EDITORS GUOZHEN SHEN | ZHENG LOU | DI CHEN

# FLEXIBLE SUPERCAPACITORS

MATERIALS AND APPLICATIONS



# **Table of Contents**

<u>Cover</u>

<u>Title Page</u>

Materials and Applications

<u>Copyright Page</u>

List of Contributors

<u>Preface</u>

1 Flexible Asymmetric Supercapacitors

1.1 Introduction

**1.2 Configurations of AFSCs Device** 

**1.3 Progress of Flexible AFSCs** 

1.4 Summary

**References** 

2 Stretchable Supercapacitors

2.1 Overview of Stretchable Supercapacitors

2.2 Fabrication of Stretchable Supercapacitor

2.3 Multifunctional Supercapacitor

<u>References</u>

<u>3 Fiber-shaped Supercapacitors</u>

3.1 Introduction

3.2 Structure of FSSCs

<u>3.3 Electrolyte</u>

3.4 Electrode

3.5 Electrode Design of FSSCs

3.6 Functionalized FSSCs

3.7 Conclusion

<u>References</u>

<u>4 Flexible Fiber-shaped Supercapacitors:</u>

4.1 Introduction to Fiber-Shaped Supercapacitors

<u>4.2 Emerging Techniques for the Fabrication of</u> <u>Fiber-Shaped Electrodes</u>

<u>4.3 Structures and Design/Configuration of Fiber-</u> <u>Shaped Electrodes</u>

4.4 Materials for Fiber-shaped Supercapacitors

4.5 Electrolytes for Fiber-Shaped Supercapacitors

<u>4.6 Performance Evaluation Metrics for Fiber-</u> <u>Shaped Supercapacitors</u>

4.7 Applications

4.8 Conclusion and Future Prospectus

<u>Acknowledgments</u>

<u>References</u>

<u>5 Flexible Supercapacitors Based on Ternary Metal</u> <u>Oxide (Sulfide, Selenide) Nanostructures</u>

5.1 Introduction

5.2 Ternary Metal Oxide

5.3 Metal Sulfide Electrodes

5.4 Metal Selenide Electrodes

5.5 Fiber-Shaped SCs

5.6 Summary and Perspectives

**Declaration of Competing Interest** 

<u>Acknowledgments</u>

<u>References</u>

<u>6 Transition Metal Oxide Based Electrode Materials for</u> <u>Supercapacitors</u>

6.1 Introduction

<u>6.2 Co<sub>3</sub>O<sub>4</sub> Electrode Materials</u>

6.3 NiO Electrode Materials

6.4 Fe<sub>2</sub>O<sub>3</sub> Electrode Materials

6.5 MnO<sub>2</sub> Electrode Materials

<u>6.6 V<sub>2</sub>O<sub>5</sub> Electrode Materials</u>

<u>References</u>

7 Three-Dimensional Nanoarrays for Flexible Supercapacitors

List of Abbreviations

7.1 Introduction

7.2 Fabrication of 3D Nanoarrays

7.3 Typical Structural Engineering of 3D

Nanoarrays for Flexible Supercapacitors

7.4 Evaluation of Flexible Supercapacitors

7.5 Conclusion

<u>Acknowledgments</u>

<u>References</u>

<u>8 Metal Oxides Nanoarray Electrodes for Flexible</u> <u>Supercapacitors</u>

8.1 Introduction

8.2 Synthesis Techniques of Metal Oxide

<u>Nanoarrays</u>

8.3 The Flexible Support Substrate for Loading Nanoarrays

8.4 The Geometry of Nanostructured Arrays

**8.5 Conclusions and Prospects** 

<u>References</u>

9 Printed Flexible Supercapacitors

List of Abbreviations

9.1 Overview of Printed Flexible Supercapacitor

9.2 Devices Structure of Printed SCs

9.3 Printable Materials for SCs

9.4 Fabrication of Flexible SCs Using Various

Printing Methods

9.5 Printed Integrated System

9.6 Perspective

<u>Acknowledgments</u>

<u>References</u>

<u>10 Printing Flexible On-chip Micro-Supercapacitors</u>

10.1 Introduction

10.2 Printable Materials for On-chip MSCs

10.3 Printing Techniques

10.4 Summary

<u>References</u>

11 Recent Advances of Flexible Micro-Supercapacitors

11.1 Introduction

11.2 General Features of Flexible MSCs

11.3 Active Materials of Flexible MSCs

11.4 Integration of Flexible MSCs

11.5 Flexible Smart MSCs

11.6 Summary and Prospects

<u>References</u>

Index

End User License Agreement

# List of Illustrations

Chapter 1

<u>Figure 1.1 (a, b) Scheme and optical image of a</u> <u>flexible acoustic device....</u>

<u>Figure 1.2 (a) The equivalent circuit of an AFSC. (b)</u> <u>Schematic illustration...</u>

<u>Figure 1.3 (a) Schematic diagram illustrates the</u> <u>growth process for preparin...</u>

<u>Figure 1.4 (a) Schematic diagram of the CC</u> <u>activation process. (b) Galvanost...</u>

<u>Figure 1.5 (a) Schematic diagram illustrating the</u> <u>synthesis procedure of MnO</u>

<u>Figure 1.6 (a) Schematics of the fabrication</u> <u>processes of metal nitride cath...</u>

<u>Figure 1.7 (a) Schematic illustration of the design</u> <u>and fabrication of the a...</u>

<u>Figure 1.8 (a) Schematic illustration of the as-</u> assembled fiber-shaped MnO<sub>2</sub>@...

<u>Figure 1.9 (a) Schematics illustration shows the</u> <u>fabrication process of an a...</u>

<u>Figure 1.10 (a) Schematic diagram of the</u> <u>fabrication procedure of an AFSC. (...</u>

Chapter 2

<u>Figure 2.1 Summary of stretchable SCs and their</u> <u>application in integrated sy...</u>

<u>Figure 2.2 Structure and voltage, energy</u> <u>distribution of 1D fiber SCs: twist...</u>

<u>Figure 2.3 Typical fabrication methods of 1D</u> <u>parallel fiber SCs: (a) Schemat...</u>

<u>Figure 2.4 (a) Schematic illustration of fabricating</u> <u>twisted SCs by wrapping...</u> <u>Figure 2.5 Schematics of the fabrication</u> <u>procedures for coaxial SCs and corr...</u>

<u>Figure 2.6 (a) Fabrication process of the</u> <u>stretchable SCs by buckling electr...</u>

<u>Figure 2.7 (a) Schematic illustration of steps for</u> <u>fabricating omnidirection...</u>

<u>Figure 2.8 (a) Schematics of the fabrication</u> <u>procedures for a MWNT/Mn<sub>3</sub>O<sub>4</sub> bas...</u>

<u>Figure 2.9 (a) Schematics of fabricating a</u> <u>stretchable MSC array on a PDMS s...</u>

<u>Figure 2.10 (a) Schematics of the fabrication</u> <u>procedures of the stretchable ...</u>

<u>Figure 2.11 (a) Optical images of the stretchable</u> <u>cellular CNT film under in...</u>

<u>Figure 2.12 (a) Schematics of a 3D stretchable SC.</u> (b) Optical images of the...

<u>Figure 2.13 (a) Schematic diagram of synthesizing</u> <u>PANI@SWCNTs sponge composi...</u>

<u>Figure 2.14 (a) Schematic illustration of the self-healing process. (b) Sche...</u>

<u>Figure 2.15 (a, b) Schematic illustration and circuit</u> <u>diagram of 2D multifun...</u>

Chapter 3

<u>Figure 3.1 (a) Schematic diagram of parallel-like</u> <u>fiber supercapacitor.(...</u>

<u>Figure 3.2 (a) Cross-sectional FE-SEM image of</u> <u>gPVAP(20) hydrogel polymer me...</u>

<u>Figure 3.3 (a) The cross-sectional SEM images of</u> <u>LSG film.(b) Side view ...</u> <u>Figure 3.4 (a) Schematic diagram showing the</u> <u>fabrication process of the soli...</u>

<u>Figure 3.5 (a) Schematics of yarn fabrication and</u> <u>yarn modified by depositio...</u>

<u>Figure 3.6 (a) Schematic illustration of the</u> <u>fabrication process of the asym...</u>

<u>Figure 3.7 (a) Schematic illustration of the</u> <u>fabrication process of a symmet...</u>

<u>Figure 3.8 (a) Overview of GMF observed by SEM.</u> <u>Scale bar: 10 mm; (b) SEM cr...</u>

<u>Figure 3.9 (a) Schematic illustration of the</u> <u>fabrication of RGO/Ni cotton ya...</u>

<u>Figure 3.10 (a) Schematic illustration of the self-healable supercapacitor; ...</u>

<u>Figure 3.11 (a) Schematic illustration showing the</u> <u>fabrication of an ultra-s...</u>

<u>Figure 3.12 (a) Schematic illustration of the typical</u> <u>structure of electroch...</u>

<u>Figure 3.13 (a) Shape recovering process of a wire-</u> <u>shaped SMSC; (b) The reve...</u>

<u>Figure 3.14 (a) Photographs of the flexible</u> <u>asymmetric FSSC at different ben...</u>

Chapter 4

<u>Figure 4.1 (a) Schematic description for the</u> <u>structure of planar supercapaci...</u>

<u>Figure 4.2 (a) Schematic description for the</u> <u>experimental procedure of wet-s...</u>

<u>Figure 4.3 (a) Schematic depiction for the</u> <u>construction process of the NiCo ...</u> <u>Figure 4.4 (a) Schematic illustration for the</u> <u>production method of the FFSC ...</u>

<u>Figure 4.5 (a) Design for the production procedure</u> of a coaxial type FFSC. (...

<u>Figure 4.6 (a) Schematic diagram representing the</u> <u>construction process of PA...</u>

<u>Figure 4.7 (a) Schematic diagram representing the</u> <u>structure of composite fib...</u>

<u>Figure 4.8 (a) Schematic diagrams for the</u> <u>fabrication of MnNiCo-CH nanoneedl...</u>

<u>Figure 4.9 Summary of recent methodologies</u> <u>implemented to improve the energy...</u>

<u>Figure 4.10 (a) Schematic design of the combined</u> <u>wire-shaped device for phot...</u>

Chapter 5

<u>Figure 5.1 (a) Schematic illustrating the fabrication</u> of the carbon textiles...

<u>Figure 5.2 SEM images of Zn-Ni-Co TOH electrodes</u> <u>obtained using different hy...</u>

<u>Figure 5.3 Schematic of the fabrication process for</u> <u>3D NiCo<sub>2</sub>O<sub>4</sub>@NiCo<sub>2</sub>O<sub>4</sub> hiera...</u>

<u>Figure 5.4 (a and b) SEM images of MnCo<sub>2</sub>O<sub>4</sub></u> <u>nanoarrays on Ni foam. (c and d) ...</u>

<u>Figure 5.5 schematic for the preparation of</u> <u>FeCo<sub>2</sub>S<sub>4</sub> hollow nanoneedle array/...</u>

<u>Figure 5.6 Schematic illustration of the design and</u> <u>fabrication of the CuCo<sub>2</sub></u>

<u>Figure 5.7 (a) SEM image of the NiCo<sub>2</sub>O<sub>4</sub> nanorod arrays, (b) SEM image of NiC...</u>

<u>Figure 5.8 (a) SEM image of ZnCoS-NSs/CC, (b)</u> <u>TEM image of Ni(OH)<sub>2</sub>@ZnCoS-NSs...</u>

<u>Figure 5.9 Schematic illustration of the two-step</u> <u>strategy for preparing net...</u>

<u>Figure 5.10 (a) Comparison of CV curves collected</u> for  $Ni_3S_2/CoNi_2S_4/NF$  and A...

<u>Figure 5.11 (a) Schematic illustration of the</u> <u>synthesis process of the compo...</u>

Figure 5.12 SC fabrication.

<u>Figure 5.13 (a and b) SEM images. (c) Charge-</u> <u>discharge cycles as a function ...</u>

<u>Figure 5.14 SEM images of the (a) Ni-Co-MOF solid</u> <u>spheres, (b) NiCo<sub>2</sub>O<sub>4</sub>, (c-d...</u>

<u>Figure 5.15 (a) Schematic illustration, (b)</u> <u>photograph, (c) equivalent circu...</u>

<u>Figure 5.16 (a) Fabrication of thread-like ASC</u> <u>based on NiCo<sub>2</sub>Se<sub>4</sub> nanosheets/...</u>

<u>Figure 5.17 (a) Schematic diagram of the assembly</u> <u>of solid-state flexible de...</u>

Chapter 6

<u>Figure 6.1 The schematic of 3D Co<sub>3</sub>O<sub>4</sub>@MnO<sub>2</sub></u> <u>heterostructures grown on Ni foam....</u>

<u>Figure 6.2 (a) Areal capacitance and specific</u> <u>capacitance of the hybrid elec...</u>

<u>Figure 6.3 (a) CV curves of the electrodes (b) CV</u> <u>curves of ASC device withi...</u>

<u>Figure 6.4 electrochemical characterization of ASC</u> <u>devices (a) charge-discha...</u> <u>Figure 6.5 Schematic of phosphate ion</u> <u>functionalized Co<sub>3</sub>O<sub>4</sub> nanosheet arrays...</u>

<u>Figure 6.6 (a) CV curves at a scan rate of 100 mV</u> <u> $s^{-1}$  (b) CV curves of...</u>

<u>Figure 6.7 Schematic of the synthesis procedure,</u> <u>the inset shows different N...</u>

<u>Figure 6.8 electrochemical performances of electrodes.</u>

<u>Figure 6.9 (a) FESEM and (b and c) TEM images of</u> <u>NiCo-LDH tetragonal microtu...</u>

<u>Figure 6.10 (a) CV curves (b) Galvanostatic charge-</u> <u>discharge curves (c) Nyqu...</u>

<u>Figure 6.11 Schematic of ZnCo<sub>2</sub>O<sub>4</sub>/MnO<sub>2</sub> composite nanocone forests (NCFs).</u>

<u>Figure 6.12 Typical SEM images of (a and b)</u> <u>ZnCo<sub>2</sub>O<sub>4</sub> NW arrays and (c and d) ...</u>

<u>Figure 6.13 Schematic of growth mechanism of  $V_2O_5$  NWAs.</u>

Chapter 7

<u>Figure 7.1 Phase diagrams of K-Mn oxide systems</u> at E = 1.2 V. (a) PH- $\mu_{K}$ 

<u>Figure 7.2 (a and b) Schematic and field-emission</u> <u>scanning electron microsco...</u>

<u>Figure 7.3 Schematic (a), FESEM (b and c), and</u> <u>TEM (d and e) images showing ...</u>

<u>Figure 7.4 (a) Schematic illustration of typical 3D</u> <u>nanowire arrays, nanotub...</u>

<u>Figure 7.5 (a) Digital photograph and schematic</u> <u>illustration of the symmetri...</u> <u>Figure 7.6 (a) SEM image of Co<sub>3</sub>O<sub>4</sub> nanowire arrays</u> <u>on nickel fibers. (b) The ...</u>

<u>Figure 7.7 (a) Schematic illustration of the</u> <u>synthesis process of the  $Co_9S_8$ ...</u>

<u>Figure 7.8 (a) Structural evolution process from</u> <u>spinel Mn<sub>3</sub>O<sub>4</sub> to birnessite-...</u>

<u>Figure 7.9 (a, c, e, and g) FESEM images of hybrid</u> <u>nanostructure of porous C...</u>

<u>Figure 7.10 (a) The experimental apparatus for</u> <u>different bending states: con...</u>

Chapter 8

<u>Figure 8.1 Schematic diagram of the metal oxide</u> <u>nanoarrays for supercapacito...</u>

<u>Figure 8.2 Solution-based method to synthesize</u> <u>metal oxide arrays. (a) SEM i...</u>

<u>Figure 8.3 NiCo<sub>2</sub>O<sub>4</sub> nanoarrays with different</u> <u>structures synthesized by solut...</u>

<u>Figure 8.4 Electrodeposition to prepare metal oxide</u> <u>arrays. (a-b) SEM images...</u>

<u>Figure 8.5 Metal oxide-based nanoarrays</u> <u>synthesized by chemical vapor deposi...</u>

<u>Figure 8.6 3D graphene foam used as facile</u> <u>scaffolds and efficient current c...</u>

<u>Figure 8.7 Flexible carbon cloth for current</u> <u>collectors. (a) Schematic illus...</u>

<u>Figure 8.8 (a) Schematic illustration of fabrication</u> procedure of 3D MnO<sub>2</sub>-Ni...

<u>Figure 8.9 (a) Schematic illustration of fabrication</u> process of CuO nanotube... <u>Figure 8.10 (a) Schematic preparation illustration</u> <u>of cyclic voltammetry oxi...</u>

<u>Figure 8.11 (a) Schematic illustration of the</u> <u>generation process of  $Co_3O_4$ @Mn...</u>

<u>Figure 8.12 1D nanowire-based arrays. (a) SEM</u> <u>image of the  $Co_3O_4$  nanowire ar...</u>

<u>Figure 8.13 1D nanotube-based arrays. (a)</u> <u>Schematic illustration of the synt...</u>

<u>Figure 8.14 2D metal oxide nanoarrays. (a) SEM</u> <u>image; (b) Galvanostatic char...</u>

<u>Figure 8.15 (a) Schematic illustration of the</u> <u>synthesis process of NiO nanof...</u>

<u>Figure 8.16 (a) Schematic illustration of the</u> <u>possible synthesis mechanism o...</u>

Chapter 9

<u>Figure 9.1 The main printing methods for flexible</u> <u>supercapacitors: inkjet [1...</u>

<u>Figure 9.2 Common device configurations for</u> <u>printed SCs: sandwiched (left) a...</u>

<u>Figure 9.3 MXene is chosen here as an example to</u> <u>show the critical elements ...</u>

<u>Figure 9.4 Representative works of inkjet-printed</u> <u>flexible SCs. (a) Optical ...</u>

<u>Figure 9.5 Representative screen-printed flexible</u> <u>SCs: (a) Schematic illustr...</u>

<u>Figure 9.6 Representative transfer-printed flexible</u> <u>SCs. (a) Schematic illus...</u>

<u>Figure 9.7 Representative 3D-printed flexible SCs.</u> (a) Schematic illustratio... <u>Figure 9.8 Representative printed integrated</u> <u>systems containing SCs. (a) Sch...</u>

Chapter 10

Figure 10.1 (a) Schematic illustration of the electrochemical exfoliation of...

<u>Figure 10.2 (a) Schematic illustration of the</u> <u>fabrication of MSCs using the ...</u>

<u>Figure 10.3 (a) Schematic illustration of direct ink-jet printing of MXene i...</u>

<u>Figure 10.4 (a) Schematic illustration of the</u> <u>fabrication of SnSe based supe...</u>

<u>Figure 10.5 (a) Optical image of the screen printing</u> <u>facility. (b) Schematic...</u>

<u>Figure 10.6 (a) Photograph of the EEG ink and</u> <u>PSSH ink. (b) Photograph of th...</u>

<u>Figure 10.7 (a) Schematic illustration of the</u> <u>stepwise fabrication procedure...</u>

<u>Figure 10.8 (a) Optical microscopy image of spray</u><u>printed patterns of GP-3.0...</u>

<u>Figure 10.9 (a) Schematic diagram of the screen</u> <u>printing process to on-chip ...</u>

<u>Figure 10.10 (a) Schematic diagram of the 3D</u> <u>printing process for MSCs. (b-d...</u>

Chapter 11

<u>Figure 11.1 Schematics of (a) conventional SCs and</u> (b) MSCs;Schematics o...

<u>Figure 11.2 (a) The fabrication process of a highly</u> <u>transparent and flexible...</u> <u>Figure 11.3 Schematic illustration of preparing</u> <u>RGO-based MSCs. (a) Fabricat...</u>

<u>Figure 11.4 (a) Schematic illustration of fabricating</u> <u>flexible RGO-based MSC...</u>

<u>Figure 11.5 Schematic illustration of fabricating</u> <u>the RGO and RGO/Mn<sub>3</sub>O<sub>4</sub> elec...</u>

<u>Figure 11.6 (a) Schematic illustration and (b) SEM</u> <u>image of the MSCs based o...</u>

<u>Figure 11.7 Schematic illustration of the fabrication</u> <u>process and optical ph...</u>

<u>Figure 11.8 (a) Schematic illustration of fabricating</u> <u>interdigitated electro...</u>

<u>Figure 11.9 (a) The fabrication process of the</u> <u>flexible MSCs based on NPG/Mn...</u>

<u>Figure 11.10 Schematic illustration the fabrication</u> <u>process of the flexible ...</u>

<u>Figure 11.11 The schematic diagram of fabricating</u> <u>all-MXene printed MSCs....</u>

<u>Figure 11.12 (a) Optical image of the self-charging</u> <u>system containing MSCs a...</u>

<u>Figure 11.13 (a) A circuit diagram of the flexible</u> <u>photodetecting system wit...</u>

<u>Figure 11.14 (a) Schematic illustration of an all-in-</u> <u>one sensing system comp...</u>

<u>Figure 11.15 (a) The fabricating process and (b)</u> <u>self-healable mechanism of ...</u>

<u>Figure 11.16 (a) Optical image of a flexible</u> <u>photodetectable MSC; (b) Photoc...</u>

<u>Figure 11.17 (a) Schematic illustrations of the</u> <u>fabrication process of flexi...</u>

# **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

# WILEY

This edition first published 2022 © 2022 John Wiley & Sons, Inc

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, except as permitted by law. Advice on how to obtain permission to reuse material from this title is available at <a href="http://www.wiley.com/go/permissions">http://www.wiley.com/go/permissions</a>.

The right of Guozhen Shen, Zheng Lou and Di Chen to be identified as the authors of the editorial material in this work has been asserted in accordance with law.

#### Registered Office

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

Editorial Office

111 River Street, Hoboken, NJ 07030, USA

For details of our global editorial offices, customer services, and more information about Wiley products visit us at <u>www.wiley.com</u>.

Wiley also publishes its books in a variety of electronic formats and by print-ondemand. Some content that appears in standard print versions of this book may not be available in other formats.

#### Limit of Liability/Disclaimer of Warranty

In view of ongoing research, equipment modifications, changes in governmental regulations, and the constant flow of information relating to the use of experimental reagents, equipment, and devices, the reader is urged to review and evaluate the information provided in the package insert or instructions for each chemical, piece of equipment, reagent, or device for, among other things, any changes in the instructions or indication of usage and for added warnings and precautions. While the publisher and authors have used their best efforts in preparing this work, they make no representations or warranties with respect to the accuracy or completeness of the contents of this work and specifically disclaim all warranties, including without limitation any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives, written sales materials or promotional statements for this work. The fact that an organization, website, or product is referred to in this work as a citation and/or potential source of further information does not mean that the publisher and authors endorse the information or services the organization, website, or product may provide or recommendations it may make. This work is sold with the understanding that the publisher is not engaged in rendering professional services. The advice and strategies contained herein may not be suitable for your situation. You should consult with a specialist where appropriate. Further, readers should be aware that websites listed in this work may have changed or disappeared between when this work was written and when it is read. Neither the publisher nor authors shall be liable for any loss of profit or any other commercial damages, including but not limited to special, incidental, consequential, or other damages.

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

# **List of Contributors**

#### Songshan Bi

Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education) College of Chemistry, Nankai University Tianjin, 300071, P. R. China

#### Hongmei Cao

Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education) College of Chemistry, Nankai University Tianjin, 300071, P. R. China

#### Cao Guan

Frontiers Science Center for Flexible Electronics, Institute of Flexible Electronics Northwestern Polytechnical University Xi'an, 710072, P.R. China

#### Mengmeng Hu

State Key Laboratory of Advanced Welding and Joining Harbin Institute of Technology (Shenzhen) Shenzhen 518055, Guangzhou, China; and Flexible Printed Electronics Technology Centre Harbin Institute of Technology (Shenzhen) Shenzhen 518055, Guangzhou, China

#### Yan Huang

State Key Laboratory of Advanced Welding and Joining Harbin Institute of Technology (Shenzhen) Shenzhen 518055, Guangzhou, China; and Flexible Printed Electronics Technology Centre Harbin Institute of Technology (Shenzhen) Shenzhen 518055, Guangzhou, China; and School of Materials Science and Engineering Harbin Institute of Technology (Shenzhen) Shenzhen 518055, Guangzhou, China

#### Muhammad Imran

Department of Chemistry, Faculty of Science King Khalid University Abha 61413, Saudi Arabia

#### Muhammad S. Javed

School of Physical Science and Technology Lanzhou University Lanzhou 730000, PR China; and Siyuan Laboratory, Guangdong Provincial Engineering Technology Research Center of Vacuum Coating Technologies and New Energy Materials, Department of Physics Jinan University Guangzhou 510632, PR China

#### Wen-Yong Lai

State Key Laboratory of Organic Electronics and Information Displays (SKLOEI), Institute of Advanced Materials (IAM) Nanjing University of Posts & Telecommunications

9 Wenyuan Road, Nanjing 210023, Jiangsu, China; and Frontiers Science Center for Flexible Electronics (FSCFE), MIIT Key Laboratory of Flexible Electronics (KLoFE) Northwestern Polytechnical University 127 West Youyi Road, Xi'an 710072, Shaanxi, China

#### La Li

State Key Laboratory for Superlattices and Microstructures Institute of Semiconductors, Chinese Academy of Science Beijing 100083, China

#### Dun Lin

MOE of the Key Laboratory of Bioinorganic and Synthetic Chemistry, The Key Lab of Low-Carbon Chem and Energy Conservation of Guangdong Province, School of Chemistry Sun Yat-Sen University, Guangzhou Guangzhou, 510275, People's Republic of China

#### Jie Liu

State Key Laboratory of Advanced Welding and Joining Harbin Institute of Technology (Shenzhen) Shenzhen, 518055, Guangzhou, China; and Flexible Printed Electronics Technology Centre Harbin Institute of Technology (Shenzhen) Shenzhen, 518055, Guangzhou, China

#### Qingjiang Liu

State Key Laboratory of Advanced Welding and Joining Harbin Institute of Technology (Shenzhen) Shenzhen, 518055, Guangzhou, China; and Flexible Printed Electronics Technology Centre Harbin Institute of Technology (Shenzhen) Shenzhen, 518055, Guangzhou, China

#### Yao Liu

State Key Laboratory of Advanced Welding and Joining Harbin Institute of Technology (Shenzhen) Shenzhen, 518055, Guangzhou, China; and Flexible Printed Electronics Technology Centre Harbin Institute of Technology (Shenzhen) Shenzhen, 518055, Guangzhou, China

#### Xihong Lu

MOE of the Key Laboratory of Bioinorganic and Synthetic Chemistry, The Key Lab of Low-Carbon Chem and Energy Conservation of Guangdong Province, School of Chemistry Sun Yat-Sen University, Guangzhou Guangdong, 510275, People's Republic of China

#### Wenjie Mai

Siyuan Laboratory, Guangdong Provincial Engineering Technology Research Center of Vacuum Coating Technologies and New Energy Materials, Department of Physics Jinan University Guangzhou, 510632, PR China

#### Ting Meng

Frontiers Science Center for Flexible Electronics, Institute of Flexible Electronics Northwestern Polytechnical University Xi'an, 710072, P. R. China

#### Zhiqiang Niu

Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), College of Chemistry Nankai University Tianjin, 300071, P. R. China

#### Guozhen Shen

State Key Laboratory for Superlattices and Microstructures Institute of Semiconductors, Chinese Academy of Science Beijing, 100083, China

#### Peng Sun

Siyuan Laboratory, Guangdong Provincial Engineering Technology Research Center of Vacuum Coating Technologies and New Energy Materials, Department of Physics Jinan University Guangzhou, 510632, PR China

#### Hua Wang

State Key Laboratory of Advanced Welding and Joining Harbin Institute of Technology (Shenzhen) Shenzhen, 518055, Guangzhou, China; and Flexible Printed Electronics Technology Centre Harbin Institute of Technology (Shenzhen) Shenzhen, 518055, Guangzhou, China

#### Jiaqi Wang

State Key Laboratory of Advanced Welding and Joining Harbin Institute of Technology (Shenzhen) Shenzhen, 518055, Guangzhou, China; and Flexible Printed Electronics Technology Centre Harbin Institute of Technology (Shenzhen) Shenzhen, 518055, Guangzhou, China

#### Panpan Wang

State Key Laboratory of Advanced Welding and Joining Harbin Institute of Technology (Shenzhen) Shenzhen, 518055, Guangzhou, China; and Flexible Printed Electronics Technology Centre Harbin Institute of Technology (Shenzhen) Shenzhen, 518055, Guangzhou, China

#### Qiufan Wang

Key laboratory of Catalysis and Energy Materials Chemistry of Ministry of Education & Hubei Key Laboratory of Catalysis and Materials Science, Hubei R&D Center of Hyperbranched Polymers Synthesis and Applications South-Central University for Nationalities 182 Minzu Road, Wuhan, 430074, China

#### Rui Wang

Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education) College of Chemistry, Nankai University Tianjin, 300071, P. R. China

#### Xiang Wu

School of Materials Science and Engineering Shenyang University of Technology China

#### Jing Xu

School of Materials Science and Engineering

Nanjing University of Science and Technology Xuanwu District, Nanjing 210094, China; and Herbert Gleiter Institute of Nanoscience Nanjing University of Science and Technology Xuanwu District, Nanjing 210094, China

#### Daohong Zhang

Key laboratory of Catalysis and Energy Materials Chemistry of Ministry of Education & Hubei Key Laboratory of Catalysis and Materials Science, Hubei R&D Center of Hyperbranched Polymers Synthesis and Applications South-Central University for Nationalities 182 Minzu Road, Wuhan 430074, China

#### Xiyue Zhang

MOE of the Key Laboratory of Bioinorganic and Synthetic Chemistry, The Key Lab of Low-Carbon Chem and Energy Conservation of Guangdong Province, School of Chemistry Sun Yat-Sen University

Guangzhou, Guangdong, 510275, People's Republic of China

#### Yizhou Zhang

State Key Laboratory of Organic Electronics and Information Displays (SKLOEI), Institute of Advanced Materials (IAM)

Nanjing University of Posts & Telecommunications 9 Wenyuan Road, Nanjing, 210023, Jiangsu, China; and Institute of Advanced Materials and Flexible Electronics (IAMFE), School of Chemistry and Materials Science Nanjing University of Information Science & Technology 219 Ningliu Road, 210044, Nanjing, Jiangsu, China

## 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

Dun Lin, Xiyue Zhang and Xihong Lu MOE of the Key Laboratory of Bioinorganic and Synthetic Chemistry, The Key Lab of Low-Carbon Chem and Energy Conservation of Guangdong Province, School of Chemistry, Sun Yat-Sen University, Guangzhou, Guangdong, 510275, People's Republic of China

# **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  $10 \,\mathrm{kW}\,\mathrm{kg}^{-1}$ ), 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).

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



Figure 1.1 (a, b) Scheme and optical image of a flexible acoustic device.

Source: Reproduced with permission from Ref. [121],  $\ensuremath{\mathbb{C}}$  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)  $3 \times 3$  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 Alair battery.

*Source:* Reproduced with permission from Ref. [15], © 2016, Wiley.