REVIEW

Nanowires

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Nanowires in Energy Storage Devices: Structures, Synthesis, and Applications

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Accompanied by the development and utilization of renewable energy sources, efficient energy storage has become a key topic. Electrochemical energy storage devices are considered to be one of the most practical energy storage devices capable of converting and storing electrical energy generated by renewable resources, which are also used as the power source of electric vehicles and portable electronic devices. The ultimate goals of electrochemical energy storage devices are long lifespan, high safety, high power, and high energy density. To achieve the above goals, researchers have attempted to use various nanomaterials to improve electrochemical performance. Among these, 1D materials play a critical role. This review classifies nanowires according to morphologies (simple nanowires, core–shell/coated nanowires, hierarchical/heterostructured nanowires, porous/mesoporous nanowires, hollow structures) and combined forms (nanowire arrays, nanowire networks, nanowire bundles) and introduces their characteristics and corresponding synthetic methods. The characteristics and advantages of nanowires in lithium-ion, sodium-ion and zinc-ion batteries, and supercapacitors, along with in situ characterization of nanowire electrode are reflected in the application examples. In the summary and outlook section, some comments are presented to provide directions for further exploring nanowire based electrochemical energy storage in the future.

1. Introduction

Due to the intensification of environmental pollution and the depletion of traditional fossil energy, the demand for renewable energy is becoming more and more urgent at present. The development and utilization of renewable energy are of

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great significance in solving the current energy crisis and environmental problems in human society.[1] Solar energy, wind energy, hydropower, and nuclear power are used as environmentally friendly and sustainable energy sources.[2] However, the seasonal characteristic, regionalism, and discontinuity make it hard to use the clean energy directly in the industries and daily life. Therefore, how to store these energy sources is a hot spot of concern. Currently, different kinds of energy storage technologies for stationary applications include mechanical, chemical, electrical, and electrochemical energy storage.[3,4] Among them, the electrochemical energy storage has higher efficiency, longer cycle life, lower cost, sustainability, and other favorable features, which has shown great prospects. Recently, lithium-ion batteries have become the mainstream of electrochemical energy storage devices, and have played an important role in smart grids, electric vehicles, and personal electronic devices.[5] However, people are still finding better alternatives, due to the scarcity of lithium resources, high prices, and safety issues.[6,7] Researches on sodium-ion batteries,[8,9] potassium-ion batteries,[10] and multivalent batteries[11] are also underway. It is hard to get ideal electrochemical energy storage devices with high power and energy density at the same time. Trying to balance the indexes, researches on the battery–supercapacitor hybrid devices have also been studied.[12] The two electrodes are the capacitive electrode and the battery-type electrode. The energy density would be improved through capacity improvement and voltage expansion.

In order to accomplish the goals above, scientists have attempted to use sundry forms of nanomaterials to improve electrochemical performance.[13] 1D nanomaterials (nanowires (NWs)/nanorods/nanotubes/nanofibers) have attracted a wide range of interests due to their unique functional characteristics. Nanowire is one of these structures that possess several practical properties, such as crystallinity, well-controlled dimensional composition, and electronic radial transport, which helps to manufacture the nanoscale systems and useful devices in electrochemical energy storage. After several decades, the application potential of nanowires in energy storage has been explored, and their advantages can partially be adapted to expectations of people on electrode materials.[14] The advantages of

nanowires are summarized as follows: 1) Nanowires provide a direct pathway for electron transfer.[15,16] 2) Nanowires provide more surface area, which results in the larger electrode–electrolyte contact area and reduced charging/discharging time.[17,18] 3) Nanowires can accommodate volume expansion, inhibit mechanical degradation, and extend cycle life.[19,20] 4) Nanowires have excellent mechanical flexibility and Young's modulus, which are of great significance for the manufacturing of microflexible electronic components.[21] Owing to the significant advantages of nanowires, the development and application in the energy storage devices have great potential.

In this review, we introduce the preparation methods based on the classification of nanowires and briefly analyze the relationship between their structures and properties. Then, according to the system classification, some application examples in energy storage are introduced. Finally, on the basis of current researches, we put forward some views on the development trend of nanowires in energy storage devices.

2. Structure Design and Synthesis of Nanowires

In order to improve energy storage performances of nanowires, various morphologies and structures have been constructed based on the original nanowires. Nanowires can be classified from two levels. From the perspective of monomer nanowires, nanowires with different shapes are prepared, such as porous nanowires and coaxial coated nanowires. Further, when combining multiple nanowire monomers in different ways, we can achieve an overall presentation of them, such as arrays or networks.

The morphology of nanowires is always serviced for better performance. In general, different morphologies can lead to different performances, which has caused great concern. In order to control the morphology and structure of materials, a lot of detailed explorations have been done. Various methods have been created in long-term research, including hydrothermal reaction,[22] electrolytic deposition,[23] calcination,[24] electrospinning,[25] microemulsion technique,[26] template method,[27] chemical vapor deposition,[28] vapor–liquid–solid (VLS) growth strategy,[29] and so on. In the review article by Mai et al.,[30] various methods of preparing nanowires for rechargeable batteries are highly summarized by the following categories: nucleation and growth,[31,32] deposition,[33,34] melt-casting, and electrospinning.[35] In fact, in order to prepare ideal nanowire products in practical applications, a combination of methods would be used to synthesize or modify nanowires with special structures in two or more steps. For instance, the common example is annealing the sample after hydrothermal reaction.[36]

Herein, we take the characteristics of morphology as a guide for the classification of nanowires, and select several typical works to briefly describe the preparation methods, morphology, and corresponding characteristics of nanowires. According to the morphology and structure of nanowires, these nanowires can be classified into simple nanowires, core–shell/coated nanowires, hierarchical/heterostructured nanowires, porous/mesoporous nanowires, and hollow structures (**Figure 1**). According to the different combined forms of nanowires,

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nanowire arrays, nanowire networks, and nanowire bundles are introduced (**Figure 2**). **Tables 1** and **2** are made to show the electrode materials, morphologies/structures, and synthesis strategies of different nanowires.

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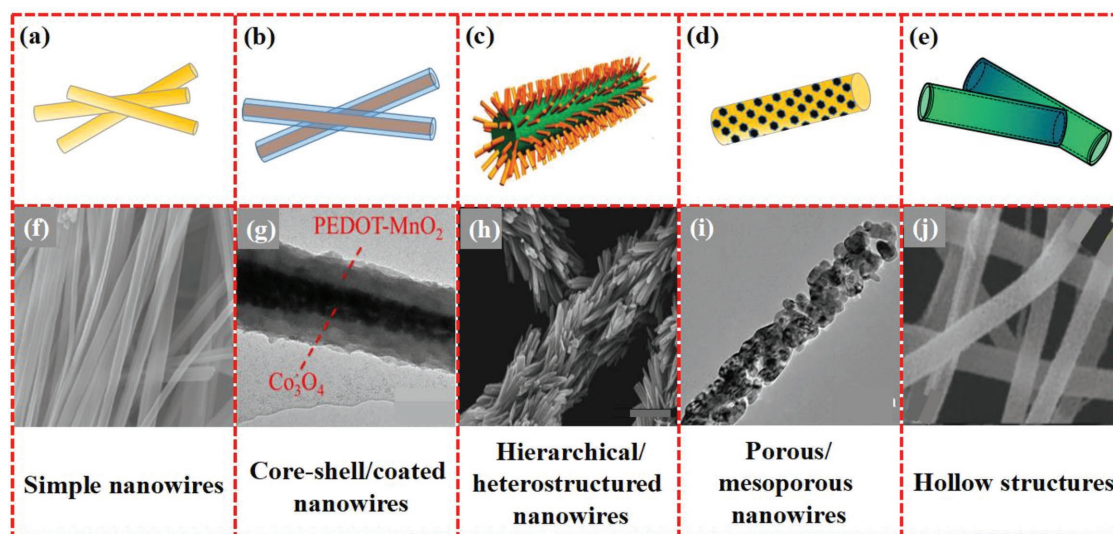
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Figure 1. Different morphologies and structures of nanowires. a–e) are schematic diagrams, and f–j) are SEM or TEM images. f) NVO nanowire. Reproduced with permission.[125] Copyright 2018, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. g) Co_3O_4/PEDOT–MnO_2 core–shell nanowire. Reproduced with permission.[169] Copyright 2014, American Chemical Society. c,h) Hierarchical $MnMoO_4$/$CoMoO_4$ heterostructured nanowires. Reproduced with permission.[26] Copyright 2011, Macmillan Publishers. i) Porous NiO/CoN interface nanowire. Reproduced with permission.[170] Copyright 2017, American Chemical Society. j) SnO2 mesoporous nanotubes. Reproduced with permission.[68] Copyright 2015, Macmillan Publishers.

2.1. Simple Nanowires

We consider that simple nanowires are ordinary and primitive nanowires, i.e., solid simple structures composed of a single substance and no other special topological structures. In fact, regulating the formation of linear shapes at the nanoscale is the key issue. To this end, a variety of strategies have been applied, such as vapor deposition, template-directed methods, and more.

Vapor deposition is a traditional method for growing nanowires, which usually uses metal particles as a catalyst to grow higher purity nanowires under vacuum conditions. By this method, different nanowires on the substances have been fabricated, such as silicon, germanium, silicon oxide, zinc oxide, etc. Morales and C.M. Lieber have done a series of works in this area. They successfully prepared single-crystal silicon and germanium nanowires using VLS growth.[29] Based on the work mentioned above He et al.[37] grew N-doped germanium nanowires on silicon substrates successfully via vapor–liquid–solid low-pressure chemical vapor deposition.

Template-directed methods are also widely used, and can be divided into hard template method and soft template method. Anodic aluminum oxide,[38] silica,[39] carbon nanotubes,[40] and molecular sieves[41] are commonly used as hard templates; common soft templates include surfactants,[42] polymers,[43] biomolecules,[44] and the like. Under the premise of templates, researchers can use electrochemical deposition, hydrothermal, solvothermal, or sol–gel methods to prepare simple nanowires of various materials.

At the same time, there are other ways, such as electrospinning, which can be used to prepare inorganic nanowires or polymer nanowires, such as zinc oxide nanowires or polycaprolactone nanofibers.[45,46] With oriented-attachment strategy, 0D nanocrystals can spontaneously form single crystal nanowires by directional attachment, such as cadmium selenide quantum wires.[47] By using molten-salt method, Dong et al.[48] developed an environmental-friendly direct electrochemical method for the mass production of silicon nanowires.

In short, based on cost and technology, hydrothermal or electrospinning is often used when simple nanowires are produced in large quantities. The methods of synthesizing simple nanowires are the basis for the synthesis of other complex nanowires structures.

2.2. Core–Shell/Coated Nanowires

Simple nanowires, sometimes, fail to meet the high requirements for electrochemical energy storage devices, e.g., the rapid charging/discharging will cause large structure expansion. Nanowires with classical core–shell structures and coated structures have been developed and exhibit better performance.[49] Obviously, the core–shell and coated nanowires have many advantages: they can provide a larger ratio of reaction contact surface area; the core serves as a good 1D electron transport path, and the outer layered material helps rapid release/intercalation of ions.[50] It turns out that the core–shell and coated nanowires of some materials show better performances.[51,52] Below, we introduce two works, using electrodeposition and gas phase reaction, respectively.

Xiong et al.[53] synthesized the Co_3O_4 nanowires hydrothermally on the prepared nickel foam and annealed them. Afterward, polypyrrole (PPy) was electropolymerized on the surface of Co_3O_4 nanowires by constant potential deposition. The electrochemical performance tests of Co_3O_4 nanowires and Co_3O_4@PPy nanowires have long-term cycle stability. It is found that the structured nanowires of Co_3O_4@PPy show better capacity performance.

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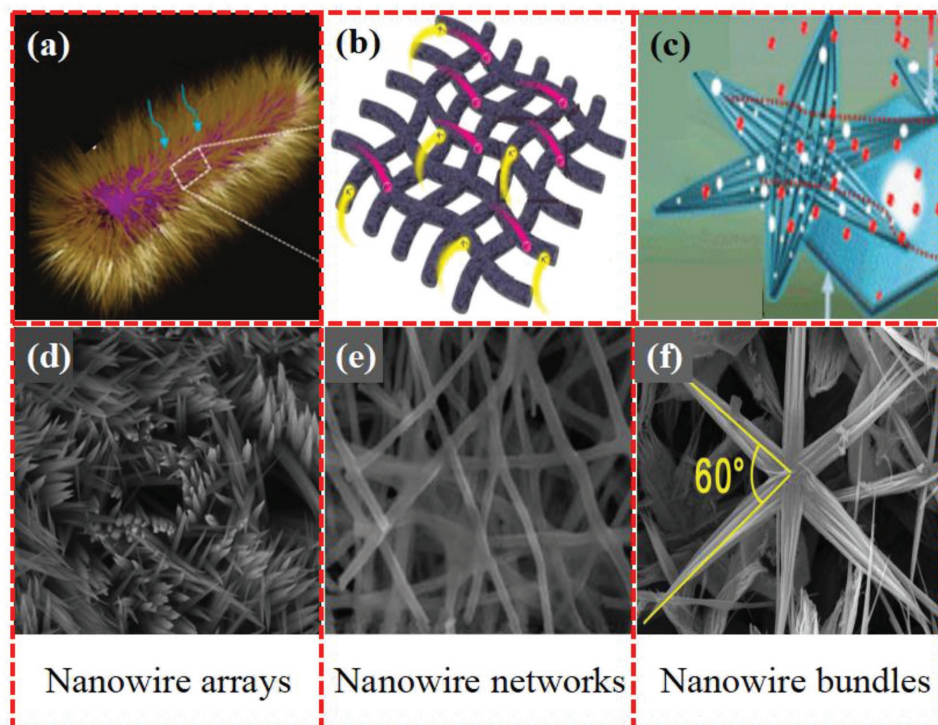ADVANCED
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Figure 2. Different combined form of nanowires. a–c) are schematic diagrams, and d–f) are SEM or TEM images. a,d) $FeCo_2O_4$ nanowire arrays. Reproduced with permission.[74] Copyright 2014, Nature Publishing Group. b,e) $K_{0.7}Fe_{0.5}Mn_{0.5}O_2$ nanowire networks. Reproduced with permission.[78] Copyright 2016, American Chemical Society. c,f) Starfish-like Co_3O_4 nanowire bundles. Reproduced with permission.[83] Copyright 2016, Springer Science Business Media Dordrecht.

The randomly assembled 2D electrode materials often suffer from serious aggregation, which results in limited cycle stability and capacity decay. It is found that covering the 2D materials on the nanowires to form core–shell nanowires can help relieve the aggregation and lead to better performances.[54,55] Choudhary et al.[56] designed and built core–shell nanowires based on simple nanowires. **Figure 3**a shows the synthesis process. The tungsten (W) foil was oxidized, spin-coated with KOH solution, and heat-treated to form a nanowire array. Then the sample was placed in an argon atmosphere containing sulfur vapor to prepare h-WO_3/WS_2 core–shell nanowires (Figure 3b,c). The nanowires are highly densely packed, with length of 8–10 µm, diameter of 150–200 nm, and an aspect ratio of about 50. Results of electrochemical test show that the capacity increases and the capacity retention rate is greater than 100% after 30 000 cycles at 100 mV s^{-1}. This work reflects the characteristics of h-WO_3/WS_2 core–shell nanowires: 1) larger surface area; 2) 1D conductive transmission channel; 3) layered 2D ion absorption; 4) high mechanical strength surface; 5) elastic current collector. The mentioned material preparation strategy can be extended to other material systems in the future.

2.3. Hierarchical/Heterostructured Nanowires

Uniform single-component electrode materials are difficult to possess both good stability and high electron/ion conductivity characteristics in electrochemical environments. Hence, it is important to design a functional electrode material that overcomes the bottleneck of the conventional 1D electrode material. Researchers have designed hierarchical/heterostructured nanowires that can enhance the structural stability of 1D nanomaterials.[57,58] Here, two classic works by Mai and co-workers about hierarchical/heterostructured nanowires are introduced. Due to the effective regulation of the structures, the electrochemical performance of nanowire material is improved.

Mai et al.[26] innovatively synthesized $MnMoO_4$/$CoMoO_4$ heterostructured nanowires (Figure 1c,h). First, $MnMoO_4$ nanowires were prepared by microemulsion method using Na_2MoO_4 and $MnCl_2$ as framework materials. Next, the $MnMoO_4$ nanowires were dispersed in water, and Na_2MoO_4 and an equal amount of $CoCl_2$ were intermittently put into the above solution. $CoMoO_4$ was attached to the framework material and gradually nucleated. The outer layer of the $CoMoO_4$ morphology can be regulated by varying the molar ratio of the manganese source to the cobalt source. This method has the characteristics of "oriented attachment" and "self-assembly" and improves the electrochemical performance of the material in a simpler way.

In some cases, the strain in the nanowires induced by the volume change could not release promptly and completely. The structure would be damaged during cycles, because of the aggregation tendency of nanowires, leading to poor cycling performance.[59,60] In order to solve the defects such as severe structural degradation, ineffective contact area, and significant self-aggregation in the electrochemical process of ordinary

Table 1. Electrode material, morphology/structure, and synthesis strategy of different nanowires. Note: There are abbreviations for some synthetic typical methods. CD = chemical deposit methods, T = template-assisted methods, CE = chemical etching methods, L = liquid phase methods, E = electrospinning methods, and EC = electrochemical methods.

Morphology/structure	Electrode material	Synthesis strategy	Ref.
Simple nanowires	Si	CD or T&CE	[29,148]
	Ge	CD	[37]
	ZnO	CD or L	[45,149]
	$H_2V_3O_8$	L	[124,150]
Core–shell/coated nanowires	C/Si	CD	[151]
	Copper/graphene	CD	[152]
	Graphene coated V_3O_7	L	[104]
	MoO_3/MoS_2	CD	[153]
	h-WO_3/WS_2	CE	[56]
	Co_3O_4/PPy	L&EC	[53]
Hierarchical/heterostructured nanowires	ZnO/CdS	L	[154]
	Vanadium oxide	E	[25]
	LiV_3O_8	E	[79]
	Zigzag $Na_{1.25}V_3O_8$	L	[61]
	$MnMoO_4/CoMoO_4$	L	[26]
Porous/mesoporous nanowires	Co_3O_4	L	[65]
	VO_2	L	[155]
	Fe_3O_4/VO_x/graphene	L	[66]
	N−C	E &CE	[156]
	Co@N−C	L	[157]
	FeS@N−C	L	[158]
Hollow structures	SiO_2	E	[159]
	Co_3O_4	L	[160]
	SnO_2 in TiO_2	T	[161]
	Tube-in-tube $CoMn_2O_4$	E	[69]
	Pea-like $Na_{0.7}Fe_{0.7}Mn_{0.3}O_2$	E	[68]

nanowires, Dong et al.[61] synthesized hierarchical zigzag $Na_{1.25}V_3O_8$ nanowires using a topological intercalation method. When synthesizing, V_2O_5, polyethylene glycol (PEG)-10K, and H_2O_2 were mixed and stirred, and the water was kept at a temperature of 180 °C for 2 days. After washing and drying, the ultralong $H_2V_3O_8$ nanowires were obtained. The previously obtained nanowires were dispersed in ethanol. Then NaOH and CTAB (hexadecyl trimethyl ammonium bromide) were added in a certain proportion to participate in chemical reactions. Finally, the samples were annealed in air at 450 °C after drying. CTAB is a sticking point of topotactical synthesis.[62] Whether or not to use CTAB was completely different for the morphologies of nanowires. The experiment shows that the hierarchical zigzag $Na_{1.25}V_3O_8$ nanowires synthesized by this strategy have better strain adaptation capability and larger electrode–electrolyte contact area. Topological intercalation can also improve robustness of the structure. The characteristics above synergistically promote cycle stability and reaction kinetics, achieving good performance for sodium-ion battery.

2.4. Porous/Mesoporous Nanowires

1D nanostructures with porous/mesoporous features can provide a larger surface area than nonporous systems. The improved effective contact area between electrode and electrolyte promotes the charge transfer and ion diffusion.[63] The void space is adapted to the volume change caused by ion insertion/ extraction, thereby relieving the structural degradation during cycles.[64]

Microemulsion systems contribute to the directional growth and alignment of 1D nanomaterials. Xu et al.[65] synthesized porous Co_3O_4 nanorods by microemulsion and calcination method. The ionic surfactant CTAB plays an important role in the synthesis process. After analysis, the formation of Co_3O_4 nanorods is converted from a layered precursor guided by a surfactant template and used as an oriented low-temperature organic molten salt medium in the initial stage of calcination. For the formation of porous structures, the decomposition of the precursor CoC_2O_4 nanorods is critical. In the test assembled into a lithium-ion battery, the prepared porous Co_3O_4 nanorod shows higher capacity and better cycle life than ordinary structured Co_3O_4 materials.

The porous nanowires have a better stress relaxation function during ion insertion/ extraction and the graphene-coated nanowires can promote electron transport effectively. As shown in **Figure 4**, An et al.[66] combined these two features and designed amorphous vanadium oxides matrixes supporting hierarchical porous Fe_3O_4/graphene nanowires (Fe_3O_4/VO_x/G-P NWs). The $FeCl_3·6H_2O$ solution was mixed with the graphene oxide dispersion, and then the NH_4VO_3 solution was added to the mixture above slowly with stirring. Hydrothermal reaction in a reactor at 180 °C for 3 h, washing and drying in H_2:Ar (5%:95%) at 500 °C for 4 h were done to obtain the Fe_3O_4/VO_x/G-P NWs. The synergistic advantage of graphene and porous nanowires provides them with a bicontinuous electron/ion channel that exhibits excellent electrochemical performance in lithium-ion batteries. It shows high cycle stability, remarkable rate performance, and high reversible capacity.

Tan et al.[67] prepared polyacrylnitrile/Mg(OH)$_2$/N,N-dimethylformamide solution for electrospinning, and etched it after preoxidation and carbonization to prepare nitrogen-doped mesoporous carbon nanofibers. Mg(OH)$_2$ is low-cost and easy to remove, which is evenly distributed in nanofibers. After chemical etching, it can form the desired mesopores. Nitrogen-doped mesoporous carbon nanofibers, which are carbonized at 900 °C, are used as electrodes for supercapacitors, exhibiting long-term cycle stability, excellent rate capability, and high specific capacitance.

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Table 2. Electrode material, morphology/structure, and synthesis strategy of different nanowires combined structures. Note: There are abbreviations for some synthetic typical methods. CD = chemical deposit methods, T = template-assisted methods, CE = chemical etching methods, L = liquid phase methods, E = electrospinning methods, and EC = electrochemical methods.

Morphology/ structure	Electrode material	Synthesis strategy	Ref.
Nanowire arrays	TiO_2	EC	[75]
	$FeCo_2O_4$	L	[74]
	$N\text{-}CoS_2$	L	[162]
	CoP	L	[163]
	$NiCo_2O_4$	L	[164]
	$TiO_2\text{-}MoO_3$	L&EC	[165]
Nanowire networks	Ni/TiO_2	E&CD	[166]
	NiO-Ni/Ag	L	[167]
	LiV_3O_8	E	[79]
	$K_{0.7}Fe_{0.5}Mn_{0.5}O_2$	E	[78]
Nanowire bundles	TiO_2	L	[168]
	Co_3O_4	L	[83]
	SnO_2	L	[81]
	$K_3V_2(PO_4)_3/C$	L	[82]

2.5. Hollow Structures

Hollow structured nanowires are often referred as nanotubes. Carbon nanotubes are widely used as one of the most important materials or carriers in energy storage devices. However, due to the limitation of the synthesis method, it is hard to prepare multielement and binary-metal oxides nanotubes. The classic work of Niu et al.[68] achieved a good breakthrough in this respect. Its pioneering method applies to a series of materials, and has high yield, low cost, and good reproducibility. They employed a universal gradient electrospinning method,

combining with a controlled pyrolysis method to synthesize various kinds of pea-like nanotubes and mesoporous nanotubes (**Figure 5**). The key to this strategy is to adjust the low, medium, and high molecular weight polyvinyl alcohol (PVA) in the precursor solution and use controlled heat treatment to obtain different nanotubes. The pea-like nanotubes consist of outer carbon nanotubes (≈20 nm thickness) and nanoparticles (100–300 nm in diameter) in the nanotubes. And the hollow nanotubes consist of ultrathin carbon nanotubes (thickness ≈5 nm and length exceeding 10 mm) and nanoparticles (about 5–20 nm in diameter) on the tube wall. Compared with traditional nanowires, these structures have higher ionic electron conductivity and larger surface area, which have greater potentials in energy storage. Mai and co-workers also used electrospinning to fabricate tube-in-tube and wire-in-tube nanotubes,[69] and cube-in-tube nanotubes[70] innovatively. In the preparation of tube-in-tube and wire-in-tube, the higher metal salt concentration contributes to the formation of a stronger metal oxide shell, while the molecular weight and ratio of PVA, the diameter of the nanofibers obtained by electrospinning, and precisely regulated pyrolysis process determine the quality of structures. The preparation principle of cube-in-tube nanotubes is basically similar to the above, but the cubic structure was prepared in advance and added to the precursor solution. The various complicated nanostructures with good performance in electrochemical energy storage demonstrate that electrospinning has great potential in building 1D nanomaterials.

2.6. Nanowire Arrays

Up to now, various strategies have been applied to construct novel nanowire array materials.[71] There are "bottom-up" methods for assembling nanowire arrays starting from atoms or molecules, and "top-down" routes for chemically etching bulk or flaky materials into nanowire arrays.[72] The array structure of the nanowires causes adjacent 1D nanostructures to be
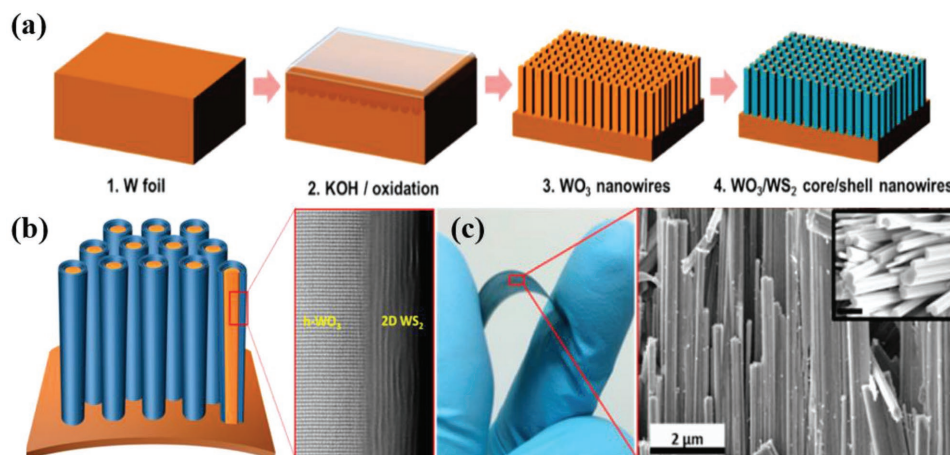

Figure 3. Fabrication process and structural characterizations of core–shell nanowires on W foils. a) Schematic for the fabrication process of h-WO$_3$/WS$_2$ core–shell nanowires on a W foil. b) Schematic illustration for one-body array of core–shell nanowire supercapacitor, and ADF-STEM image of the nanowire. c) Optical image of as-prepared core–shell nanowires on a W foil under mechanical bending (left). Corresponding SEM image (right) shows high-density, well-aligned nanowires along with their faceted surface (inset). The scale bar in the inset is 500 nm. Reproduced with permission.[56] Copyright 2016, American Chemical Society.
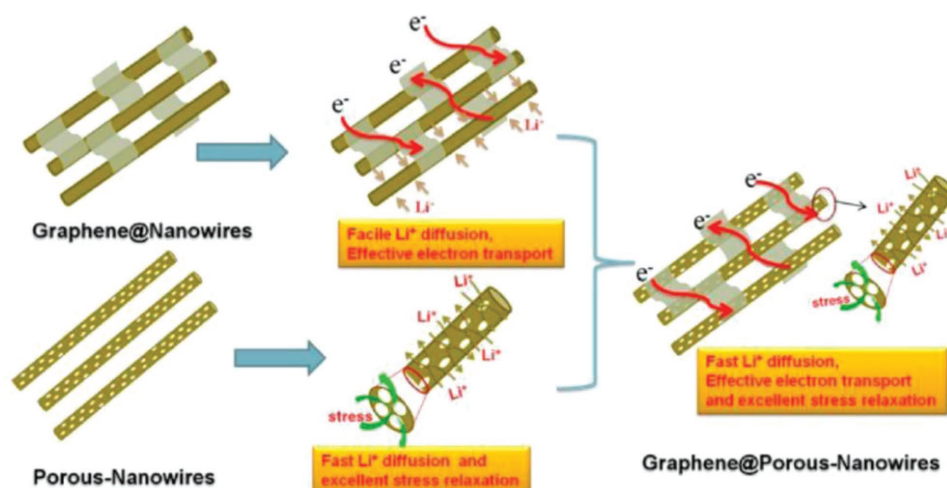
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Figure 4. Schematic illustration of the porous nanowire composites with fast Li$^+$ diffusion, effective electron transport, and excellent stress relaxation during Li$^+$ extraction/insertion. Reproduced with permission.[66] Copyright 2014, American Chemical Society.

separated from each other and allows most of the electrolyte to easily access the surface of the nanowires and its performance will be improved.[73]

With "bottom-up" method, Chodankar et al.[74] designed and prepared FeCo$_2$O$_4$ nanowire arrays (Figure 2a,d) with the stainless steel mesh. After hydrothermal treatment, the sample was annealed in the atmosphere. The obtained FeCo$_2$O$_4$ nanowire array appears a unique layered mesoporous structure, exhibits good surface property, and enhances the electrode/electrolyte interaction by minimizing the circulation path of electrolyte ions and electrons.

Salari et al.[75] prepared TiO$_2$ nanotube arrays (TNTA) using anodization method to be part of "top-down" strategy. Using titanium and platinum foils as the anode and the cathode, respectively, self-organized TNTA was synthesized using 9:1 volume ratio by weight of glycerin/water and 0.2% of NH$_4$F as an electrolyte. The anodization reaction was carried out for 17 h at a constant voltage of 15 V to form tubular TiO$_2$ arrays on one side of the current collector. After drying in air, the samples were annealed in an argon atmosphere at 600 °C for 5 h. The micro-supercapacitors made of these as electrode material have higher volumetric capacitance and energy density than conventional titanium oxide microcapacitor devices using a carbon-based electrode and an organic electrolyte.

2.7. Nanowire Networks

The interconnected networked nanowire structures have a stable layered framework structure, rapid ion diffusion channels, and a 3D electron transport network, which have potentials in energy storage.[76,77] We select three works which built nanowire networks with different strategies and achieved excellent performance.

Wang et al.[78] prepared Fe/Mn-based layered oxide interconnected nanowires (Figure 2b,e). Polyvinylpyrrolidone, CH$_3$COOK, iron (III) acetylacetonate, and manganese (II) acetylacetonate were mixed in deionized water. The electrospinning

method was used to deliver the solution to the metal needle at a constant flow rate of 0.4 mL h^{-1}, and nanowires were fabricated at a high voltage of 21.0 kV. The obtained product was sintered in air at 300 °C. Then it was kept in argon atmosphere at 800 °C for 8 h to obtain an interconnected K$_{0.7}$Fe$_{0.5}$Mn$_{0.5}$O$_2$ nanowire network. The electrochemical performance of the nanowire networks in potassium-ion battery is significantly better than that of K$_{0.7}$Fe$_{0.5}$Mn$_{0.5}$O$_2$ particles.

Ren et al.[79] designed and built layered LiV$_3$O$_8$ nanowire networks through a polymer cross-linking strategy by electrospinning. The cross-link between PVA and polyethylene oxide (PEO) not only facilitates electrospinning, but also promotes a gentle multistep degradation process when samples are calcined. The proposed formation mechanism is shown in Figure 2b,e. The special structure provides more stable structure, larger effective contact area, and lower charge transfer resistance.

Liu et al.[80] synthesized Ag nanowires (ANWs) by hydrothermal method and spin-coated it on fluorine doped tin oxide (FTO) conductive glass. Then, Ni layer was electrodeposited on the surface of Ag nanowires. The sample was annealed to get NiO-Ni/ANWs/FTO electrode materials. During the annealing process, similar to the welding method, the silver nanowires were connected as networks, which improves the stability of the material. ANWs act as excellent conductors that can help improve NiO performance.

2.8. Nanowire Bundles

Nanowire bundles are formed by adjacent nanowires. The remarkable electrochemical properties of nanowire bundles could be attributed to their particular features of structures. For example, the highly stable skeleton can facilitate cycle stability, and the large porosity of nanowire bundles can lead to rapid ion diffusion and high rates performances. Nanowire bundles with a large surface area provide wider electrode/electrolyte contact area and more active sites, resulting in superior electrochemical performance.[81]
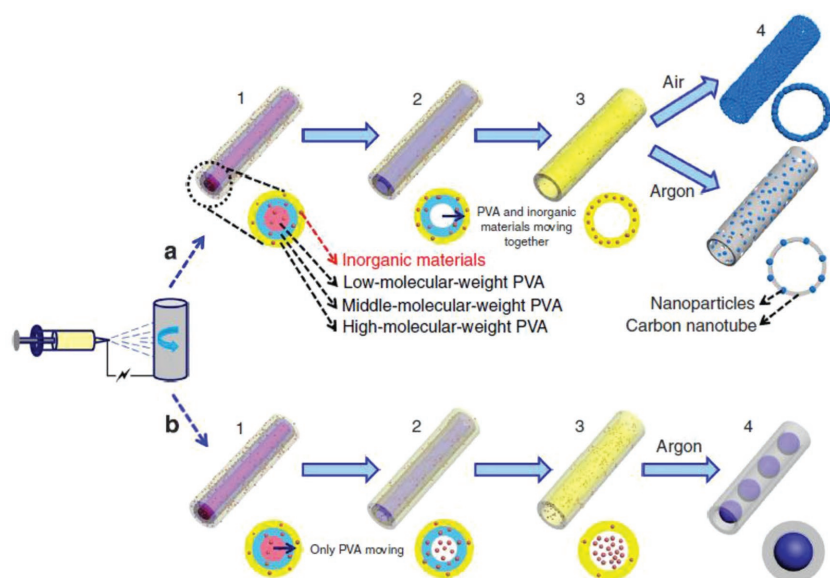
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Figure 5. Schematics of the gradient electrospinning and controlled pyrolysis method. a) Preparation process of mesoporous nanotubes. (1) After the electrospinning process, the low-, middle-, and high-molecular-weight PVA tend to be distributed into three layers in the radial direction of composite nanowires. (2) As the temperature is slowly increased, the inner low-weight PVA first pyrolyses and moves toward the boundary of the low-/middle-weight PVA, carrying the inorganic materials. Then the middle-weight PVA pyrolyses and moves toward the high-weight PVA as well. (3) All of the preliminary pyrolysed PVA and inorganic materials converge together in the tube walls. (4) After sintering in air, all of the PVA pyrolyse and uniform mesoporous nanotubes are obtained, which are composed of tiny inorganic nanoparticles. On the other hand, after high-temperature sintering under argon, PVA carbonize, uniform mesoporous nanotubes are also obtained, which consist of inorganic nanoparticles and carbon nanotubes. The mesopores result from the decomposition of the inorganic materials and a part of PVA polymers. b) Preparation process of pea-like nanotubes. (1) After the electrospinning process, the composite nanowires are directly and immediately placed into a furnace in air, which is preheated to and maintained at 300 °C. (2, 3) All of the PVA decompose at the same time and rapidly move toward the outer high-weight PVA layer without carrying the inorganic materials, leaving them in the center. (4) After high-temperature sintering under argon, the outer PVA carbonize and the inner inorganic materials develop into nanoparticles, forming pea-like nanotubes. Reproduced with permission.[68] Copyright 2015, Macmillan Publishers.

$K_3V_2(PO_4)_3/C$ nanowire bundles coated with conductive carbon, which have porous nanostructure and highly stable framework (**Figure 6**), were fabricated by Wang et al.[82] using an organic acid-assisted method. The diameter of single nanowire is in the range of 150–500 nm, but can reach 1 μm when they are clustered into bundles. The length is about 5–30 μm. The carbon layer on surface also prevents the aggregation and ensures effective electronic contact between adjacent nanowires, thereby exhibiting better structural stability and an extremely long cycle life.

Gao et al.[83] synthesized 3D starfish-like Co_3O_4 nanowire bundles on nickel foam (Co_3O_4-oNF) by a simple hydrothermal method (Figure 2c,f). $CoCl_2 \cdot 6H_2O$, $CO(NH_2)_2$, and NH_4F were first formulated into solution, and then the preactivated nickel foam was immersed in the solution and placed against the inner wall of Teflon-lined autoclave. Reaction was carried out at 120 °C for 10 h and pink precursors were grown. After washing and drying, the obtained precursor was heated in tube furnaces at 400 °C. Then the sample was sonicated, washed, and dried at room temperature. The overall height of a highly symmetrical (60° angle) starfish Co_3O_4 nanowire bundles is 15 μm, while the diameter is ≈270 nm (Figure 2c,f). The 3D starfish Co_3O_4 was self-assembled by mesoporous Co_3O_4 nanowires, and the samples provided significantly enhanced specific capacitance and high cycle stability. After annealing, the surface became swelled and rough compared to the precursor. It turns out that the porous structure produced by the decomposition of
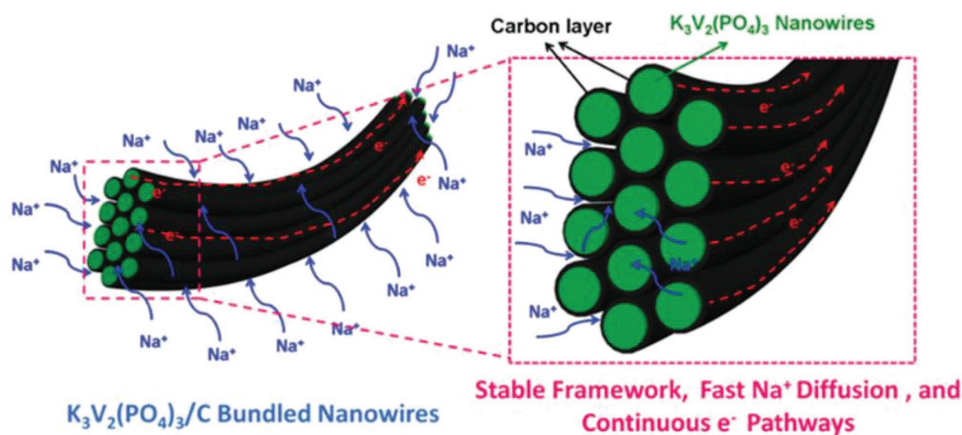

Figure 6. Schematic illustration of the $K_3V_2(PO_4)_3/C$ bundled nanowires with stable framework, fast Na^+ diffusion, and high electronic conductivity. Reproduced with permission.[82] Copyright 2015, Wiley-VCH.

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the precursor can promote the rapid transport of electrons and ions in the electrochemical reaction.

3. Applications of Nanowires in Energy Storage

The development of electrochemical energy storage technology is very fast and has gone through several stages. Lead–acid battery[84,85] is the earliest commercial energy storage battery system. In addition, electrochemical energy storage mainly includes metal-ion batteries,[86,87] metal–sulfur batteries,[88,89] flow batteries,[90,91] metal–air batteries,[92,93] and supercapacitors.[94] With the deep research of nanowires, some achievements have been made. Here, we choose to introduce the application of nanowires in lithium-ion, sodium-ion, zinc-ion batteries, and supercapacitors. At the same time, in situ characterization of nanowire electrode is also mentioned as key member.

3.1. Lithium-Ion Batteries

Currently, rechargeable lithium-ion batteries have become the main source of power for most electronic products. As we know, in 1991, Sony developed the first commercial lithium-ion battery which started a new chapter. In that battery system, the cathode material is made of lithium cobaltate and the anode is made of coke. After that, researchers have pursued on exploring and optimizing the electrode materials. Up to now, the main research object of cathode materials is Li−M−O (M = V, Mo, Co, Mn) salt, polyanion salt, nonmetallic element (sulfur, selenium, iodine), etc. The research direction of anode materials mainly includes lithium metal, carbon materials, lithium titanium oxides, silicon-based materials, and more.

With the development of technology, nanocrystallization is a highly concerned topic in improving the performance of electrode materials. Due to the increased specific surface area, shortened diffusion path, and improved electronic conductivity of nanomaterials, the rate performance and structural stability are significantly improved. For example, silicon is a promising anode material. Each silicon atom can accommodate 4.4 lithium atoms, and its theoretical capacity reaches 4000 mAh g^{-1} or more, which is almost 10 times of that of carbon materials.[95] However, because of the large volume expansion (even up to 400%), silicon is easy to be pulverized during charging and discharging processes, resulting in the poor stability and short cycle life.[96] In view of this, Cui and co-workers produced nanowire structure as the anode of lithium-ion batteries. The first charge/discharge capacity and the second were 4277/3124 and 3541/3193 mAh g^{-1}, respectively. Then its capacity remained practically steady within 10 cycles. Compared with other structures such as bulk and microspheres, nanowire is more stable and has an increased capacity.[97] Meanwhile, other anode electrode materials were made into different nanostructures, such as nanospheres, nanowires, etc., which showed great performance in lithium-ion battery. The works on nanowires were particularly striking, e.g. carbon,[98] TiO_2,[99] SnO_2,[100] and Co_3O_4 nanowires[101] showed better cycle performance than the bulk materials. It can be attributed to great strain relaxation

during lithium insertion/extraction, short electron/ion transport paths, as well as high electrode/electrolyte contact area of nanowire structures.

Although nanowires show great potential in lithium-ion batteries, their cycle lifespan and capacity are still limited. The optimization of nanowires is mainly divided in to two stream: carbon layer coating and prelithiation.[102,103]

Yan et al.[104] prepared V_3O_7 nanowire templated graphene scrolls (VGSs) through "oriented assembly" and "self-scroll" strategies. There are internal cavities between the nanowire and the graphene roll, the construction process of which depends on the system energy, the reaction time, and the curvature of the nanowires (**Figure 7**a,b). This material exhibits the great performance in the lithium-ion battery with a capacity retention of 87.3% after 400 cycles at 2000 mA g^{-1} and a specific capacity of 321 mAh g^{-1} at 100 mA g^{-1}. The coasted graphene can significantly improve the battery performances of the V_3O_7. The VGSs with only 5 wt% graphene exhibit conductivity and capacity of 27 and 4.5 times of the simple V_3O_7 nanowires (at a large current density of 3000 mA g^{-1}). The good cycle stability and electrical conductivity are shown in Figure 7c,d. An et al.[66] combined these two characteristics ingeniously and designed the amorphous vanadium oxides matrixes supporting hierarchical porous Fe_3O_4/graphene nanowires. The synergistic advantages of graphene and porous nanowires provide a bicontinuous electron/ion pathway, which exhibits great electrochemical performance for lithium-ion batteries. It shows remarkable rate capability (5 A g^{-1}) and high reversible capacity (1146 mAh g^{-1}). The capacity retention remains 99% after 100 charge/discharge cycles at 2 A g^{-1}. Li et al.[105] synthesized core–shell porous carbon coating SiO_x nanowires (pC-SiO_x NWs) and used them as anode materials for lithium-ion batteries. It has a lower cost, a stable cycle life, and a higher specific capacity (100 cycles at 100 mA g^{-1} and 150 cycles at 500 mA g^{-1}, the capacities are kept at 1060 and 623 mAh g^{-1}, respectively). The method has advantages of easy material synthesis, construction process, and good reproducibility, which can be combined with prelithiation technology and has a good application prospect.

The diffusion of lithium ions in electrode is the sticking point to the performance. Ionic intercalation can alter the interlaminar structure of the material, which affects diffusion performance. Zhao et al.[106] performed theoretical calculations and experimental investigations on more than 20 nanomaterials: 5 typical cathode materials and their alkali metal ion intercalation compounds A−M−O (A = Li, Na, K, Rb; M = V, Mo, Co, Mn, Fe−P). They discovered that in the electrode material, the appropriate alkali metal ions are embedded to increase the layer spacing, which can improve the cycle performance and rate capability (**Figure 8**). In addition, this work provides a reliable strategy to regulate the diffusion channels of certain intercalation compounds, offering a good inspiration for future related research.

Metal chalcogenides have gradually attracted attentions for lithium-ion batteries.[107,108] Luo et al. did lots of works on the Sb_2Se_3 nanowires. First, the researchers used hydrazine hydrate ($N_2H_4 \cdot H_2O$), sodium selenite (Na_2SeO_3), antimony acetate ($Sb(CH_3COO)_3$), and other substances mixed hydrothermal synthesis of ultralong Sb_2Se_3 nanowires,[109] followed by vacuum filtration to produce free-standing membrane
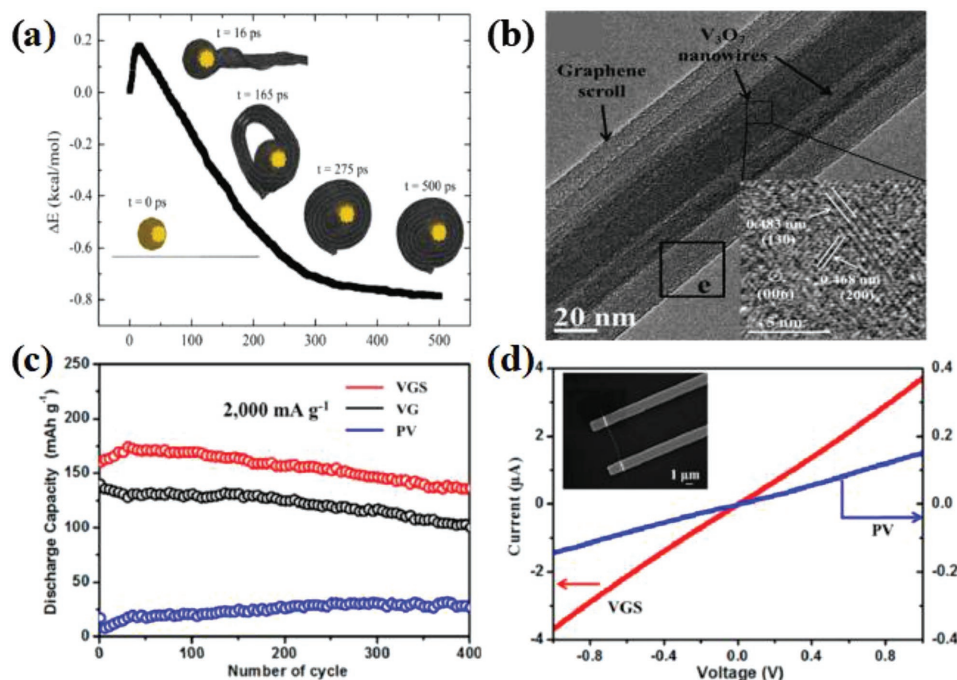
Figure 7. a) Change in per-carbon energy during the wrapping of a graphene sheet onto a nanowire to form a GS (graphene scrolls) (the insets are a series of simulation configurations of the formed GSs). b) TEM images of VGS (the inset gives an HRTEM image of a V_3O_7 nanowire in GSs). c) Galvanostatic discharge profiles of VGS (red line), VG (V_3O_7 nanowire/graphene) (black line), and PV (pure V_3O_7 nanowires) (blue line) at 2000 mA g^{-1} tested between 4 and 1.5 V. d) Single-nanowire transport properties of VGS and PV (the inset is the SEM image of a VGS single-nanowire device). Reproduced with permission.[104] Copyright 2013, American Chemical Society.

consisting of Sb_2Se_3 nanowire, which shows great flexibility. When used as the anode of lithium-ion battery, it has good cycling stability and a capacity of 614 mAh g^{-1} at 100 mA g^{-1}. Later, they tried to use $SbCl_3$ as a source of germanium. Using a new microwave synthesis method, the uniform single-crystal Sb_2Se_3 nanowires was synthesized with stirring. This Sb_2Se_3 nanowire,[110] when used as an anode of a lithium-ion battery, can provide a high reversible capacity of 650.2 mAh g^{-1} and a capacity retention of 63.8% at 100 mA g^{-1} after 1000 cycles at 1000 mA g^{-1}. It can be seen that the application prospect of Sb_2Se_3 nanowires in lithium-ion batteries is good, and the relevant research strategies are available for other nanowires in energy storage research.

3.2. Sodium-Ion Batteries

However, lithium-ion batteries are not likely the ideal choice when used in future large-scale energy storage systems, due to the limitations of lithium resources. The abundant sodium has lower cost than lithium, and the sodium and lithium ions have similar electrochemical processes in the battery.[111] Therefore, sodium-ion batteries are considered to be one of the best alternatives to lithium-ion batteries.[112]

However, since the radius of Na$^+$ is about 70% larger than the radius of Li$^+$, the diffusion of Na$^+$ during charging and discharging is kinetic hesitating. It results in low diffusion coefficient, large volume expansion, and poor cycle performance.[113] In the case, 1D nanostructures with easy pressure-release and short ion diffusion distance are essential for high-speed and long-life sodium-ion batteries. Researchers are constantly looking for more reliable electrode materials for sodium-ion batteries. In order to meet the practical application, the sodium-ion battery electrode has a longer service life, good rate performance, and higher energy density, and it is important to enhance the ion diffusion and reduce the influence of the electrochemical reaction process on the crystal structure of the electrode.[114]

Vanadium oxides are rich in sources, low in cost, and have large interlayer spacing and theoretically high specific capacities.[115] Therefore, they are considered as one of the better sodium-ion battery electrode materials.[116] Wang et al.[117] prepared flexible $H_2V_3O_8$ nanowire films by a simple hydrothermal and suction filtration process. The $H_2V_3O_8$ nanowire film without additives exhibited a high specific capacity of 1688 mAh g^{-1} at 10 mA g^{-1}. There was almost no capacity loss, and no damage to the $H_2V_3O_8$ nanowire film was found after 100 cycles. Through in situ detection, it was discovered that the ratio of capacitive charge storage to total capacity was relatively large, while the crystal structure of $H_2V_3O_8$ was highly reversible during the insertion/extraction of sodium ions. This study lays the foundation for the further study of sodium-ion batteries using vanadium oxide and the development of flexible devices.

More progress has been made on the research of vanadium-based nanowires. In a simple $Na_{1.25}V_3O_8$ (NVO) nanowire, the strain cannot be fully and rapidly released and the crystal structure is unstable. So the nanowires are easy to aggregate and the structure is damaged during cycling, resulting in poor cycle performance. By carefully designing and optimizing electrode materials, Dong et al.[61] synthesized hierarchical zigzag
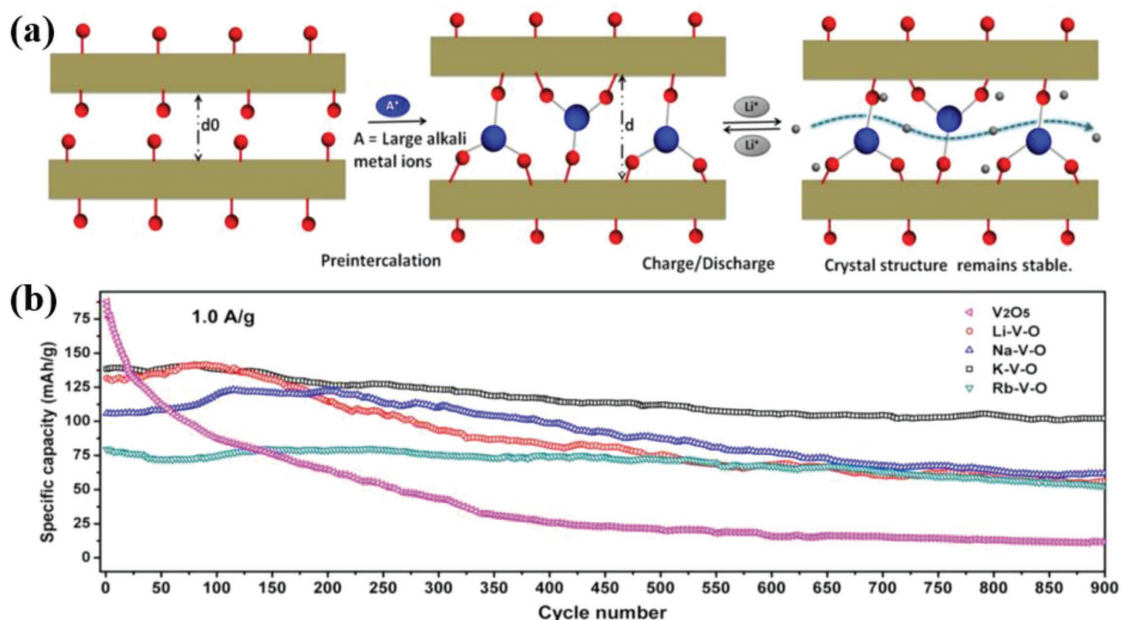
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Figure 8. a) Schematic representation of large alkali metal ion intercalation. b) Cycling performance of A–V–O nanowires at the charge/discharge rate of 1.0 A g^{-1}. Reproduced with permission.[106] Copyright 2015, American Chemical Society.

NVO nanowires using a topological intercalation method. Comparing with ordinary NVO nanowires, it maintains better structural integrity during cycling, increased electrode–electrolyte contact area, and more suitable stress release. In summary, the optimization of the shape and structure of the electrode material leads to better cycle performance. Wang et al.[82] prepared $K_3V_2(PO_4)_3$/C-bundle nanowires with porous nanostructure, a highly stable framework, and conductive carbon coating. Its capacity is stable and its cycle stability is obviously improved. This is an effective strategy for promoting the electrochemical performance of sodium-ion batteries.

3.3. Zinc-Ion Batteries

Lithium metal resources are limited and expensive, and these factors have limited the development of lithium-ion batteries.[118] Zinc has a high overpotential of low equilibrium potential and hydrogen reaction, and is an element having a low standard potential among all elements that can be efficiently reduced from an aqueous solution. Among the metal elements that can be stabilized in aqueous solution, the energy of zinc is also high. At the same time, metal zinc is rich in resources, low toxicity, and easy to handle. Therefore, the low price, high safety, no environmental pollution, and high power secondary zinc-ion battery is the ideal green battery system.[119]

Recently, zinc-ion batteries have received widespread attention. Zinc-ion batteries have superior electrochemical performance compared to other types of batteries. In general, their advantages are mainly reflected in the following points.

(1) Zinc-ion batteries have the advantages of ordinary batteries and supercapacitors, which can achieve higher energy density and power density at the same time. According to the galvanostatic charge/discharge results, power density, and energy density calculation formula, the power density can be calculated as high as 12 kW kg^{-1}, which is higher than that of ordinary batteries in the market. The energy density of zinc-ion batteries can reach 320 Wh kg^{-1}, which is about 15 times that of a supercapacitor.[120]

(2) Zinc-ion batteries have good rate performance. Zinc-ion batteries can be slowly discharged at low current densities and quickly discharged at high current densities.[121]

(3) The cost of zinc-ion batteries is low. The zinc-ion battery has a simple manufacturing process and can be assembled in the air, which greatly reduces the manufacturing cost. At the same time, metal zinc is rich in resources and is a low-priced metal. At present, regardless of the hydrogen fuel cell or lithium-ion battery in the market, electrode materials and manufacturing costs are still high, which limit its application range.[122]

(4) Zinc-ion batteries are environmental-friendly and safe. The electrolytes, zinc metal, and inorganic salts used in zinc-ion batteries are nontoxic, and no contaminants will be produced during the production and application of batteries. Therefore, zinc-ion batteries are green batteries.

It has to be said that zinc-ion batteries still have some limitations. The rapid decay of capacity and dissolution of the electrode material and poor cycle stability hinders their widespread application.[123] Researchers have continued to improve their overall performance such as cycle stability through new attempts.

He et al.[124] used a layered $H_2V_3O_8$ nanowire as a cathode material for the first time in zinc-ion batteries. The water-based zinc-ion battery shows a capacity of 423.8 mAh g^{-1} at 0.1 A g^{-1}, excellent cycle stability, and a capacity retention rate of 94.3% after 1000 cycles. The in situ tests confirm the

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reversible intercalation mechanism and discusses the electrochemical kinetics of its cathode. Later, they developed the sodium ion stabilized vanadium oxide nanowire cathode for zinc-ion batteries. The work reported on the design and construction of $Zn//Na_{0.33}V_2O_5$ (NVO) batteries.[125] The NVO electrode provides high capacity (367.1 mAh g^{-1}, 0.1 A g^{-1}) with long-term cycling stability (capacity retention over 93% after 1000 cycles) and good rate performance. The researchers tested the single nanowire device and verified the increase in conductivity due to sodium ion embedding. The layered nanowire electrode material exhibits great potential, and the indigenous ions can be pillars to stabilize the layered structure, enhancing cycling stability.

On the basis of the above NVO, Hu et al.[126] used the structural water to improve performance. They developed a more durable zinc-ion battery system with aqueous $Zn(CF_3SO_3)_2$ electrolyte and $Na_2V_6O_{16}\cdot1.63H_2O$ nanowire cathode. This kind of nanowires can provide a high specific capacity of 352 mAh g^{-1} at 50 mA g^{-1}. After 5000 cycles at 5000 mA g^{-1}, the capacity retention rate is 90%, and the cycle performance is good. However, the general NaV_3O_8 nanowires maintained only 17% of the initial capacity after 4000 cycles of 5000 mA g^{-1}. By comparison, the structural water of the material can play an important role in improving the electrochemical performance of certain cathode materials.

Wu et al.[127] used α-MnO_2 nanowires as the cathode of a zinc-ion battery. To solve the problems of rapid capacity decay and material dissolution, researchers coated α-MnO_2 nanowires with graphene. Graphene scroll-coated α-MnO_2 nanowires exhibit higher capacity, increased conductivity, and good rate performance compared to bare α-MnO_2 nanowires. The zinc-ion battery also has a fairly long-term cycle stability (specific capacity reaches 145.3 mAh g^{-1} at 3000 A cycle. The retention rate is as high as 94% after 3000 cycles). Characterization of in situ X-ray diffraction (XRD), galvanostatic intermittent titration technique (GITT), and X-ray photoelectron spectroscopy (XPS) clarifies the two-step intercalation mechanism in which Zn ions are first inserted into the layer and then inserted into the MnO_2 framework tunnel. This strategy provides new ideas for the development of aqueous zinc-ion batteries and even other types of electrode material optimization.

3.4. Supercapacitors

Supercapacitor, also called electrochemical capacitor or ultracapacitor, is an important energy storage device, which possesses long cycle life (>10^5 cycles), high power density (>10 kW kg^{-1}), and high rate capability with fast charge/discharge capability within seconds.[128] In some cases, it can be used with batteries, and may even replace batteries because of their higher power density compared with the batteries.

Nanowires are widely used in supercapacitors. The electrode materials for supercapacitors can be roughly divided into three categories: carbon-based materials,[129] conductive polymer materials,[130] and metal oxide materials.[131] At the same time, researchers have also discovered new types of special 1D nanomaterials, such as metal sulfides and nitride nanowires and composite products of above materials.

We have found that 1D carbon materials, in addition to providing capacity in supercapacitor applications, are more of a carrier for other substances. More hybrid or composite materials have also been used as electrodes for supercapacitors. Yang et al.[132] prepared a photoresist/chitosan-coated carbon nanotube (CHIT-CNT) composite, and fabricated a carbon/CHIT-CNT micro-supercapacitor on the silicon wafer. It has a high capacitance and energy density, along with a remarkable cycle performance, whose capacitance was maintained at 99.9% after 10 000 cycles of voltammetry cycles. Using a similar strategy, Yang et al.[133] mixed MoS_2@rGO (reduced graphene oxide) and multiwalled carbon nanotubes with photoresist, repeated spin coating, and then made fingers on silicon wafer. The all-solid-state micro-supercapacitor made after pyrolysis has high energy density, good capacitance retention, and excellent cycle performance. Among various materials introduced above, many of them are used in supercapacitors, such as h-WO_3/WS_2 core–shell nanowires,[56] Co_3O_4@PPy nanowires,[53] $MnMoO_4$/$CoMoO_4$ heterostructured nanowires[26] mesopores, and nitrogen-doped mesoporous carbon nanofibers.[67] Their structural characteristics bring significant advantages in its application, so we would not repeat them here.

Recently, researches on supercapacitors are developed with the goal of being lightweight, portable, and flexible. Some micro-supercapacitors have been made, but they still have limitations and bottleneck in practice.[134] First of all, at present, the manufacturing process of the micro-supercapacitor is relatively complicated, and the high cost and low output result in a decrease in its practicality. Second, most micro-supercapacitors rely on predesigned substrates, which have poor flexibility and are incompatible with basic components such as cloth, paper, or plastics. There is still a gap in the implementation of wearable devices. Finally, some of the micro-supercapacitors do not match the existing electric devices.[135] Therefore, the low-cost manufacturing method of the highly durable reliable system micro-supercapacitors is of great significance. Interestingly enough, researchers are constantly trying to come up with new strategies to help it better fit into real-life applications. Here, we highlight two works with innovation and development potential.

It is reported that Zhu et al.[136] manufactured a transferable, highly durable, substrate-versatile, and high-performance all-polymer micro-supercapacitor (µSC) with plug-and-play function. They used electrochemical deposition ways to grow polypyrrole nanowires (PPy NW) on the patterned FTO. Then they used heat releasing tape to pick up electrodes and transfer them to any other substrate, such as fabric, paper, and tape. In subsequent in-depth studies, the PPy NW µSC even can be transferred onto the window, china, leaf, wood, cloth, and wall, which displays the excellent substrate versatility of the as-developed transfer process (**Figure 9**a). Whether under flat state, after being wadded up or being rolled up, the PPy NW µSC shows the perfect performance durability after being transferred and under various mechanical deformations (Figure 9b–g). Therefore, they proposed the concept of "µSC bank," which can be connected in parallel or in series on paper substrate to meet the needs of different situations. The manufacturing cost can be reduced to ≈0.1 USD cm^{-2}. Meanwhile, PPy NW µSCs appeared with an ultrahigh energy density of 15.25 mWh cm^{-3}

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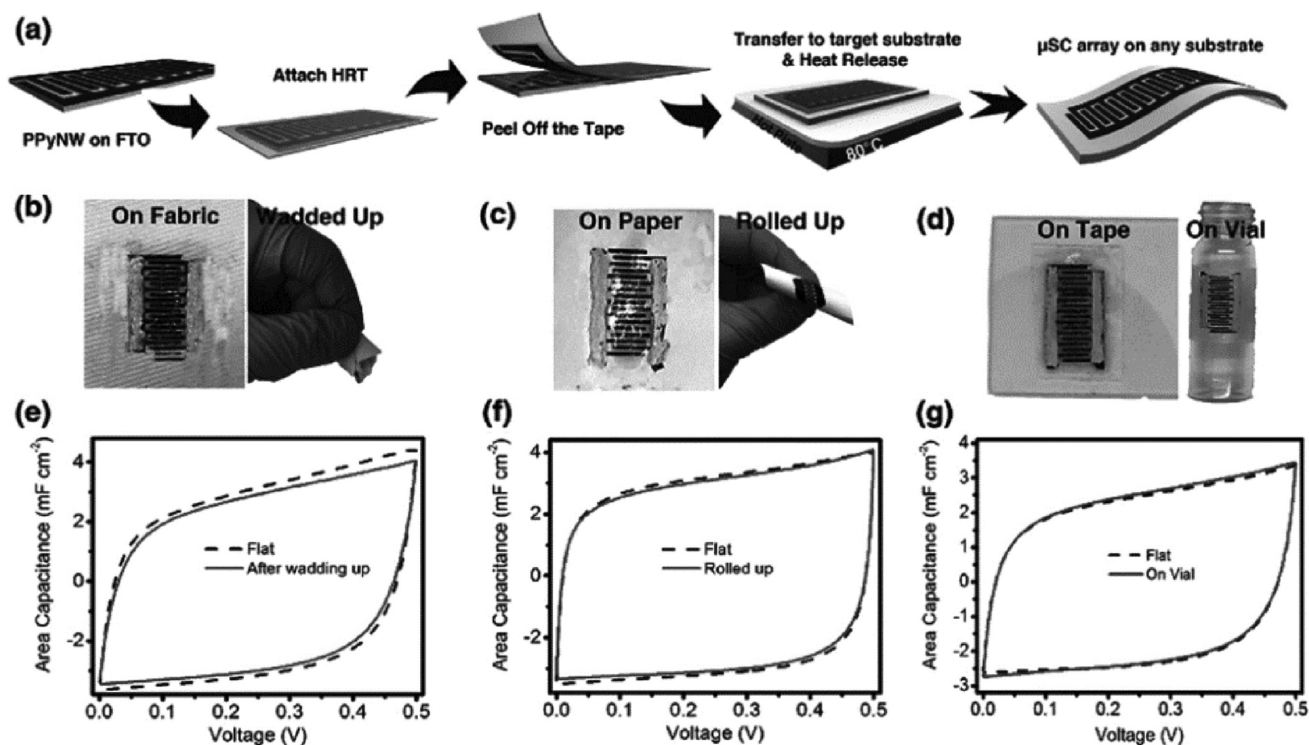MATERIALS

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Figure 9. a) Schematic illustration of the process for transferring PPy NW µSCs to target substrates. b) Digital photographs of the PPy NW µSC on textile and being wadded up, c) on paper and being rolled up, and d) on plastic tape and being attached onto the vial. e) CV curves of the PPy NW µSC on textile under flat state and after being wadded up, f) the PPy NW µSC on paper under flat state and being rolled up, and g) the PPy NW µSC on plastic tape under flat state and on vial (all the CV curves were recorded under the scan rates of 60 mV s⁻¹). Reproduced with permission.[136] Copyright 2017, Wiley-VCH.

at a high power density of 0.89 W cm⁻³. More importantly, the plug-and-play function of this kind of device was achieved by wiring and attaching the PPy NW µSCs to a variety of electric devices.

Lv et al.[137] developed a new kind of supercapacitor that can be directly edited into the desired shape (**Figure 10**). The electrode of this editable supercapacitor consists of CNTs and ultralong MnO_2 nanowires (MNWs) sandwiched by nanocellulose fibers (NCFs). Among them, MNWs and CNTs provide capacity and good electrical conductivity, and NCFs are used to enhance the mechanical properties of the electrodes and prevent short circuits. The supercapacitors use Cu tape as substrate to load materials. When we need to use it, we can cut it into any shape we need, just like the art of paper-cutting (Figure 10b). The supercapacitors have good specific capacitance, and also have advanced cycle stability (95% capacitance retention after 10 000th cycles), because of the interconnected multilayer structures and fabric-like microstructures. As excellent flexible energy storage devices with plug-and-play functionality, after 10 000 stretch–release tests at 400% elastic tensile strain, they retained ≈98% of initial capacitance. In further tests and comparisons, the MNW film has a higher specific capacitance than the MnO_2 nanoflowers (MNFs) electrode at all discharge current densities, indicating its excellent performance and charge storage capacity. The high aspect ratio MNW evenly dispersed and interlaced without obvious aggregation, resulting in rapid electron conduction. However, the nanoflower structure tends

to agglomerate and has less contact with the CNTs network. The more uniform the distribution of MNWs compared to the random distribution of MNFs, the greater the possibility of electrolyte contact with the active material, which facilitates better wetting of the electrode. In addition, contact angle measurements confirm that the graded porous network on the MNW electrode also promotes hydrophilic wetting of the electrolyte more effectively than the MNF electrode. The hydrophilicity of the electrode further promotes ion conduction. From these perspectives, the advantages of nanowires in supercapacitors are proved.

3.5. In Situ Characterization of Nanowire Electrode

Although tremendous materials have been developed and improved for the application in energy storage devices, the complex reaction mechanism still poses challenge on the researchers.[138] Basically, three types are demonstrated for metal-ion batteries,[139] i.e., intercalation, conversion, and alloying reaction. For electrode materials in battery, ions can intercalate and extract reversibly with a reversible lattice evolution. To capture this process, some structure characterization methods are applied to in situ characterization of electrode materials, such as XRD,[140,141] transmission electron microscope (TEM),[142,143] Raman spectra.[140] In case of nanowire materials, due to the unique 1D structure geometry, in situ characterization becomes
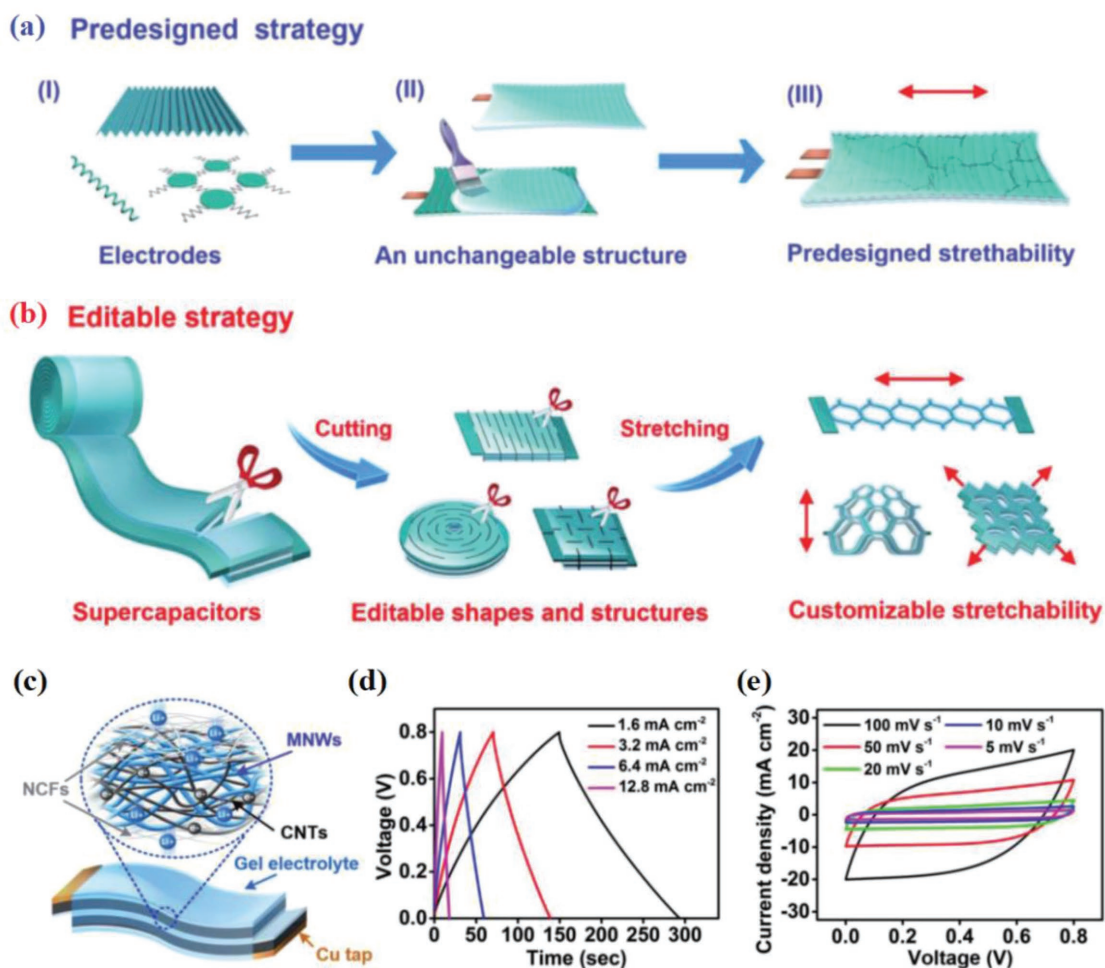
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Figure 10. Schematics for the assembling process of stretchable supercapacitors through a) predesigned strategy and b) their editable strategy. The predesigned strategy (a) can only apply an unchangeable structure, and requires three steps to prepare stretchable supercapacitors: I) predesigning electrodes into stretchable architectures (e.g., upper: wave-like structure, bottom left: spring-like fiber structures, bottom right: serpentine bridge-island structure), II) coating the structured electrodes with gel electrolyte, and III) overlapping structured electrodes for assembling of stretchable supercapacitors with predesigned stretchability. The mismatches between predesigned structures of electrodes and substrates/gel electrolytes may result in severe stress concentrations at interfaces that initiate microcracks and facilitate the crack propagation during stretching. While the editable strategy (b) only needs to cut the supercapacitors into desirable shapes and structures, the customizable structures, such as honeycomb-like structures, pyramid pop-up structure, living-hinge structure, and so on, make the as-prepared supercapacitors stretchable in an arbitrary direction. The red arrows indicate the stretchable direction of the as-prepared supercapacitors with customizable structures. c) Schematic illustration of supercapacitor construction (side view). d) Galvanostatic charging–discharging and e) cyclic voltammetry (CV) curves of flexible supercapacitors based on MNW70-NCF film electrodes at different scanning rates. Reproduced with permission.[137] Copyright 2017, Wiley-VCH.

a more efficient approach. Briefly, nanowire with an idealized model makes for a good connection to a micro circuits and ensures high-resolution observation of the microstructure and lattice evolution for a single material.

Due to the high-resolution of a local nanosized region, TEM gives prior to the characteristic of single nanowires in characterization. In 2010, Huang et al. reported the first in situ TEM work on the lithiation process of SnO_2 nanowire.[142] They made a nano-electrochemical device on the TEM holder (**Figure 11**a), which enables a microbattery setup with $LiCoO_2$ as cathode and ionic liquid as electrolyte. They found that the lithiation process goes along the axial direction of nanowire and results in the irreversible structure damage. Subsequently, many nanowires are studied by in situ TEM, such as ZnO

nanowire, SiO_2 nanowire, Si nanorod, $LiMn_2O_4$ nanowire, and MnO_2 nanowire. In addition to the observation, the evolution of nanomorphology, and study of the mechanical properties, in situ TEM also plays an important role in studying the energy storage mechanism. In a recent work by Lee et al., they investigate the lithiation mechanism of MnO_2 by in situ TEM.[144] The electrochemical reaction mechanism of the unique tunnel structure is not clear, though MnO_2 shows great performance. According to the results of in situ TEM, they proved that the fastest diffusion path is along the tunnels and the atomic position during the reaction procedure has been uncovered.

Although in situ TEM can realize high-resolution analysis of single nanowire, the high vacuum limits the operation condition and the precise control of lithium rate is a hard work.
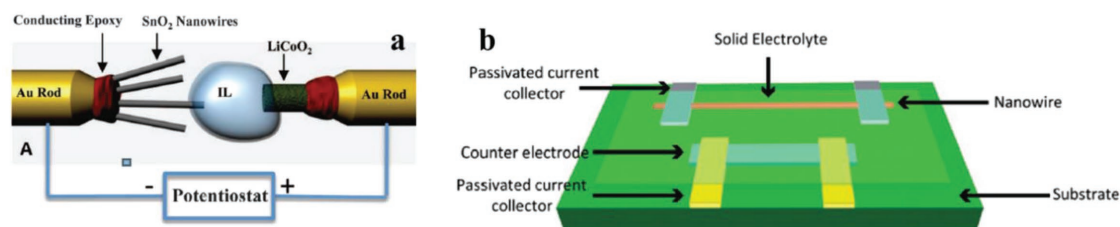
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Figure 11. a) Schematic of the experimental setup of in situ TEM. Reproduced with permission.[142] Copyright 2010, American Association for the Advancement of Science. b) Schematic diagram of a single nanowire electrode device design. A single vanadium oxide nanowire or Si nanowire is the work electrode, and HOPG or $LiCoO_2$ nanofilm is the counter electrode. The electrolyte is the PEO–$LiClO_4$–PC–EC polymer. Reproduced with permission.[145] Copyright 2010, American Chemical Society.

To create a moderate condition for battery, researches fabricated on-chip devices to realize the in situ characterization. As shown in Figure 11b, Mai et al. designed the first all-solid single nanowire battery,[145] where a single vanadium oxide nanowire or silicon nanowire acts as working electrode, PEO–$LiClO_4$–PC–EC polymer acts as electrolyte, and HOPG/$LiCoO_2$ acts as counter electrode. It is notable that the electrical transport measurement of single nanowire under different charge states has been realized on this platform. Moreover, in situ Raman spectra played a significant role in characterizing the structure destruction of single Si nanowire. Subsequently, Mai and co-workers fabricated the multicontact devices with different exposure state to study the mechanism of Li/Na ion transport.[111] They demonstrated an axial transport path of ion in a confined channel and the radial path for open and immersed condition. Similarly, they also found that Na ion caused heavier structure degradation as its larger volume. Afterward, they fabricated a MnO_2 nanowire/MoS_2 nanosheet heterostructure and designed two different measurement configurations[146] (charge from MnO_2 or MoS_2). The experiment results demonstrated that the unidirectional transport of electrons decide the measured capacity of a heterostructured material. In the field of in situ characterization, on-chip electrochemical devices have brought great potentials and maximized the advantages of nanowires.

4. Summary and Outlook

In this review, nanowires in electrochemical energy storage devices are discussed. Nanowires are classified according to different structures and combinations, including simple nanowires, core–shell/coated nanowires, hierarchical/heterostructured nanowires, porous/mesoporous nanowires, hollow nanowires and nanowire arrays, nanowire networks, and nanowire bundles. The various morphologies of nanowires have shown great application potential in electrochemical energy storage devices. To the point, the applications of different nanowires in lithium-ion, sodium-ion, zinc-ion batteries and supercapacitors systems are introduced. In situ characterization of nanowire electrode is mentioned as an important strategy for detecting energy storage mechanism.

In summary, homogeneous single-component electrode materials (simple nanowires) usually fail to meet the high-performance demands. By constructing special 1D nanostructures, researchers have given nanowires greater contact area and

higher stability. It embodies the importance of combining multiple advantages, designing functional 1D nanostructures, and overcoming limitations of different active substances in electrochemistry. Core–shell/coated nanowires provide large surface area and more stable structure through combinations of different materials, providing continuous electron and ion transfer channels. In hierarchical/heterostructured nanowires, the strain energy caused by volume change is relatively rapidly released and has good reversibility in electrochemical cycles. Porous/mesoporous nanowires overcome the limitations of poor ion and electron conductivity for electrode materials and low volume energy density, and exhibit excellent electrochemical performance in different electrochemical energy storage devices. Hollow structured nanowires also called nanotubes, whose hollow space can be loaded with other active materials, making them exhibit better electrochemical performance. Nanowire arrays, nanowire networks, and nanowire bundles combine the nanowires monomers to further enhance their overall electrochemical performance.

At the same time, although some progress has been achieved in the construction of 1D nanostructures, the standards for optimizing these materials into mature products that can be commercialized have not been reached, and there are opportunities for further enhancements. How to conduct small-scale experiments from achieving mass production is still challenging. The improved materials processing, better equipment, and more efficient manufacturing methods are needed. In the future, the demands for energy storage devices with high performance will be enormous, which requires continuous improvement of electrode materials, and we still have a long way to go.

Here, we would like to propose some ideas, and these directions may make significant progress in the field of energy storage in the future (**Figure 12**).

4.1. Revelation of the Reaction Mechanism

It is significant to actively uncover the internal mechanism of the nanowires for energy storage, including ion insertion/extraction, electron transfer, material strain, reaction potential, interface contact, etc. Most of the batteries and supercapacitors have the problem of capacity decay after recycling. Only by deep understanding of the mechanism and targeted improvement of materials can breakthroughs be made. Researchers should optimize their solutions based on existing testing methods. For example, a series of in situ inspections is a very good way to
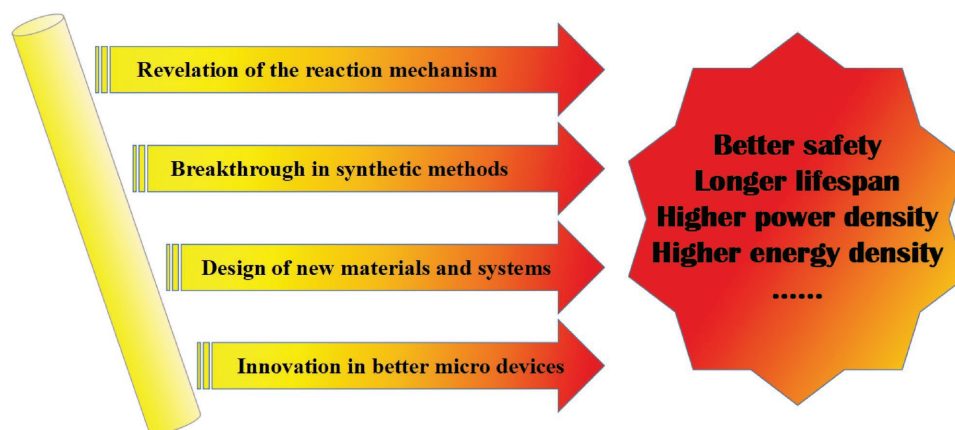
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Figure 12. Schematic illustration of some directions of advanced nanowires for electrochemical energy storage devices in the future.

explore the mechanism.[138] Compared with ex situ detection, it can reflect the dynamic changes of materials in charge/discharge more intuitively. For instance, single nanowire devices have advantages in this regard and can be used to monitor electrode reactions and material changes.[145,147]

4.2. Breakthrough in Synthetic Methods

Some new synthetic methods are mentioned above, which make the morphology and structure of the nanowires adjustable and help to improve performance in energy storage. We should combine knowledge of chemistry, physics, and materials science to delve into the microscopic processes and internal mechanisms of synthesis to achieve accurate design. For example, bionics is a key consideration. Biological tissues or molecules can be used as templates for synthetic nanowires, and biological enzymes also have the effect of inducing and promoting the reaction. There have been some precedents for some applications. Then, in order to achieve a breakthrough in the synthetic methods, the researchers are advised to combine the new ideas with the traditional synthetic methods effectively, so that the synthesized nanowires would have higher feasibility, suitable cost, and good performance.

4.3. Design of New Materials and Systems

The development of science and technology is always a gradual process and a process of continuous trial. It is expected that there will be ideal electrochemical energy storage devices with higher power density, higher energy density, lower cost, and higher cycle performance in the future. In the context of understanding the basic principles and performances, it is necessary to design and construct some new 1D nanomaterials for energy storage. With the development of computer technology and numerical simulation software, we will be able to use big data and other means to assist in the design of new materials, which can be efficient and save resources. At the same time, to develop better systems outside the existing systems, a variety of different metal-ion batteries, metal–air batteries, and hybrid-supercapacitors are worth exploring. Innovative research

involving electrolytes is also worth discussing. For example, solid-electrolyte is a potential direction.

4.4. Innovation in Better Microdevices

The advantages of 1D nanostructures determine that they are important part of developing new flexible, transparent, wearable devices. It is currently a hot field to miniaturize energy storage devices, combine them with micro/nano sensors and energy conversion devices, and ensure their safety and feasibility, as mentioned in this review. A new generation of on-chip smart devices requires more convenient design and manufacturing methods, more advanced micro/nano processing technology, and strong environmental compatibility. In the future, it is foreseeable that it will become one of the most important carriers in intelligent life, and thus change the way of human life.

Conflict of Interest

The authors declare no conflict of interest.

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