

Mini Review

Recent Advances of Flexible Electrospun Nanofibers-based Electrodes for Electrochemical Supercapacitors: A Minireview

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Flexibility has been identified as the most important factor in the foldable or bendable electrochemical supercapacitors (ESs), which include: electrical double-layer capacitors, and pseudo-capacitors. In this minireview, electrospun polymeric nanofibers (PNFs) and carbon nanofibers (CNFs) based composite electrodes for flexible electrochemical supercapacitors are reviewed in detail. During the past three decades, various electrospun composite electrodes have been developed, and their advantages and disadvantages in ESs are discussed through extensive analysis of literature. Additionally, this paper also discusses and predicts some futuristic research directions based on results published in literature. It is no doubt that electrospinning technology will continue to play an important role in flexible supercapacitor technology.

Keywords: Flexible Supercapacitor; Electrospun polymeric nanofibers; Electrospun carbon nanofibers; Energy storage

1. INTRODUCTION

Since the 21th century, with the rapid development of the global economic and industrial technology, the ecological problems and environmental pollution have caused by overusing the fossil fuels.[1, 2] Therefore, the utilization of efficient and clean energy has become a significant research topic in energy conversion and storage field. In recent years, some of the most effective and advanced technologies for novel electrochemical energy structures are lithium ion batteries (LIBs),[3-5] fuel cells,[6-8] and electrochemical supercapacitors (ESs).[9-11] Among these environmental benignity energy storage devices, supercapacitors (SCs) have attracted increasing attention mainly due to their high power density, long service life, fast charge-discharge and reliable safety features. As a result, ESs have been widely applied in hybrid electric vehicles (HEVs), portable electronics, and large industrial

equipment as renewable energy power sources.[12-14] According to their operating mechanisms, ESs can be classified into two types: electrochemical double layer capacitors (EDLCs) and pseudocapacitors. EDLCs store charges directly via electrostatic ion absorption forming electrical double layers (EDLs) on the surface of electrodes, resulting in limited energy density.[15] Alternatively, pseudocapacitors store more electric energy than EDLCs due to reversible redox reactions at the interface of the electrode material with the electrolyte.[16] From this regard, recent attention has been focused on the increase of the energy density of EDLCs and the design of the high performance pseudocapacitive electrode materials.

In the past three decades, the development of flexible electronic equipment, such as wearable displays, implantable bio-sensors and bendable mobile phones, has attracted tremendous attention.[17] However, current ESs devices are usually bulky, rigid and heavy, which cannot meet the high requirements of flexible electronics. Compared with conventional energy storage devices, flexible ESs are lightweight, foldable, bendable and even wearable.[18, 19] In order to provide continual energy and stable current output, flexible ESs must possess higher energy density and power density. Therefore, in the foreseeable future, improving the electrochemical performance of flexible ESs with shape-conformability, and excellent mechanical properties has been proven to be a promising avenue.[20-22] However, the greatest challenge in achieving flexible ESs with excellent electrochemical performance and flexibility is the selection and design flexible electrodes with high capacity.

Electrospinning is a scalable, simple and effective manufacturing technique to produce flexible nanofibers via applying a high voltage to a polymer solution.[23-26] The nanofiber structure is dependent on the spinneret design, spinning condition and polymer-salt precursor, and the fiber diameter can be controlled by changing the viscosity and electric conductivity of the polymer solutions, and the applied voltage.[27, 28] Electrospun nanofibers (ENFs), especially polymeric nanofibers (PNFs) and carbon nanofibers (CNFs) with diameters ranging from sub-nanometers to several micrometers, have brought synergic advantages of excellent flexibility and relatively high specific surface areas. Therefore, ENFs electrodes show promising perspectives for the construction of flexible ESs due to their superior mechanical properties and high electrochemical performance (**Fig. 1**). In order to fully utilize these superior advantages of electrospun PNFs and CNFs materials, modification of PNFs and CNFs with other functional materials for fabricating interesting hybrid nanostructures has become another hot issue in present research and technological enterprise. Different types of functional materials, such as transition metal oxides (TMOs), transitional metal sulfides/nitrides/carbides, Transition metal chalcogenides (TMDs) and layered double hydroxides (LDHs), have been incorporated into PNFs and CNFs substrates to form high-performance electrodes.[29, 30] These hybrid composites have some synergistic properties includes high theoretical capacity, excellent electrical conductivity, high specific surface areas and exceptional mechanical flexibility/strength, which will significantly enhance the energy storage performance far beyond pure PNFs and CNFs.

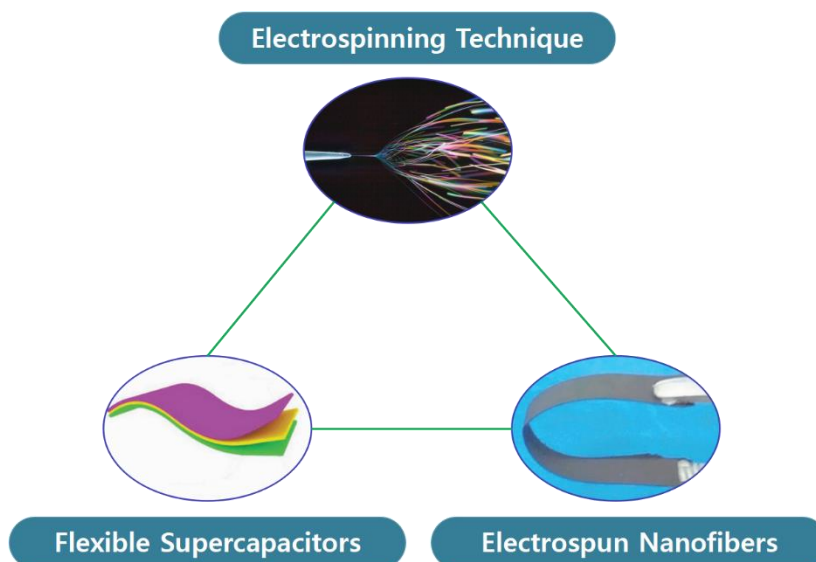


Figure 1. The scheme illustrates the typical process from electrospinning technique to electrospun nanofibers and flexible supercapacitors.

Despite there are many excellent reviews regarding electrochemical energy storage and conversion so far,[31-33] there are very few mentioned on flexible ENF-based electrodes for supercapacitors. Herein, this minireview research focuses on the recent advances and future developing direction of flexible ENF-based electrodes for supercapacitors, including PNFs and CNF-based hybrid nanomaterials. The aim of research on the flexible ENF-based electrodes is to develop electrodes that possess excellent electrochemical capacity, good cyclic stability and rate capability as well as high energy density and power density. Therefore, in the second section, we introduces the fundamental principles and influencing parameters of electrospinning technique. In the next section, the most recent advances in the design and preparation of various flexible PNF- and CNF-based electrodes for supercapacitors. Lastly, some summaries and perspectives on the futuristic developing trends of flexible ENF-based electrodes are highlighted.

2. ELECTROSPINNING

The history of electrospinning technique can be traced back to the early 1990s based on Cooley and Morton's reports.[34, 35] In 1914, John Zeleny firstly established a mathematical model to investigate the influence of electrical forces on liquids by researching the behavior of liquid droplets at the end of iron capillaries.[36] In 1930s and 1940s, there are a large number of patents and research papers on the principles and apparatus. Formhals successfully produced electrospun fibers with a modified electrospinning device to overcome the traditional advantage of drying system in 1934.[37, 38] In 1936, Charles Norton used air-blast to prevent assist fiber formation during electrospinning with melt liquids for the precursor.[39] In 1966, Sir Geoffrey Ingram Taylor has put forward the theoretical "Taylor cone" model, which modeled the conical geometry of liquid droplets.[40] After that in the 1980s and 1990s, only very few publications and patents were published in electrospinning research field. Until

1990s, since Prof. Reneker employed high voltage to charge the polymer solution to produce a series of fibers with diameter less than 5 μm , the electrospinning technology has gained considerable attentions and booming development.[41, 42] **Fig. 2** indicates a schematic of typical electrospinning set-up which contains three parts: a high voltage source, a spinneret/nozzle and a conductive collector. Based on electrostatic field between nozzle and collector, the polymer nanofibers is elongated, solidified and finally collected on the surface of conductive collector.[43-46]

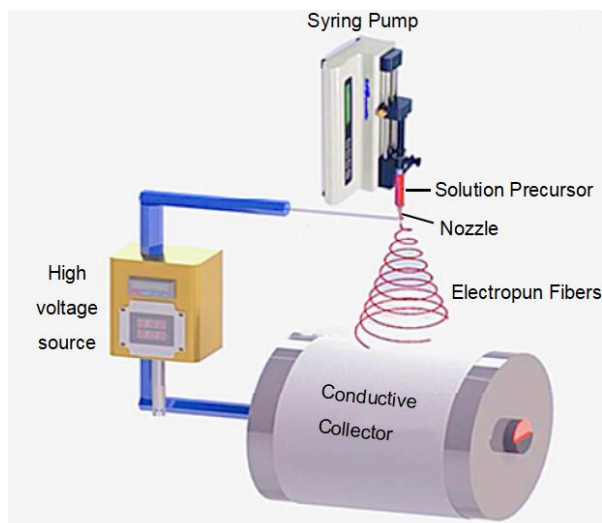


Figure 2. Typical schematic of electrospinning process. This figure has been republished with permission of the Royal Society of Chemistry, from [Hierarchical electrospun nanofibers for energy harvesting, production and environmental remediation, P. S. Kumar, J. Sundaramurthy, S. Sundarajan, V. J. Babu, G. Singh, S. I. Allakhverdiev, S. Ramakrishna, *Energy & Environmental Science*, 7, 3192-3222, 2014; permission conveyed through Copyright Clearance Center, Inc.].

2.1. Fundamental principles

Electrospinning is an unique method using electrostatic forces to fabricate ultra-fine fibers from polymer, polymer composite solutions or melts, and the fibers have thinner diameters and higher surface areas than those produced from other conventional spinning processes.[47, 48] By using this advanced technique, various nanofibers including polymers, carbon materials, inorganic materials and their hybrid composites can be constructed.[49-51] Moreover, the basic principles of other techniques, such as pesticide sprayers and electrostatic precipitators, are similar with electrospinning process, which works based on electrical repulsive forces. Typically, in the electrospinning process, a high voltage electrostatic potential (typically in the range of 5-30 kV) is applied to charge the polymer solutions to induce the ejection of a liquid jet from the tip of the syringe through a spinneret, including single, co-axial and multi-spinneret.[52, 53] Before the polymer solution is ejected from the tip of the syringe, the electrically conducting spinneret and the collector should be separated at an optimum distance (typically in the range of 10-25 cm). The jet extends through spiraling loops, as the loops diameter increase, the jet grows longer and thinner, resulting in the solidification of the polymer precursor as the solvent evaporates, and then

it collects on the target.[54-56] Because of the high stretching of jets, the polymer molecules would highly oriented in the fibers, which have been proved by polarized FT-IR and polarized Raman spectroscopy in very recent reports.[57, 58]

Generally, These collected ENFs have two types, namely random and aligned nanofibers, both of which have outstanding characteristics including ultra-high surface-to-volume ratio, ability to produce porous nanofibers with highly interconnected pores, and controllable surface morphology.[59-61] The electrospinning using simple plate collectors often produces nonwoven or random nanofiber mats, and using a disc or cylinder with high rotating speed results in aligned nanofiber mats.[62, 63] ENFs have various morphologies, such as core-shell,[64-68] sea-island,[69] hollow,[70] porous and dense structures,[46, 71, 72] which can be achieved by adjusting electrospinning parameters including applied electric field, solution concentration, feed rate and distance between the spinneret and collector.

2.2. Influencing parameters

The applied electric field, which controls the electrostatic forces working on the polymer jet in the “Taylor cone”, has played a crucial role in ultimate fiber formation in electrospinning process. The proper applied voltage can stabilize the electrospinning process that only occurs at an electric field of 1-2 kV/cm as the distance between spinneret tip and collector is changed to 5 cm. Additionally, it is worth noting that the applied electric field also had a powerful effect on fiber diameters. The higher the applied electric field, the longer the fiber average length and the thinner the fiber diameters.[73, 74] Meanwhile, the critical voltage has specific relation with molecular weight of polymer precursor, and higher molecular weight causes the increase of the viscosity. Increasing the voltage value could also result in increasing of the spinning current, and further lead to incidence of beaded morphology and the reduction of surface area.

Viscosity and surface tension of solution are another two important factors influencing the bead formation and the fiber diameters. Viscosity is a functional characteristic of the concentration of solution and molecular weight of the polymer. The polymer precursor solution must have a sufficiently high viscosity to produce bead-free fibers, while a high molecular weight ensures the viscosity.[75, 76] Generally speaking, the increased viscosity results in increasing of the fiber diameter. When the viscosity is too low, polymer particles are obtained by electrospraying. At a higher viscosity, smooth fibers can be produced instead of beaded fibers because the polymer chain entanglements are higher. Both the inherent characteristic of polymer and the type of solvent determine the surface tension, while the surface tension of solutions should be kept low to produce smooth fibers by avoiding the formation of beads. Remarkably, the concentration of the solution has negligible impact on surface tension. Based on this finding, solvents with a relatively low surface tension, such as *N,N'*-Dimethylformamide (DMF), *N*-Methyl pyrrolidone (NMP) and Dimethylacetamide (DMAc), may increase the spinnability because it is more likely to form fibers.[77-82]

The feed rate of polymer solutions is very important because it determines not only the fiber morphology but also the electrospinning efficiency.[83-85] By increasing the solution feeding rate, a smooth fiber structure and uniform fiber diameter obtained instead of spindle-like beads. Moreover, the

factor of flow rate cannot be ignored and highly related to the applied voltage. In general, high flow rate often requires high voltage, which could ensure a stable cone-jet mode and a continuous electrospinning process.

Apart from the above, other process parameters including collector, the electrical conductivity of precursor, solvent volatility and ambient humidity, also affect the fiber structure and diameter. **Fig. 3** illustrates four commonly used rotating drum collectors.[86] The fiber diameter can be controlled by adjusting the collector rotating speed, while higher rotating speed can improve the fiber orientation due to molecular chains' alignment in the direction of fiber axis. Increasing electrical conductivity can lead to fine-diameter fibers, while the fiber structure did not obtain at the ultrahigh conductivity of solution, because Taylor cone will not occur in electrospinning process. It is highly required that suitable solvent volatility to avoid the self-dissolution of nanofibers in the collector. However, if the solvent evaporates too fast, the polymer solution may quickly solidify on the spinneret tip and block it. Ambient humidity, which also affects both the fiber processability and morphology, should be kept at a low level to ensure the obtained fibers stable in moisture atmosphere.



Figure 3. Different collectors for electrospinning. This figure has been republished with permission of an open-access article of Springerlink.com, from [Review for application of electrospinning and electrospun nanofibers technology in textile industry, M. Mirjalili, S. Zohoori, *Journal of Nanostructure in Chemistry*, 6, 207-213, 2016.].

3. FLEXIBLE PNFs-BASED ELECTRODES

As one of the advanced energy storage devices,[87] ESCs provide better power density than batteries due to the long life cycle, high safety and environmental affability.[88, 89] Since 1977, Hideki Shirakawa discovered that polyacetylene has an excellent electronic conductivity and earned a Nobel Prize in Chemistry in 2000,[90] various conducting polymers (CPs) have gained considerable interest for SC electrodes in energy storage applications.[91, 92] However, most of the CPs is not suitable for application in SC electrodes due to its limited accessible surface area. Fortunately, electrospinning, which is a scalable technique to produce flexible one dimensional (1D) nanofibers with a relatively high surface area, can solve the above issues adequately. Polyaniline (PANI), as a typical conducting polymer, has shown promising perspective as an electrochemical active material for SCs.[93, 94] In 2015, Liu

[95] proposed a highly flexible and foldable sandwiched symmetric all-solid-state SCs, which consisted of flexible electrospun polyaniline/carbonized polyimide (PANI/CPI) nanofibers electrode (**Fig. 4a**). Remarkably, the PANI/CPI nanocomposite membrane electrode generates superior specific capacity of 379 F g^{-1} at 0.5 A g^{-1} and long cycle life with a capacity retention of 94% after 1000 cycles at 1 A g^{-1} (**Fig. 4b and c**).

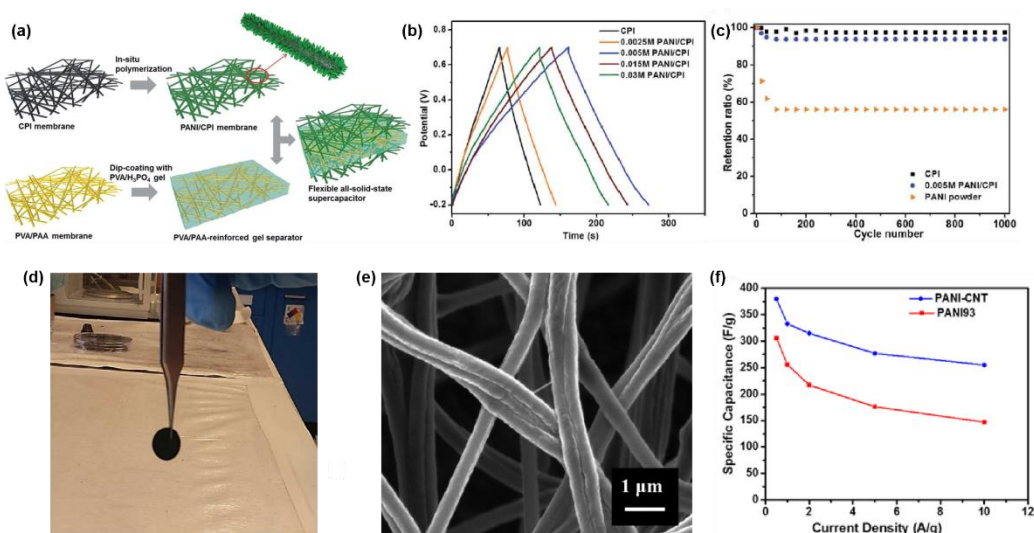


Figure 4. (a) Schematic for the preparation of flexible and foldable all-solid-state supercapacitors consisting of electrospun PANI/CPI composite membranes and PVA/PAA nanofiber membrane-reinforced gel separator; (b) Charge-discharge curves at a current density of 0.5 A g^{-1} ; (c) Plots of cycle life tests of supercapacitors at a current density of 1 A g^{-1} . This figure has been republished with permission of the Royal Society of Chemistry, from [Electrospun polymer nanofiber membrane electrodes and an electrolyte for highly flexible and foldable all-solid-state supercapacitors, Y. Miao, J. Yan, Y. Huang, W. Fan, T. Liu, *RSC Advances*, 5, 26189-26196, 2015; permission conveyed through Copyright Clearance Center, Inc.]. (d) Digital photos of freestanding nanofiber electrodes; (e) SEM images of PANI-CNT electrospun fibers with an average nanofiber diameter of $491 \pm 86 \text{ nm}$; (f) CV curves of symmetric PANI-CNT capacitor at different scan rates. This figure has been reprinted with permission from (Supercapacitor Electrodes Based on High-Purity Electrospun Polyaniline and Polyaniline–Carbon Nanotube Nanofibers, S. K. Simotwo, C. DelRe, V. Kalra, *ACS applied materials & interfaces*, 8, 21261-21269, 2016). Copyright (2016) American Chemical Society.

To circumvent the problem that the pure PANI solution is difficult to prepare due to its limited solubility and dispersion in most organic solvents, an electrospinnable polymer such as polyethylene oxide (PEO) can be usually added to PANI to form electrospinnable polymer solution. For instance, Kalra [96] designed high purity polyaniline (PANI) nanofibers by using high molecular weight PEO as an electrospinnable polymer to successfully produce PANI/PEO nanofibers, and further fabricated PANI/CNT/PEO nanofibers via a single step electrospinning process to enhance the conductivity and cyclic stability of the electrode (**Fig. 4d and e**). Both PANI and PANI-CNT flexible electrodes exhibited promising electrochemical performance, including high specific capacitances (308 and 385 F g^{-1} at a current density of 0.5 A g^{-1}) and high specific capacitance retentions (70 and 81.4% at a current density of 2 A g^{-1} after 1000 cycles; **Fig. 4f**). Subsequently, in 2018, Vijayakumar [97] reported a flexible

Polyaniline/Polyvinyl alcohol/Graphene Oxide (PANI-PVA-GO) nanofibers as freestanding and binder-free SC electrode through electrospinning process. The flexible PANI/PVA/GO electrode reached a maximum specific capacitance of 438.8 F g^{-1} , which is higher than the PANI/PVA electrode (143.3 F g^{-1} at 100 mV s^{-1}).

Besides PANI, other polymers such as polyamide-66 (PA66), Nylon-6 (PA-6) and Polyindole (Pind) are also used as active materials in ESCs. In 2014, Hu [98] integrated electrospun polyamide 66 (PA66) nanofiber and reduced graphene oxide (rGO) nanosheets to fabricate porous flexible electrode, which demonstrated superior mass loading and capacity. In this research article, GO nanosheets were self-assembled on PA66 nanofibers by electrospinning and subsequently dip-coating in the first step; and then rGO nanosheets dispersed onto the nanofibers through hydrazine vapor reduction method. The obtained flexible RGO/PA66 nanofibers exhibited a high area capacity (0.931 F cm^{-2}), approximately 4.4 times higher than that of rGO-coated PA66 microfibers electrode (0.213 F cm^{-2}). A highly flexible and transparent Polyaniline/Nylon-6/Cellulose Acetate (PANI-PA-CA) electrode fabricated by in situ polymerization of PANI nanowires on Nylon-6 nanofiber-reinforced cellulose acetate thin film substrates was reported by Kim [99]. The prepared PANI-PA-CA electrode exhibited not only excellent transparency optimal and flexibility, but also superior specific capacitance of 402 F g^{-1} at a current density of 0.3 A g^{-1} , and long cyclic stability (capacitance retention of 61% after 1000 cycles). Polyindole (Pind) was previously less studied but recently gained considerable attention in the energy storage field. Zhu fabricated high surface area Pind/CNTs nanofibers by electrospinning technique. In their research report, 10 wt.% addition of CNTs can significantly enhance the conductivity and stability of Pind. As a result, the bind-free Pind/CNTs electrode showed great capacitance improvements of 476 F g^{-1} at a current density of 1.0 A g^{-1} compared to the pure Pind electrode (238 F g^{-1}). Moreover, they proposed an all-solid-state ESCs device, where stainless steel fabric was used as current collector, and PVA/ H_2SO_4 gel was used as electrolyte. Remarkably, the ESC device exhibited a high power density of 426 W kg^{-1} , which is higher than those of other Pind-based electrodes such as $\text{Co}_3\text{O}_4/\text{CNT}/\text{Pind}$ and $\text{V}_2\text{O}_5/\text{Pind}/\text{AC}$ composites. This work has set a stage for Pind-based electrode materials to compete with other CPs for ESCs.[100]

4. FLEXIBLE CNFs-BASED ELECTRODES

4.1. Flexible polymer derived CNFs electrodes

In the past few decades, carbon nanofibers (CNFs) have been widely investigated as the most promising electrode materials for ESCs. At present, electrospinning process still is the main preparation method of polymer derived free-standing CNFs with outstanding electrical conductivity, high surface area and excellent mechanical strength. The as-fabricated flexible CNFs prepared by electrospinning polymer precursor such as Polybenzimidazol (PBI),[101] Polyimide (PI),[102] photopatternable epoxy (SU-8),[103] Phenolic resin,[104, 105] and polyacrylonitrile (PAN)[106] as carbon sources were usually have a specific capacitance of 175 F g^{-1} .

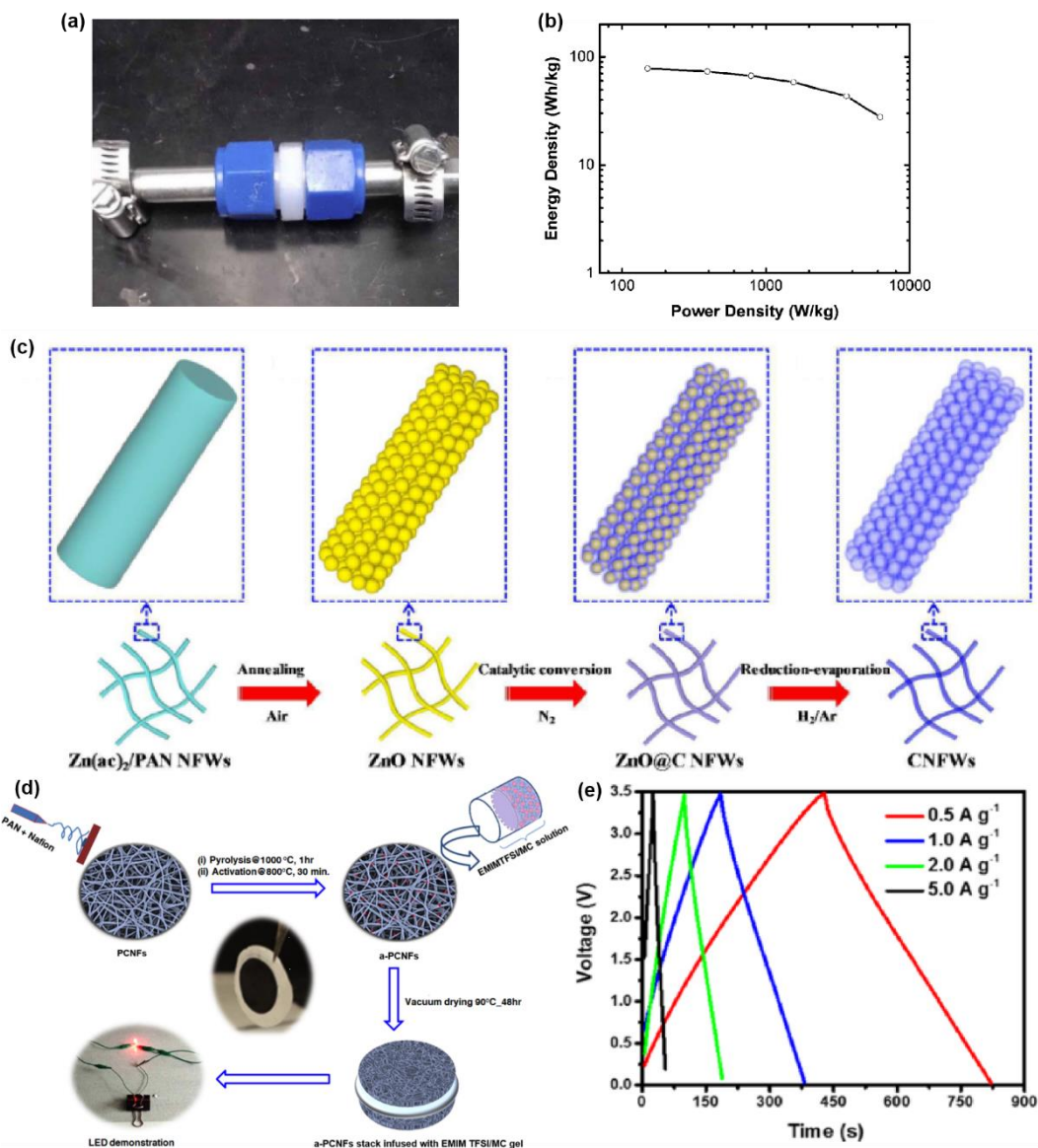


Figure 5. (a) Picture of a Swagelok cell setup used for electrochemical testing; (b) Ragone plot of an activated porous carbon nanofibers. This figure has been republished with permission of the Royal Society of Chemistry, from [Binder-free three-dimensional high energy density electrodes for ionic-liquid supercapacitors, C. Tran, D. Lawrence, F. W. Richey, C. Dillard, Y. A. Elabd, V. Kalra, *Chemical Communications*, 51, 13760-13763, 2015; permission conveyed through Copyright Clearance Center, Inc.]. (c) Schematic illustration of the fabrication procedure of CNFWs; This figure has been republished with permission of the Royal Society of Chemistry, from [Porous ultrathin carbon nanobubbles formed carbon nanofiber webs for high-performance flexible supercapacitors, L. Wang, G. Zhang, X. Zhang, H. Shi, W. Zeng, H. Zhang, Q. Liu, C. Li, Q. Liu, H. Duan, *Journal of Materials Chemistry A*, 5, 14801-14810, 2017; permission conveyed through Copyright Clearance Center, Inc.]. (d) Schematic illustration of the fabricated solid-state symmetric device; (e) Capacitance at different current densities. This figure has been reprinted with permission from (Highly Durable, Self-Standing Solid-State Supercapacitor Based on an Ionic Liquid-Rich Ionogel and Porous Carbon Nanofiber Electrodes, S. K. Simotwo, P. R. Chinnam, S. L. Wunder, V. Kalra, *ACS applied materials & interfaces*, 9, 33749-33757, 2017). Copyright (2017) American Chemical Society.

Yang [101] successfully prepared activated CNFs through electrospinning PBI solutions to nanofibers, followed by carbonization and activation, the obtained CNFs activated at 850 °C by steam showed the highest specific capacitance of 178 F g⁻¹. Using Swagelok cell for electrochemical testing, a binder-free porous carbon nanofiber electrode for room temperature ionic-liquid ESC is proposed in Tran's article (**Fig. 5a**), The electrochemical device provides a high energy density and power density (**Fig. 5b**). [103] By carbonization of electrospinning PI/SiO₂ hybrid composite nanofibers and removing the SiO₂ additive, Wang [107] fabricated the flexible CNFs that possessed high capacitance retention of 70% after 10000 cycles. Phenolic resin has been also widely used to produce CNFs due to its high carbon yield and low cost. The first report about phenolic resin based CNFs was in 2012 by Liu group, [108] which exhibited excellent specific capacitance up to 171 F g⁻¹. Recently, Ling [109] presented a facile and effective method by electrospinning, carbonization and silica removal to prepare flexible CNF electrodes, which used phenolic resin as carbon precursor, and partially-hydrolyzed tetraethyl orthosilicate (TEOS) as sacrificial template. The as-fabricated flexible CNFs delivered high specific capacitances of 274 F g⁻¹ at a current density of 0.1 A g⁻¹ and long-term electrochemical stability with a capacitance retention of 90% after 5000 cycles.

PAN nanofibers are typically used as precursors to produce nitrogen-doped CNFs through electrospinning. In 2004, Lee [112] firstly reported on the preparation of PAN-based activated CNFs (460-1160 m² g⁻¹) as a flexible electrode with the specific capacitance of 91-134 F g⁻¹ at a current density of 1 mA cm⁻². Generally, the fabrication of PAN-based carbon materials needs chemical or physical activation procedure in many literatures. [113, 114] Besides these two methods, a flexible PAN-based CNF paper was obtained [115] by simultaneously carbonized and activated in CO₂ atmosphere, and exhibited a specific capacitance value up to 150 F g⁻¹ at a current density of 50 A g⁻¹. There is no doubt that the morphology of CNF electrode often determines the specific surface area and the specific capacitance. Thus, Duan [110] applied ZnO as removal templates, and combined electrospinning technique to produce a new kind of free-standing carbon nanofiber webs (CNFWs) with interconnected porous ultrathin carbon nanobubbles (**Fig. 5c**). As a result, this free-standing CNFW electrode exhibited superior electrochemical performances because this unique fibrous-bubbled structure can not only provide fast electron transport paths but also ion transport channels. Analogously, Gupta [116] designed linear tube carbon nanofibers (LTCNFs) through electrospinning PAN and PS polymer blend solutions followed by thermal treatment to remove PS templates. Furthermore, CNFs have been also prepared from PAN-hybrid composites precursors, such as PAN/PVP, [117, 118] PAN/pitch, [119, 120] PAN/PMHS, [121] Poly(acrylonitrile-co-vinylimidazole), [122] PAN/PMMA, [123] PAN/APEG, [124] PAN/PAA, [125] etc. Kalra [126] reported a specific capacitance of 142 F g⁻¹ at 0.5 A g⁻¹ with freestanding PAN/Nafion derived CNF electrodes and silica-based ionic liquid gel electrolytes. Soon after, the same group constructed three-dimensional CNFs prepared through electrospinning PAN/Nafion blend solutions followed by a pyrolysis carbonization process, [111] and synthesized ion gels by the entrapment of EMImTFSI in a methyl cellulose matrix (**Fig. 5d**). As a remarkable result, an outstanding specific capacitance of 153 F g⁻¹ at 20 mV s⁻¹ was obtained because the electrode framework creates electrons and ion-conducting pathways (**Fig. 5e**). Yang [127] used PAN/PmAP blends as carbon precursor to produce flexible nitrogen-doped porous CNF mats by electrospinning method, and followed by thermal stabilization and carbonization. The as-obtained SCs showed high specific capacitance and

good cycling stability due to the high effective surface area, excellent conductivity and high nitrogen content.

4.2. Flexible CNF-based composite electrodes

An ideal flexible electrode should generally have a combination of outstanding mechanical strength and excellent specific capacitance.[128, 129] Although flexible CNFs have been widely studied as electrode for ESCs, the use of individual CNFs is limited due to unsatisfactory capacitance in high-performance flexible supercapacitors.[130] Therefore, to meet the demands of flexible supercapacitors, designing and developing CNF-based composite electrodes has aroused increasing interest, especially integrated CNFs and pseudo-capacitance materials or other carbon materials like carbon nanotube, graphene, etc.

CNFs-polyaniline composites: It is well known that PANI is one of the most promising candidates for supercapacitors among pseudo-capacitance materials owing to its simple fabrication process, low cost, extremely high specific capacitance and environmental stability (**Fig.6a and b**).[131, 132] However, great volume expansion/shrinkage of PANI during long term charge/discharge processes will destroy electrode backbone, and further result in poor cycle life and rate capability. Therefore, to address this critical challenge, researchers have shown keen interest in compositing PANI and CNFs, which can integrate the advantages of high power output of CNFs and high energy output of PANI (**Fig. 6c, d, and e**).[133, 134] For an instance, Zhou [135] successfully prepared cross-linked N-doped carbon nanofiber network (CLCF) as flexible electrode with a high specific capacitance of 223 F g^{-1} at 0.5 A g^{-1} and superior rate capability of 78.5 % of the initial capacitance at 0.5 A g^{-1} . Moreover, CLCF could be used as scaffold for supporting PANI to form CLCF/PANI composite, which exhibited a higher specific capacitance of 300 F g^{-1} at 0.5 A g^{-1} and no obvious capacitance loss even when the ESC device was bended to 180° . Wang [136] applied electrospinning method to fabricated free-standing coal based carbon nanofiber (CBCNF) paper, which used as a supporting scaffold to grow PANI nanowires, and the obtained composite electrode displayed an extremely high specific capacitance of 1257 F g^{-1} at a current density of 0.5 A g^{-1} . Recently, Ding [137] reported a highly flexible carbon black doped carbon nanofiber/PANI membrane with exceptional electrochemical performance, including a superior specific capacitance of 501 F g^{-1} at 0.5 A g^{-1} and outstanding capacitance retention of 91% after 5000 cycles. Additionally, they successfully fabricated solid-state symmetric supercapacitor device comprised of H_3PO_4 -PVA gel membrane, which can power on a set of LEDs when charged, and no obvious capacitance change can be observed at different bending angles even after 500 bending cycles.

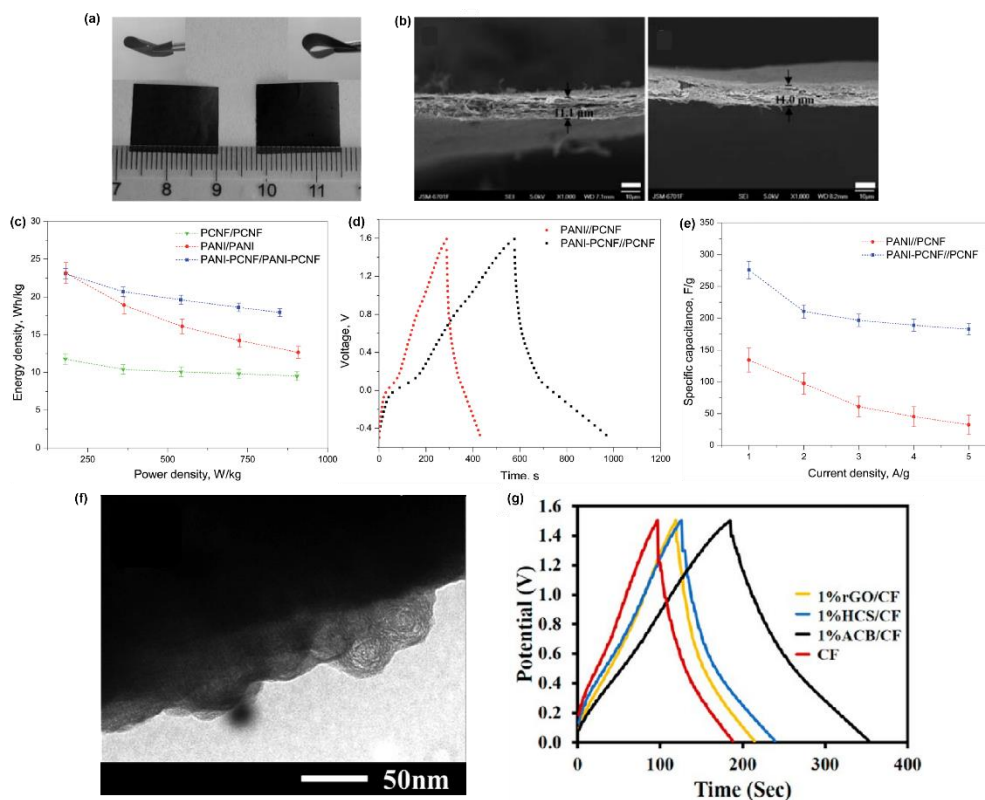


Figure 6. (a) Digital camera images of the CNF paper (left) and the CNF-PANI composite paper (right); (b) Side-view SEM images of the CNF paper (left) and the CNF-PANI composite paper (right); This figure has been republished with permission of the Royal Society of Chemistry, from [Fabrication of carbon nanofiber-polyaniline composite flexible paper for supercapacitor, X. Yan, Z. Tai, J. Chen, Q. Xue, *Nanoscale*, 3, 212-216, 2011; permission conveyed through Copyright Clearance Center, Inc.]. (c) Ragone plots of PANI-based symmetric supercapacitors; (d) Galvanostatic charge–discharge curves of PANI-based asymmetric supercapacitors; (e) Specific capacitances of PANI-based asymmetric supercapacitors; This figure has been republished with permission of the Royal Society of Chemistry, from [Free-standing polyaniline-porous carbon nanofiber electrodes for symmetric and asymmetric supercapacitors, M. Dirican, M. Yanilmaz, X. Zhang, *RSC Advances*, 4, 59427-59435, 2014; permission conveyed through Copyright Clearance Center, Inc.]. (f) TEM image of carbon fiber composites with 1 wt.% rGO; (g) GCDs of carbon-based nanofiber composite with ACB, HCS, and rGO at 1 wt.%. This figure has been reprinted with permission from (Electrospinning of Carbon–Carbon Fiber Composites for High-Performance Single Coin-Cell Supercapacitors: Effects of Carbon Additives and Electrolytes, P. Suktha, M. Sawangphruk, *Industrial & Engineering Chemistry Research*, 36, 10078-10086, 2017). Copyright (2017) American Chemical Society.

CNFs-carbon nanotube composites: Hou [139] used electrospinning technique to incorporated latex nanoparticles (LNPs) and multiwalled carbon nanotubes (MWCNTs) in PAN nanofibers, and then carbonization to form CENF/LNPs/MWCNTs electrode. Compared the porous CENFs without MWCNTs, the freestanding and binder-free composite electrode with MWCNTs possessed higher specific surface area, meso-porosity percentage, as well as better electrochemical performance. More recently, a flexible CNF/CNT electrode was prepared through sol-gel, electrospinning, and chemical vapor deposition (CVD) processes in Xie's report.[140] After deposited with MnO₂, the obtained CNF/CNT/MnO₂ electrode showed high specific capacitance of 631 F g⁻¹ at 0.9 A g⁻¹ and extremely

long-term cycling stability of 95% after 1500 cycles. Moreover, the assembled symmetric SCs possessed maximum energy density of $19.11 \text{ W h kg}^{-1}$ and maximum power density of $25,000 \text{ W kg}^{-1}$. This work would offer a promising and highly valuable method to produce conductive self-supporting scaffold for high-performance energy storage devices.

CNFs-graphene composites: Graphene, as a single-atomic thickness of carbon atoms, has been predicted one of the most promising candidate for SCs due to its high electrical conductivity, large specific surface, superior mechanical strength and excellent thermal conductivity (**Fig 6f and g**). [138] After being integrated with CNFs, graphene can improve the physical and chemical properties of composite electrode. [141, 142] By using PAN/GNS as electrospun precursor, Yan [143] prepared a binder-free and flexible CNF/GNS paper electrode via electrospinning process and followed with high temperature carbonization. Benefited from the synergistic effect from CNF and GNS, the paper electrode showed a high specific capacitance of 197 F g^{-1} , which is 24% higher than that of pure CNF electrode. Qiu [144] demonstrated a freestanding carbon nanofiber/graphene (CNF/G) electrode via in-situ electrospinning and simultaneously spraying process. The as-obtained composite electrode exhibited a specific capacitance of 183 F g^{-1} , which is 1.6 times higher than that of CNF without graphene, because the CNF web could prevent the agglomeration of graphene.

CNFs-metal oxides composites: Metal oxides, such as transitional metal oxides, [145] binary/ternary metal oxides, [146, 147] and RuO_2 , [148, 149] have been studied for the supercapacitors in order to increase the energy density owing to their fast faradic surface redox reactions. However, all these potential metal oxides electrodes often suffer from their intrinsically poor electrical conductivity and low ionic diffusion constant. Therefore, to overcome these challenges, developing CNFs/metal oxides hybrid materials is an effective strategy to improve their electrochemical performance. More importantly, CNFs can be used as flexible scaffolds to effectively grow nanostructured metal oxides to form freestanding electrodes for wearable and foldable supercapacitors. [150-152] Kang [153] fabricated a flexible asymmetric supercapacitor with MnO_2/CNF composites as positive electrode and activated CNFs as negative electrode in aqueous electrolyte, which exhibited high energy density of 30.6 Wh kg^{-1} and power density of 20.8 kW kg^{-1} . By electrospinning, chemical vapor deposition and in-situ redox deposition process, Xie [154] prepared a freestanding CNT/CNF/ MnO_2 electrode and further assembled flexible symmetric supercapacitor device. Remarkably, the flexible device presented a high energy density of 3.88 Wh kg^{-1} at power density of 7 kW kg^{-1} and outstanding capacitance retention of 70% after 100 bending cycles, indicating a superior flexibility. Analogously, Liu [155] reported a flexible NiCo_2O_4 doped carbon nanofibers (NCCNF) by the combination of electrospinning and co-deposition method, which can be used as a highly conductive scaffold to grow δ -phase and γ -phase MnO_2 nanomaterials (**Fig. 7a**). The obtained flexible NCCNF@ MnO_2 hybrid electrode, including nanosheet and nanorod structure, has high specific surface areas and three-dimensional network, which result in remarkable specific capacitances of 918 F g^{-1} and 827 F g^{-1} , respectively. ZnCo_2O_4 , as a typical spinel structure, has been vertically grown on porous CNFs in Qu's recent report [156] via a facile electrospinning and hydrothermal method (**Fig. 7b and c**).

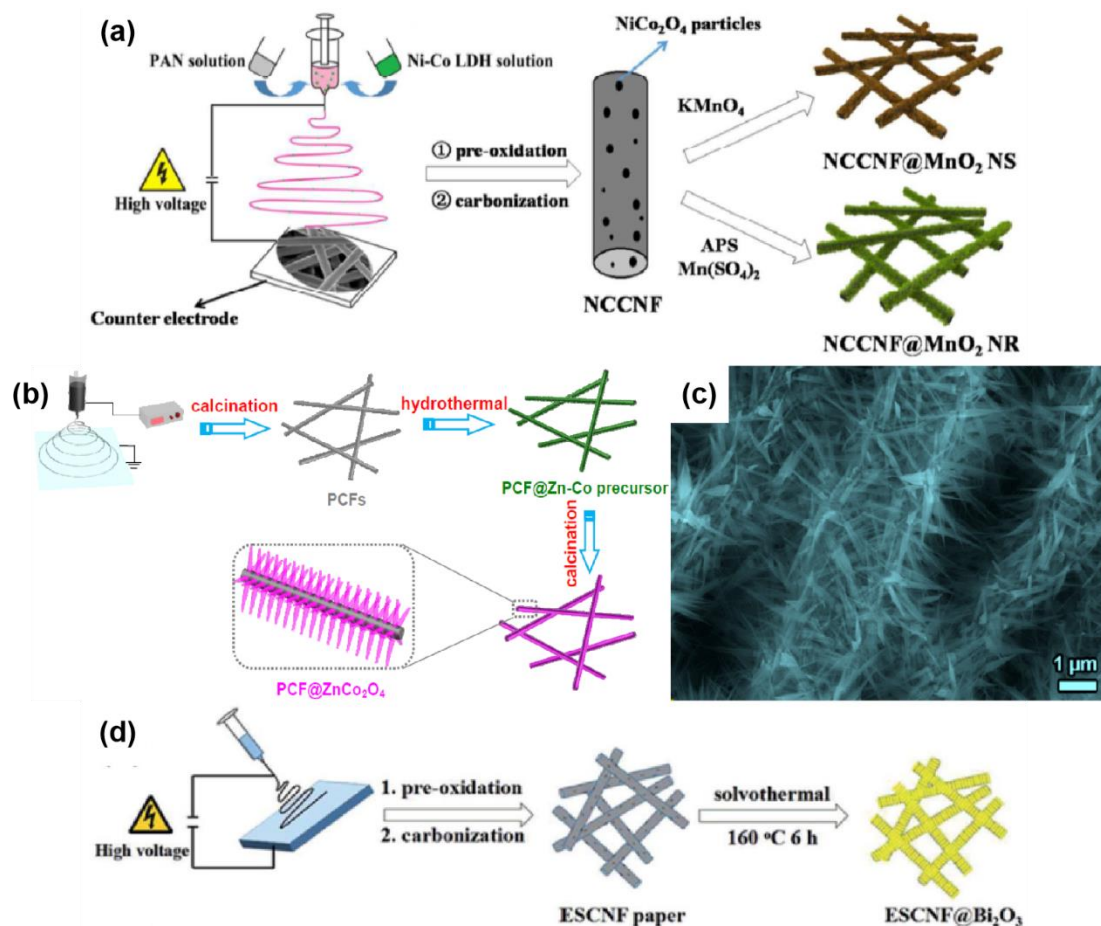


Figure 7. (a) Schematic illustration for the preparation of NCCNF@MnO₂ NS and NR hybrid membranes; This figure has been reprinted with permission from (Flexible Hybrid Membranes of NiCo₂O₄-Doped Carbon Nanofiber@MnO₂ Core–Sheath Nanostructures for High-Performance Supercapacitors, F. Lai, Y. Miao, Y. Huang, T. Chung, T. Liu, *The Journal of Physical Chemistry C*, 24, 13442-13450, 2015). Copyright (2015) American Chemical Society. (b) Schematic illustration of the fabrication of PCF@ZnCo₂O₄ hybrid; (c) SEM image of PCF@ZnCo₂O₄ hybrid; This figure has been republished with permission of the Royal Society of Chemistry, from [Hierarchical core–shell heterostructure of porous carbon nanofiber@ZnCo₂O₄ nanoneedle arrays: advanced binder-free electrodes for all-solid-state supercapacitors, H. Niu, X. Yang, H. Jiang, D. Zhou, X. Li, T. Zhang, J. Liu, Q. Wang, F. Qu, *Journal of Materials Chemistry A*, 3, 24082-24094, 2015; permission conveyed through Copyright Clearance Center, Inc.]. (d) Schematic illustration for the fabrication of ESCNF@Bi₂O₃ negative electrode. This figure has been republished with permission of the Royal Society of Chemistry, from [A bismuth oxide nanosheet-coated electrospun carbon nanofiber film: a free-standing negative electrode for flexible asymmetric supercapacitors, L. Li, X. Zhang, Z. Zhang, M. Zhang, L. Cong, Y. Pan, S. Lin, *Journal of Materials Chemistry A*, 4, 16635-16644, 2016; permission conveyed through Copyright Clearance Center, Inc.].

Benefiting from three-dimensional hierarchical structural features, the binder-free PCF@ZnCo₂O₄ electrode exhibited a high specific capacitance of 1384 F g⁻¹ at 2 mV s⁻¹, and achieved high energy density (49.5 Wh kg⁻¹) as well as power density (222.7 W kg⁻¹) in all-solid-state asymmetric supercapacitor with PCFs as negative electrode. Very recently, As shown in **Fig. 7d**, Lin [157] reported a flexible and foldable asymmetric supercapacitor device with the freestanding ESCNF@Bi₂O₃ as

negative electrode and CF@NiCo₂O₄ as positive electrode, which achieved a high energy density of 25.1 Wh kg⁻¹ and ultra-high power density of 786.2 W kg⁻¹.

Beyond these above-mentioned CNF-based hybrid electrodes, other composite electrodes, such as CNF-metal hydroxide,[158] CNF-Mg,[159] CNF-PS,[160] CNF-Pt,[161] CNF-Ag[162] and CNF-metal sulfides[163] have also attracted considerable attention due to their high specific capacity and power density. For some examples, Liu [164] successfully grew Ni-Co LDH nanorods on CNFs via electrospinning and co-deposition process. Recently, by using coaxial electrospinning and hydrothermal method, Chen [165] prepared a freestanding hierarchical 1D CNFs- 2D NiCo₂S₄ electrode, which could effectively decrease the ion diffusion resistance and increase the specific surface area.

5. SUMMARY AND FUTURE OUTLOOK

In this review article, we have systematically highlighted the recent progress in flexible and wearable supercapacitors by applying electrospun nanofibers as electrode materials. Nowadays, 1D nanofibers have made great achievements in electrochemical energy and conversion field due to its promising advantages of exceptional mechanical flexibility/strength, definable porosity and relatively high specific surface areas. In this regard, electrospinning technique is an ideal and efficient method to produce uniform nanofibers with diameters ranging from sub-nanometers to several micrometers. In addition to the advantages of various morphologies and controllable porosity, the ENFs have also used as supporting scaffold to uniformly grow active pseudo-capacitance materials to form hierarchical heterostructures, which could provide more active sites for the electrochemical reactions and further enhance the electrochemical performance. Although great development in flexible ENFs and the hybrid electrodes has been achieved, there are still numerous drawbacks and challenges need to be conquered towards commercialization and practical applications.

i) In a technical aspect, although a large number of electrospinning theoretical models have been proposed, the accurate models still need to be improved to reduce the time for parameters optimization. Therefore, developing and innovating reliable theoretical models with abilities of simulating influence of spinning parameters and predicting the fiber diameters may be important to increase the electrospinning efficiencies and decrease the fabrication cost in industries.

ii) More attention should be focused on the high-performance electrode materials with a high active surface area, excellent conductivity and mechanical properties, which ensure better integrity to form binder-free electrode with a short ion transfer path. Furthermore, designing some intriguing structures, such as hollow and core-shell nanofiber, have recently received a great number of attention. Additionally, such hierarchical materials could be applied in other research areas like batteries,[166-168] electrocatalysis,[169, 170] photocatalysis,[171, 172] solar cells[173-175] and wearable electronic fabrics.

iii) Despite ENF-based hybrid composites used as binder-free electrode materials have been studied extensively in the past years, the flexible supercapacitors devices is still in the infancy stage. Planar- or fiber-shaped supercapacitors will be a promising research direction in the near future. However, some important parameters of ENFs, such as mechanical properties, stretchability and optical

transparency have not been quantitatively and systematically investigated during the electrochemical process.

Although a large number of difficulties and challenges exist, electrospinning technique still is a productive method to produce uniform nanofibers with some interesting structures. The combination of electrospinning with other techniques like hydrothermal, co-precipitation, CVD or electrochemical deposition still is a powerful and versatile way to form high-performance electrode materials. With the fast development of materials science and engineering, we believe the flexible and wearable supercapacitors with exceptional electrochemical and mechanical performance will expedite many progresses, and boost the commercialization of smart and flexible electronics in the future.

References

1. S. Wilke, B. Schweitzer, S. Khateeb, S. Al-Hallaj, *J. Power Sources*, 340 (2017) 51-59.
2. D. Wang, *Int. J. Electrochem. Sci.*, (2019) 102-113.
3. J. Zhou, J. Qin, X. Zhang, C. Shi, E. Liu, J. Li, N. Zhao, C. He, *ACS Nano*, 9 (2015) 3837-3848.
4. W. Li, Y. Yang, G. Zhang, Y. Zhang, *Nano Lett.*, 15 (2015) 1691-1697.
5. H. Sun, *Int. J. Electrochem. Sci.*, (2019) 219-227.
6. J. Shui, W. Min, D. Feng, L. Dai, *Sci. Adv.*, 1 (2015) e1400129-e1400129.
7. B. Huang, X. Wang, H. Fang, S. Jiang, H. Hou, *Mater. Lett.*, 234 (2019) 354-356.
8. Y. Liu, *Int. J. Electrochem. Sci.*, (2019) 196-204.
9. F. Lai, Y. Huang, L. Zuo, H. Gu, Y. Miao, T. Liu, *J. Mater. Chem. A*, 4 (2016) 15861-15869.
10. R. Zhao, K. Li, R. Liu, M. Sarfraz, I. Shakir, Y. Xu, *J. Mater. Chem. A*, 5 (2017) 19098-19106.
11. K. Li, Y. Huang, J. Liu, M. Sarfraz, P. O. Agboola, I. Shakir, Y. Xu, *J. Mater. Chem. A*, 6 (2018) 1802-1808.
12. K. Yuan, Y. Xu, J. Uihlein, G. Brunklaus, L. Shi, R. Heiderhoff, M. Que, M. Forster, T. Chasse, T. Pichler, T. Riedl, Y. Chen, U. Scherf, *Adv. Mater.*, 27 (2015) 6714-6721.
13. J. Han, K. Lu, Y. Yue, C. Mei, C. Huang, Q. Wu, X. Xu, *Ind. Crop. Prod.*, 128 (2019) 94-107.
14. Q. Ding, X. Xu, Y. Yue, C. Mei, C. Huang, S. Jiang, Q. Wu, J. Han, *ACS Appl. Mater. Interf.*, 10 (2018) 27987-28002.
15. A. González, E. Goikolea, J. A. Barrena, R. Mysyk, *Renew. Sust. Energ. Rev.*, 58 (2016) 1189-1206.
16. A. M. Abioye, F. N. Ani, *Renew. Sust. Energ. Rev.*, 52 (2015) 1282-1293.
17. J. Han, Y. Yue, Q. Wu, C. Huang, H. Pan, X. Zhan, C. Mei, X. Xu, *Cellulose*, 24 (2017) 4433-4448.
18. Y. Yang, H. Fei, G. Ruan, C. Xiang, J. M. Tour, *Adv. Mater.*, 26 (2014) 8163-8168.
19. Y. Shi, L. Pan, B. Liu, Y. Wang, Y. Cui, Z. Bao, G. Yu, *J. Mater. Chem. A*, 2 (2014) 6086-6091.
20. F. Grote, Z. Yu, J. Wang, S. Yu, Y. Lei, *Small*, 11 (2015) 4666-4672.
21. X. Chen, H. Lin, J. Deng, Y. Zhang, X. Sun, P. Chen, X. Fang, Z. Zhang, G. Guan, H. Peng, *Adv. Mater.*, 26 (2014) 8126-8132.
22. W. Xiong, X. Hu, X. Wu, Y. Zeng, B. Wang, G. He, Z. Zhu, *J. Mater. Chem. A*, 3 (2015) 17209-17216.
23. W. Xu, Y. Ding, S. Jiang, J. Zhu, W. Ye, Y. Shen, H. Hou, *Eur. Polym. J.*, 59 (2014) 129-135.
24. S. Jiang, Y. Chen, G. Duan, C. Mei, A. Greiner, S. Agarwal, *Polym. Chem.*, 9 (2018) 2685-2720.
25. S. Chen, G. He, A. A. Carmona-Martinez, S. Agarwal, A. Greiner, H. Hou, U. Schröder, *Electrochem. Commun.*, 13 (2011) 1026-1029.
26. S. Gao, G. Tang, D. Hua, R. Xiong, J. Han, S. Jiang, Q. Zhang, C. Huang, *J. Mater. Chem. B*, 7 (2019) 709-729.

27. S. Jian, J. Zhu, S. Jiang, S. Chen, H. Fang, Y. Song, G. Duan, Y. Zhang, H. Hou, *RSC Adv.*, 8 (2018) 4794-4802.
28. D. Lv, R. Wang, G. Tang, Z. Mou, J. Lei, J. Han, S. D. Smedt, R. Xiong, C. Huang, *ACS Appl. Mater. Interfaces*, 11 (2019) 12880-12889.
29. B. Zhang, F. Kang, J. M. Tarascon, J. K. Kim, *Prog. Mater. Sci.*, 76 (2016) 319-380.
30. S. Peng, L. Li, J. K. Y. Lee, L. Tian, M. Srinivasan, S. Adams, S. Ramakrishna, *Nano Energy*, 22 (2016) 361-395.
31. X. Peng, L. Peng, C. Wu, Y. Xie, *Chem. Soc. Rev.*, 43 (2014) 3303-3323.
32. L. Li, Z. Wu, S. Yuan, X. Zhang, *Energ. Environ. Sci.*, 7 (2014) 2101.
33. M. Zhi, C. Xiang, J. Li, M. Li, N. Wu, *Nanoscale*, 5 (2013) 72-88.
34. J. F. Cooley, Apparatus for electrically dispersing fluids, 1902.
35. W. J. Morton, Method of dispersing fluids. US, 1902.
36. J. Zeleny, *Phys. Rev.*, 3 (1914) 69-91.
37. F. Anton, Method and apparatus for the production of fibers, US, 1938.
38. C. G. Formhals, Multiple barrel gun, US, 1944.
39. A. Dvornik, Method of and apparatus fob, 1937.
40. G. Taylor, *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences*, 291 (1966) 145-158.
41. J. Doshi, D. H. Reneker, *Industry Applications Society Meeting*, 1693 (1993) 1698-1703.
42. D. H. Reneker, I. Chun, *Nanotechnology*, 7 (1999) 216-223.
43. P. S. Kumar, J. Sundaramurthy, S. Sundarajan, V. J. Babu, G. Singh, S. I. Allahverdiev, S. Ramakrishna, *Energ. Environ. Sci.*, 7 (2014) 3192-3222.
44. D. Lv, M. Zhu, Z. Jiang, S. Jiang, Q. Zhang, R. Xiong, C. Huang, *Macromol. Mater. Eng.*, 303 (2018) 1800336.
45. D. Hua, Z. Liu, F. Wang, B. Gao, F. Chen, Q. Zhang, R. Xiong, J. Han, S. K. Samal, S. C. Smedt, C. Huang, *Carbohydr. Polym.*, 151 (2016) 1240-1244.
46. Z. Guo, G. Tang, Y. Zhou, S. Liu, H. Hou, Z. Chen, J. Chen, C. Hu, F. Wang, S. C. Smedt, *Carbohydr. Polym.*, 169 (2017) 198-205.
47. M. Zhu, R. Xiong, C. Huang, *Carbohydr. Polym.*, 205 (2019) 55-62.
48. W. Ma, M. Zhang, Z. Liu, C. Huang, G. Fu, *Environ. Sci. Nano*, 5 (2018) 2909-2920.
49. S. Zhou, G. Zhou, S. Jiang, P. Fan, H. Hou, *Mater. Lett.*, 200 (2017) 97-100.
50. G. Duan, A. R. Bagheri, S. Jiang, J. Golenser, S. Agarwal, A. Greiner, *Biomacromolecules*, 18 (2017) 3215-3221.
51. L. Liu, H. Bakhshi, S. Jiang, H. Schmalz, S. Agarwal, *Macromol. Rapid Comm.*, 39 (2018) e1800082.
52. W. Ma, J. Zhao, O. Oderinde, J. Han, Z. Liu, B. Gao, R. Xiong, Q. Zhang, S. Jiang, C. Huang, *J. Colloid Interf. Sci.*, 532 (2018) 12-23.
53. M. Zhu, D. Hua, M. Zhong, L. Zhang, F. Wang, B. Gao, R. Xiong, C. Huang, *Colloid Interf. Sci. Commun.*, 23 (2018) 52-58.
54. X. Shi, Z. Xu, C. Huang, Y. Wang, Z. Cui, *Macromolecules*, 51 (2018) 2283-2292.
55. M. Zhu, D. Hua, H. Pan, F. Wang, B. Manshian, S. J. Soenen, R. Xiong, C. Huang, *J. Colloid Interf. Sci.*, 511 (2018) 411-423.
56. Z. Jiang, H. Zhang, M. Zhu, L. Dan, J. Yao, R. Xiong, C. Huang, *J. Appl. Polym. Sci.*, 135 (2017) 45766.
57. H. Xu, S. Jiang, C. Ding, Y. Zhu, J. Li, H. Hou, *Mater. Lett.*, 201 (2017) 82-84.
58. H. Yang, S. Jiang, H. Fang, X. Hu, G. Duan, H. Hou, *Spectrochimic. Acta. A*, 200 (2018) 339-344.
59. C. Luo, S. D. Stoyanov, E. Stride, E. Pelan, M. Edirisinghe, *Chem. Soc. Rev.*, 41 (2012) 4708-4735.
60. M. Zhu, J. Han, F. Wang, W. Shao, R. Xiong, Q. Zhang, H. Pan, Y. Yang, S. K. Samal, F. Zhang, C. Huang, *Macromol. Mater. Eng.*, 302 (2017) 1600353.

61. W. Ma, S. K. Samal, Z. Liu, R. Xiong, S. C. Smedt, B. Bhushan, Q. Zhang, C. Huang, *J. Membrane Sci.*, 537 (2017) 128-139.
62. Y. Chen, L. Sui, H. Fang, C. Ding, Z. Li, S. Jiang, H. Hou, *Compos. Sci. Technol.*, 174 (2019) 20-26.
63. G. Duan, S. Liu, S. Jiang, H. Hou, *J. Mater. Sci.*, 54 (2019) 6719-6727.
64. Z. Sun, E. Zussman, A. L. Yarin, J. H. Wendorff, A. Greiner, *Adv. Mater.*, 15 (2010) 1929-1932.
65. G. Duan, A. Greiner, *Macromol. Mater. Eng.*, (2019) 1800669.
66. K. Molnar, A. J. Hajdu, M. Zrinyi, S. Jiang, S. Agarwal, *Macromol. Rapid Comm.*, 38 (2017).
67. W. Ma, Z. Guo, J. Zhao, Q. Yu, F. Wang, J. Han, H. Pan, J. Yao, Q. Zhang, S. K. Samal, S. C. Smedt, C. Huang, *Sep. Purif. Technol.*, 177 (2017) 71-85.
68. W. Ma, Q. Zhang, S. K. Samal, F. Wang, B. Gao, H. Pan, H. Xu, J. Yao, X. Zhan, S. C. Smedt, C. Huang, *RSC Adv.*, 6 (2016) 41861-41870.
69. R. Liu, N. Cai, W. Yang, W. Chen, H. Liu, *J. Appl. Polym. Sci.*, (2009) NA-NA.
70. X. Zhang, V. Aravindan, P. S. Kumar, H. Liu, J. Sundaramurthy, S. Ramakrishna, S. Madhavi, *Nanoscale*, 5 (2013) 5973-5980.
71. V. J. Babu, A. S. Nair, Z. Peining, S. Ramakrishna, *Mater. Lett.*, 65 (2011) 3064-3068.
72. S. Jayaraman, V. Aravindan, P. S. Kumar, W. Ling, S. Ramakrishna, S. Madhavi, *Chem. Commun.*, 49 (2013) 6677-6679.
73. C. J. Buchko, L. Chen, Y. Shen, D. C. Martin, *Polymer*, 40 (1999) 7397-7407.
74. S. Megelski, J. S. Stephens, D. B. Chase, J. F. Rabolt, *Macromolecules*, 35 (2002) 8456-8466.
75. H. Fong, I. Chun, D. H. Reneker, *Polymer*, 40 (1999) 4585-4592.
76. G. Duan, S. Liu, H. Hou, *E-Polymers*, 18 (2018) 569-573.
77. P. Gupta, C. Elkins, T. Long, G. L. Wilkes, *Polymer*, 46 (2005) 4799-4810.
78. C. Wang, A. C. Hsu, J. Lin, *Macromolecules*, 39 (2006) 7662-7672.
79. S. Jiang, B. Uch, S. Agarwal, A. Greiner, *ACS Appl. Mater. Interfaces*, 9 (2017) 32308-32315.
80. J. Zhu, S. Jiang, H. Hou, S. Agarwal, A. Greiner, *Macromol. Mater. Eng.*, 303 (2018) 1700615.
81. S. Jiang, D. Han, C. Huang, G. Duan, H. Hou, *Mater. Lett.*, 216 (2018) 81-83.
82. S. Jiang, N. Helfricht, G. Papastavrou, A. Greiner, S. Agarwal, *Macromol. Rapid Commun.*, 39 (2018) e1700838.
83. S. V. Fridrikh, J. Yu, M. P. Brenner, G. C. Rutledge, *Phys. Rev. Lett.*, 90 (2003) 144502.
84. J. Tao, S. Shivkumar, *Mater. Lett.*, 61 (2007) 2325-2328.
85. W. Ma, Q. Zhang, D. Hua, R. Xiong, J. Zhao, W. Rao, S. Huang, X. Zhan, F. Chen, C. Huang, *RSC Adv.*, 6 (2016) 12868-12884.
86. M. Mirjalili, S. Zohoori, *J. Nano.Chem.*, 6 (2016) 207-213.
87. Q. Guo, X. Zhou, X. Li, S. Chen, A. Seema, A. Greiner, H. Hou, *J. Mater. Chem.*, 19 (2009) 2810.
88. S. He, X. Hu, S. Chen, H. Hu, M. Hanif, H. Hou, *J. Mater. Chem.*, 22 (2012) 5114.
89. M. S. Javed, S. Dai, M. Wang, Y. Xi, Q. Lang, D. Guo, C. Hu, *Nanoscale*, 7 (2015) 13610-13618.
90. H. Shirakawa, E. J. Louis, A. G. Macdiarmid, C. K. Chiang, A. J. Heeger, *J. Chem. Soc.*, 16 (1977) 578-580.
91. K. Wang, H. Wu, Y. Meng, Z. Wei, *Small*, 10 (2014) 14-31.
92. W. Jiang, D. Yu, Q. Zhang, K. Goh, L. Wei, Y. Yong, R. Jiang, J. Wei, Y. Chen, *Adv. Funct. Mater.*, 25 (2015) 1063-1073.
93. J. M. Ko, J. H. Nam, J. H. Won, K. M. Kim, *Synthetic Met.*, 189 (2014) 152-156.
94. Q. Hao, X. Xia, W. Lei, W. Wang, J. Qiu, *Carbon*, 81 (2015) 552-563.
95. Y. Miao, J. Yan, Y. Huang, W. Fan, T. Liu, *RSC Adv.*, 5 (2015) 26189-26196.
96. S. K. Simotwo, C. DelRe, V. Kalra, *ACS Appl. Mater. Interfaces*, 8 (2016) 21261-21269.
97. A. Rose, K. G. Prasad, T. Sakthivel, V. Gunasekaran, T. Maiyalagan, T. Vijayakumar, *Appl. Surf. Sci.*, 449 (2018) 551-557.
98. M. Tebyetekerwa, S. Yang, S. Peng, Z. Xu, W. Shao, D. Pan, S. Ramakrishna, M. Zhu, *Electrochim. Acta*, 247 (2017) 400-409.

99. Y. Wang, S. Li, S. Hsiao, W. Liao, P. Chen, S. Yang, H. Tien, C.M. Ma, C. Hu, *Carbon*, 73 (2014) 87-98.
100. K. Devarayan, D. Lei, H. Kim, B. Kim, *Chem. Eng. J.*, 273 (2015) 603-609.
101. C. Kim, S. Park, W. Lee, K. Yang, *Electrochim. Acta*, 50 (2004) 877-881.
102. Q. Liu, Y. Wang, L. Dai, J. Yao, *Adv. Mater.*, 28 (2016) 3000-3006.
103. P. F. Jao, K. T. Kim, G. J. Kim, Y. K. Yoon, *J. Micromech. Microeng.*, 23 (2013) 114011.
104. C. Ma, Y. Li, J. Shi, Y. Song, L. Liu, *Chem. Eng. J.*, 249 (2014) 216-225.
105. J. Sheng, C. Ma, Y. Ma, H. Zhang, R. Wang, Z. Xie, J. Shi, *Int. J. Hydrogen Energ.*, 41 (2016) 9383-9393.
106. C. Tran, D. Lawrence, F. W. Richey, C. Dillard, Y. A. Elabd, V. Kalra, *Chem. Commun.*, 51 (2015) 13760-13763.
107. B. Wang, G. Lu, Q. Luo, T. Wang, *J. Nanomater.*, 2016 (2016) 1-7.
108. C. Ma, Y. Song, J. Shi, D. Zhang, M. Zhong, Q. Guo, L. Liu, *Mater. Lett.*, 76 (2012) 211-214.
109. C. Ma, S. Ruan, J. Wang, D. Long, W. Qiao, L. Ling, *J. Colloid. Interf. Sci.*, 531 (2018) 513-522.
110. L. Wang, G. Zhang, X. Zhang, H. Shi, W. Zeng, H. Zhang, Q. Liu, C. Li, Q. Liu, H. Duan, *J. Mater. Chem. A*, 5 (2017) 14801-14810.
111. S. K. Simotwo, P. R. Chinnam, S. L. Wunder, V. Kalra, *ACS Appl. Mater. Interfaces*, 9 (2017) 33749-33757.
112. C. Kim, K. S. Yang, W. J. Lee, *Electrochem. Solid Lett.*, 7 (2004) A397.
113. C. Kim, K. S. Yang, *Appl. Phys. Lett.*, 83 (2003) 1216-1218.
114. C. Kim, B. T. Ngoc, K. S. Yang, M. Kojima, Y. A. Kim, Y. J. Kim, M. Endo, S. Yang, *Adv. Mater.*, 19 (2007) 2341-2346.
115. E. J. Ra, E. R. Piñero, Y. H. Lee, F. Béguin, *Carbon*, 47 (2009) 2984-2992.
116. S. Bhoyate, P. K. Kahol, B. Sapkota, S. R. Mishra, F. Perez, R. K. Gupta, *Surf. Coat. Tech.*, 345 (2018) 113-122.
117. H. Niu, J. Zhang, Z. Xie, X. Wang, T. Lin, *Carbon*, 49 (2011) 2380-2388.
118. X. Li, Y. Zhao, Y. Bai, X. Zhao, R. Wang, Y. Huang, Q. Liang, Z. Huang, *Electrochim. Acta*, 230 (2017) 445-453.
119. B. H. Kim, K. S. Yang, Y. A. Kim, Y. J. Kim, B. An, K. Oshida, *J. Power Sources*, 196 (2011) 10496-10501.
120. S. H. Kim, B. H. Kim, *Synthetic Met.*, 242 (2018) 1-7.
121. B. H. Kim, K. S. Yang, H. G. Woo, K. Oshida, *Synthetic Met.*, 161 (2011) 1211-1216.
122. K. H. Jung, W. Deng, D. W. Smith, J. P. Ferraris, *Electrochem. Commun.*, 23 (2012) 149-152.
123. B. H. Kim, K. S. Yang, J. P. Ferraris, *Electrochim. Acta*, 75 (2012) 325-331.
124. K. Huang, M. Li, Z. Chen, Y. Yao, X. Yang, *Electrochim. Acta*, 158 (2015) 306-313.
125. G. Duan, H. Fang, C. Huang, S. Jiang, H. Hou, *J. Mater. Sci.*, 53 (2018) 15096-15106.
126. D. W. Lawrence, C. Tran, A. T. Mallajoyula, S. K. Doorn, A. Mohite, G. Gupta, V. Kalra, *J. Mater. Chem. A*, 4 (2016) 160-166.
127. A. Choudhury, J. H. Kim, S. S. Mahapatra, K. S. Yang, D. J. Yang, *ACS Sustain. Chem. Eng.*, 5 (2017) 2109-2118.
128. K. Huang, Y. Yao, X. Yang, Z. Chen, M. Li, *Mater. Chem. Phys.*, 169 (2016) 1-5.
129. J. Ding, H. Zhang, X. Li, Y. Tang, G. Yang, *Mater. Design*, 141 (2018) 17-25.
130. C. Arup, D. Baban, M. S. Sinha, K. D. Won, Y. K. Seung, Y. D. Joo, *Nanotechnology*, 29 (2018) 165401.
131. X. Yan, Z. Tai, J. Chen, Q. Xue, *Nanoscale*, 3 (2011) 212-216.
132. G. Xue, J. Zhong, Y. Cheng, B. Wang, *Electrochim. Acta*, 215 (2016) 29-35.
133. M. Dirican, M. Yanilmaz, X. Zhang, *RSC Adv.*, 4 (2014) 59427-59435.
134. F. O. Agyemang, G. M. Tomboc, S. Kwofie, H. Kim, *Electrochim. Acta*, 259 (2018) 1110-1119.
135. Y. Cheng, L. Huang, X. Xiao, B. Yao, L. Yuan, T. Li, Z. Hu, B. Wang, J. Wan, J. Zhou, *Nano Energy*, 15 (2015) 66-74.

136. X. Song, J. Guo, M. Guo, D. Jia, Z. Sun, L. Wang, *Electrochim. Acta*, 206 (2016) 337-345.
137. N. Iqbal, X. Wang, A. A. Babar, J. Yan, J. Yu, S. Park, B. Ding, *Adv. Mater. Interf.*, 4 (2017) 1700855.
138. Y. Zeng, X. Li, S. Jiang, S. He, H. Fang, H. Hou, *Mater. Lett.*, 161 (2015) 587-590.
139. J. Zhou, J. Chen, S. Han, H. Zhao, J. Bai, Z. Yang, X. Mu, Y. Liu, D. Bian, G. Sun, Z. Zhang, X. Pan, E. Xie, *Carbon*, 111 (2017) 502-512.
140. Q. Dong, G. Wang, H. Hu, J. Yang, B. Qian, Z. Ling, J. Qiu, *J. Power Sources*, 243 (2013) 350-353.
141. P. Suktha, M. Sawangphruk, *Ind. Eng. Chem. Res.*, 56 (2017) 10078-10086.
142. W. K. Chee, H. N. Lim, Z. Zainal, I. Harrison, Y. Andou, N. M. Huang, M. Altarawneh, Z. Jiang, *Mater. Lett.*, 199 (2017) 200-203.
143. W. K. Chee, H. N. Lim, Y. Andou, Z. Zainal, A. A. Hamra, I. Harrison, M. Altarawneh, Z. Jiang, N. Huang, *J. Energ. Chem.*, 26 (2017) 790-798.
144. Z. Tai, X. Yan, J. Lang, Q. Xue, *J. Power Sources*, 199 (2012) 373-378.
145. B. H. Kim, C. H. Kim, K. S. Yang, A. Rahy, D. J. Yang, *Electrochim. Acta*, 83 (2012) 335-340.
146. H. K. Sang, I. K. Yong, J. H. Park, J. M. Ko, *Int. J. Electrochem. Soc.*, 4 (2009) 1489-1496.
147. D. Lei, X. Li, M. K. Seo, M. S. Khil, H. Y. Kim, B. S. Kim, *Polymer*, 132 (2017) 31-40.
148. K. S. Yang, B. H. Kim, *Electrochim. Acta*, 186 (2015) 337-344.
149. B. H. Kim, C. H. Kim, D. G. Lee, *J. Electroanal. Chem.*, 760 (2016) 64-70.
150. S. Lin, Y. Lu, Y. Chien, J. Wang, P. Chen, C. Ma, C. Hu, *J. Power Sources*, 393 (2018) 1-10.
151. D. G. Lee, C. M. Yang, B. H. Kim, *J. Electroanal. Chem.*, 788 (2017) 192-197.
152. S. Y. Kim, J. H. Wee, C. M. Yang, B. H. Kim, *J. Electroanal. Chem.*, 801 (2017) 403-409.
153. J. Wang, Y. Yang, Z. Huang, F. Kang, *Carbon*, 61 (2013) 190-199.
154. T. Wang, D. Song, H. Zhao, J. Chen, C. Zhao, L. Chen, W. Chen, J. Zhou, E. Xie, *J. Power Sources*, 274 (2015) 709-717.
155. F. Lai, Y. Miao, Y. Huang, T. Chung, T. Liu, *J. Phys. Chem. C*, 119 (2015) 13442-13450.
156. H. Niu, X. Yang, H. Jiang, D. Zhou, X. Li, T. Zhang, J. Liu, Q. Wang, F. Qu, *J. Mater. Chem. A*, 3 (2015) 24082-24094.
157. L. Li, X. Zhang, Z. Zhang, M. Zhang, L. Cong, Y. Pan, S. Lin, *J. Mater. Chem. A*, 4 (2016) 16635-16644.
158. Z. Tai, J. Lang, X. Yan, Q. Xue, *J. Electrochem. Soc.*, 159 (2012) A485-A491.
159. C. Ma, J. Sheng, C. Ma, R. Wang, J. Liu, Z. Xie, J. Shi, *Chem. Eng. J.*, 304 (2016) 587-593.
160. S. Y. Kim, B. H. Kim, *J. Power Sources*, 328 (2016) 219-227.
161. A. Aboagye, Y. Liu, J. G. Ryan, J. Wei, L. Zhang, *Mater. Chem. Phys.*, 214 (2018) 557-563.
162. Y. I. Kim, E. Samuel, B. Joshi, M. W. Kim, T. G. Kim, M. T. Swihart, S. S. Yoon, *Chem. Eng. J.*, 353 (2018) 189-196.
163. W. Zong, F. Lai, G. He, J. Feng, W. Wang, R. Lian, Y. Miao, G. Wang, I. P. Parkin, T. Liu, *Small*, 14 (2018) e1801562.
164. F. Lai, Y. Huang, Y. Miao, T. Liu, *Electrochim. Acta*, 174 (2015) 456-463.
165. Y. Xiao, H. Jun, Y. Xu, H. Zhu, K. Yuan, Y. Chen, *J. Mater. Chem. A*, 6 (2018).
166. K. Fu, L. Xue, O. Yildiz, S. Li, H. Lee, Y. Li, G. Xu, L. Zhou, P. D. Bradford, X. Zhang, *Nano Energy*, 2 (2013) 976-986.
167. S. Wang, L. Xia, L. Yu, L. Zhang, H. Wang, X. Lou, *Adv. Energy Mater.*, 6 (2016) 1502217.
168. S. H. Chung, P. Han, R. Singhal, V. Kalra, A. Manthiram, *Adv. Energy Mater.*, 5 (2015) 1500738.
169. L. Xia, S. Wang, G. Liu, L. Ding, D. Li, H. Wang, S. Qiao, *Small*, 12 (2016) 853-859.
170. Y. Zhao, Q. Lai, J. Zhu, J. Zhong, Z. Tang, Y. Luo, Y. Liang, *Small*, 14 (2018) e1704207.
171. T. Liu, Y. Guo, Y. Yan, F. Wang, C. Deng, D. Rooney, K. N. Sun, *Carbon*, 106 (2016) 84-92.
172. J. Fu, B. Zhu, W. You, M. Jaroniec, J. Yu, *Appl. Catal. B: Environ.*, 220 (2018) 148-160.
173. T. Zhang, Y. Hou, V. Dzhagan, Z. Liao, G. Chai, M. Loffler, D. Olianias, A. Milani, S. Xu, M. Tommasini, D. R. Zahn, Z. Zheng, E. Zschech, R. Jordan, X. Feng, *Nat. Commun.*, 9 (2018) 1140.

174. I. Jeong, J. Lee, K. L. Joseph, H. I. Lee, J. K. Kim, S. Yoon, J. Lee, *Nano Energy*, 9 (2014) 392-400.
175. H. Elbohy, A. Aboagye, S. Sigdel, Q. Wang, M. H. Sayyad, L. Zhang, Q. Qiao, *J. Mater. Chem. A*, 3 (2015) 17721-17727.

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