an array of field-effect heterojunctions on textile. *Source:* Reproduced with permission from Ref. [14], © 2017, NPG. (h, i) Fabrication and optical image of the fiber-shaped Al-air battery. *Source:* Reproduced with permission from Ref. [15], © 2016, Wiley.

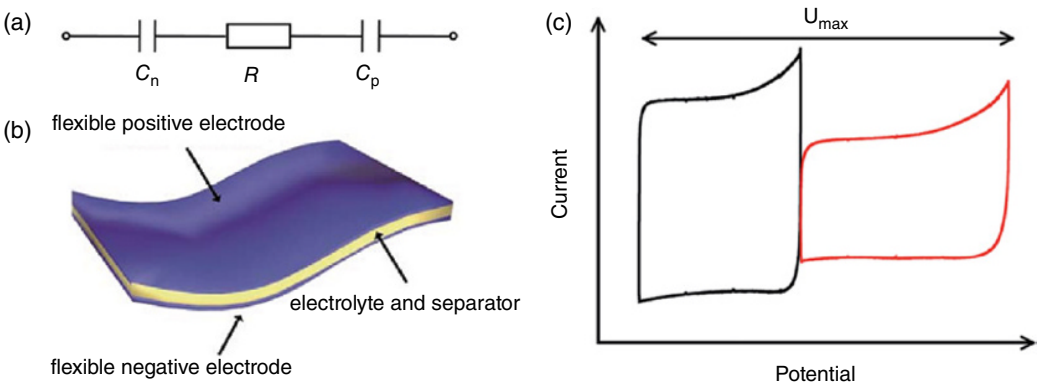

Figure 1.2 (a) The equivalent circuit of an AFSC. (b) Schematic illustration of the typical configuration of AFSCs and (c) Cyclic voltammograms (CV) curves as schematic illustrations of typical AFSCs. *Source:* Reproduced with permission [30]. © 2016, Royal Society of Chemistry.

The maximum C value of the FSCs can be reached when C_n is equal to C_p. Thus, early investigations focused on the symmetric flexible supercapacitors (SFSCs) with cathodes and anodes being identical for achieving higher device capacitance [31–34]. However, due to their limited potential voltage (<1 V in aqueous electrolyte), the energy density of SFSCs is still unsatisfactory. Notably, the V of a FSC device related to the capacitive potential range of electrodes. Thus, asymmetric flexible supercapacitors (AFSCs), also called hybrid SCs or battery-capacitor SCs, are designed with different electrodes configured together (Figure 1.2b) [24–28]. By making use of the distinct capacitive potential range, AFSCs have been widely proven to effectively achieve high operating voltages (even >2 V in aqueous electrolyte) as well as optimized capacitance after balancing the charge between the specific positive and negative electrodes (Figure 1.2c) [30, 35]. In addition, they have several important advantages including small size, low weight, ease of handling, excellent reliability, and a wider range of operating temperatures. Therefore, AFSCs have become one of the most promising energy storage devices for flexible and wearable electronics.

In this context, to achieve high electrochemical performance while maintaining good mechanical stability, FSCs with asymmetric structure could realize further gains, and thus arouse global efforts in relative research. This chapter enumerates some typical newly developed AFSCs in terms of structure design of electrode materials and device's configuration engineering. We first focus on the guidelines on the material design and charge balance of a typical AFSC device. Furthermore, different types of various newly developed AFSCs, including sandwich-type, fiber-type, and the other type of AFSCs devices, are illustrated based on various electrode materials. Finally, the future developing trends and challenges are discussed to provide certain reference to readers on how to contrive this device.

1.2 Configurations of AFSCs Device

Specifically, AFSCs device can be fabricated by constructing two flexible dissimilar electrodes (a Faradaic positive electrode and a capacitor-type negative electrode), a separator and, in most cases, quasi-solid-state electrolyte in a soft package. Among various types of quasi-solid-state

electrolytes, gel polymer electrolytes have been extensively used in FSCs due to its relatively high ionic conductivity [36–40]. Soft and bendable plastics including polyethylene terephthalate (PET) [41–44], polydimethylsiloxane (PDMS) [45], and ethylene/vinyl acetate copolymer (EVA) film [46] are typically used as packaging materials for FSC devices.

Considering that the fundamental limit of energy storage capability is largely determined by the electrode material, either the material choice or structure design of electrode materials are of vital importance. Apart from directly fabricated freestanding films like carbon nanotube (CNT) films [47, 48] and graphene films [49, 50], previous reports for FSCs indicate that the flexible electrodes can also rely on a flexible substrate such as thin metal foils [51, 52], polymer substrates [53], textiles [54], and papers [55], to provide flexibility. The main differences between the AFSCs and SFSCs are that the AFSCs require that the positive and negative electrodes are not the same, but they need to be matched well. Electrode materials that are dominated by Faradaic reactions such as metal oxides (RuO_2 [56, 57], MnO_2 [58–64], CoO [60, 65–67] NiO [68–70], V_2O_5 [71, 72], etc.), metal sulfides ($NiCo_2S_4$ [73–75], MoS_2 [76], CoS_2 [77, 78], NiS [58, 63, 79, 80], etc.) and conductive polymers (polyaniline (PANI) [32, 81], polypyrrole (PPy) [82, 83], poly (3,4-ethylenedioxythiophene) (PEDOT) [84, 85] etc.) are normally applied as positive electrodes in AFSCs due to their high specific capacitance and relatively higher potential window. Notably, carbon-based materials (activated carbon [60, 66, 67], graphene [59, 86], CNTs [87], carbon fibers [88–90] etc.), metal nitrides (TiN [20], VN [91], MoN [92], etc.), and some metal oxides (FeO*x* [93], MoO*x* [94] etc.) are usually employed as negative electrodes because of their fast charging/discharging rate and suitable working window at negative potential.

However, before they are assembled in an AFSC, the matching problems of the two electrodes with different theoretical capacitance need to be solved [91]. As for an AFSC, the charge balance will follow the relationship q+ = q−. The charge stored by each electrode depends on the specific capacitance (C), the potential range for the charge/discharge process (E) and the mass of the active electrode material (m), following the Eq. (1.3):

$$q = C \times E \times m \tag{1.3}$$

In order to get q+ = q− at the typical current density, the mass balancing will follow the Eq. (1.4):

$$\frac{m_+}{m_-} = \frac{C_- \times E_-}{C_+ \times E_+} \tag{1.4}$$

In this way, the suitable mass ratio between the positive electrode (m+) and negative electrode (m−) is defined, which is much closed to the mass loading of the active materials of positive and negative electrode in typical AFSCs.

1.3 Progress of Flexible AFSCs

1.3.1 Sandwich-Type AFSCs

To date, the most widely applied configuration of AFSCs is sandwich-type AFSCs, which stacks two flexible flat electrodes face-to-face with an ionic conductive separator and liquid/gel electrolyte in the middle of the two electrodes to isolate direct contact. AFSCs with such shape holds great potential in future applications in flexible planar electronic devices, such as flexible display, wristbands, membrane-type sensors, etc. [24]

1.3.1.1 Carbon-Based Anodes

The most reliable anode materials for sandwich-type AFSCs are carbon-based materials with significant excellence in conductivity and mechanical stability, such as graphene, CNTs, carbon fibers, etc. [24, 25, 27, 56, 95–97] For example, Zhai et al. [98] successfully synthesized hydrogenated MnO_2 nanorods (H-MnO_2) on carbon cloth (CC) via electrodeposition followed by annealing in hydrogen atmosphere (Figure 1.3a), and loaded reduced graphene oxide (RGO) on CC using vacuum process. The obtained H-MnO_2 cathode and RGO anode were assembled as flexible solid-state AFSC with LiCl/PVA gel electrolyte and a separator sandwiched in between. The as-fabricated sandwich-type AFSC (denoted as H-MnO_2//RGO) exhibited a reliable operating voltage window as wide as 1.8 V and extraordinary mechanical tolerance to bending (Figure 1.3b). Owing to the significantly wide potential window, the device achieved a high energy density of 0.25 mWh cm^{-3} at power density of 1.01 W cm^{-3}, which has surpassed many SFSCs and some AFSCs previously reported. To verify the feasibility of the AFSCs device as energy storage device for wearable electronics, two H-MnO_2//RGO devices were tailored on a laboratory coat in series and able to power an electronic watch (Figure 1.3c). Recently, Yu and his co-workers [25] reported a sandwich-type AFSC with CNT-textile anode and MnO_2/graphene-textile cathode, which achieved an operating potential window of 1.5 V and a maximum energy density of 12.5 W h kg^{-1}. Choi et al. [56] developed a solid-state AFSC based on an ionic liquid functionalized chemically modified graphene (IL-CMG) film as anode and a hydrous RuO_2-ILCMG composite film as cathode, which reached a high output voltage of 1.8 V and thus delivered a maximum energy density of 19.7 W h kg^{-1} and

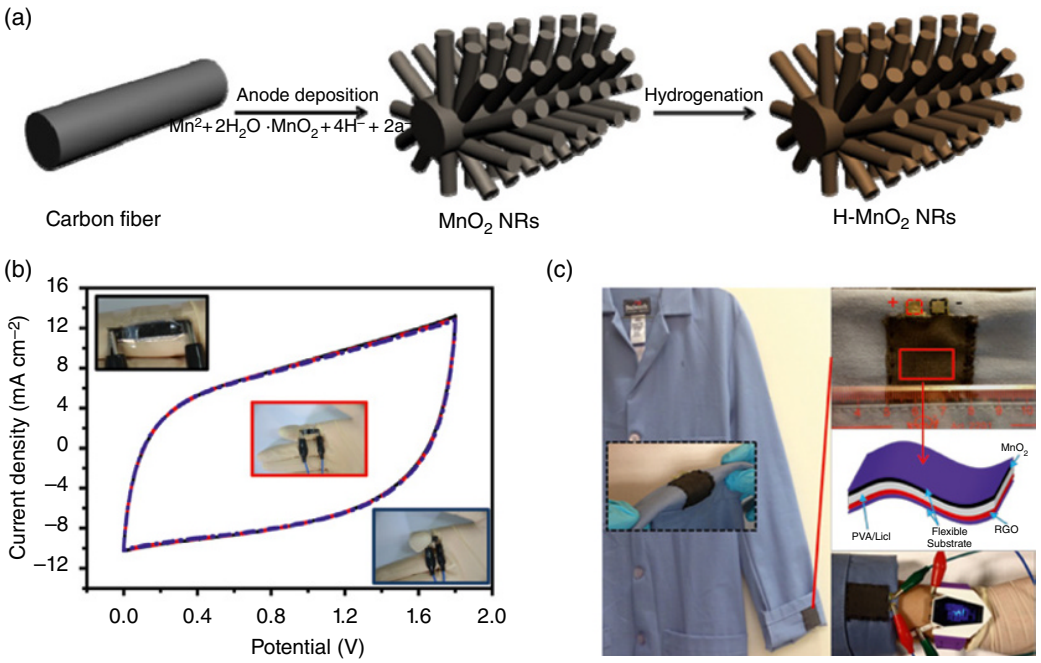

Figure 1.3 (a) Schematic diagram illustrates the growth process for preparing H-MnO_2 NRs on carbon cloth substrate. (b) CV curves obtained at different bent conditions at 200 mV s^{-1}. Insets are the photos of ASCs device on finger. (c) Schematic diagram and photo images of wearable ACS in real applications (sewing on the clothes model and powering electronic watch). *Source:* Reproduced with permission [98]. © 2014, Elsevier Publishing.

maximum power density of 6.8 kW kg^{-1}. Moreover, the as-fabricated device exhibited superior cyclic stability even when bent or twisted.

Unfortunately, most carbon-based anodes are relatively low in capacitance due to the electrochemical double layer energy storage mechanism. To this end, effective strategies of achieving high-energy-dense AFSCs has been extensively developed by employing pseudocapacitive anodes such as functionalized carbon, transition metal oxides, transition metal nitrides, conductive polymers, etc. [90] Recently, Wang et al. [90] creatively applied electrochemical activation to CC (Figure 1.4a), which were rarely employed as SC electrode materials because of its intrinsic low capacitance as a result of the small surface area and poor electrochemical activity [32]. The obtained electrochemically activated carbon cloth (EACC) anode was coupled with MnO_2@TiN loaded on CC as cathode to fabricate a novel sandwich-type AFSC (denoted as MnO_2@TiN//EACC) with an extended operation voltage window of 2 V (Figure 1.4b). Besides the broadened voltage window, the impressively boosted capacitance of EACC due to the roughened surface and the introduction of oxygen-containing groups on the surface for redox reactions also contribute to an excellent energy density as high as 1.5 mWh cm^{-3}, which enables its successful application in powering light emitting diode (LED) indicator even under bent condition (Figure 1.4c).

1.3.1.2 Transition Metal Oxide Anodes

Transition metal oxides can generate reversible redox reactions on the surface or even in the bulk during charging/discharging, which results in much higher capacitances compared to carbon-based anodes. By integrating transition metal oxides with flexible current collectors as

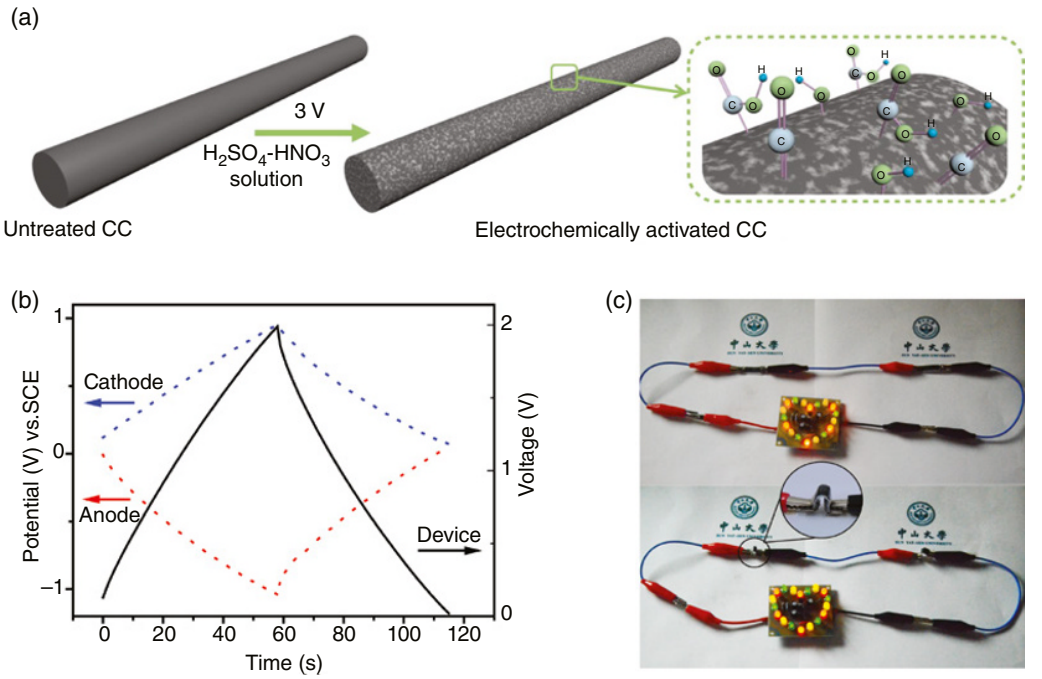

Figure 1.4 (a) Schematic diagram of the CC activation process. (b) Galvanostatic charge/discharge curve and potential distribution curve for the MnO_2@TiN//EACC device at 6 mA cm^{-2}. (c) A LED indicator powered by the tandem straight and bended MnO_2@TiN//EACC devices. *Source:* Reproduced with permission [90]. © 2015, Wiley-VCH.

pseudocapacitive anodes, the energy density of AFSC can be drastically enhanced. For example, Yang et al. [54] grew α-MnO_2 nanowires (NWs) and amorphous Fe_2O_3 nanotubes (NTs) on flexible carbon textile as the pseudocapacitive cathode and anode respectively (Figure 1.5a) to fabricate a sandwich-type flexible asymmetric pseudocapacitor (Figure 1.5b). The as-fabricated sandwich-type AFSC operates at a maximum cell voltage of 1.6 V (Figure 1.5c) and delivers high energy density of 0.55 mWh cm^{-3} (Figure 1.5d). Two devices connected in series can readily operate a blue LED after charging (Figure 1.5d inset), indicating the potential of the AFSC in future applications. Similarly, a novel flexible all-solid-state asymmetric SC fabricated with a carbon-fabric-loaded WO_{3-x}/MoO_{3-x} core/shell nanowires anode and a polyaniline cathode was reported by Xiao and his co-workers. The device showed satisfactory energy density (1.9 mWh cm^{-3}), impressive cyclic stability, as well as good mechanical flexibility.

1.3.1.3 Transition Metal Nitride Anodes

Owing to the high conductivity and transition metal sites with multiple valence states, transition metal nitrides are emerging as promising pseudocapacitive anode materials with fast and reversible redox reactions. Many transition metal nitrides have been exploited for AFSCs, such as

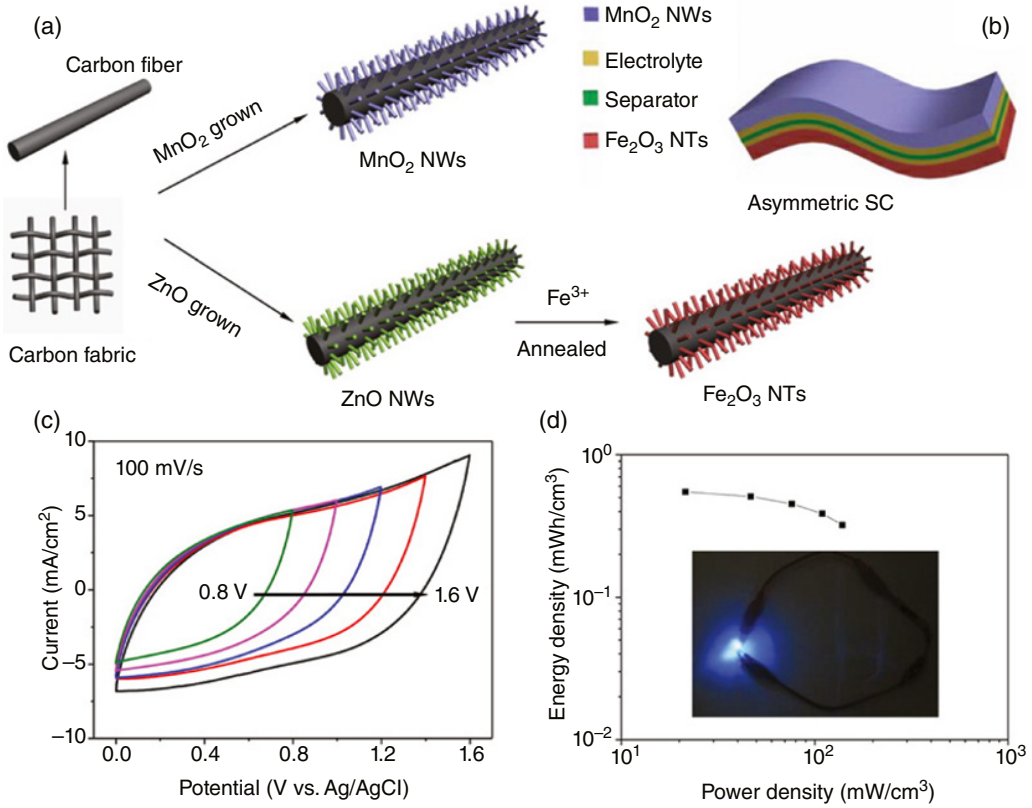

Figure 1.5 (a) Schematic diagram illustrating the synthesis procedure of MnO_2 NWs and Fe_2O_3 NTs on carbon cloth. (b) Schematic sketch illustrating the designed asymmetric supercapacitor device. (c) CV curves of the assembled solid-state AFSC device collected in different scan voltage windows. (d) Ragone plots of the solid-state AFSC device. Inset shows a blue LED powered by the tandem AFSC devices. *Source:* Reproduced with permission [54]. © 2014, American Chemical Society.

titanium nitride, vanadium nitride, tungsten oxynitride, iron nitride, etc., with high performances comparable to transition metal oxide anodes [91, 99–101]. For instance, Fan's group successfully fabricated an all-metal nitrides solid-state asymmetric SC, where the titanium nitride (TiN) cathode and iron nitride (Fe_2N) anode were grown on CC-loaded graphene nanosheets (GNS) using atomic layered deposition followed by calcination under ammonia atmosphere (Figure 1.6a).

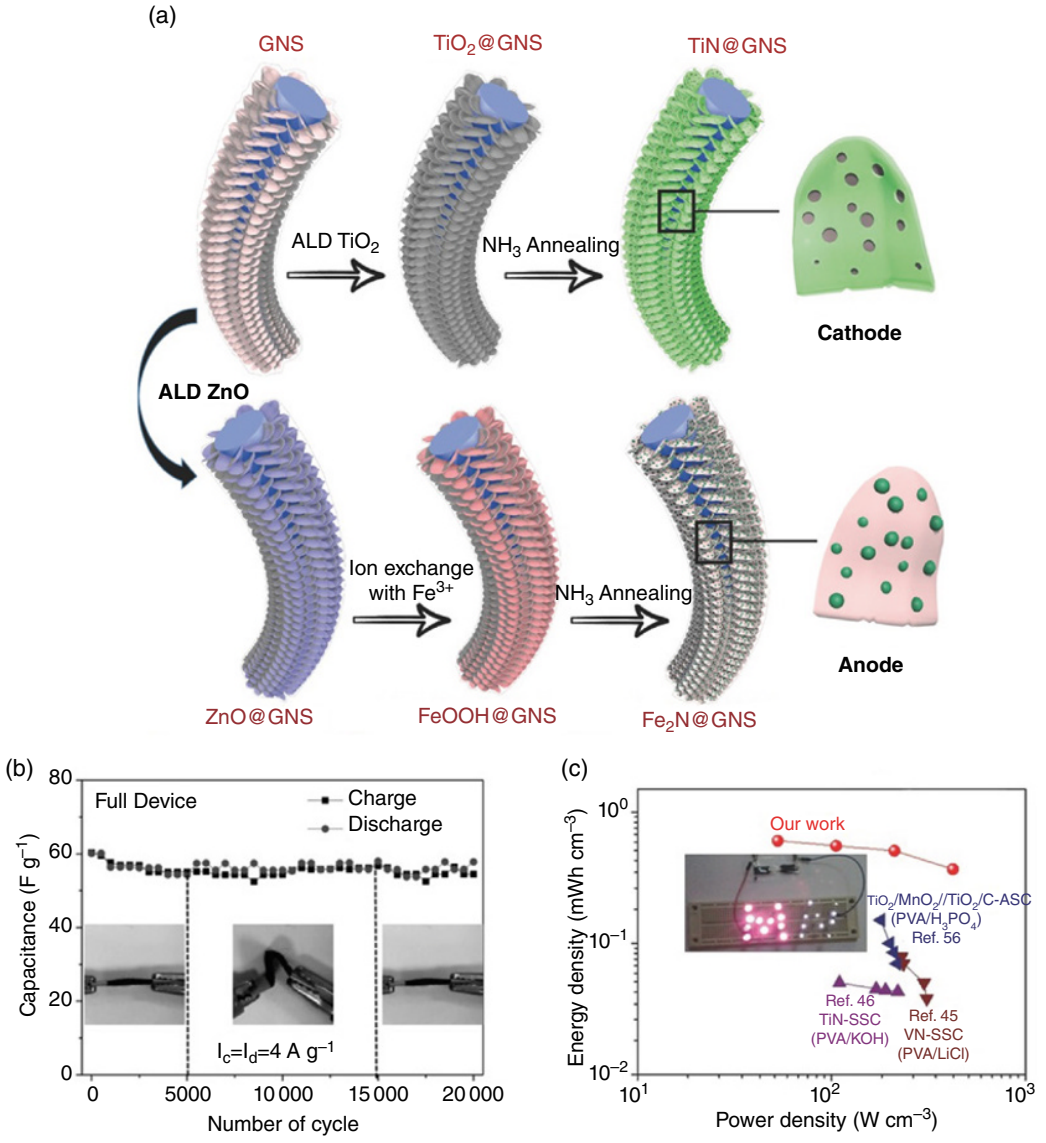

Figure 1.6 (a) Schematics of the fabrication processes of metal nitride cathode and anode materials. (b) Cycling performance of full device at $4\,A\,g^{-1}$ in 20 000 cycles with different bending situations. (c) Ragone plots of quasi-solid-state TiN-Fe_2N AFSC in comparison with other PVA-based solid electrolyte SFSCs and AFSCs. Inset: pink and white LEDs in parallel are lit up by two full devices in tandem. *Source:* Reproduced with permission [101]. © 2015, Wiley-VCH.

The porous configuration of TiN and homogeneous distribution of Fe_2N nanoparticles contribute to the extraordinary cycling durability (≈98% capacity retention after 20 000 cycles) of the fabricated quasi-solid-state AFSC device using PVA/LiCl polymer gel as neutral electrolyte (Figure 1.6b). The AFSC device achieved a maximum energy density of 0.61 mWh cm^{-3} and a maximum power density of 422.7 mW cm^{-3}, which were substantially higher than those of transition-metal-nitride-based SCs and PVA-based solid-state SCs (Figure 1.6c). Lu's group has reported various AFSCs using CC-loaded transition metal nitride anodes in recent years. For example, they used neutral PVA/LiCl polymer gel electrolyte to effectively stabilize porous VN NWs anode, and paired it with VO_x NWs cathode to assemble a stable and high-performance quasi-solid-state AFSC device with a high output voltage of 1.8 V [91]. Furthermore, the VO_x//VN-AFSC device was able to deliver an impressive volumetric capacitance of 1.35 F cm^{-3}, a highest energy density of 0.61mWh cm^{-3} and extraordinary cycling stability with 12.5% loss of capacitance after 10 000 cycles. They also prepared holey tungsten oxynitride (WON) nanowires on CC through the annealing of WO_3 precursor nanowires in ammonia atmosphere [100]. The as-fabricated AFSC device with WON NWs anode and MnO_2 cathode could deliver a high working voltage of 1.8 V and volumetric capacitance of 2.73 F cm^{-3}. The maximum energy density of MnO_2//WON AFSC device was 1.27 mWh cm^{-3} at a power density of 0.62 W cm^{-3}, which has transcended many reported AFSC devices.

1.3.1.4 Conductive Polymer Anodes

Conductive polymers are promising candidates as pseudocapacitive materials owing to their good conductivity and reversible redox reactions during charging/discharging, but they are mostly applied as cathode materials while rarely studied as anode materials for AFSCs. Recently, Wang et al. synthesized 150 WO_3@PPy nanowires on carbon fibers as the anode and grew $Co(OH)_2$ nanowires on carbon fabric as the cathode for AFSC device. The as-fabricated AFSC device exhibited apparent pseudocapacitive behavior within a stable potential range of 0–1.6 V. The maximum volumetric capacitance of 2.8 F cm^{-3} was achieved at a scan rate of 20 mV s^{-1}. Moreover, the asymmetric supercapacitor (ASC) device delivered an energy density as high as 1.03 mWh cm^{-3}.

1.3.2 Fiber-Type ASCs

Despite distinct advances, the planar-shaped SCs are still insufficient in deformability for weaving into textiles or integrating into linear-shaped electronics. In this regard, researchers have creatively assembled electrodes with one-dimensional geometry to fabricate fiber-type AFSCs. Fiber-shaped AFSCs have been developed into multiple configurations including parallel type, wrap type, coaxial-helix type and two-ply yarn type, in order to effectively meet the demands of different wearable energy textiles, including sensing [102–104], communication [105], and storage [106].

1.3.2.1 Parallel-Type Fiber AFSCs

For a parallel-type fiber AFSC, two fiber-shaped electrodes are assembled side-by-side, separated by gel/polymer electrolyte, and finally supported on a flat substrate [60, 107–109]. For instance, Yu et al. [109] reported a parallel type all-solid-state asymmetric micro-SC using MnO_2-deposited rGO/SWCNT fiber as the cathode (denoted as GCF/MnO_2-10) and an N-doped rGO/SWCNT fiber as the anode (denoted as GCF/N2) (Figure 1.7a). By fully utilizing the potential window of both cathode (0 ~ 0.9 V) and anode (−0.9 ~ 0 V), the device showed a high output voltage of 1.8 V (Figure 1.7b). Excellent electrochemical performances such as good cycling stability

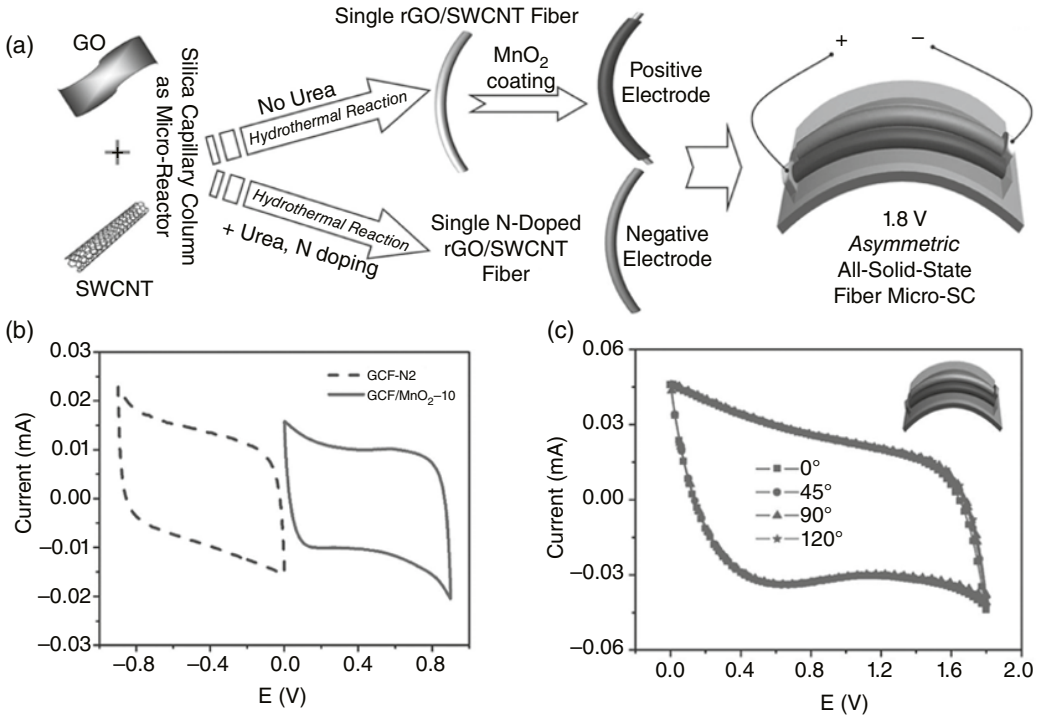

Figure 1.7 (a) Schematic illustration of the design and fabrication of the asymmetric fiber-based micro-SC. (b) Comparative CV curves obtained for the GCF-N2 and GCF/MnO_2-10 fibers at the scan rate of 10 mV s^{-1}. (c) CV curves of one asymmetric micro-SC, which are bended at different angles. *Source:* Reproduced with permission [109]. © 2014, Wiley-VCH.

(87% capacitance retention after 10 000 cycles), high energy density (5 mW h cm^{-3}) and power density (929 mW cm^{-3}) were also achieved. Furthermore, such device geometry exhibited promising mechanic stability under different bending states (Figure 1.7c). This asymmetric micro-SC device was testified as a reliable power source for a ZnO film-based UV photodetector, suggesting its promising potential in future applications.

1.3.2.2 Wrap-Type Fiber AFSCs

The design of a wrap-type AFSC is very similar to that of a parallel-type fiber AFSC, which encapsulates two electrodes into a protective flexible tube instead of placing them on a flexible substrate [53, 59, 62, 110–112]. Recently, Lu and his co-workers [112] successfully synthesized N and low valence-state Mo dual-doped MoO_3 nanowires on carbon fibers, which was coupled with MnO_2@TiN-loaded carbon fiber cathode and sealed with heat-shrinkable tube to fabricate a wrap type solid-state ASC (denoted as MnO_2@TiN//N-MoO_{3-x}) (Figure 1.8a). The galvanostatic charge/discharge (GCD) curves of MnO_2@TiN//N-MoO_{3-x} with different current densities in Figure 1.8b indicate that the stable operating voltage of the device reaches a significantly high value of 2.0 V. The ASC device also shows superior rate capability when current density increased by 15 folds (Figure 1.8c). More importantly, the excellent flexibility and mechanic robustness enabled the fiber AFSC device to perfectly maintain its electrochemical performances in bent and even knotted conditions (Figure 1.8d). Benefiting from the ultrahigh output voltage and Faradaic

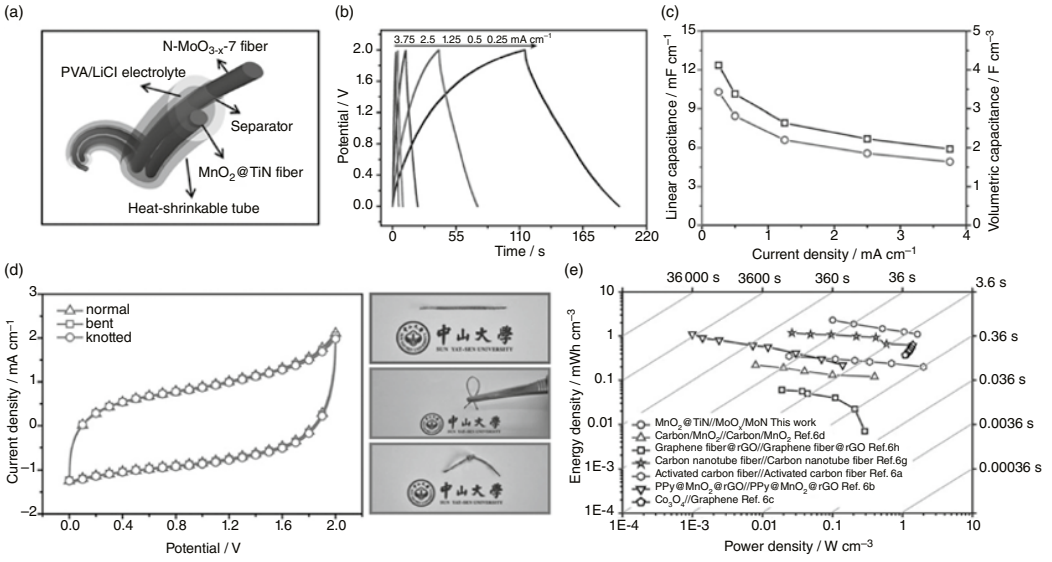

Figure 1.8 (a) Schematic illustration of the as-assembled fiber-shaped MnO_2@TiN//N-MoO_{3-x}-ASC device. (b) GCD curves of our fiber-shaped AFSC device. (c) Linear capacitances and volumetric capacitances of the fiber-shaped AFSC device as a function of current density. (d) CV curves collected at 100 mV s^{-1} for the fiber-shaped AFSC device under different conditions (left) and corresponding device pictures (right). (e) Ragone plots for the fiber-shaped AFSC device and other recently reported fiber-shaped FSCs. *Source:* Reproduced with permission [112]. © 2016, Wiley-VCH.

electrodes with improved conductivity, the MnO_2@TiN//N-MoO_{3-x} device exhibited a maximum energy and power density of 2.29 mW h cm^{-3} and 1.64 W cm^{-3} respectively, outperforming many other fiber-shaped SC devices reported (Figure 1.8e).

1.3.2.3 Coaxial-Helix-Type Fiber AFSCs

By helically wrapping a wire shape axial electrode with another wire electrode, coaxial-helix-type ASCs with core–shell cable-like structures have been creatively explored [86, 113–117]. For example, the Thomas group [117] fabricated a novel cable-like coaxial-helix-type AFSC as illustrated in

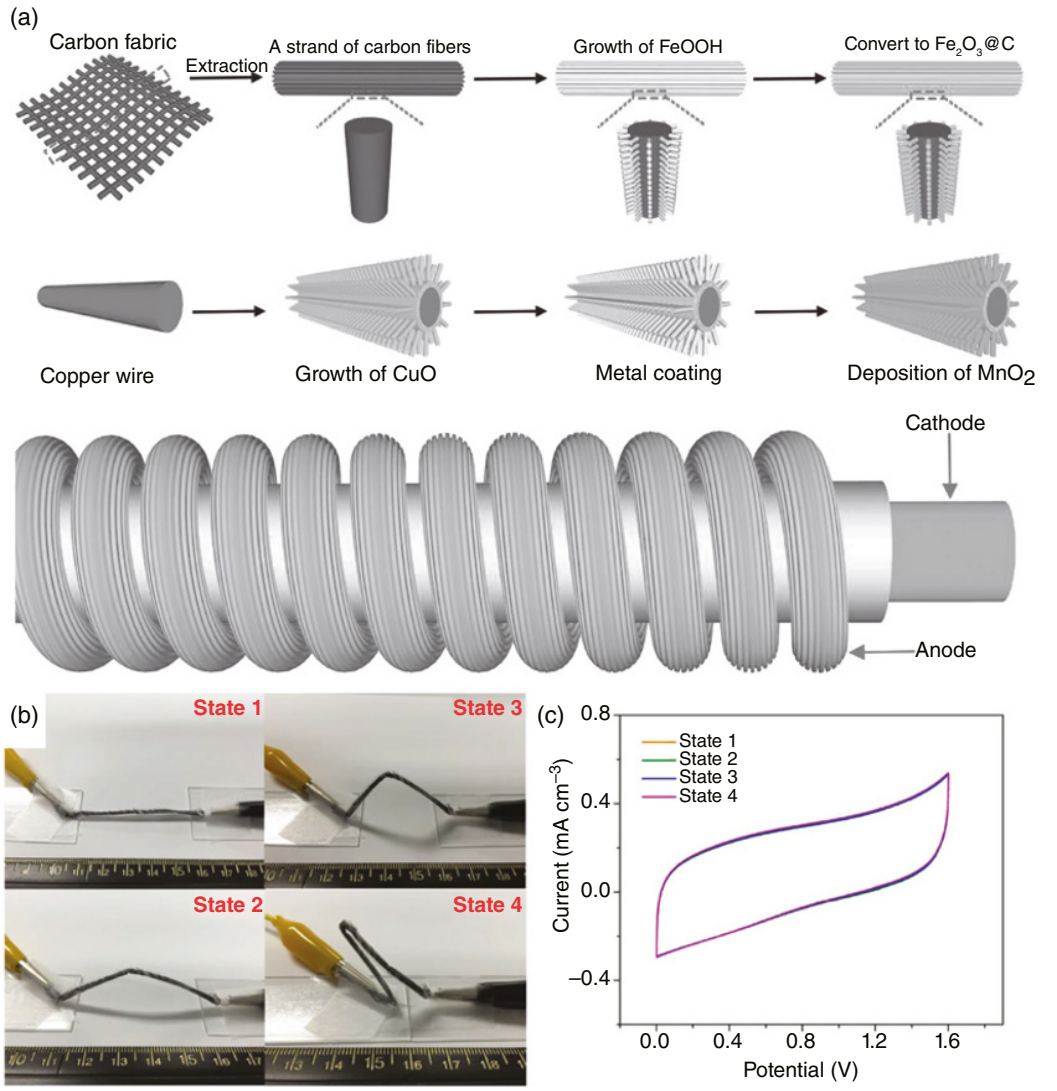

Figure 1.9 (a) Schematics illustration shows the fabrication process of an anode and a cathode, respectively, and the structure of a coil-type asymmetric supercapacitor electrical cable. (b) Optical images of a coil-type asymmetric supercapacitor electrical cable at different bending states. (c) CV curves obtained at different bending states at 200 mV s^{-1}. *Source:* Reproduced with permission [117]. © 2015, Wiley-VCH.