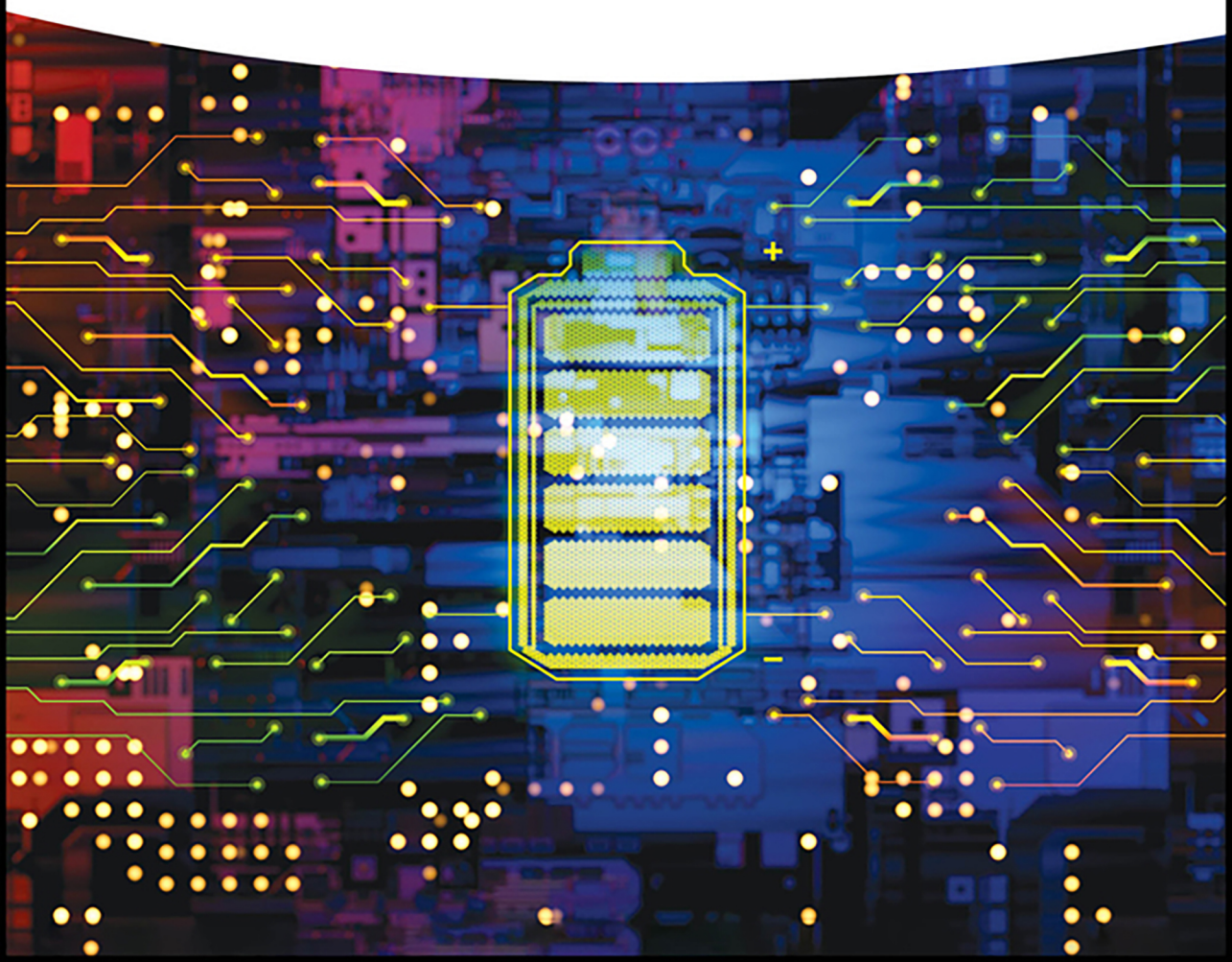


Edited by Liqiang Mai

# Nanowire Energy Storage Devices

Synthesis, Characterization, and Applications





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*Edited by Liqiang Mai*

#### **The Editor**

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## Contents

### Preface *xi*

<b>1</b>	<b>Nanowire Energy Storage Devices: Synthesis, Characterization, and Applications</b>	<b>1</b>
1.1	Introduction	1
1.1.1	One-Dimensional Nanomaterials	1
1.1.1.1	Nanorods	3
1.1.1.2	Carbon Nanofibers	3
1.1.1.3	Nanotubes	3
1.1.1.4	Nanobelts	5
1.1.1.5	Nanocables	6
1.1.2	Energy Storage Science and Technology	6
1.1.2.1	Mechanical Energy Storage	7
1.1.2.2	Electromagnetic Energy Storage	9
1.1.2.3	Electrochemical Energy Storage	9
1.1.3	Overview of Nanowire Energy Storage Materials and Devices	13
1.1.3.1	Si Nanowires	15
1.1.3.2	ZnO Nanowires	17
1.1.3.3	Single Nanowire Electrochemical Energy Storage Device	18
	References	19
<b>2</b>	<b>Fundamentals of Nanowire Energy Storage</b>	<b>27</b>
2.1	Physical and Chemical Properties of Nanowires	27
2.1.1	Electronic Structure	27
2.1.2	Thermal Properties	29
2.1.2.1	Melting Point	29
2.1.2.2	Thermal Conduction	30
2.1.3	Mechanical Properties	31
2.1.4	Adsorption and Surface Activity	32
2.1.4.1	Adsorption	33
2.1.4.2	Surface Activity	33
2.2	Thermodynamics and Kinetics of Nanowires Electrode Materials	34
2.2.1	Thermodynamics	34

2.2.2	Kinetics	34
2.3	Basic Performance Parameters of Nanowires Electrochemical Energy Storage Devices	35
2.3.1	Electromotive Force	36
2.3.2	Operating Voltage	36
2.3.3	Capacity and Specific Capacity	36
2.3.4	Energy and Specific Energy	37
2.3.5	Current Density and Charge–Discharge Rate	37
2.3.6	Power and Specific Power	38
2.3.7	Coulombic Efficiency	38
2.3.8	Cycle Life	38
2.4	Interfacial Properties of Nanowires Electrode Materials	38
2.4.1	Interface Between Nanowire Electrode Materials and Electrolytes	38
2.4.2	Heterogeneous Interfaces in Nanowire Electrode Materials	40
2.5	Optimization Mechanism of Electrochemical Properties of Nanowires Electrode Materials	42
2.5.1	Mechanism of Electron/Ion Bicontinuous Transport	42
2.5.2	Self-Buffering Mechanism	44
2.6	Theoretical Calculation of Nanowires Electrode Materials	44
2.7	Summary and Outlook	48
	References	49
<b>3</b>	<b>Design and Synthesis of Nanowires</b>	<b>51</b>
3.1	Conventional Nanowires	51
3.1.1	Wet Chemical Methods	51
3.1.1.1	Hydrothermal/Solvothermal Method	52
3.1.1.2	Sol–Gel Method	53
3.1.1.3	Coprecipitation Method	54
3.1.1.4	Ultrasonic Spray Pyrolysis Method	55
3.1.1.5	Electrospinning Method	55
3.1.2	Dry Chemical Method	57
3.1.2.1	High-Temperature Solid-State Method	57
3.1.2.2	Chemical Vapor Deposition Method	58
3.1.3	Physical Method	59
3.2	Porous Nanowires	60
3.2.1	Template Method	60
3.2.1.1	Template by Nanoconfinement	60
3.2.1.2	Template by Orientation Induction	62
3.2.2	Self-Assembly Method	63
3.2.3	Chemical Etching Method	64
3.3	Hierarchical Nanowires	65
3.3.1	Self-Assembly Method	65
3.3.2	Secondary Nucleation Growth Method	68
3.4	Heterogeneous Nanowires	69
3.4.1	Heterogeneous Nucleation	69



3.4.2	Secondary Modification	71
3.5	Hollow Nanowires	73
3.5.1	Wet Chemical Method	73
3.5.2	Template Method	73
3.5.3	Gradient Electrospinning	76
3.6	Nanowire Arrays	79
3.6.1	Template Method	79
3.6.2	Wet Chemical Method	81
3.6.3	Chemical Vapor Deposition	83
3.7	Summary and Outlook	86
	References	88
<b>4</b>	<b>Nanowires for In Situ Characterization</b>	<b>95</b>
4.1	In Situ Electron Microscopy Characterization	95
4.1.1	In Situ Scanning Electron Microscopy (SEM) Characterization	95
4.1.2	In Situ Transmission Electron Microscope (TEM) Characterization	97
4.2	In Situ Spectroscopy Characterization	101
4.2.1	In Situ X-ray Diffraction	101
4.2.2	In Situ Raman Spectroscopy	106
4.2.3	In Situ X-ray Photoelectron Spectroscopy	108
4.2.4	In Situ XAS Characterization	108
4.3	In Situ Characterization of Nanowire Devices	111
4.3.1	Nanowire Device	111
4.3.2	Nanowire Device Characterization Example	111
4.4	Other In Situ Characterization	115
4.4.1	In Situ Atomic Force Microscopy Characterization	115
4.4.2	In Situ Nuclear Magnetic Resonance	117
4.4.3	In Situ Neutron Diffraction	119
4.4.4	In Situ Time-of-Flight Mass Spectrometry	121
4.5	Summary and Outlook	123
	References	124
<b>5</b>	<b>Nanowires for Lithium-ion Batteries</b>	<b>131</b>
5.1	Electrochemistry, Advantages, and Issues of LIBs Batteries	131
5.1.1	History of Lithium-ion Batteries	131
5.1.2	Electrochemistry of Lithium-ion Batteries	132
5.1.2.1	Theoretical Operation Potential	133
5.1.2.2	Theoretical Specific Capacity of Electrode Materials and Cells	133
5.1.2.3	Theoretical Specific Energy Density of an Electrochemical Cell	134
5.1.3	Key Materials for Lithium-ion Batteries	134
5.1.3.1	Cathode	134
5.1.3.2	Anode	135
5.1.3.3	Electrolyte	135
5.1.3.4	Separator	136
5.1.4	Advantages and Issues of Lithium-ion Batteries	137

5.2	Unique Characteristic of Nanowires for LIBs	138
5.2.1	Enhancing the Diffusion Dynamics of Carriers	138
5.2.2	Enhancing Structural Stability of Materials	138
5.2.3	Befitting the In Situ Characterization of Electrochemical Process	139
5.2.4	Enabling the Construction of Flexible Devices	139
5.3	Nanowires as Anodes in LIBs	139
5.3.1	Alloy-Type Anode Materials (Si, Ge, and Sn)	139
5.3.1.1	Lithium Storage in Si Nanowires	139
5.3.1.2	Lithium Storage in Ge Nanowires	142
5.3.1.3	Lithium Storage in Sn Nanowires	145
5.3.2	Metal Oxide Nanowires	146
5.3.3	Carbonaceous Anode Materials	148
5.4	Nanowires as Cathodes in LIBs	151
5.4.1	Transition Metal Oxides	151
5.4.2	Vanadium Oxide Nanowires	153
5.4.3	Iron Compounds Including Oxides and Phosphates	157
5.5	Nanowires-Based Separators in LIBs	160
5.6	Nanowires-Based Solid-State Electrolytes in LIBs	163
5.7	Nanowires-Based Electrodes for Flexible LIBs	168
5.8	Summary and Outlook	174
	References	175

<b>6</b>	<b>Nanowires for Sodium-ion Batteries</b>	<b>185</b>
6.1	Advantages and Challenges of Sodium-ion Batteries	185
6.1.1	Development of Sodium-ion Batteries	185
6.1.2	Characteristic of Sodium-ion Batteries	186
6.1.2.1	The Working Principle of Sodium-ion Battery	186
6.1.2.2	Advantages of Sodium-ion Batteries	186
6.1.3	Key Materials for Sodium-ion Batteries	187
6.1.3.1	Cathode	188
6.1.3.2	Anode	188
6.1.3.3	Electrolyte	189
6.1.3.4	Separator	189
6.1.4	Challenges for Sodium-ion Batteries	191
6.2	Nanowires as Cathodes in Sodium-ion Batteries	193
6.2.1	Layered Oxide Nanowires	193
6.2.2	Tunnel-type Oxide Nanowires	195
6.2.3	Polyanionic Compound Nanowires	196
6.3	Nanowires as Anodes in Sodium-ion Batteries	200
6.3.1	Carbonaceous Materials and Polyanionic Compounds	200
6.3.1.1	Graphitized Carbon Materials	200
6.3.1.2	Amorphous Carbon Materials	201
6.3.1.3	Carbon Nanomaterials	201
6.3.2	Polyanionic Compounds	203
6.3.3	Metals and Metal Oxides	206

6.3.3.1	Metal Nanowires	206
6.3.3.2	Transition Metal Oxide Nanowires	207
6.3.4	Metal Sulfides	215
6.3.4.1	Molybdenum Sulfide and Its Composites	216
6.3.4.2	Tungsten Sulfide and Its Composites	216
6.3.4.3	Stannic Sulfide and Its Composites	218
6.3.4.4	Nickel Sulfide, Ferrous Sulfide and Their Composites	218
6.4	Summary	220
	References	220
<b>7</b>	<b>Application of Nanowire Materials in Metal-Chalcogenide Battery</b>	<b>229</b>
7.1	Lithium–Sulfur Battery	230
7.1.1	Sulfur–Carbon Nanowire Composite Cathode Materials	231
7.1.2	Conductive Polymer Nanowire/Sulfur Composite Cathode Materials	236
7.1.3	Metal Compound Nanowires/Sulfur Composite Cathode Materials	237
7.2	Sodium–Sulfur Battery and Magnesium–Sulfur Battery	243
7.2.1	Sodium–Sulfur Battery	243
7.2.2	Magnesium–Sulfur Battery	247
7.3	Lithium–Selenium Battery	249
7.3.1	Reaction Mechanism of Lithium–Selenium Battery	250
7.3.2	Selenium-Based Cathode Materials	251
7.3.3	Existing Problems and Possible Solutions	256
7.4	Summary and Outlook	257
	References	258
<b>8</b>	<b>Application of Nanowires in Supercapacitors</b>	<b>263</b>
8.1	Nanowire Electrode Material for Electrochemical Double-Layer Capacitor	265
8.1.1	The Application of Carbon Nanotubes in EDLCs	266
8.1.2	The Application of Carbon Nanofibers in EDLCs	267
8.2	Nanowire Electrode Materials for Pseudocapacitive Supercapacitors	269
8.2.1	Metal Oxide Nanowire Electrode Materials	269
8.2.2	Conducting Polymer Nanowire Electrode Materials	271
8.3	Nanowire Electrode Materials of Hybrid Supercapacitors	272
8.3.1	Hybrid Supercapacitor Based on Aqueous Electrolyte	274
8.3.1.1	Carbon/Metal Oxide	274
8.3.1.2	Carbon/Conductive Nanowire Polymer	276
8.3.2	Other Electrolyte System Hybrid Supercapacitors	277
8.3.2.1	Organic Electrolyte System	277
8.3.2.2	Redox-Active Electrolyte System	278
8.3.3	Solid Electrolyte or Quasi-Solid-State Hybrid Supercapacitor	279

8.4	Summary and Outlook	279
	References	280
<b>9</b>	<b>Nanowires for Multivalent-ion Batteries</b>	<b>285</b>
9.1	Nanowires for Magnesium-Ion Battery	285
9.1.1	Vanadium-Based Nanowires for MIBs	286
9.1.2	Manganese-Based Nanowires for MIBs	289
9.1.3	Other Nanowires for MIBs	290
9.2	Nanowires for Calcium-Ion Batteries	292
9.3	Nanowires for Zinc-Ion Batteries	293
9.3.1	Vanadium-Based Nanowires for ZIBs	294
9.3.2	Manganese-Based Nanowires for ZIBs	295
9.4	Nanowires for Aluminum Ion Batteries	296
9.5	Summary and Outlook	298
	References	299
<b>10</b>	<b>Conclusion and Outlook</b>	<b>305</b>
10.1	Structure Design and Performance Optimization of 1D Nanomaterials	305
10.2	Advanced Characterization Methods for 1D Nanomaterials	308
10.3	Applications and Challenges of Nanowire Energy Storage Devices	314
10.3.1	Application of Nanowire Structures in Lithium-ion Batteries	314
10.3.2	Applications of Nanowire Structures in Na-ion Battery	315
10.3.3	Applications of Nanowire Structures in Other Monovalent-ion Batteries	316
10.3.4	Application of Nanowires in Lithium–Sulfur Batteries	316
10.3.5	Application of 1D Nanomaterials in Supercapacitors	318
10.3.6	Nanowires for Other Energy Storage Devices	319
10.3.6.1	Metal Air Batteries	319
10.3.6.2	Multivalent-ion Battery	320
10.3.6.3	Metal Sulfur Batteries	320
	References	322
	<b>Index</b>	<b>327</b>

## Preface

With the increasing prominence of worldwide energy crisis, materials science and nanotechnologies have become the key to the fields of new energy storage and utilization. With the in-depth study of nanotechnologies, nanoenergy storage materials are in the rapid development stage. Especially, owing to their excellent chemistry, electricity, thermal, mechanical, and other properties, nanowire materials exhibit unique electron and ion transport characterization, making them distinctive among nanomaterials. From this perspective, nanowire energy storage devices (ESDs) show outstanding electrochemical and energy storage characteristics. And nanowire materials also have more unique advantages in the construction of micro and nanoenergy storage devices and the assembly of flexible ESDs. To this end, nanowire materials offer various opportunities to address the challenges of advanced ESD, thus attracting the great attention and strong interest of the majority of scientific researchers.

In this book, we present a comprehensive discourse on nanowire energy storage devices (ESDs) from the perspective of synthesis, characterization, and applications. This publication is structured into 10 chapters, each with coherent connections and distinct focal points. Readers can read systematically or selectively, according to their needs.

The **Chapter 1** is written by *Prof. Liqiang Mai and Wen Luo*. **Chapter 1** intends to offer an all-sided introduction to one-dimensional nanomaterials, energy storage science and technology, and review the nanowire energy storage materials and devices.

The **Chapter 2** is written by *Prof. Liqiang Mai and Chaojiang Niu*. **Chapter 2** summarizes the physicochemical characteristics of nanowire, the unique advantages of nanowires as electrode materials, the basic performance parameters of nanowire electrochemical ESDs, the optimization mechanism of electrochemical performance, and briefly introduces the theoretical calculations related to nanowire electrode materials.

The **Chapter 3** is written by *Prof. Liqiang Mai and Lin Xu*. **Chapter 3** focuses on the common synthesis methods and growth mechanisms of various types of nanowire materials based on the classification of nanowires with different morphologies.

The **Chapter 4** is written by *Prof. Liqiang Mai and Xiaocong Tian*. **Chapter 4** briefly introduces various characterization methods and summarizes the progress in the characterization of nanowires up to now. Chapter 4 will also discuss the

future of characterization for nanowires and give perspectives on the opportunities of nanowires in post-lithium energy storage systems.

The **Chapter 5** is written by *Prof. Liqiang Mai and Ya You*. **Chapter 5** elaborates the application of nanowires in lithium-ion batteries, discusses the unique characteristic of nanowires for energy storage, and gives perspectives on the opportunities of nanowires in post-lithium energy storage systems.

The **Chapter 6** is written by *Prof. Liqiang Mai and Ting Zhu*. **Chapter 6** summarizes the application of nanowire cathode and anode materials in sodium-ion batteries. The synthesis, characterization, and reaction mechanism of the nanowires are completely demonstrated. The perspectives on the development of nanowires in sodium-ion batteries are also discussed in this chapter.

The **Chapter 7** is written by *Prof. Liqiang Mai and Xu Xu*. **Chapter 7** expounds the principles and applications of various new batteries from the perspective of nanowire electrode materials and explains the characteristics and advantages of nanowire electrode materials in new batteries.

The **Chapter 8** is written by *Prof. Liqiang Mai and Liang Zhou*. **Chapter 8** focuses on one-dimensional nanomaterials applied to three typical capacitors, including Electric double-layer capacitors (EDLCs), pseudocapacitive supercapacitors, and hybrid supercapacitors. The relationship between one-dimensional structure and performance of capacitors is explored, which could provide theoretical guidance for the deeper improvement of nanowire-based supercapacitors.

The **Chapter 9** is written by *Prof. Liqiang Mai and Qinyou An*. **Chapter 9** introduces a broader application of nanowire ESDs in the various fields of multivalent-ion batteries, such as magnesium-ion battery, calcium-ion battery, zinc-ion battery, and aluminum-ion batteries. In the chapter, we also give a simple summary and outlook on nanowires for multivalent-ion batteries.

The last chapter is written by *Prof. Liqiang Mai and Wen Luo*. **Chapter 10** provides a systematic conclusion and outlook on nanowire ESD and gives perspectives on the structure design, performance optimization, and advanced characterization methods of 1D nanomaterials. Moreover, in this chapter, we also intend to present a broad picture of micro-nano device structure optimization and fabrication process improvement for different applications.

This book is available for institutions of higher learning and scientific research units engaged in the development of nanomaterials and ESDs research related researchers and practitioners to use, also can be used as institutions of higher learning materials, chemical energy, physical and related professional teachers, graduate, and senior undergraduate professional reference book. Overall, despite the best efforts of the author, due to the limitations of level and time, it is inevitable that there will be some mistakes and omissions in the book. We sincerely hope that the readers will contact us with valuable suggestions for its continued improvement.

Finally, I would like to thank all the contributors to this book. We thank the support of the National Key Research and Development Program of China (2020YFA0715000), the National Natural Science Foundation of China (51832004, 52127816, 51802239, 52172233).

## 1

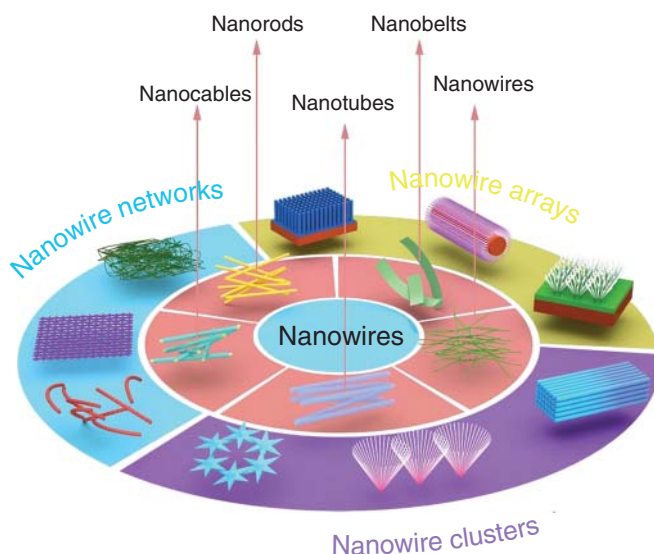
# Nanowire Energy Storage Devices: Synthesis, Characterization, and Applications

## 1.1 Introduction

### 1.1.1 One-Dimensional Nanomaterials

As an important member of the large family of nanomaterials, one-dimensional nanowire (NW) materials, including nanorods, nanotubes, nanobelts, and nanocables, have gradually received attention from researchers (Figure 1.1). A NW can be defined as a one-dimensional structure that is less than 100 nm in the lateral direction (there is no limitation in the longitudinal direction). The aspect ratio of a part of a NW is more than 1000 [1]. According to their different compositions, NWs can be divided into different types, including metal NWs (such as Ni, Pt, and Au), semiconductor NWs (such as InP, Si, and GaN), and insulator NWs (such as SiO<sub>2</sub> and TiO<sub>2</sub>). NW materials have important implications for theoretical research and technical applications. This kind of material has peculiar physical and chemical properties, such as the transition from metal to insulator, super mechanical strength, high luminous efficiency, lower laser threshold, and enhanced thermoelectric coefficient [2].

The research on NWs can be traced to the early 1960s. In 1964, Wagner and Ellis [3] used vapor–liquid–solid (VLS) growth to epitaxially grow Si single crystal whiskers on a single crystal Si(111) substrate, creating a precedent for Si NW research. In 1975, Givargizov [4] conducted a systematic study on the process of VLS growth and gave a reasonable VLS growth mechanism for NWs. In 1998, Morales [5] and Zhang et al. [6] used laser ablation deposition (LAD) to successfully grow Si NWs. NW materials exhibit unique optical, electrical, and magnetic properties that many bulk materials do not have. Therefore, they have an extremely important position in the field of producing nanodevices, various sensors, microtools, micro-electrodes, device-integrated connection lines, and next-generation EL display devices. Current research results show that many one-dimensional nanomaterials have demonstrated essential applications. For example, Huang et al. [7] grew ZnO NW array with a diameter of 20–150 nm and a length of about 10  $\mu$ m through a vapor-phase transport process on a sapphire substrate, successfully preparing



**Figure 1.1** Schematic diagram of different types of nanowires and their secondary structures.

nanolasers in 2001. In 2007, Prof. Lieber from Harvard University and his team developed the first single NW solar cell [8]. They reported a solar cell prepared by a single coaxial silicon nanowire (SiNW), which adopts a p-i-n coaxial structure. The synthesis and application of NWs have become hot spots for scientists in recent years because of their unique advantages. Prof. Mai from Wuhan University of Technology and his team designed and assembled the first single NW electrochemical energy storage device to reveal the intrinsic mechanism of electrochemical performance degradation in 2010 [9]. In the same year, Huang et al. [10] used in situ TEM to observe the lithiation phenomenon of a single NW of  $\text{SnO}_2$  for the first time. In 2012, Kouwenhoven from Delft University of Technology and his team verified the hypothesis that Majorana fermions in NWs are coupled with superconductors [11]. In 2014, Prof. Cheng from Monash University and his team built a wearable pressure sensor using gold nanowires [12]. In 2019, scientists from Cambridge University, King's College London, Peking University, Zhejiang University, Shanghai Jiao Tong University, and other universities developed the first single NW spectrometer in the world [13]. In 2020, researchers from Chinese Academy of Sciences demonstrated a new flexible dual- NW structure consisting of a GeSn layer with Sn content of 10% heteroepitaxially grown on the sidewall of a Ge NW by molecular beam epitaxy (MBE), which effectively suppressed the formation of defects at the GeSn/Ge interface and greatly reduced the dark current and static power consumption of the photodetector with GeSn/Ge dual-NW structure [14]. NWs and devices with various structures have been continuously developed, and their applications in scientific research and industrialization have become increasingly extensive with the continuous progress of nanotechnology.



The important development process is shown in Figure 1.2. This book focuses on the introduction of NW materials in electrochemical energy storage.

#### 1.1.1.1 Nanorods

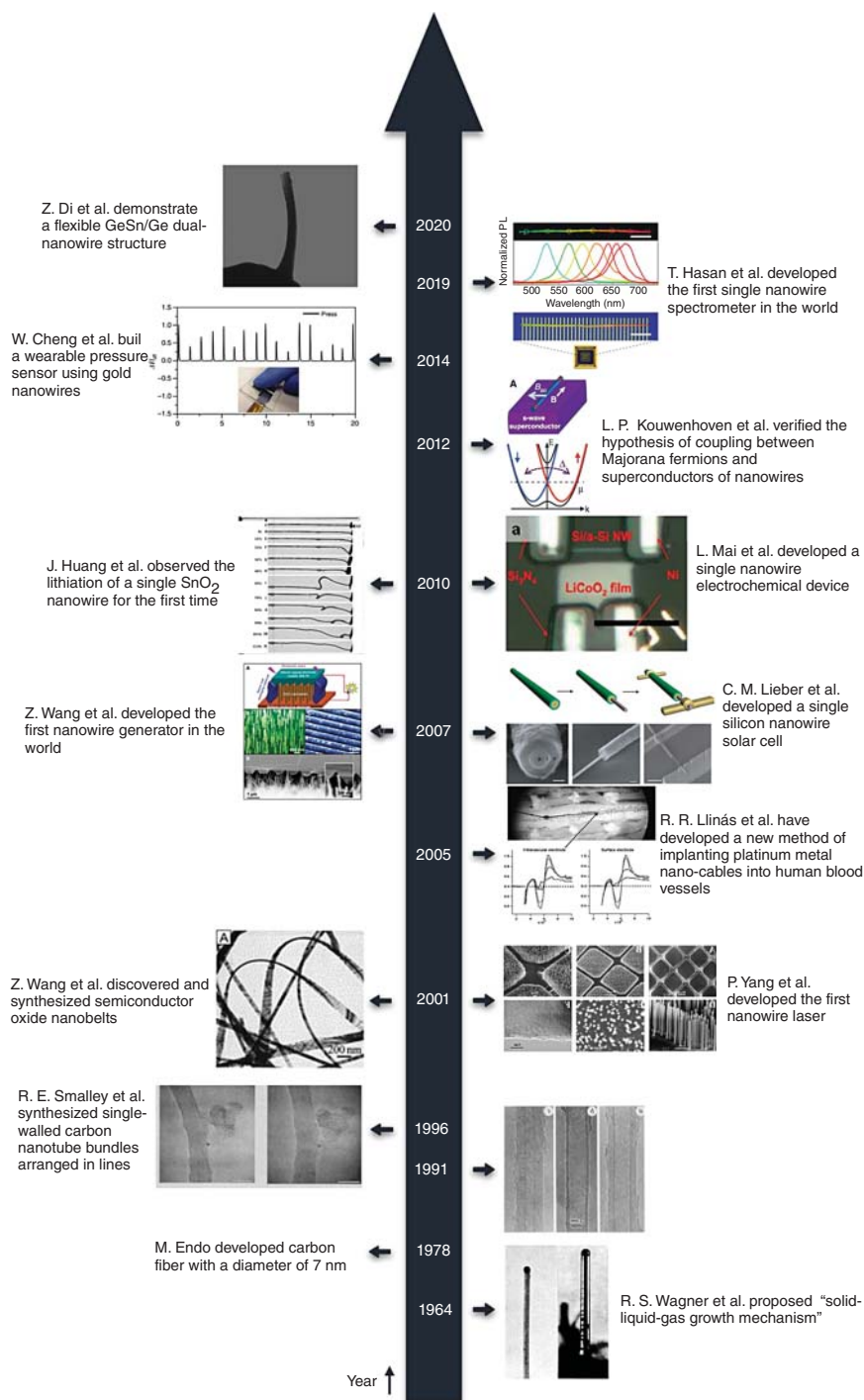
Nanorods and NWs are well-known one-dimensional nanostructures, which are frequently used not only in nano-electromechanical systems but also in biomedical treatments, dentistry, production of energy from solar cells, and humidity-sensitive analysis [15]. Nanorods consist of rod-like nanoparticles. Its length is usually much larger than its size in the two-dimensional direction and can achieve a macroscopic magnitude. It should be noted that there is no strict distinction between NWs and nanorods. Generally, those with a large slenderness ratio are called nanofibers, and those with a small aspect ratio are called nanorods. The dividing line is located at  $1\text{ }\mu\text{m}$ . The preparation methods for nanorods mainly adopt VLS growth and template-based synthesis. Nanorods can also be formed by using LAD. Panasonic, the U.S. Bureau of Standards and Metrology, and the University of Florida have done a large quantity of work in this area, using the pulsed laser method to successfully prepare one-dimensional SiNWs and boron nitride nanotubes. The one-dimensional nanomaterial synthesized by this method has the advantages of high purity, large output, and uniform diameter. Researchers at the University of Minnesota and Princeton University successfully prepared a quantum disk in 1998. This disk is a nano-array system composed of magnetic nanorods with a density of  $109\text{ bit cm}^{-2}$ .

#### 1.1.1.2 Carbon Nanofibers

Carbon nanofibers (CNFs) are  $\text{sp}^2$ -based linear, noncontinuous filaments that are different from carbon fibers, which are continuous with diameter of several micrometers [16]. They are a new type of quasi-one-dimensional carbon material that has attracted more attention in recent years. Its diameter is generally  $50\text{--}200\text{ nm}$ , the length is  $50\text{--}100\text{ }\mu\text{m}$ , and the aspect ratio is  $100\text{--}500$ . Its structure and performance are in the transition state between ordinary carbon fiber and carbon nanotubes, and are formed by stacking nano-sized graphite sheets at different angles to the axial direction of the fiber in space [17]. One-dimensional CNFs have many superior properties, so their application prospects are extensive. CNFs have pores on molecular level over the surface and also have pores inside, as well as a large specific surface area [18]. Therefore, it can absorb a large amount of gas and is a potential hydrogen storage material. It can also be used as a high-efficiency adsorbent, catalyst, and catalyst carrier [19]. CNFs also have high electrical conductivity and can be used as cathode materials for lithium-ion secondary batteries and electrodes for electric double-layer capacitors [20].

#### 1.1.1.3 Nanotubes

Carbon nanotubes, the one-dimensional allotropes of carbon, have attracted significant research interest ever since their discovery due to their outstanding material properties. Carbon nanotubes are a typical representative of nanotubes. In the 1970s,



**Figure 1.2** Important development history of nanowire materials. Source: Refs. [3–14].

M. Endo from the University of Orléans in France successfully synthesized carbon fibers with a diameter of 7 nm, but he did not carefully evaluate and characterize the structure of these carbon fibers [21]. Until 1991, Iijima [22] of the Japanese NEC company discovered carbon nanotubes for the first time with a high-resolution electron microscope. Since then, nanomaterials have attracted widespread attention in the global scientific research field. In 1996, the famous American Nobel Prize winner Smalley and others synthesized single-walled carbon nanotube (SWNT) bundles arranged in rows, which signifies that scientists can prepare batches of NWs in a controlled manner [23]. Xie and coworkers [24] from Institute of Physics, Chinese Academy of Sciences, have achieved the directional growth of carbon nanotubes and successfully synthesized ultra-long (millimeter-level) carbon nanotubes, reported the synthesis of strong, highly conducting, and transparent SWNT films in 2007.

Because carbon nanotubes have the advantages of large specific surface area, good electrical conductivity, and high chemical stability, they have also been widely used for electric double-layer supercapacitor electrodes or as conductive additives in other electrochemical energy storage systems, such as pseudocapacitors and metal ion batteries [25]. At the same time, the internal and surface bond states of carbon nanotubes are different, and there is a phenomenon of incomplete coordination of surface atoms, which leads to an increase in active sites on the surface. These characteristics make carbon nanotubes one of the ideal catalyst support materials [26]. In addition, carbon nanotubes are also expected to be used for field emission tubes, field emission flat panel displays, microwave generators, gas discharge tubes, and fluorescent lamps, and their nano-scale hollow pipes also make them have great potential for hydrogen storage [27].

#### 1.1.1.4 Nanobelts

It is difficult to maintain stability during large-scale industrial production of carbon nanotubes, slowing the research of nanomaterials. In 2001, Prof. Zhonglin Wang and his team used the high-temperature solid gas phase method to discover and synthesize semiconductor oxide nanobelt structures for the first time in the world [28]. Then, they successfully synthesized the ribbonlike structure of broadband semiconductor systems such as zinc oxide, tin oxide, indium oxide, cadmium oxide, and gallium oxide. The purity of these ribbonlike structure materials is as high as 95%, and they have the advantages of large output, perfect structure, clean surface, no internal defects, and no dislocations. In 2007, Zhonglin Wang and his team developed the first NW generator in the world [29].

The cross section of the nanobelt is a narrow rectangular structure with a bandwidth of 30–300 nm, a thickness of 5–10 nm, and length of up to several millimeters. Compared with carbon nanotubes, silicon, and compound semiconductor linear structures, nanobelts are the only broadband semiconductor one-dimensional ribbon structures that have been found to have a controllable structure, be defect-free, and have more unique and superior features of structure and physical properties than carbon nanotubes. Although nanobelts lack the high structural strength of cylindrical nanotubes, they can ensure the necessary stability of electronic equipment and the uniformity of the material structure during mass production because

of their superior performance, which is very important in nanophysics research and nanodevice applications. This structure is an ideal system for researching the transport processes of light, electricity, and heat in one-dimensional functional and smart materials. It can enable scientists to use single oxide nanobelts to make nanometer-sized gas and liquid sensors, nanofunctions, and smart optoelectronic components, laying a solid foundation for nanooptoelectronics [30].

#### 1.1.1.5 Nanocables

In 1997, French scientists C. Colliex and his team found a sandwich-geometry C–BN–C tube in the product obtained by analyzing the arc discharge. Because its geometry is similar to that of a coaxial cable and the diameter is at the nanometer level, it is called a coaxial nanocable [31]. In 1998, Zhang et al. [32] used laser ablation to synthesize a coaxial nanocable with a diameter of tens of nanometers and a length of 50  $\mu\text{m}$ . Their experiment shows that if the mixed powder of BN, C, and  $\text{SiO}_2$  is used as the raw material, a single-core nanocable can be formed with  $\beta$ -SiC core wire inside and amorphous  $\text{SiO}_2$  single wire outside. If  $\text{Li}_3\text{N}$  is added to the raw materials, a coaxial nanocable with another structure can be formed, that is, the core is SiC, the middle layer is amorphous  $\text{SiO}_2$ , and the outermost layer is BNC with a graphite structure. At the same time, Meng et al. [33] developed a new coaxial nanocable preparation method, which is sol–gel and carbothermal reduction with evaporation–condensation, and successfully synthesized a coaxial nanocable with SiC semiconductor core and  $\text{SiO}_2$  insulator on the outer layer. After 2000, people have successfully prepared hundreds of coaxial nanocables using different synthesis methods and different kinds of materials, such as  $\text{SiGaN/SiO}_x\text{N}_y$  [34], Fe/C [35], Ag/polypyrrole [36], GaP/ZnS [37], CdSe/ $\text{TiO}_2$  [38], and three-layer structure of Ag/ $\text{SiO}_2$ /ppy [39] and Nd/FM (FM = Fe, Co, Ni)/PA66 [40].

Coaxial nanocables play a crucial role in the fields of biomedicine, nano-electronic devices, nano-microprocessing, and testing technology. In terms of practical applications, the components in the ultrahigh-density-integrated circuit are mainly connected by nanocable coupling; hence, the nanocable also plays an important role in the connection line. Considering the research on solar cells, the US National Renewable Energy Laboratory has developed a kind of solar cell with high-energy conversion using coaxial nanocable. Respecting medical research, in 2005, scientists in the United States and Japan successfully developed a new method of implanting platinum metal nanocables with a diameter of 1% of human hair into human blood vessels and hoped that one day it would help doctors treat certain human diseases [41]. Nanocables can also be used as probes for miniature detectors on important nano-resolution detectors such as field emission detectors, biological detectors, and atomic force microscopes [42]. It is believed that with the continuous discovery of new special properties of nanocables, coaxial nanocables will also become a new force in the field of NW materials.

#### 1.1.2 Energy Storage Science and Technology

The widespread application of fossil fuels (oil, coal, and natural gas) has greatly promoted the rapid development of the world economy. Nowadays, the improvement

of the world economy is still largely based on the use of fossil fuels. However, with the continuous consumption of nonrenewable energy, traditional fossil fuels such as oil, coal, and natural gas will eventually face exhaustion. It is predicted that the life span of coal, natural gas, and oil will be less than 100 years on average if calculated at the current rate of fossil fuel consumption. The global demand for energy will reach 28 TW by 2050 [43], which is equivalent to the energy produced by consuming 1010 tons of oil each year. Obviously, one of the biggest issues of the twenty-first century is the energy crisis. The deterioration of the energy crisis will lead to a world economic crisis, which in turn leads to an intensification of economic conflicts. At the same time, major problems such as environmental pollution and global warming caused by the growing consumption of fossil fuels pose a severe threat to the sustainable development of mankind. Therefore, energy and environmental issues have become international issues that threaten human survival and development. In summary, the development of renewable energy is the key to solving energy and environmental problems and is the only choice for human beings to achieve sustainable development. Renewable energy mainly includes solar energy, biomass energy, wind energy, hydropower, geothermal energy, and tidal energy. The most important way to solve energy and environmental problems is to vigorously develop renewable energy. However, renewable energy sources such as solar and wind energy are discontinuous and have large, unpredictable, and variable characteristics. Their acquisition and output are unstable, and their energy density is low, which has a great impact on the reliability of the power grid. It is difficult to integrate into the grid. Hence, how to achieve effective conversion and storage between various energy forms is particularly important. The development of energy storage technology can effectively solve this problem enabling renewable energy to be stored and applied in a stable form. In addition, with energy storage technology as the development direction of the future power grid, smart grids can adjust grid peak using energy storage devices, increasing the capacity of the transmission and distribution system and optimizing efficiency. Energy storage technology can be widely used for the generation, transmission, distribution, and usage of the entire power industry. In this book, energy storage mainly refers to electrical energy storage. It is a technology in which electrical energy is stored in another form and released when needed, which can effectively solve the above problems.

The existing energy storage methods are mainly divided into the following categories: electrochemical energy storage (lead-acid batteries, flow batteries, alkaline metal secondary batteries, multivalent ion batteries, metal-chalcogenide batteries, supercapacitors, etc.); mechanical energy storage (pumped hydro storage, flywheel energy storage, compressed air energy storage, etc.); electromagnetic energy storage (superconducting energy storage); and latent heat storage.

#### **1.1.2.1 Mechanical Energy Storage**

The essence of mechanical energy storage is that electrical energy is converted into mechanical energy for storage. There are three main types of mechanical energy storage technologies that have been applied in industry: pumped hydro storage, flywheel energy storage, and compressed air energy storage.

### ***Pumped Hydro Storage***

Pumped hydro storage is currently the most mature and widely used energy storage technology in the world, which is mainly used for system backup and peak load and frequency modulation. The energy storage system is equipped with two storage reservoirs: the upper reservoir and the lower reservoir. Water is pumped from the lower reservoir to the upper reservoir when storing electricity. Water flows from the upper reservoir to the pump location when using electricity, and the potential energy of the water flow is used to drive the turbine to generate electricity. Pumped hydro energy storage has the longest life cycle (30–60 years), the largest number of cycles (10 000–30 000 times) and the largest capacity (500–8000 MWh) compared with other energy storage [44]. However, the disadvantage is that the site selection is greatly affected by the geographical location and the construction period is long as well as the investment cost is high.

### ***Compressed Air Energy Storage***

Compressed air energy storage system (CAES) uses gas turbine energy to generate electricity. The air compression system consumes excess electricity to compress the air and store it in underground salt mines, abandoned quarries, or large ground storage tanks when storing electricity. The stored air is released from the air storage chamber and burned with fuel when using electricity. The produced gas, with its high temperature and pressure, drives the gas turbine to generate electricity. The system construction investment and power generation cost are lower than pumped hydro storage. Besides, it has the following advantages: long service life (20–40 years), large capacity, and large quantities of charge–discharge cycles. It has wide applications in the fields of power production, transportation, and consumption, including peak shaving and valley filling, power load balancing, renewable energy access, and backup power supplies [45]. It has broad application prospects in conventional power systems, renewable energy, distributed function systems, and smart grids. However, the negative aspects of CAES are obvious. To begin with, its energy density is low. To make matters worse, it depends on large gas storage chambers and causes fossil fuel consumption and environmental pollution.

### ***Flywheel Energy Storage***

Flywheel energy storage and power generation technology uses the conversion between electrical and kinetic energy to store and generate energy. The flywheel is connected to the power grid, and the electrical energy provided by the power grid drives the flywheel to rotate at a high speed, converting the electrical energy into kinetic energy and storing it when storing energy. The rotating flywheel drives the motor to generate electricity, converting kinetic energy into electrical energy when using energy. Compared with other energy storage technologies, flywheel energy storage has the advantages of high energy conversion efficiency (85–95%), non-polluting, simple maintenance, free from geographical environment restrictions, and continuous operation [46]. Mainly used for uninterruptible power supply (UPS), grid peak shaving, and frequency control. However, short power generation times and high equipment costs are important factors restricting its development.

### 1.1.2.2 Electromagnetic Energy Storage

Superconducting magnetic energy storage (SMES) is the most common energy storage technology for electromagnetic energy storage. SMES system directly stores electromagnetic energy in the superconducting coil. The stored electromagnetic energy is sent back to the grid or other loads when electricity is needed. SMES system has unique benefits that other energy storage technologies do not have. SMES systems can store energy almost lossless for a long time (conversion efficiency exceeds 90%) [47], release energy rapidly, have a small size, and are environmentally friendly. The low-frequency power oscillation of the grid can be reduced or eliminated, and the active and reactive power can be adjusted more easily with the existence of SMES system. Therefore, SMES can improve the stability of the power system and enhance the controllability of power generation with new energy. However, its short board is high in cost, complicated in process, and operating conditions.

### 1.1.2.3 Electrochemical Energy Storage

The principle of electrochemical energy storage is that electrical energy is converted into chemical energy for storage. It includes various types of batteries (lead–acid batteries, nickel-metal hydride (NiMH) batteries, lithium-ion batteries, etc.) and supercapacitors. Electrochemical energy storage is convenient and safe, is not restricted by region, has less environmental pollution, is not restricted by Carnot cycle in energy conversion, and has high conversion efficiency compared with other methods [48]. Electrochemical energy storage is the most important component in the field of energy storage. Since Le Clancy invented lead-acid batteries in 1859, various chemical batteries involving different energy storage systems have been developing in the direction of high capacity, high power, low pollution, long service life, and high safety to meet the needs of different fields. At present, lithium-ion battery has the advantages of high energy density, high conversion efficiency (close to 100%), long cycle life, and low self-discharge. They have been widely used in various electronics and electric vehicles and are gradually being deployed in the field of large-scale energy storage. Many large-scale lithium battery energy storage demonstration systems and bases have been built in most countries. However, in 2018, the U.S. Geological Survey Mineral and Commodity Summaries showed that the global lithium reserves could not meet the rapid development of global electric vehicles [49]. Thus, in order to meet the rapid development of electric vehicles and the increasing demand for energy storage devices in other fields, other types of secondary batteries and energy storage devices have also been significantly developed, such as new alkaline metal secondary batteries (sodium ion battery, potassium ion battery), multivalent ion batteries (magnesium ion battery, zinc ion battery, aluminum ion battery, etc.), metal-chalcogenide batteries, metal-oxygen batteries, and supercapacitors. The common types of electrochemical energy storage involved and their main characteristics are shown in Table 1.1. Electrode materials are the core component of energy storage devices. Improving the performance of chemical energy storage equipment by exploring and developing new energy storage materials has become a global issue, which has received great attention and support from all countries.

**Table 1.1** Common types of electrochemical energy storage and their main advantages and disadvantages.

Type of battery	Mechanism of energy storage	Analysis of advantages and disadvantages
Lead-acid batteries	$\text{PbO}_2 + 2\text{H}_2\text{SO}_4 + \text{Pb} \leftrightarrow 2\text{H}_2\text{O} + 2\text{PbSO}_4$	Pros: mature technology and low cost Cons: short cycle life and pollution problem
NiMH batteries	$\text{Ni(OH)}_2 + \text{M} \leftrightarrow \text{NiOOH} + \text{MH}$	Pros: withstand overcharge and over discharge, strong capability of high rate discharge, safety and high power density Cons: low voltage and low energy density
Monovalent ion batteries	Embedding reaction, alloying reaction, conversion reaction	Pros: mature technology for lithium-ion batteries, small self-discharge, light weight, small size, high working voltage, environmentally friendly, no memory effect, charging rapidly and high energy capacity Cons: internal impedance is high, the working voltage changes greatly and the capacity decays quickly
Multivalent ion batteries	Embedding reaction, alloying reaction, conversion reaction	Pros: the theoretical volume ratio is high, and the anode has rich metal resources Cons: multivalent ions have a large radius, the polarization phenomenon is serious, and configuring a suitable electrolyte is difficult
Metal-chalcogenide batteries	The anode (M) is mainly the deposition and dissolution reaction of metal ions, and the oxidation-reduction reaction of the chalcogen element (X) occurs in the cathode. The reaction of the entire battery system can be summarized as: $\text{M} + \text{X} \leftrightarrow \text{MX}$	Pros: high energy density Cons: low power density, short cycle life, immature system, and difficult to achieve commercialization
Metal-air batteries	Catalytic materials are used to catalyze the oxygen or pure oxygen in the air as the cathode active material, the metal is the anode, and the ammonium chloride or caustic solution is used as the electrolyte to participate in the electrochemical reaction.	Pros: relatively low cost and stable output voltage Cons: low power density, short cycle life, and low output voltage

(Continued)



Table 1.1 (Continued)

Type of battery	Mechanism of energy storage	Analysis of advantages and disadvantages
Supercapacitors	Electric double layer, pseudocapacitance (underpotential deposition, redox reaction, and embedded pseudocapacitance)	Pros: high power density and good cycle stability Cons: low energy density and low output voltage
Flow batteries	A high-performance battery that uses positive and negative electrolytes is separated and circulate, respectively	Pros: long cycle life Cons: low energy storage density

**Lead-Acid Batteries**

The basic chemical composition of all types of lead-acid battery is the same. In the charged state, the cathode is lead dioxide, the anode is metallic lead, and the electrolyte is sulfuric acid solution. In the discharge state, the main components of the positive and negative electrodes are lead sulfate. The global lead-acid battery industry has always been larger than other batteries because of a series of advantages such as low cost, high working voltage, safety, and reliability that other batteries cannot replace [50]. Lead-acid batteries have a long history of development, and the technology is mature and is now widely used in many fields. In the automotive industry, lead-acid batteries are used for the starting, ignition, and lighting of various cars, motorcycles, and ships. In the electric vehicle industry, lead-acid batteries provide power for electric cars and electric bicycles. In addition, the market demand for lead-acid batteries in the communications industry is huge. In addition, when new energy sources generate electricity, it also needs to be supplied with lead-acid batteries [51]. Lead-acid batteries can replace expensive gas and oil turbine generators to meet load balancing requirements as an alternative power supply method during peak electricity consumption.

**NiMH Batteries**

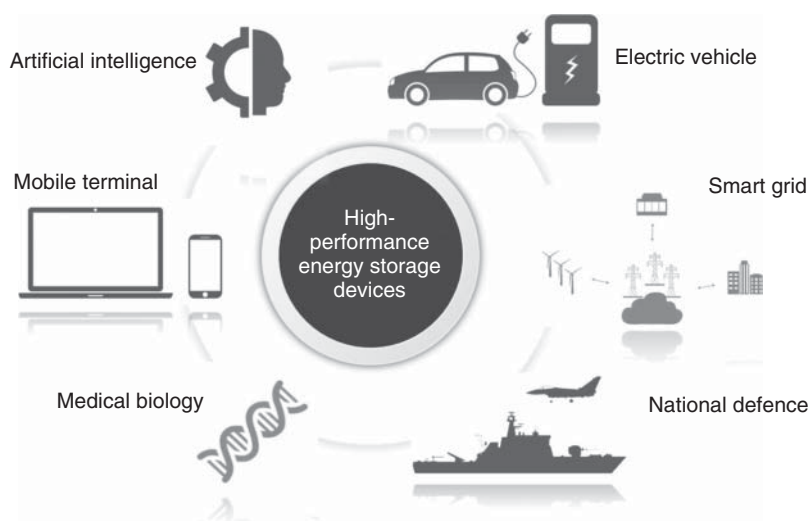
NiMH batteries are a new generation of high-energy secondary batteries that replace Ni–Cd batteries [52]. NiMH batteries are a kind of green battery compared with lead-acid batteries. The cathode of NiMH battery is  $\text{Ni(OH)}_2$ . The anode material is metal hydride (MH). The electrolyte is an aqueous potassium hydroxide solution. In the field of small batteries, although the energy density of NiMH batteries is higher than Ni–Cd batteries, its energy density is lower than that of lithium-ion batteries. Therefore, at present, the market utilization rate of NiMH batteries is lower than that of lithium-ion batteries. There are also some electric tools that retain NiMH batteries, like sweeping robots. In the automotive industry, NiMH batteries are used as power batteries. NiMH batteries have outstanding advantages compared with lithium-ion batteries and hydrogen fuel cells, which mainly show in their fast charging and discharging speeds, high mass-specific power, and good stability.

In addition, the energy storage batteries currently used in smart grids mainly include lead-acid batteries, lithium-ion batteries, sodium-sulfur batteries, all-vanadium flow batteries, and NiMH batteries. Among them, lead-acid batteries will produce lead pollution, and many European countries have gradually banned lead-acid batteries. Li-ion batteries are not yet mature in large-scale integration technology. The technology of NiMH batteries as a smart grid energy storage system is relatively mature, with good safety performance and long service life [53].

### ***Monovalent Ion Batteries***

Lithium-ion batteries are the most representative of monovalent ion batteries. It mainly realizes charge and discharge through repeated insertion and extraction of lithium ions between the positive and negative electrodes. Lithium ions are extracted from the cathode material and inserted into the anode material through the electrolyte, and the anode material is in a lithium-rich state when charging. The situation is opposite when discharging. Before the advent of lithium-ion batteries, NiMH batteries were widely used in the portable electronic equipment industry. After the advent of lithium-ion batteries, they are superior to NiMH batteries in terms of weight, capacity, and power. The energy density of lithium-ion batteries is greater than that of NiMH batteries, the self-discharge phenomenon is weakened, as well as the charging time is shorter. Lithium-ion battery energy storage technology currently occupies a leading position in the energy storage industry and has been widely used in electric vehicles, smart grids, cutting-edge defense equipment, biomedicine, portable devices, artificial intelligence, etc., as shown in Figure 1.3.

However, large-scale applications of lithium-ion batteries are still limited, and security and high cost are the main influencing factors. The current commercial cathode materials for lithium-ion batteries are mainly  $\text{LiCoO}_2$ ,  $\text{LiMn}_2\text{O}_4$ , and  $\text{LiFePO}_4$ . The anode materials are mainly carbon materials and  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  [54]. The electrolyte is a nonaqueous organic electrolyte. In recent years,  $\text{LiFePO}_4$



**Figure 1.3** Main application areas of high-performance energy storage devices.

has received widespread attention around the world due to its better safety and high-rate discharge performance, and its application in electric vehicles and grid energy storage has been rapidly promoted [55].

### ***Multivalent Ion Batteries***

There is an increasing demand for lithium-ion batteries in various fields due to their continuous development. The shortage of lithium resources is one of the important factors hindering the development of lithium-ion batteries. In order to alleviate this problem, multivalent ion batteries, including magnesium ion batteries, zinc ion batteries, aluminum ion batteries, and calcium ion batteries, have been rapidly developed. Multivalent ion batteries have higher safety performance and lower cost than lithium ion batteries. Moreover, multivalent ion batteries directly use metals as negative electrode materials, so they have the potential to greatly increase the energy density of the batteries compared with lithium ion battery using carbon materials as negative electrodes. Therefore, it has good application value and development prospects in the fields of large-scale energy storage and civil batteries. Unfortunately, multivalent ion batteries are still in the research stage, and the strong polarization effect and high requirements for electrolyte are important factors that limit the development of multivalent ion batteries [56].

### ***Supercapacitors***

Supercapacitors are different from traditional batteries. The energy storage mechanism of supercapacitors was divided into physical energy storage and chemical energy storage. The physical mechanism is that a double layer structure formed by the interface of electrode/electrolyte with porous carbon material with high specific surface area is used for energy storage [57]. The chemical mechanism is that the rapid, reversible redox reactions between electrodes and electrolyte are used for energy storage (pseudocapacitance) [58]. Therefore, according to different energy storage mechanisms, supercapacitors can be divided into electric double layer supercapacitors (EDLC), pseudocapacitors, and hybrid capacitors (both physical energy storage and chemical energy storage). It combines the advantages of traditional capacitors and batteries, not only has the advantages of high discharge power of electrostatic capacitors, but also has a large charge storage capacity, as same as batteries. Its capacity can reach the farad level or even thousands of farad levels. At the same time, it has the advantages of high power density, good cycle stability, strong temperature adaptability, and being environmentally friendly. Supercapacitors are currently widely used in different market areas such as auxiliary peak power, backup power, storage of renewable energy, and alternative power supplies. More importantly, it also has very broad market prospects in industrial control, wind and solar power generation, transportation, military industry, and other directions [59].

## **1.1.3 Overview of Nanowire Energy Storage Materials and Devices**

Nanomaterials have a high specific surface area and excellent activity. When used as a battery electrode material, it has a large contact area with the electrolyte and

a short ion diffusion distance, which can effectively improve the electrical activity of the material. It also has significant advantages when used as a high-power battery electrode material. At the same time, a reasonable design of nanostructures is beneficial to alleviate stress release during cycling, and is conducive to improving the stability of the structure in order to obtain a longer cycle life. For this reason, research on large-capacity, high-power, long-life, and low-cost electrochemical energy storage technology based on new nano-electrode materials is one of the frontiers and areas of focus in the low-carbon economy era. Lithium-ion batteries, supercapacitors, and lithium-air batteries have been extensively studied due to their respective advantages, but traditional electrode materials are still difficult to meet the needs of high capacity and high power. Numerous researches have shown that the electrochemical properties of electrode materials are closely related to their scale, internal crystal structure, and apparent morphology. NW electrode materials, due to their unique anisotropy, rapid axial electron transmission, and radial ion diffusion characteristics, are suitable for the design, integration, and performance control of alkali metal ion batteries, supercapacitors, transparent flexible energy storage devices, and hybrid devices.

In recent years, the development of nanowires has shown diversified characteristics, including multilayer NWs, NW clusters, nanotube clusters, NW clusters, and other one-dimensional NW materials with composite structures that have been able to develop rapidly. It is used for the tip of a scanning tunneling microscope, nanodevices, ultralarge integrated circuit wires, optical fibers, micro-drills in microelectronics, electrode materials for energy hunting systems, active materials for catalytic systems such as photocatalysis and electrocatalysis, and electrode materials for energy storage systems (such as metal ion batteries and supercapacitors). This chapter focuses on the electrochemical energy storage system by discussing the physical and chemical properties, synthetic chemistry, and practical applications of NW electrode materials.

There are many ways to synthesize NW materials, such as hydrothermal methods [60], electrospinning methods [61], and template methods [62]. Various directional control methods can synthesize NW materials with different morphologies. However, the physical and chemical properties of NWs will be different, and the external properties will also be different. With the progress of technology, NW materials have also developed, from conventional NWs to ultra-long NWs [63], mesoporous NWs [64], dendritic NWs [65], etc. The uniformity, controllability, and electrochemical properties of NW materials have been continuously improved with the continuous optimization of the structure. The specific preparation methods for different NW structures will be described in detail in Chapter 3.

One-dimensional NW materials have the following advantages for electrochemical energy storage. Firstly, compared to granular nanomaterials, NW electrode materials provide transmission paths with continuous axial electron and radial ion transmission paths, which endow NW materials with better rate performance. Secondly, NW materials can directly grow on the substrate of metal or carbon material. It can be used as a framework to composite with other materials without the addition of a binder, constructing a complex and multi-element electrode

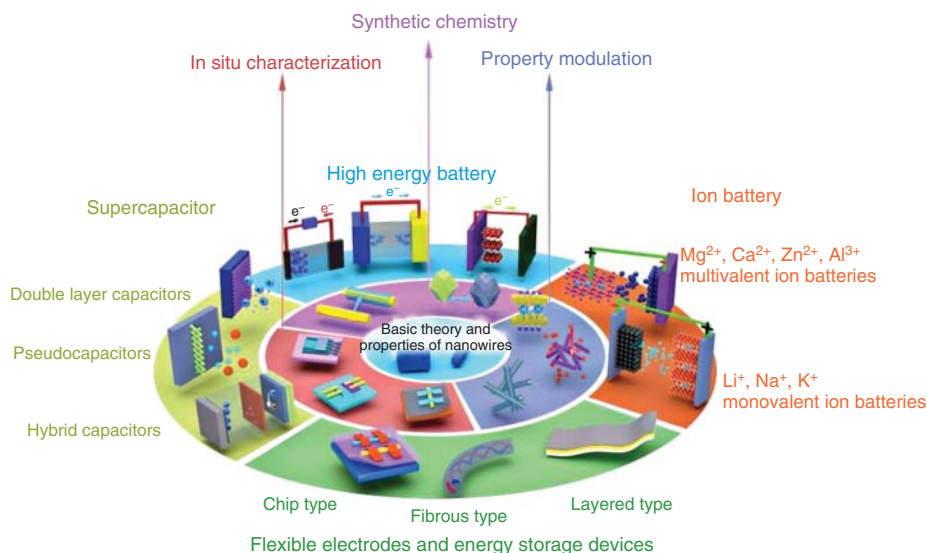
structure. Thirdly, NW materials have geometric characteristics, which are tens of microns in length and tens of nanometers in diameter, making it easy to make a single NW electrochemical device for in situ electron microscopy and spectroscopy characterization [66].

At the same time, the use of NW materials for electrochemical energy storage also has the following challenges. Firstly, when semiconductor NWs are used for electrochemical energy storage, their poor conductivity requires additional conductive agents or conductive material coatings like carbon coatings, which increases the complexity of the electrode construction process. Besides, the continuous charging and discharging processes will cause the deterioration of the material structure, which will affect the axial electron conduction of the NW material, thus affecting the cycle stability of the battery. Additionally, the materials in the electrode network created by overlapping NWs are largely in point contact with one another, which reduces the conductivity of the entire electrode and raises the internal resistance of the battery [66]. In view of the advantages and challenges of using NW materials for energy storage, researchers have proposed a variety of optimization strategies and designed and constructed NW electrode materials with various structures.

Energy storage materials and devices with high energy density, good power density, and long service lives are major requirements for the development of new energy vehicles, smart grids, and cutting-edge national defense equipment. However, rapid capacity decay and difficulty balancing energy and power density are major bottlenecks, restricting the development of high-performance energy storage materials and device technologies. In order to solve the above bottlenecks, the author of this book has been committed to the research of NW energy storage materials and devices in combination with the advantages of NW materials described above. The author and his team focused on basic research and application development of NW electrode materials in basic theory, controlled growth, performance regulation, device assembly, in situ characterization, and energy storage applications. They designed and assembled the first single NW solid-state energy storage device for monitoring capacity decay in real-time and took the lead in realizing the large-scale preparation and application of high-performance NW energy storage devices and key materials, achieving many innovative research results. The main research content of the NW energy storage devices involved in this book is shown in Figure 1.4.

#### 1.1.3.1 Si Nanowires

Silicon materials have the characteristics of high specific capacity ( $4200 \text{ mAh g}^{-1}$ ) that other materials cannot achieve as negative electrode materials. It has attracted the attention of researchers and is the third-generation negative electrode material that can replace graphite materials [67]. In addition, as silicon element is generally nontoxic, abundant, and widely available, new systems may have cost and recycling benefits. The application of silicon in lithium batteries originated in the 1970s. Nelson et al. [68] and Sharma et al. [69] reported that the phenomenon of reversible lithiation and delithiation of silicon at high temperature. Subsequently, researchers such as Weydanz et al. [70], Gao et al. [71], Limthongkul et al. [72], Li et al. [73],



**Figure 1.4** Main research contents of nanowire energy storage devices.

and Obrovac et al. [74] conducted in-depth research and gradually improved the reversible lithium storage mechanism of silicon materials.

Nanotechnology applied to silicon materials can resolve the volume expansion of silicon-based anode materials during cycle. The volume expansion phenomenon will cause structure collapse of the active materials and shedding of the current collector to lose electrical contact when the lithium ions are released, thereby affecting the cycle's performance. Yue et al. [75] used nanosilicon powders with different sizes (5, 10, and 20 nm) to prepare anode materials and found that silicon particles with a particle size of 10 nm have the highest specific capacity after electrochemical tests. One-dimensional NWs and nanotubes can also improve the problem of volume expansion, except for zero-dimensional nanoparticles. SiNWs have many excellent properties that are different from those of general silicon materials, such as electron transport, field emission characteristics, surface activity, and quantum confinement [76]. Therefore, it has a wide range of application prospects in the manufacture of low-dimensional nanodevices [77]. At present, the preparation and application of nanodevices such as SiNW transistors, sensors, and NW batteries have been realized.

The battery made with SiNWs as the anode has better storage capacity than the battery made with traditional graphite as the anode. Traditional graphite anodes need six carbon atoms to store one Li<sup>+</sup>, while one Si atom can store four Li<sup>+</sup>. However, a large number of moving Li atoms with high speed will break the Si in a battery made of Si thin layers or Si ions and will also destroy the bond between Si and the substrate, weakening the power storage capacity. Cui et al. of Stanford University prepared Si NWs on a stainless steel substrate and then made a lithium ion battery with SiNWs, which not only increased the anode capacity of the battery but also ensured that the SiNWs never fell off the substrate after a series of expansion

and contraction experiments. This is because the shape of the SiNWs enables the Si atomic lattice to expand and contract rapidly along the NW, thereby alleviating the structural strain and making the NW firmly adhere to the metal substrate. In this way, the stored electricity of Si anodes is 10 times higher than that of traditional graphite anodes [78].

### 1.1.3.2 ZnO Nanowires

The band gap of ZnO nanowires at room temperature is 3.37 eV. ZnO hardly produces any light scattering under natural light. In addition, its thermal ionization energy under room temperature is low (26 meV) [79] and much lower than the exciton binding energy (60 meV), so the ZnO NWs have great exciton stability. The crystal structure of ZnO NWs has intrinsic defects that can cause energy transitions to emit light at various energy levels. ZnO NWs show unique properties in the fields of thermodynamics, electricity, optics, and magnetism [80].

Bae et al. [81] reported that ZnO NWs have a larger electron concentration and field-effect mobility than bulk ZnO. Choi et al. [82] developed a kind of composite nanofiber containing insulating  $\text{ZnGa}_2\text{O}_4$  nanocrystals as components for building field-effect transistors (FET). The composite NW material has excellent electrical properties and high field effects. This is because the insulating spinel phase of  $\text{ZnGa}_2\text{O}_4$  effectively blocks the flow of electrons through  $\text{In}_2\text{O}_3$  and ZnO nanocrystals. Moreover, based on low-pressure chemical vapor deposition (LPCVD) technology, a series of ZnO NWs have been grown on  $\text{SiO}_2/\text{Si}$  and SiNWs/Si substrates. These composite nanomaterials have quasi-lasting photoconductivity and enhanced ohmic  $I$ - $V$  characteristics [83]. Moon et al. [84] obtained ZnO–NiO mixed oxide nanostructures by electrospinning. After measuring their electrical conductivity, they found that the value increased with increasing temperature, which can be attributed to the thermal emission of the carrier from the grain boundary energy state. Park et al. [85] showed that, compared with pure ZnO, the prepared ZnO/N-doped carbon nanotube nanocomposite has higher electron mobility. In addition, the work of Khurana et al. [86] revealed that the electron transfer kinetics of ZnO graphene composites is faster than those of pure ZnO NWs.

The application of ZnO NW materials in energy storage is generally used as the window layer of solar cells or the photoanode of dye-sensitized solar cells. ZnO NWs can be combined with certain polymers, graphene, or quantum dots to form hybrid photovoltaic devices. In 2005, Lévy-Clément et al. [87] took the lead in using CdSe-sensitized p-CuSCN layer and n-ZnO NWs to form a heterojunction solar cell and achieved a conversion efficiency of 2.3%. Liu et al. [88] used ZnO NW/ $\text{Sb}_2\text{S}_3$ /P3HT structure to fabricate an organic/inorganic hybrid solar cell and achieved a conversion efficiency of 2.9%. Then, Park et al. [89] grew vertically arranged ZnO NWs on graphene surfaces and constructed a hybrid solar cell with PEDOT:PEG as the interface layer and PbS quantum dots as the hole transport layer, obtaining a conversion efficiency of 4.2% under AM1.5 light conditions. In addition, Chen et al. [90] produced a dye-sensitized solar cell with vertical array of ZnO NWs and studied the effect of NW length on the photovoltaic performance of solar cells. The results indicate that the length of the ZnO NW increases with increasing conversion efficiency.

### 1.1.3.3 Single Nanowire Electrochemical Energy Storage Device

Mai et al. [9] used the unique anisotropy of NWs to design and assemble an all-solid-state electrochemical energy storage device with single NWs that can be used for in situ diagnosis and micro-nanosystem support power supply. This device can detect the electrical conductivity and law of structural changes of the NWs during cycle test without adding conductive additives or binders. Using a single vanadium oxide NW as a working electrode shows that after a shallow discharge with a current of 100 pA, the conductance of the NW drops by 2 orders of magnitude. After shallow charging, the conductance returns to the original level. This result indicates that the structural change of the NWs caused by the insertion and extraction of lithium ions is reversible in the case of shallow charge and discharge. After 400 seconds of deep discharge at 100 pA, the conductivity of the NWs irreversibly decrease by 5 orders of magnitude, showing that the structure undergoes permanent changes. The direct connection between the NW electrical transport and charging and discharging states has been established through research on the in situ characterization platform based on the all-solid-state single NW device. This also inherently reveals the scientific law of the capacity attenuation of NW energy storage devices. In other words, the capacity decay of NW electrode material and rapid decline of conductivity are directly related to structural deterioration. Huang et al. [10] designed and constructed a battery system with single-crystal  $\text{SnO}_2$  NWs as anode and lithium cobalt oxide as cathode. Using TEM technology to observe the morphological changes of the NWs during charging and discharging, it is found that when lithium ions are inserted into the NWs, it will cause violent volume expansion, elongation, and curling deformation. It is worth noting that no matter how severe the deformation is, the nanowire always maintains structural integrity during the cycle process, which further verifies the superior performance of the nanomaterial as an electrode.

Based on the characterization of single NW materials, the increasingly limited nature of their structure and morphology has been discovered. It needs to be modified to improve its electrochemical performance. Commonly used methods include pre-embedding technology to modify one-dimensional NWs, surface modification hierarchical nanowires, internal structure optimization NWs, and synergy optimization NWs. Pre-embedding technology is an effective method to increase the carrier concentration and improve the conductivity of the NW electrode without destroying the morphology [91]. Hierarchical structure NW materials include dendritic structure NW materials and coaxial NW materials. When dendritic NW materials are used as electrodes, they can provide more ion transmission paths, higher electronic conductivity, more active sites, and effectively inhibit the self-aggregation of nanomaterials [92]. The preparation of coaxial NW materials is relatively easy to realize. This structure is usually used to improve the structural stability of the material, enhance the electrical conductivity, and buffer the stress and strain of the internal material [93]. In addition, the specific surface area of the NW, the contact area between electrolyte and electrode material, and reactive sites can be improved by effectively combining the advantages of one-dimensional nanostructures and mesoporous structures to construct mesoporous NWs, providing free space for



stress release in the reaction [94]. The synergistic effect of surfactants can change the orientation of the nanowires and reduce their interface resistance [95].

Single NW devices have good applications in different energy conversion devices. A single NW device used in a solar cell can increase the conversion efficiency of solar energy by up to 40%. The thermal conductivity of one-dimensional NW materials is completely different from that of bulk materials [96], as thermoelectric devices can effectively improve thermal energy utilization. In addition, a single nanodevice can be used as an efficient electrocatalyst in electrocatalytic hydrogen production devices. It can effectively enhance the charge injection of the electrode material and improve the catalytic activity of the catalyst by reducing the contact resistance between the electrode and the material [97].

It is necessary to understand some basic theories of NW energy storage materials when the composition of the material is determined, such as thermodynamic and kinetic characteristics and important electrochemical performance parameters. These will be introduced in detail in Chapter 2. After that, we will consider the method used to synthesize the required NW materials, whether hierarchical NWs or porous NWs, hydrothermal or electrospinning, which will be discussed in Chapter 3. In order to study the electrochemical mechanism of the synthesized NWs, in situ characterization methods are needed to provide convincing evidence. Chapter 4 lists some in situ characterization methods, including detailed descriptions of single NW devices, in situ electron microscopy, and in situ spectroscopy. Chapters 5–9 of this book show readers the application of NW electrode materials in a variety of electrochemical systems, leading readers to the forefront of nanowire energy storage materials and devices.

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