

Review

Recent Progress in Flexible Graphene-Based Composite Fiber Electrodes for Supercapacitors

Songmei Wu

Department of Textile and Garment, Anhui Vocational and Technical College, Hefei 230011, China; wusm@uta.edu.cn

Abstract: Graphene has shown the world its fascinating properties, including high specific surface area, high conductivity, and extraordinary mechanical properties, which enable graphene to be a competent candidate for electrode materials. However, some challenges remain in the real applications of graphene-based electrodes, such as continuous preparation of graphene fibers with highly ordered graphene sheets as well as strong interlayer interactions. The combination of graphene with other materials or functional guests hence appears as a more promising pathway via post-treatment and in situ hybridism to produce composite fibers. This article firstly provides a full account of the classification of graphene-based composite fiber electrodes, including carbon allotropy, conductive polymer, metal oxide and other two-dimensional (2D) materials. The preparation methods of graphene-based composite fibers are then discussed in detail. The context further demonstrates the performance optimization of graphene-based composite fiber electrodes, involving microstructure design and surface modification, followed by the elaboration of the application of graphene-based composite fiber electrodes in supercapacitors. Finally, we present the remaining challenges that exist to date in order to provide meaningful guidelines in the development process and prospects of graphene-based composite fiber electrodes.



Citation: Wu, S. Recent Progress in Flexible Graphene-Based Composite Fiber Electrodes for Supercapacitors. *Crystals* **2021**, *11*, 1484. <https://doi.org/10.3390/cryst11121484>

Academic Editors: Guorui Wang, Changhong Cao, Mahdi Hamidi and Rajratan Basu

Received: 4 November 2021

Accepted: 24 November 2021

Published: 30 November 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the author. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

Keywords: graphene; composite; flexible electrode; wearable electronics

1. Introduction

Stretchable and flexible electronics have gained tremendous attention and indicated a mainstream direction in modern electronics. They can be integrated comfortably and compliantly onto the compliant and dynamically deformable human body, in striking contrast to conventional rigid electronics devices [1,2]. In this context, flexible materials are required to fulfill these specific demands. Given the high flexibility, deformability, breathability, comfortability, weavability and lightweight of fibers and textiles, they are deemed as competent candidates for constructing wearable devices [3–5]. Smart textiles, integrating textiles with electronic technology, are hence expected to revolutionize personalized healthcare and play a crucial role in the continuing progress of human society.

To power wearable devices, the design and fabrication of energy conversion and storage devices has recently become the research focus. In particular, supercapacitors are promising energy storage devices which can complement batteries in miniaturized portable electronics, because they offer high power density, long lifetime, high charge/discharge rate and excellent cycle stability [6,7]. Commonly, based on the working mechanism, supercapacitors can be divided into electric double-layer capacitor (EDLC) and pseudo-capacitors [8–10]. Specifically, the energy storage of an EDLC originates from the separation of anions and cations in the electrolyte at the interface between the electrode material and electrolyte [11]. Pseudo-capacitors (also called faradaic capacitors) rely on the fast and reversible Faradaic oxidation-reduction reaction on the surface of the electrode material, which gives rise to electron charge transfer [12]. It is therefore clear that the electrode material acts as a key factor that determines the energy storage capability of supercapacitors [13].

Generally, a flexible fiber supercapacitor is comprised of conductive fibers as electrodes and electrolyte as a separator, where electrode materials essentially necessitate high flexibility, high mechanical strength, and excellent electrochemical performance [14,15]. So far, a variety of fiber-shaped electrodes has been developed. Polymer fibers with high deformability and mechanical strength as well as low cost can be simply exploited as electrode substrates; however, their poor conductivity greatly suppresses the electrochemical performance of the resulted fiber electrode. To this end, polymer fibers are usually composited with metals/metal oxide or carbon nanotubes (CNTs) to improve the conductivity [16,17]. Even so, the limited content of the conductive materials on the polymer fiber electrode results in a low capacitance of the polymer substrate fiber supercapacitor, which affects its working performance in practical applications. In addition, the complex process of metal coating and CNT growth (for example, by physical and chemical vapor deposition) will increase the cost of fabrication of fiber electrodes. By contrast, metal wires intrinsically possess high electrical conductivity that benefits the ion transport in electrolyte and reduces internal resistance, thus improving the electrochemical performance of fiber electrodes [18]. Nevertheless, the high density of metal wires poses significant challenges for metal wire-based fiber supercapacitors to achieve both high mass capacitance and volume capacitance at the same time. Compared to polymer fibers, metal wires also present higher rigidity and hardness, which are adverse to the stretchability and flexibility of devices. Moreover, some metal wire electrodes have high chemical activity, and possibly induce the chemical reaction between the electrolyte and the metal wire itself. Unlike insulated polymer fibers and heavy metal wires, fiber electrodes based on carbon nanomaterial, such as graphene and CNT, show advantages of high electrical conductivity, light weight, impressive flexibility and mechanical strength, as well as excellent chemical stability, making them optimal candidate materials for fiber electrodes of supercapacitors [19–21].

Extensive studies have found that graphene outperforms other carbon materials in terms of electrical and thermal conductivity as well as weavability when used for fiber electrodes [22–27]. As an emerging material in the field of energy storage, graphene has shown the world its fascinating properties, such as high impermeability [28–30], high electron mobility [31], high thermal conductivity [32,33], superlubricity [34–36], extraordinary elasticity and stiffness [37,38]. Particularly, the high electrical conductivity of graphene sheets could avoid the inclusion of conductive additives and enhance the energy density of graphene-based electrodes. Furthermore, its huge specific surface area facilitates the accessibility of electrolytes to graphene sheets. For instance, the intrinsic electrochemical double layer capacitance of monolayer graphene was reported to be around $21 \mu\text{F}/\text{cm}^2$ [39], which theoretically yields an electrochemical double layer capacitance up to $\sim 550 \mu\text{F}/\text{g}$ for a graphene-based supercapacitor, if the entire surface area of graphene could be fully utilized. The atomic thickness combined with high aspect ratio also renders graphene electrodes with excellent mechanical flexibility, allowing graphene sheets to be assembled into fibers and films with robust mechanical stability [40,41]. From the perspective of industrial production and application, graphene oxide (GO) and reduced graphene oxide (rGO) are more easily accessible, scalable, and cost-effective in contrast to pristine graphene. Graphene oxide, as a well-known chemically exfoliated derivative, can be dispersed into various solvents due to the presence of carboxylic and hydroxyl groups [42,43]. These oxygen functional groups also provide strong interactions with other materials, thus facilitating the assembly process to form composite fibers. Although the introduction of defects results in a mechanical degradation of GO, the denser stacking structure and strong interfacial bonding allow a more efficient stress transfer between GO layers; therefore, the GO-based fibers exhibit even better mechanical performance than pristine ones. Furthermore, GO can be transformed back into rGO, with partial restoration of the graphitic structure accomplished by chemical or thermal reduction [44]. Both the electrical conductivity and mechanical stiffness/strength are improved, which are favorable for the design of graphene-based fiber electrodes. The low cost and high solution processability further benefit the mass production of materials and devices.

Graphene fibers, as a one-dimensional (1D) macroscopic graphene assembly, have demonstrated superior physical properties, including high Young's modulus (~ 400 GPa), tensile strength (~ 2.2 GPa) [45], electrical conductivity ($\sim 2.2 \times 10^7$ S/m) [46], and thermal conductivity (~ 1575 W/mK) [47]. However, the creation of graphene fibers still presents difficulties in fabrication of continuous and highly ordered graphene sheets with strong interlayer interactions. One effective way is to integrate graphene fibers with other materials or functional guests via post-treatment and in situ hybridism to produce composite fibers [48,49]. In this article, differing from previous reviews [27,50–53], we narrow the scope to graphene-based composite fibers and present their applications in electrodes for flexible supercapacitors. The article is organized based on the classification of composite materials, offering a guideline in light of material selection, which is instrumental for the design of high-performance supercapacitors oriented to a specific application on demand. Special emphasis is then placed on the material preparation, configuration design, and electrochemical performance. In addition, existing challenges and future prospects are also presented toward improving the energy storage performance of graphene-based composite fiber supercapacitors and accelerating their applications on the wearable electronics.

2. Classification of Graphene-Based Composite Fiber Electrodes

The combination of graphene fibers with other functional materials is capable of optimizing their specific properties while maintaining the structural order in composite fibers. The introduced guest molecules cover a wide range of compositions, from ions to carbon materials, polymers, and metal oxides. Note that some insulating organic polymers such as poly(vinylidene fluoride) (PVDF), poly(tetrafluoroethylene) (PTFE), and carboxy methyl cellulose (CMC) have been used to adhere the electrode material to the current collector [54]. However, they usually limit the electrical conductivity, reduce ionic conductivity due to their hydrophobicity, and degrade specific capacitance by adding inactive weight to the electrode. Therefore, they are out of the discussion here and we will focus on those materials with an active role in the total capacitance of the supercapacitors favoring the synergistic effects.

2.1. Carbon Allotropy

Carbon-based materials, including graphene, CNTs, carbon nanofibers, and activated carbon, commonly consist of the main active materials for electrodes of supercapacitors [24]. Integrating graphene with different carbon allotropes can leverage the respective advantages to produce graphene composite materials with unique properties. For example, CNT dispersions were mixed with graphene oxide (GO) to produce composite fiber electrodes, as shown in Figure 1a, and the stacked graphene sheets were successfully aligned to the axis of the fiber (Figure 1b). The morphology of the CNT/GO fiber in the SEM image (Figure 1c) was found to be distinctive with highly porous and rugged surfaces as compared to that of the pristine graphene fiber. Furthermore, the intercalation of CNTs in graphene fibers as spacers can increase the interlayer spacing between graphene layers and make a contribution to the effective ion accessibility of graphene. Meanwhile, the increased porosity also improved the ion exchange efficiency. Consequently, the electrical conductivity and hence specific capacitance were both augmented [55–57]. Their synergistic effect resulted in obvious enhancements in the electrochemical performance [58].

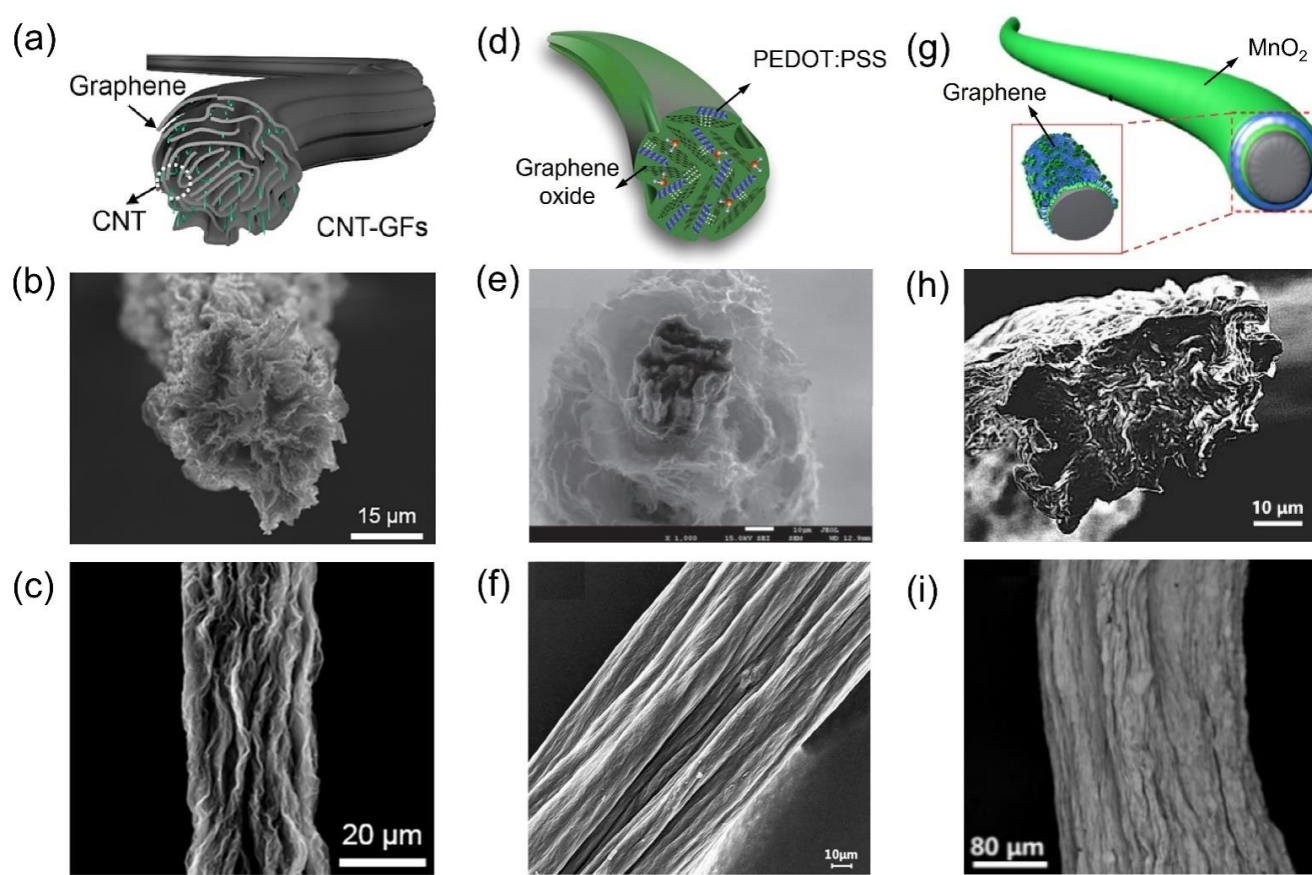


Figure 1. (a) Schematic, (b) surface SEM image, and (c) cross section SEM image of graphene/CNT composite fiber [55] (copyright permission American Chemical Society 2019); (d) Schematic, (e) surface SEM image, and (f) cross section SEM image of graphene/PEDOT:PSS composite fiber [58,59] (copyright permission Elsevier 2018, Wiley-VCH 2013); (g) Schematic, (h) surface SEM image, and (i) cross section SEM image of graphene/MnO₂ composite fiber [60,61] (copyright permission Elsevier 2021, Wiley-VCH 2020).

2.2. Conductive Polymer

Conductive polymers, such as polyacetylene (PA), polyaniline (PANI), polypyrrole (PPy), poly(3,4-ethylenedioxythiophene) (PEDOT) and polythiophenes (PTs) are intrinsically conductive thanks to the presence of the π -conjugated bond structures [62]. The instability of the capacitors based on conductive polymers during long-term charge/discharge cycling is one of their most lethal deficiencies. It has been demonstrated that, in the graphene/PANI composite, graphene acts as the framework for sustaining PANI nanofibers to prevent the fibers from severely swelling and shrinking during cycling, improving the cyclic stability [63]. In turn, as typical pseudocapacitive materials, conductive polymers will bring extra capacitance to graphene electrodes through the Faraday process [64–66]. Typically, the graphene-based composite fiber can be created either by randomly mixing or surface coating of polymer on graphene fibers. For the former, the resulted polymer composite can present different microscopic architectures depending on the preparation methods. Specifically, the methods relying on the fluid assembly can generate layered structures, where the graphene plays a templating role to arrange the ordering of hierarchical structures over a long range. For example, Qu's group [67] designed a microfluidic spinneret through which GO and polyvinyl alcohol (PVA)/alginate sodium component can be spontaneously extruded from one outlet, producing a GO/PVA-alginate/GO layered structure. The laminar flow within one microfluidic spinneret ensured the clear boundary of each component without unwanted mixing. In contrast to random distribution of graphene in a polymer matrix, polymer chains are more effectively absorbed or grafted

onto graphene sheets and fill in the interlayer galleries within the layered architecture. In this case, the restacking of the graphene sheets can be prohibited, and the specific surface area of the composites is accordingly increased because of the uniform distribution of graphene sheets. As shown in Figure 1e,f, more wrinkles with many pores are introduced inside the composite fibers, and largely facilitate the sufficient exposure of graphene sheets to the electrolyte for the access of ions, which benefits the electrochemical performance as well [55]. More importantly, the consequent layer microstructures are reminiscent of nacles with brick-mortar features. Instead of weak van der Waals (vdW) interactions, stronger physical or chemical crosslinks (e.g., hydrogen bond) will be formed between graphene layers, thus improving simultaneously the strength and toughness of graphene fibers [68–71]. The enhanced mechanical performance is critical to the stability and durability of energy devices.

2.3. Metal Oxide

Previous studies showed that the use of nanostructured metal oxides (such as MnO_2 , Fe_3O_4 , NiO) as faradaic electrodes is helpful for an energy density increase [72]. In supercapacitors, metal oxides afford higher pseudo-capacitance through bulk redox reactions compared to carbon materials; however, the large volume variation-induced structural change destroys the stability of electrodes, leading to severe capacity fading during charge/discharge processes [73]. To this end, fabrication of graphene/metal oxide composites is expected to be an effective and practical method to alleviate stability issues. First of all, graphene serves as a support for uniformly anchoring or dispersing metal oxide nanostructures with well-defined sizes, shapes and crystallinity, as depicted in the schematic in Figure 1g. Secondly, as shown in Figure 1h,i, graphene sheets and metal oxide nanorods can be evenly dispersed in the fibers. Graphene assists to suppress the volume change and particle agglomeration of metal oxides during the charge–discharge process. Thirdly, graphene plays as a 2D conductive template for building a 3D interconnected conductive porous network to improve the electrical conductivity and charge transport of pure metal oxides. Furthermore, metal oxides between graphene layers can restrict the aggregation and restacking of graphene sheets induced by vdW forces, as well as increasing the available electrochemical active surface area. Due to these synergistic effects, integration of metal oxides and graphene in a composite fully leverages each active component and accounts for excellent electrochemical performance [73].

2.4. Other Layered Materials

Atomically thin nanosheets, such as clay and other 2D materials, exhibit similar surface morphology and rich electrical, thermal, and electrochemical properties as graphene. Integration of these 2D nanosheets into graphene fibers can on one hand facilitate the scalable production; on the other hand, they also remedy the mechanical or transport defects of graphene fibers and translate their fascinating attributes into macroscopic assemblies. For example, montmorillonite (MMT) was also considered for effective sub-size spacers to induce looser restacking but also to avoid causing the non-linkage of graphene sheets [74]. Beyond that, a large amount of Si–O and –OH groups on clay endow it with high hydrophilicity, which not only improves the interface strength with graphene sheets, but also benefits the dispersion in aqueous solution that fits for the spinning process [75]. Consequently, the improved hydrophilicity and orderly aligned graphene sheets within the graphene/clay composite fibers facilitate the electrolyte diffusion and absorption across the fiber, thus accounting for enhanced capacitive performance compared to pure graphene fibers.

3. Preparation Methods of Graphene-Based Composite Fibers

The preparation methods dictate the precision of graphene-based electrodes and play a significant role in the electrochemical performance of supercapacitors. Several earlier reviews have comprehensively discussed the manufacturing and processing of graphene fibers [52,76,77]. Commonly used methods including hydrothermal method [78], wet spin-

ning [57], and dry spinning methods [79] were introduced in detail. Besides, there are also some other preparation techniques reported in the literature, such as the chemical vapor deposition (CVD)-assisted method [80,81] and electrophoretic self-assembly method [82], as summarized in Figure 2. Herein, we instead pay attention to the approaches to fabricate graphene-based fibers in composite form. Generally, we can either mix the graphene and other complementary materials in spinning solutions before the fiber production or deposit graphene coating on as-prepared fibers.

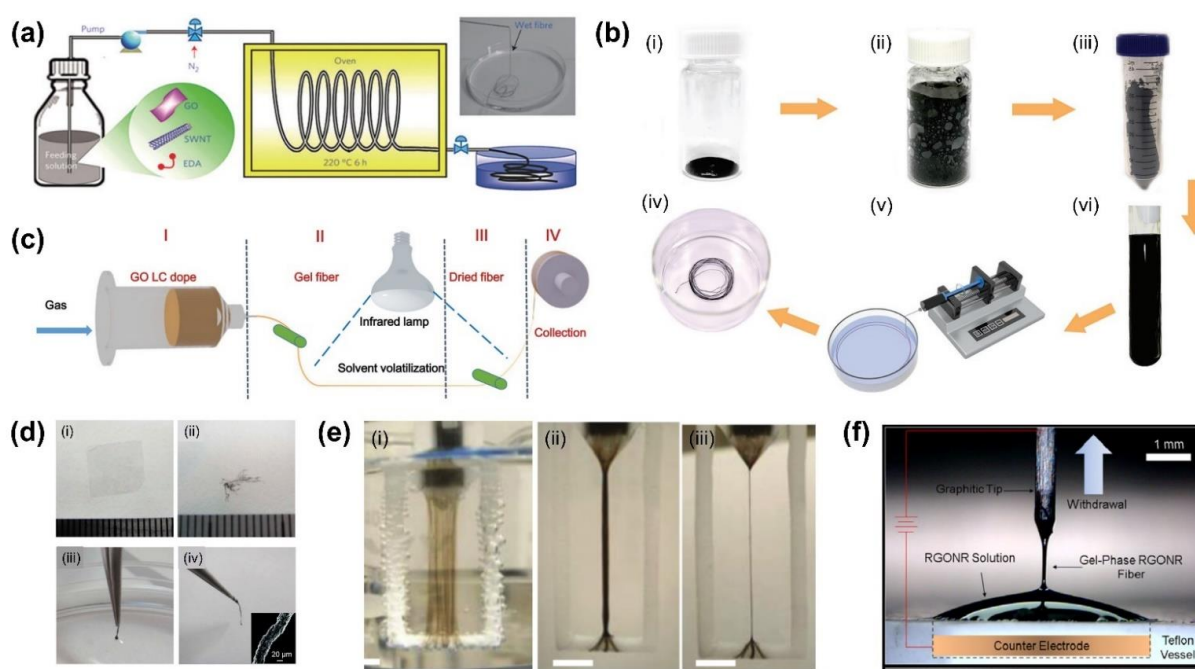


Figure 2. (a) Schematic of the hydrothermal fabrication procedures of CNT/graphene fibers [78] (copyright permission Nature Publishing Group 2014); (b) Schematic illustration of the fabrication of the wet-spun CNT/graphene hybrid fiber [57] (copyright permission Wiley-VCH 2017); (c) Schematic illustration of the dry spinning process with a concentrated organic dispersion of GO [79] (copyright permission The Royal Society of Chemistry 2017); (d) CVD graphene film to fiber self-assembly [80] (copyright permission American Chemical Society 2011); (e) Illustration of the sequential step process of graphene nanoribbon yarn fabrication [81] (copyright permission Wiley-VCH 2012); (f) Photograph of a reduced graphene oxide nanoribbon fiber formed by the electrophoretic self-assembly method [82] (copyright permission IOP Publishing 2012).

3.1. Solution Mixing

Solution mixing is the most widely applied method for production of graphene-based composites. Commonly, graphene suspension is mixed with a second phase (e.g., CNT, polymer resin, metal oxide, etc.) either in the same solvent or in a mixed solvent via the shear mixing or stirring process. Then the continuous fibers can be collected by wet spinning or other fiber preparation methods as discussed above. For example, Zeng et al. [57] have developed hybrid CNT/graphene fibers using the wet-spinning strategy, followed by electrodeposition of PANI to achieve a high-performance composite supercapacitor. Therein, thermally exfoliated graphene flakes are dissolved in chlorosulfonic acid without aggregation and mixed with liquid-crystal CNTs as a spinning solution. One thing should be noted: that, for aqueous spinning solutions in most studies, GO is usually used as starting material. This is because pristine graphene is bonded by weak vdW interactions, which makes it difficult to prepare for spinning solutions where the graphene flakes can be uniformly dissolved and to reform graphene sheets into a fixed attachment. Instead, introduction of oxygen functional groups can improve the interlayer bonding and facilitate the dispersion of graphene into water or polar organic solvents [42]. Therefore, after the spinning process, the dried GO fibers require subsequent reduction processes to repair the lattice defects of the graphene structure

and recover electrical conductivity. Chemical reduction processes by chemical reagents, photocatalysis, or electrochemical reduction, and the thermal reduction via thermal annealing and microwave have been extensively conducted [83].

3.2. In Situ Polymerization

In situ polymerization is another effective approach to prepare graphene/polymer composites with uniform dispersion and strong interface of graphene sheets in polymer matrix. In this case, graphene materials are mixed and swollen in a monomer solution firstly and then ultrasonically dispersed in the solution. The polymerization process commences via heat or radiation with the presence of a specific oxidizing agent. Finally, the composites are used to produce fibers via melt spinning, electrostatic spinning, wet spinning, or other abovementioned ways. Jiang et al. [84] have reported the fabrication of polyacrylic acid (PAA) and GO composite fibers via the in situ polymerization method. Therein, the acrylic acid and initiator were firstly mixed with GO aqueous solution with the aid of ultrasound. Upon in situ polymerization of acrylic acid at 60 °C, the homogenous GO/PAA gel was prepared, which was used to collect fibers by the melt spinning process, as shown in Figure 3a. In addition, in situ polymerization can also be employed to fabricate polymer coating wrapping around wet-spun graphene fibers. For instance, Zhang et al. [85] demonstrated the preparation of graphene/PANI composite fibers by in situ polymerization of aniline monomer on graphene fibers synthesized by the wet-spinning method and a chemical reduction process.

3.3. CVD Growth

Chemical vapor deposition (CVD) is a relatively developed technology to grow large-area and high-quality graphene films [86]. Graphene can be deposited on a temporary metal substrate and then transferred onto the textile preforms or directly deposited on the textile preforms. The growth process is carried out under a vapor phase, whereby the starting material of graphene is initially prepared in vapor form, flowed, and subjected to a very high temperature along with the targeted substrate; hence, the coating films present a very fine and even morphology [87]. Xiong et al. [88] have documented a catalyst-free process to grow graphene perpendicularly on carbon fiber cloth with the plasma-enhanced CVD method. Likewise, Zeng et al. [89] demonstrated a 3D graphene assembly achieved by vertically growing graphene sheets on carbon nanofibers (Figure 3b). The rich nanosized pores were found to benefit from a high electrical conductivity.

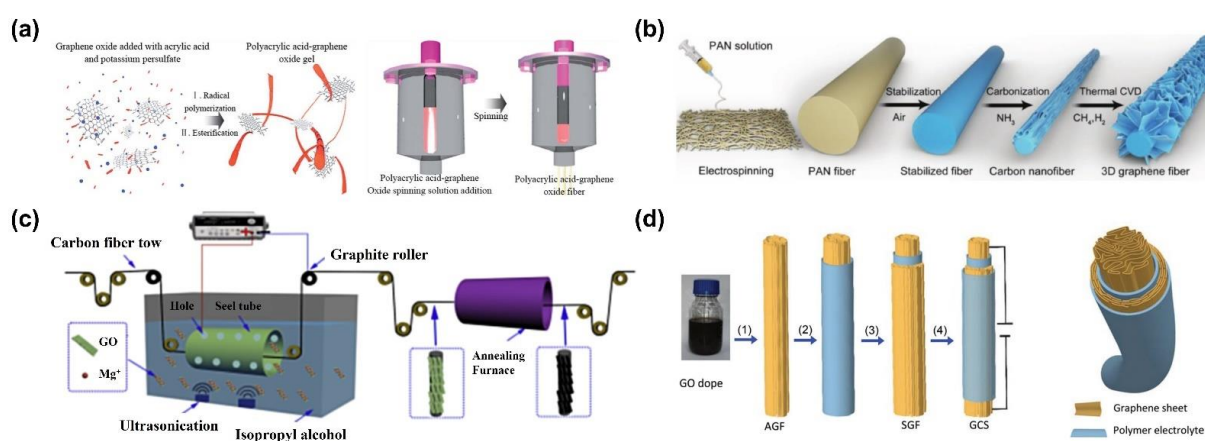


Figure 3. (a) Preparation of GO/PAA gels where the PAA is in situ polymerized in GO aqueous solution, and subsequent spinning of composite fibers [84] (copyright permission Royal Society of Chemistry 2013); (b) Preparation of composite fibers by thermal CVD growth of graphene on electrospun PAN nanofibers [89] (copyright permission Wiley-VCH 2017); (c) The scheme of EPD deposition of GO onto carbon fiber surfaces [90] (copyright permission Elsevier 2016); (d) Schematic illustration of the fabrication process of a graphene coaxial fiber supercapacitor via wet-spinning, chemical reduction and multiple dip-coating of polymer electrolyte and GO gel [91] (copyright permission Royal Society of Chemistry 2015).

3.4. Electrophoretic Deposition

The negatively charge, high mobility, as well as abundant hydrophilic oxygen-containing functional groups on GO make it suitable for electrophoretic deposition (EPD) solution. Typically, fiber or textile preforms are mounted onto the anode, towards which the negatively charged GO moves when an electrical voltage is applied to the electrodes immersed in the solution, until GO sheets are deposited on the surface of fibers. Despite of the advantages, including high deposition rate and throughput, good uniformity and controlled thickness of the coating films, there still remain some drawbacks with the EPD method, such as generation of bubbles in the electrolysis process. To this end, water can be replaced by isopropyl alcohol to serve as the electrolytic solution as presented in Figure 3c, which helps increase the dispersibility of GO and the deposition efficiency [90].

3.5. Direct Coating

Coating graphene and its derivatives on fibers is a direct way to prepare composite supercapacitor electrodes. Commonly used methods include dip coating and spray coating. Zhao et al. [91] designed and prepared a novel graphene-based coaxial fiber supercapacitor with two electrodes of a core fiber and a dip-coated cylinder sheath, as depicted in Figure 3d. The axial graphene fiber was firstly assembled by liquid crystal wet-spinning from GO followed by the chemical reduction. A polyvinyl alcohol (PVA) gel layer was then dip-coated on the graphene fiber, acting as the electron separator between the two electrodes. Subsequently, the polymer-coated graphene fiber was dip-coated in GO solution to form a GO gel layer, which is conductive after chemical reduction by hydroiodic acid. Finally, the dip coating of the PVA layer was repeated to fabricate an integrated supercapacitor. A similar coaxial fiber supercapacitor was also realized for hybrid graphene/MnO₂ systems by multiple dip coating processes [61]. As the device performance greatly rests on the adhesion between coating layer and fibers, additives or binders such as carbon black and polyvinylidene fluoride (PVDF) were used to improve the interfacial interactions, while maintaining the electrical conductivity at the electrode material/substrate interface [92]. The details of preparation of different graphene-based composite fibers are listed in Table 1.

Table 1. Preparation of different graphene-based composite fibers.

Electrodes	Preparation Methods	Electrolyte	Agents	Time/Temperature	Ref.
Graphene + Carbon Allotropy					
rGO/CNT	Wet spinning + hydrothermal activation	PVA/KOH	H ₂ O ₂ + NH ₄ OH	Chemical reduction with HI at 80 °C for 6 h; Dried at 60 °C for 30 min	[55]
SWNT/nitrogen-doped rGO	Hydrothermal process in fused-silica capillary column	PVA/H ₃ PO ₄	ethylenediamine	Hydrothermal reaction at 220 °C for 6 h; Dried at room temp. for 4 h	[78]
GO/CNT	Biscrolling method	PVA/H ₃ PO ₄	NA	Chemical reduction with HI at 80 °C for 8 h; Dried in vacuum for 12 h	[93]
rGO/CNT	Low-temperature chemical reduction assembly method	NA	Vitamin C	Dried in air at 40 °C	[94]
rGO/CNT	Dry spinning of CNT fiber + dip coating of GO	PVA/H ₃ PO ₄	NA	NA	[95]
Graphene/active carbon	Wet spinning	PVA/H ₃ PO ₄	NA	Chemical reduction with HI at 95 °C for 12 h; Dried at 60 °C for 12 h	[96]
rGO/active carbon	Wet spinning	PVA/LiCl	KOH	Chemical reduction with HI at 95 °C for 12 h; Dried at room temp. overnight	[97]

Table 1. Cont.

Electrodes	Preparation Methods	Electrolyte	Agents	Time/Temperature	Ref.
Graphene + Conductive Polymer					
rGO/PEDOT:PSS	Hydrothermally process in a sealed mold pipe	PVA/H ₃ PO ₄	Vitamin C	Chemical reduction at 90 °C	[98]
rGO/PEDOT:PSS rGO//PANI rGO/PPy	Wet spinning + in situ polymerization	PVA/H ₂ SO ₄	NA	Chemical reduction with HI at 65 °C for 6 h;	[99]
Graphene/PANI	Wet spinning + thermal annealing + dip coating	PVA/H ₂ SO ₄	NA	Thermal annealing at 800 °C for 3 h; Dip coating at 0 °C for 24 h under slight stirring	[49]
Graphene/PPy	Wet spinning	PVA/H ₂ SO ₄	NA	Chemical reduction with HI at 80 °C for 8 h	[100]
rGO/PANI	Macromolecular self-assembly	PVA/H ₂ SO ₄	NA	Reduction at 180 °C for 12 h	[62]
Graphene + Metal Oxide					
rGO/MnO ₂	Wet spinning + electrodeposition	PVA/H ₃ PO ₄	NA	Chemical reduction with HI at 80 °C	[48]
rGO/MnO ₂	Wet spinning	PVA/H ₃ PO ₄	NA	Dried at 60 °C in vacuum; Reduction at 85 °C for 24h	[101]
Graphene/MnO ₂	Self-assembly of CVD graphene + MnO ₂ deposition	PVA/H ₃ PO ₄	NA	CVD growth at 1000 °C within 5 min with Ar/H ₂ /CH ₄ ; MnO ₂ deposition at 80 °C for 6 min	[102]
GO/MnO ₂	Electrochemically electrolyzing GO on graphene fiber + MnO ₂ deposition	PVA/H ₃ PO ₄	NA	Baked in an oven at 230 °C for 2 h	[103]
Graphene + Layered Materials					
rGO/MoS ₂	Wet spinning + hydrothermal process	PVA/H ₂ SO ₄	NA	Chemical reduction with HI/acetic acid at 90 °C for 8 h; Hydrothermal reaction at 200 °C for 24 h	[104]
rGO/MoS ₂	Hydrothermal process	PVA/H ₂ SO ₄	NA	Hydrothermal reaction at 220 °C for 6 h; Dried in air for 2 h	[105]
rGO/Mxene	Wet spinning	PVA/H ₃ PO ₄	NA	Chemical reduction with HI/acetic acid at 90 °C for 12 h	[106]
rGO/Mxene	Wet spinning + twisting	PVA/H ₂ SO ₄	NA	NA	[107]
rGO/Mxene	Wet spinning	PVA/H ₂ SO ₄	NA	Chemical reduction with HI/acetic acid at 85 °C for 12 h	[108]
rGO/clay	Non-liquid-crystal spinning	PVA/H ₂ SO ₄	NA	Chemical reduction with HI/acetic acid at 85 °C for 9 h; Dried at 60 °C in vacuum	[74]

4. Performance Optimization of Graphene-Based Composite Fiber Electrodes

The electrochemical performance of graphene-based composite fiber electrodes is determined by numerous factors, such as the preparation method, graphene flake size, the selection of second phase material and its concentration in composite [52]. In reality, these factors essentially affect the microstructure and interfaces in composite fibers. Therefore, while different optimization strategies have been proposed, they can be briefly classified into two categories: (1) microstructure design and (2) surface modification. The ultimate purpose is to prevent the restacking of graphene sheets and increase the specific surface area, eventually realizing the enhancement of the electrochemical performance of fiber electrodes.

4.1. Microstructure Design

The ideal carbon electrode should have a hierarchical porous structure, including a mass of micropores (pore size < 2 nm) to promote charge storage, an appropriate amount of narrowly distributed mesopores (diameter ~ 2 –50 nm) to increase ion transport, and a small number of macropores (diameter > 50 nm) serving as the buffer region [109–112]. Design of a hierarchical porous carbon-based fiber electrode is very important for the creation of high-performance supercapacitors. In this scenario, Zheng et al. [113] developed a scalable and cost-effective method to prepare hierarchically porous core-sheath graphene-based fiber electrodes with a rational pore size distribution (88–97% micropores, 0–8.3% mesopores, and 1.9–4.2% macropores) and high specific surface area (up to $416.4 \text{ m}^2/\text{g}$), as shown in Figure 4. The hierarchical architecture was achieved by decorating wet-spun graphene fiber with carbonized phenol formaldehyde (CPF) resin containing small-size graphene (SG). The encompassment of CPF and small-size graphene synergistically brought about ultrahigh micro-porosity and increased electrical conductivity, promoting ion storage and transport performance. Qu's group recently has fabricated all graphene core-sheath fibers, in which a graphene fiber core is wrapped by a sheath of 3D porous network-like graphene framework through an electrochemically electrolyzing process. The high electronic conduction of the graphene fiber and the high specific surface area of 3D graphene network combined contributed to the electrochemical performance of the fiber-based supercapacitor [59].

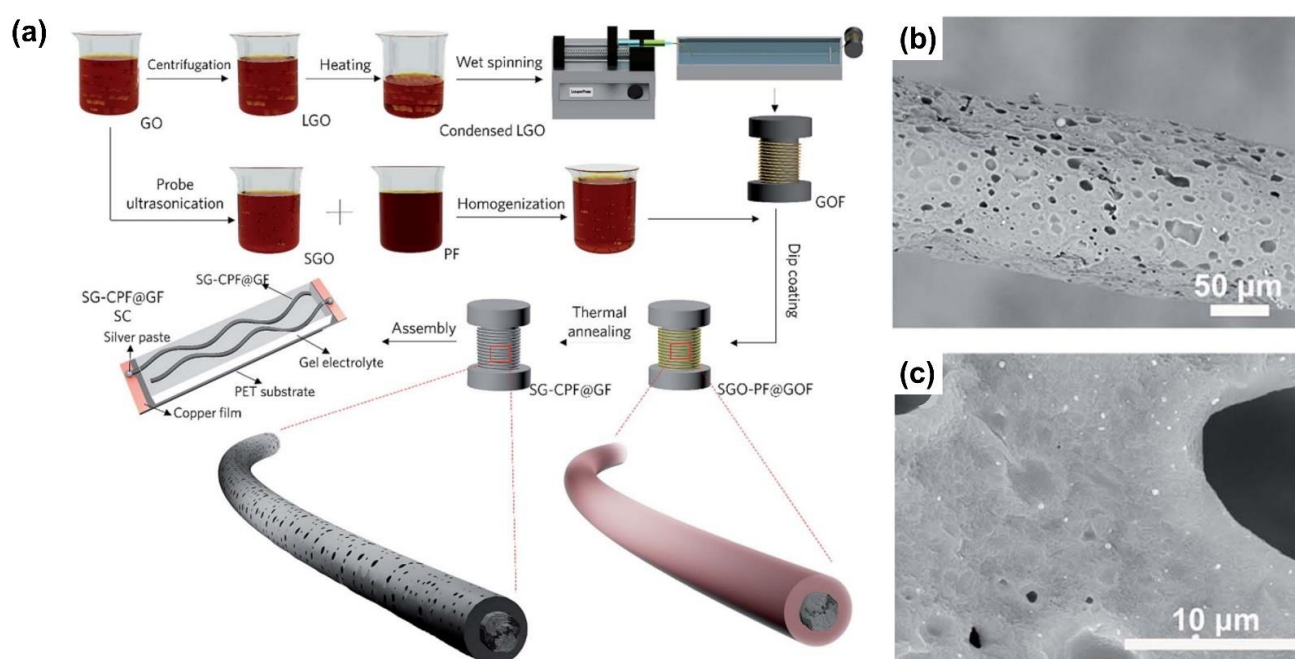


Figure 4. (a) Schematic illustration showing the roadmap for producing hierarchically porous core-sheath graphene-based fiber electrodes; (b,c) SEM imaging showing the typical porous structure along the fiber axis, confirming the presence of mesopores and macropores [113] (copyright permission Royal Society of Chemistry 2018).

In fact, during the wet spinning process, the drying of graphene fibers typically leads to a shrinkage and the induced capillary force forces graphene sheets to contract inward and buckle into a wrinkled structure of varying conformations [79]. With amplitudes ranging from nanometers to micrometers, multiscale wrinkles can also significantly increase the porosity and hence specific surface area of electrode materials, yielding remarkable electrochemical and energy-storing properties. For example, Zhang et al. [114] compared the effect of different preparation methods (i.e., thermal reduction vs. chemical reduction) on a flexible fibrous graphene electrode's performance. As shown in Figure 5a,b, the surface of the fiber electrode reduced by hydroiodic acid exhibits distributed wrinkles, which are caused by turbostratic stacking of graphene sheets, and the cross-section image consequently presents obvious pores. In contrast, the wrinkles after thermal reduction almost disappear, giving rise to a uniform and intact surface; the graphene sheets are also partially connected according to the cross-section images, as shown in Figure 5c,d. This is because of the graphitization of GO during the high temperature annealing process. This would hinder the electrolyte ions' diffusion and result in poor capacitance performance.

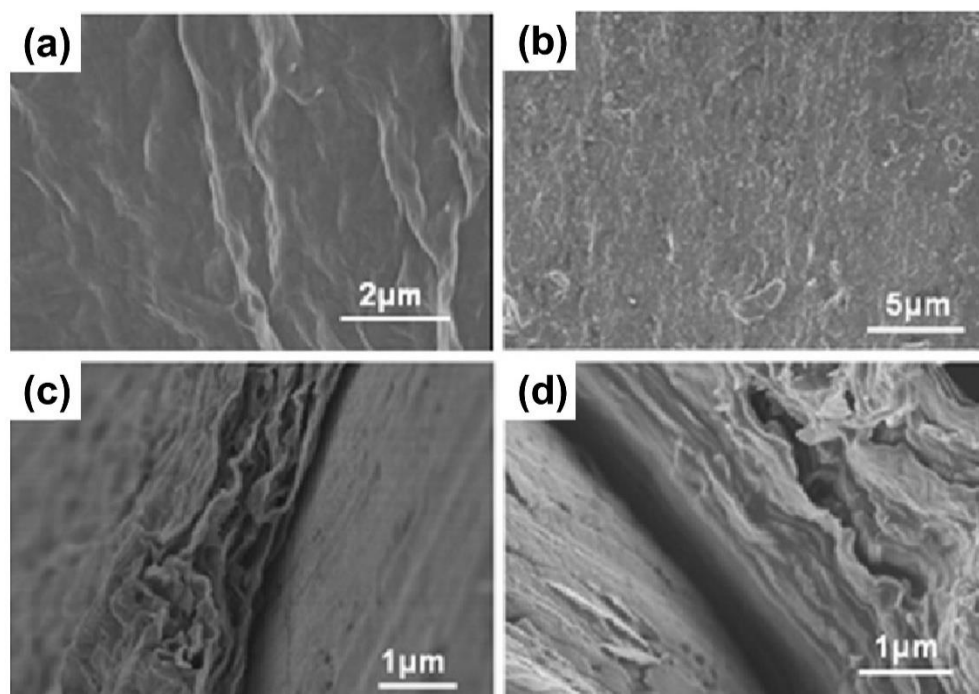


Figure 5. (a) Top and (b) cross-section SEM image of the graphene-based fiber electrode by chemical reduction; (c) Top and (d) cross-section SEM image of the graphene-based fiber electrode by thermal reduction [114] (copyright permission Wiley-VCH 2020).

In addition, the wrinkled structure also favors the flexibility as well as interfacial bonding of graphene-based composite fibers [115]. Nonetheless, from the mechanical perspective, these voids and random wrinkles also act as defects within graphene fibers (Figure 6) and are fatal to the mechanical and durability performance of composite fibers. Defect engineering strategies are therefore required to tune the wrinkled structure and porosity of graphene-based fiber, in order to reach a balance between the mechanical degradation and the electrochemical performance enhancement. In this respect, Gao's group [45] has carried out a series of studies exploiting a continuous stretching strategy to attain the optimal alignment of GO sheets, allowing the possibility of voids and an inhomogeneous structure. As a consequence, the as-obtained graphene fiber exhibited an ultrahigh stiffness and tensile strength, as well as high electrical conductivity attributed to the suppressed defects.



Figure 6. Structural model and corresponding electron images of multiscale defects in graphene-based fibers, including rough surface with random wrinkles, inhomogeneous core-sheath structure, default stacking and voids, and amorphous laminates of defective graphene sheets [45] (copyright permission Wiley-VCH 2016).

4.2. Surface Modification

Introducing hetero-molecules/atoms into graphene-based fibers not only improves their specific properties, but also extends their functionalities. Generally, functional groups or heteroatoms containing oxygen, nitrogen, and sulfur can be introduced to reconstruct and optimize hybrid graphene composite fibers through surface modification without damaging the 3D order. In particular, nitrogen or sulfur doping can effectively increase the capacitance of carbon-based materials, while oxygen-containing functional groups have been also demonstrated to endow graphene with tunable physical and chemical properties to achieve desirable applications. For example, Liu et al. [46] investigated the effects of different dopants on the conductivity of graphene fibers by doping graphene fibers at high temperatures. They found that doping of FeCl_3 , bromine, and potassium could all increase the conductivity of graphene fibers, setting the new records for graphene fibers reported in the literature. The obtained high conductivities were ascribed to the effective increment in carrier concentration after doping as well as the high carrier mobility stemming from graphene building blocks. Nitrogen-doped graphene fiber electrodes were also synthesized by microfluidic-directed strategy, as shown in Figure 7a [116]. The nitrogen-active site was found to contribute to enhancing the surface charge density and the interaction with ions in the electrode, leading to ultra-large capacitance and record high output energy density. Chen et al. [117] reported a hydrothermal process for controlled synthesis and structural modification of the nitrogen-doped graphene hydrogel by employing organic amine and graphene oxide as precursors. The organic amine not only offered a nitrogen source to obtain the nitrogen-doped graphene but was also an important modification to control the assembly of graphene sheets in 3D structures, giving rise to an enhancement of the electrochemical performance for supercapacitors. Even at an ultrafast charge/discharge rate of 185 A/g, with a specific capacitance of 113.8 F/g, a high power density of 205.0 kW/kg can be achieved. Besides that, 95.2% of the capacitance was retained at a current density of 100 A/g after 4000 cycles.

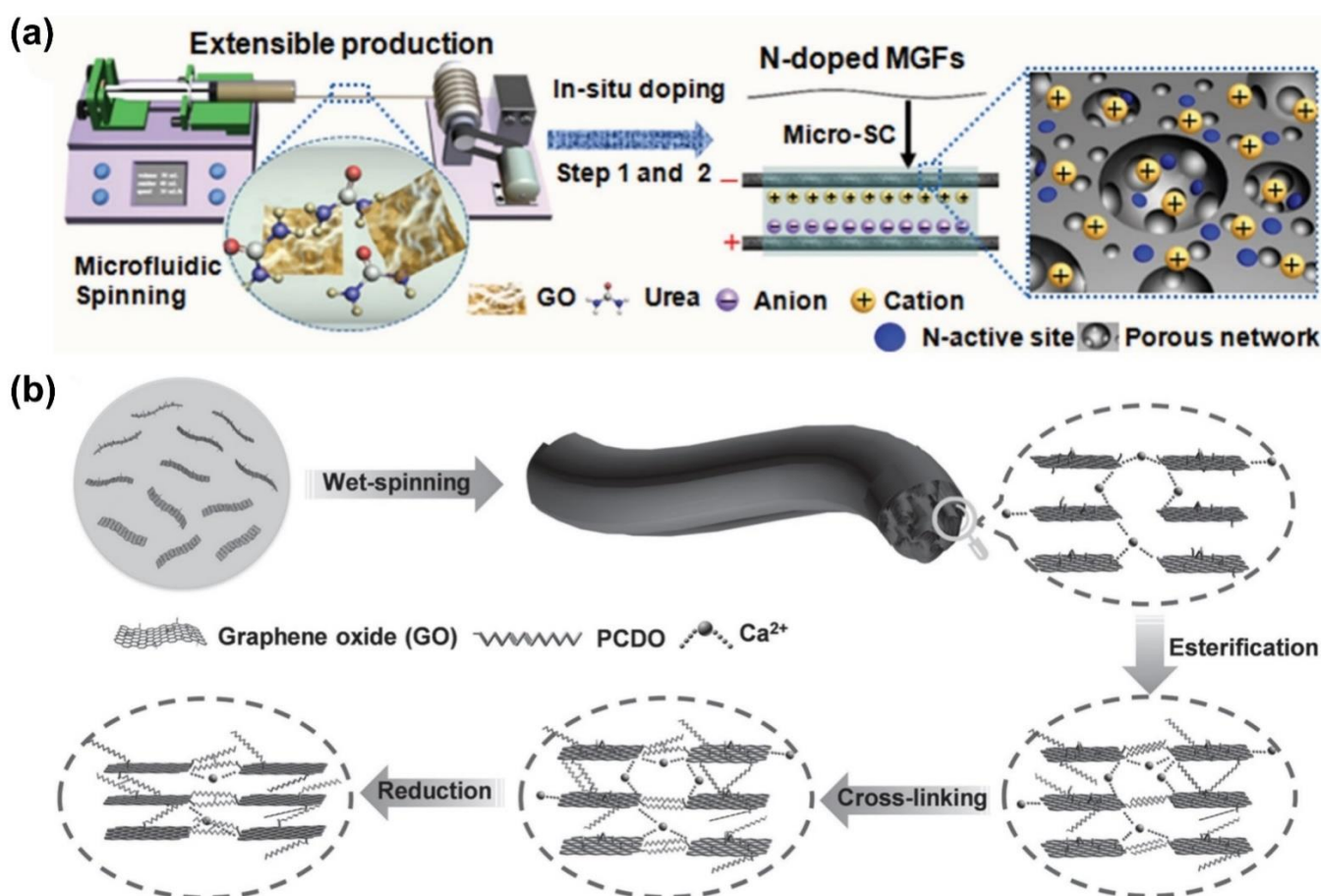


Figure 7. (a) Schematic illustration of the preparation of N-doped microfluidic-directed graphene fibers [116] (copyright permission Wiley-VCH 2017); (b) Schematic illustration of the preparation process for the bioinspired rGO-Ca²⁺-PCDO fibers [118] (copyright permission Wiley-VCH 2016).

Furthermore, surface modification is also deemed as an effective approach for interface engineering, which leads to stronger interfacial interactions and higher mechanical properties of graphene-based composites. Inspired by the design principles originating from nacre, Zhang et al. [69,118] performed chemical functionalization on graphene fibers by constructing synergistic interfacial interactions of covalent bonding, ionic bonding, and π - π interactions (Figure 7b). The reinforced graphene fibers displayed significantly enhanced the tensile strength and toughness, as well as higher electrical performance than neat graphene fibers.

5. Electrochemical Performance of Graphene-Based Composite Fiber Electrodes in Supercapacitors

5.1. Carbon Allotropy/Graphene

Carbon allotropes such as CNT offer combined remarkable properties including high flexibility, tensile strength, electrical conductivity, and mechanical and thermal stability. Therefore, the integration of CNTs and graphene into fibers will lead to synergistic enhancement of properties and functions. Yu et al. [78] proposed a scalable synthesis of a hierarchically structured carbon microfiber made of an interconnected network of aligned single-walled CNTs with interposed nitrogen-doped rGO sheets. The capacitor electrodes made from these fibers have a specific volumetric capacity of 305 F/cm³ in H₂SO₄ and 300 F/cm³ in PVA/H₃PO₄ electrolytes. Unfunctionalized few-walled CNTs were also used to dispersed into GO suspension and spun into composite fibers [119]. The introduction of CNTs significantly improved the conductivity up to 210.7 S/cm. Consequently, the wire-shaped supercapacitors exhibited a high volumetric capacity of 38.8 F/cm³ and en-

ergy density of 3.4 mWh/cm^3 , as well as excellent charge/discharge performance. Later, Sun et al. [93] synthesized CNT-graphene composite fibers by incorporating graphene nanosheets among neighboring CNTs (Figure 8a), playing a role of effective bridges to improve the charge transport. The as-obtained wire-shaped supercapacitor displayed a high specific capacitance of 31.50 F/g , much higher than that for pure CNT fibers (5.83 F/g) under the same conditions, as presented in Figure 8b,c. Using a low-temperature chemical reduction assembly method with vitamin C as the reducing agent, Jiang et al. [94] prepared flexible rGO/CNT hybrid fibers with an interconnected network architecture that showed excellent mechanical strength and volumetric high energy density. The volumetric specific capacitance of the rGO/CNT electrode was estimated to be 559.9 F/cm^3 , and the qualitative specific capacitance was 59.76 F/g at a high current density of 1 A/g , which is higher than that of single rGO fibers. Park et al. [55] developed porous CNT-graphene hybrid fibers for all-solid-state symmetric supercapacitors through the wet-spinning method followed by a hydrothermal activation process. The optimized volume capacitance could reach as high as 60 F/cm^3 ; meanwhile the energy density was increased to 4.83 mWh/cm^3 . This was ascribed to the continuous solvated ion pathways through the fibers.

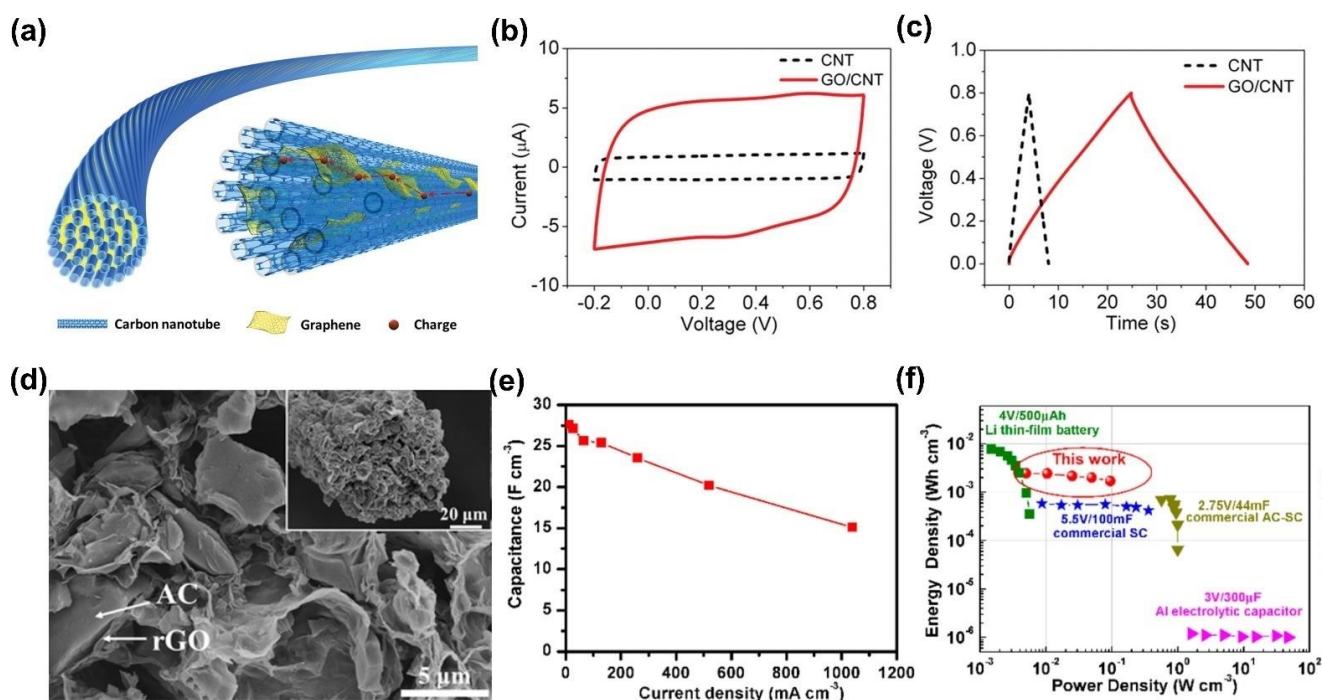


Figure 8. (a) Schematic illustration of the structure of the graphene/CNT composite fiber; (b) Current–voltage and (c) galvanostatic charge–discharge curves of wire-shaped supercapacitors with bare CNT and GO/CNT composite fibers as electrodes, respectively [93] (copyright permission Wiley-VCH 2014); (d) SEM image of activated carbon/rGO fibers; (e) Specific capacitance of AC fiber-based all-solid-state supercapacitors at various current densities; (f) Energy and power densities of the AC fiber-based all-solid-state supercapacitors compared with those of commercially available energy-storage systems [96] (copyright permission American Chemical Society 2016).

In addition to CNTs, GO was also leveraged as dispersant and binder to fabricate activated carbon (AC) fibers, as shown in Figure 8d [96]. A flexible all-solid-state supercapacitor was then constructed by twisting two AC fiber electrodes with PVA/ H_3PO_4 electrolyte, which showed a specific capacitance of 27.6 F/cm^3 at 13 mA/cm^3 and 20.2 F/cm^3 at 520 mA/cm^3 , corresponding to mass capacitance of 43.8 and 32.1 F/g , respectively (Figure 8e). Furthermore, the Ragone plot in Figure 8f gives the maximum energy density of the AC fiber-based all-solid-state supercapacitors, which is up to 2.5 mWh/cm^3 at a power density of 5 mWh/cm^3 , superior to those of commercially available supercapacitors. Ho et al. [97] recently synthesized activated graphene by KOH-based activation of exfoli-

ated graphite oxide, which was then incorporated in graphene fibers by employing GO as a dispersant and binder in the wet-spinning process, followed by subsequent chemical reduction treatment. The hierarchically porous structure of activated graphene significantly increased the specific surface area up to $2868.7 \text{ m}^2/\text{g}$. The obtained supercapacitor exhibited the highest areal capacitance of $145.1 \text{ mF}/\text{cm}^2$ at $0.8 \text{ mA}/\text{cm}^2$, corresponding to an areal energy density and power density of $5.04 \text{ } \mu\text{Wh}/\text{cm}^2$ and $0.50 \text{ mW}/\text{cm}^2$, respectively. Furthermore, the supercapacitor showed a long-term stability with a capacitance retention of $\sim 91.5\%$ after 10,000 cycles.

5.2. Conductive Polymer/Graphene

As typical pseudocapacitive materials, conducting polymers with high redox pseudocapacitive charge, low cost and ease of preparation are one of the most important active materials for supercapacitors. Modifying graphene with conductive polymers to form functional composites is deemed as an effective way to enhance the capacitance performance. Sasikala et al. [99] reported a PEDOT/graphene core-shell fiber where N and Cu co-doped porous graphene fiber was uniformly coated with PEDOT shell layers, presenting high electrical conductivity and superb electrochemical performance. The macropores not only endowed the fiber with a huge specific surface area, but also served as an electrolyte reservoir providing more open channels for the infiltration of electrolytes. As a result, the assembled fiber supercapacitors showed a high volumetric specific capacitance of $263.1 \text{ F}/\text{cm}^3$ and energy density of $7.0 \text{ mWh}/\text{cm}^3$.

By twisting two fiber electrodes with a gel polymer electrolyte between them, a twisted fiber configuration enables the fiber electrodes to contact more closely; therefore, more efficient ion transport is achieved. Ding et al. [100] fabricated a diameter-controlled graphene/polypyrrole (PPy) fiber via the wet-spinning strategy, which provided an advantageous platform as flexible, lightweight electrodes for supercapacitors. The flexible all-solid-state fiber supercapacitor was then created by intertwining two graphene/PPy fiber electrodes pre-coated with PVA/ H_2SO_4 gel polyelectrolyte. The capacitance was obtained to be $107.2 \text{ mF}/\text{cm}^2$ at a current density of $0.24 \text{ mA}/\text{cm}^2$, which was found to maintain stability during a long-term repetitive straight-to-bending process. The energy density was also kept consistent in the range of 6.6 to $9.7 \text{ } \mu\text{Wh}/\text{cm}^2$. Core-sheath porous PANI nanorods/graphene hybrid fibers were achieved by in situ chemical polymerization [49]. In addition to the electrical double-layer capacitance contributed by graphene fibers and faradaic pseudo-capacitance offered by PANI, the mesopores resulted from the interconnected PANI nanorods further facilitated the solvated ions' transport from the electrolyte into electrodes, endowing the as-assembled twisted fiber supercapacitors with a volumetric capacitance of $357.1 \text{ mF}/\text{cm}^2$ and energy density of $5.7 \text{ mWh}/\text{cm}^3$ or $7.93 \text{ } \mu\text{Wh}/\text{cm}^2$.

Hollow graphene-based fibers have recently drawn attention as the tubular structures expose more internal area that benefits electrochemical applications. Qu et al. [98] prepared a hollow rGO/PEDOT:PSS hybrid fiber electrode, as depicted in Figure 9a. The hollow structure favors both the exterior and interior active surface area accessible to the electrolyte. The consequent electrical conductivities could reach $4700 \text{ S}/\text{m}$ even without taking the hollow interior into account. Besides that, the as-assembled supercapacitor gave rise to a high specific areal capacitance of $304.5 \text{ mF}/\text{cm}^2$, corresponding to an ultrahigh energy density of $27.1 \text{ } \mu\text{Wh}/\text{cm}^2$ (Figure 9b). The specific capacitance was also highly stable and maintained as almost constant after the specific capacitance remained almost unchanged after bending for 500 times and can be maintained by 96% after 10,000-cycle loading (Figure 9c). According to the comparison with other fiber-shaped supercapacitors in Figure 9d, the achieved electrochemical performance represented the highest areal capacitance and areal energy density.

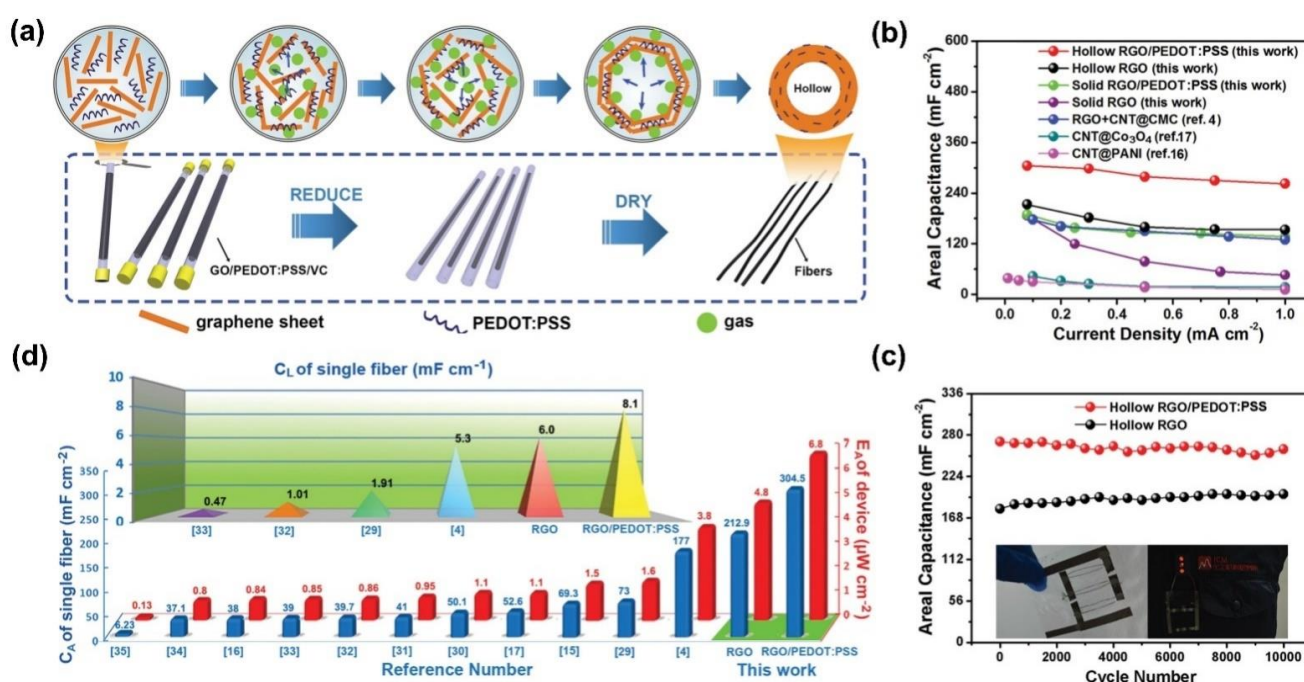


Figure 9. (a) Schematic illustration of preparation of hollow rGO/conducting polymer composite fibers; (b) Areal specific capacitances of composite fiber supercapacitors at increasing current densities; (c) Long-term cyclic stability of the composite fiber supercapacitors; (d) Comparison of the electrochemical performances of composite fiber supercapacitors with that of the other fiber-shaped supercapacitors in areal specific capacitance (C_A), length specific capacitance (C_L), and areal energy density (E_A) [98] (copyright permission Wiley-VCH 2016).

5.3. Metal Oxide/Graphene

Among different metal oxides, MnO_2 is one of the most promising materials for low-cost and environment-friendly electrochemical capacitor devices with high specific capacitance [120,121]. Earlier demonstrations included the solution-based synthesis of graphene/ MnO_2 nanostructured textiles as high-performance supercapacitor electrodes [122], which yields high specific capacitance up to 315 F/g, as shown in Figure 10a–c. Furthermore, embedding MnO_2 nanorods into graphene sheets has been demonstrated to be efficient in increasing the electrochemical performance of graphene fibers due to the presence of hierarchically porous structures and high pseudo-capacitance of MnO_2 nanorods. The assembled all-solid-state hybrid fiber supercapacitors exhibited a high volumetric capacitance (66.1 F/cm³) and energy density (5.8 mWh/cm³) [101]. Li et al. [102] fabricated a graphene fiber-based solid-state supercapacitor with MnO_2 nanoparticle deposition. The maximum areal capacitance of the hybrid flexible graphene– MnO_2 composite electrode was increased to 42.02 mF/cm², which is almost 20 times higher than that of a graphene fiber capacitor without MnO_2 . Accordingly, the energy density was also increased from 7.38×10^{-5} to 1.46×10^{-3} mWh/cm². Qu's group prepared an all-solid-state flexible fiber supercapacitor, wherein graphene fibers with a sheath of 3D graphene network was coated with MnO_2 nanoflowers [103]. Sharing the same electrochemical mechanism as discussed above, the supercapacitors presented a significantly enhanced capacitive performance, with a measured area-specific capacitance of 9.1–9.6 mF/cm², combined with a robust tolerance to mechanical deformation. More recently, an all-in-one graphene and MnO_2 composite hybrid supercapacitor fiber device has been developed by Yu's group, as shown in Figure 10d [48]. In contrast to twisted configuration, the all-in-one design effectively eliminated any circuit shortage and reduced the charge-transfer pathway. The synergetic effect of MnO_2 nanoparticles and graphene sheets endows the supercapacitors with a higher specific volumetric capacitance of 29.6 F/cm³ without severe capacitance fading at a high

bending angle or voltage scan rate, but also remarkable flexibility and tensile strength that can be easily woven into conductive textiles.

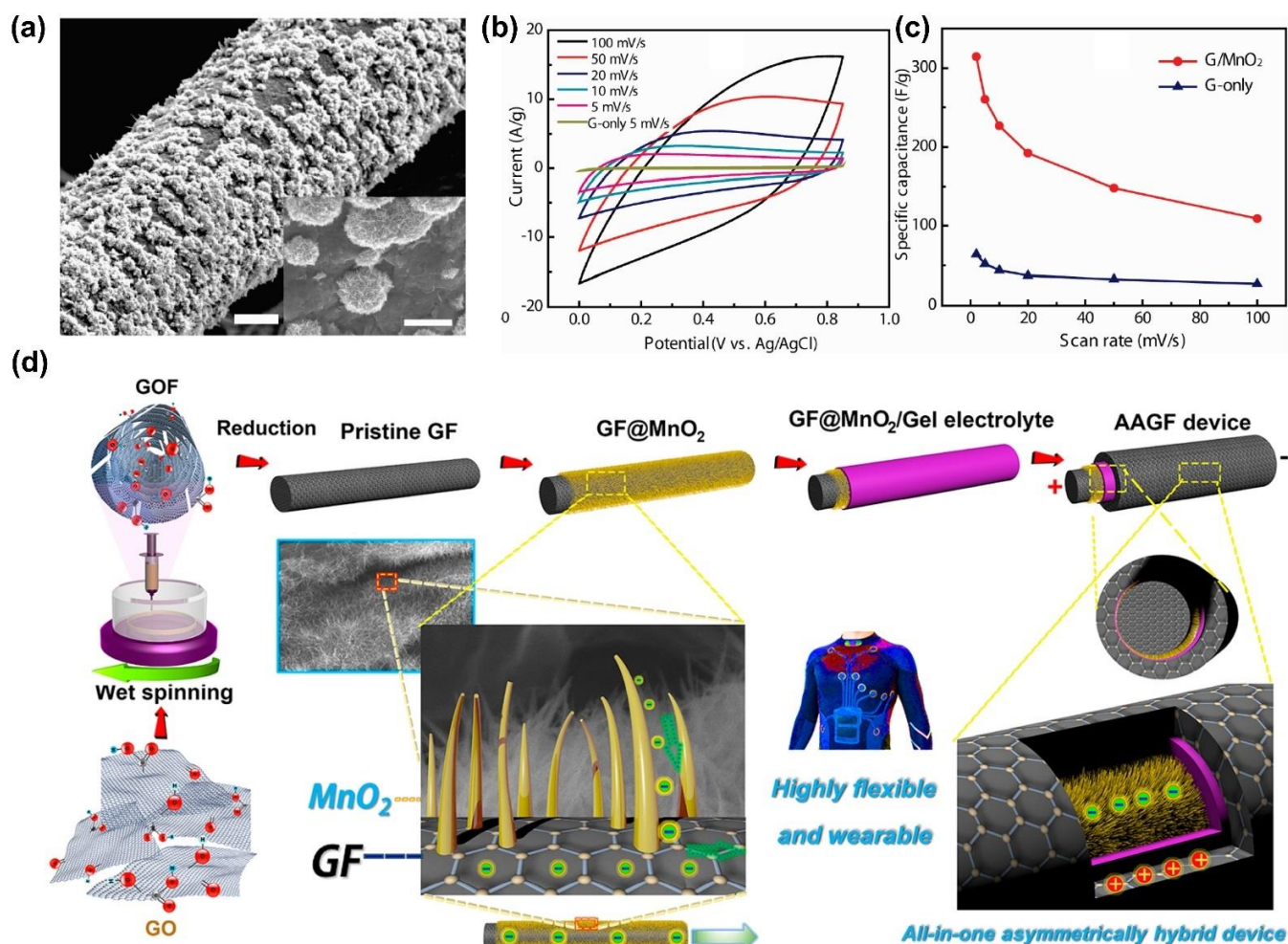


Figure 10. (a) SEM image of a typical graphene fiber with conformal coating of MnO₂ nanostructures; (b) Cyclic voltammograms for graphene/MnO₂-textile electrode at different scan rates in 0.5 M aqueous Na₂SO₄ electrolyte; (c) Comparison of specific capacitance values between graphene/MnO₂-textile and graphene nanosheets-only textile at different scan rates [122] (copyright permission American Chemical Society 2011); (d) Schematic illustration of the fabrication route to asymmetric graphene fiber all-in-one device, including wet spinning of GO fibers, reduction of fiber to form core graphene fiber, growth of MnO₂ layer, gel electrolyte coating, and outer graphene layer coating [48] (copyright permission American Chemical Society 2017).

5.4. Other 2D Materials: Graphene and Clay/Graphene

Two-dimensional materials such as MoS₂ and MXene have been successfully incorporated into graphene fibers to improve their electrochemical properties. In particular, Tang et al. [104] designed a hierarchical graphene/MoS₂ core-shell fiber by growing radially aligned 2D MoS₂ arrays on the surface of graphene fibers. The solid supercapacitor displayed a superior capacitance of 189.73 mF/cm², almost 260 times higher than that of pure graphene fibers. In addition, the energy density can reach as high as 14.665 μWh/cm² (6.5 mWh/cm³). Recently, an intercalated rGO/MoS₂ composite fiber has been synthesized by a one-step hydrothermal process [105]. Large graphene sheets constructed a robust skeleton intercalated by MoS₂ nanosheets filling the micropores in the hybrid fibers, as depicted in Figure 11a. The combination of the excellent electrical conductivity of rGO with the outstanding electrochemical activity of MoS₂ renders a highest specific capacitance of

368 F/cm³ for the resulting fiber-shaped supercapacitor compared with previous reports (Figure 11b).

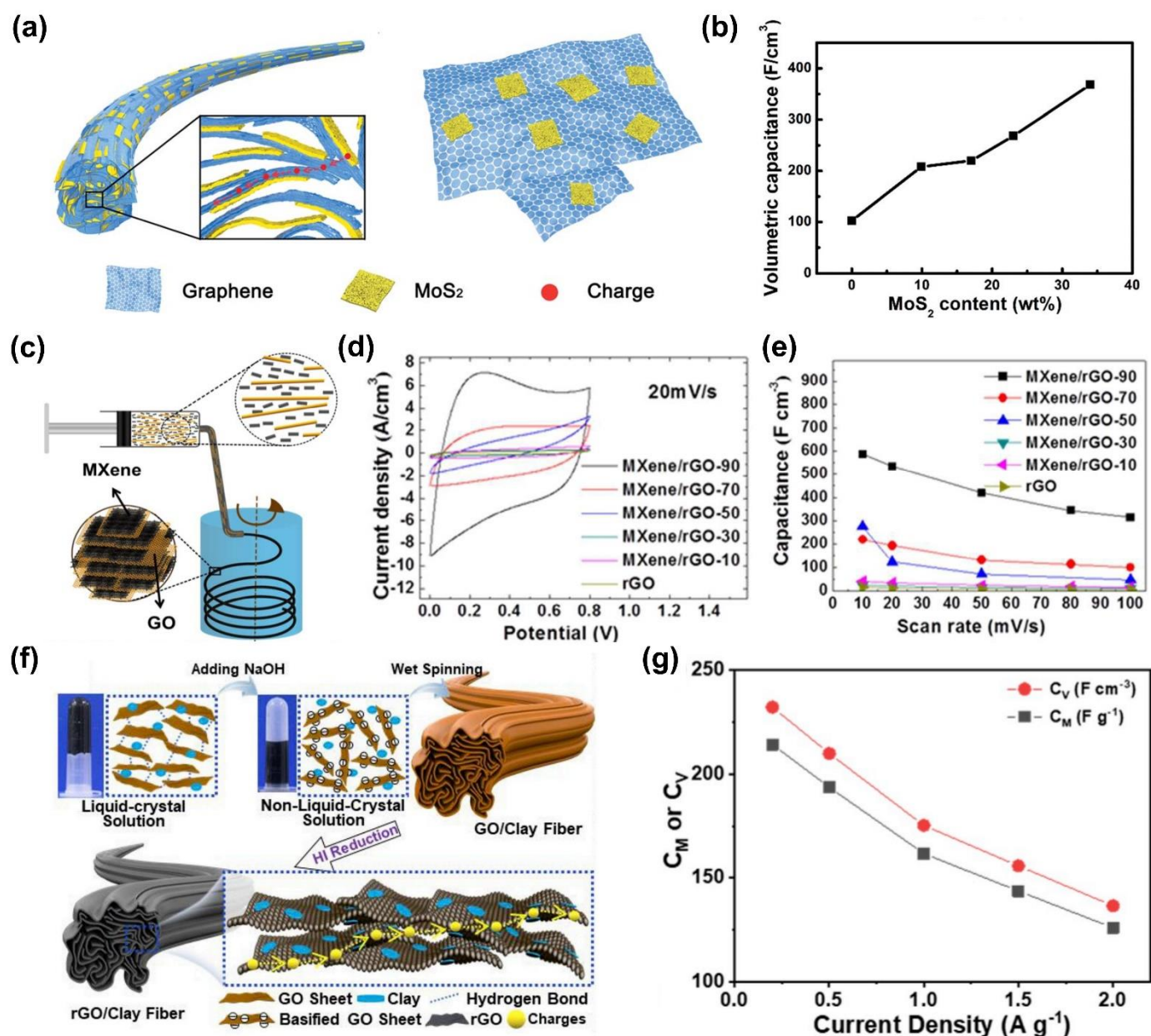


Figure 11. (a) Schematic illustration of the intercalated nanostructure of the graphene/MoS₂ hybrid fiber, where small MoS₂ sheets are epitaxially grown on large graphene sheets; (b) Dependence of volumetric capacitance on the MoS₂ content in the supercapacitor [105] (copyright permission The Royal Society of Chemistry 2017); (c) Schematic illustration of wet-spinning process for the MXene/GO fiber; (d) Current–voltage curves and (e) volumetric capacitances at different scan rates of the fabricated solid state MXene/rGO supercapacitors with various MXene contents [106] (copyright permission The Royal Society of Chemistry 2017); (f) Schematic illustration of the fabrication process of rGO/clay hybrid fibers; (g) Specific capacitance at different current density of rGO/clay fiber [74] (copyright permission Elsevier 2020).

Since MXene is also a promising candidate for supercapacitors, Gao's group developed a wet-spinning assembly strategy for continuous fabrication of composite fibers through a synergistic effect between GO liquid crystals and MXene nanosheets, as presented in Figure 11c [106]. The reduction enabled an increase of the conductivity of the MXene/rGO fibers from 2.7×10^3 S/m to 2.9×10^4 S/m. The consequent fiber-constructed flexible supercapacitors exhibited a record high volumetric capacitance (586.4 F/cm³) and high

areal capacitance (372.2 mF/cm^2), far exceeding those of neat GO fibers (16.4 F/cm^3 and 7.8 mF/cm^2) (Figure 11d,e). Similarly, He and co-authors demonstrated the fabrication of individual rGO/MXene-based fibers with carefully engineered hierarchical structures [108]. They paid more attention to the effect of the liquid electrolyte mediation and lateral size of MXene sheets on the electrical, mechanical, and electrochemical properties. The obtained rGO/MXene supercapacitors showed capacitance of 342.6 mF/cm^2 , which is 17 times higher than that of neat rGO fibers (19.16 mF/cm^2). Moreover, the electrolyte mediation was found to further increase the areal capacitance up to 550.96 mF/cm^2 , exceeding that of most state-of-the-art fiber electrodes. In terms of the size effect, the larger flake of MXene in the hybrid fibers was demonstrated to result in higher conductivity and mechanical strength as well as better electrochemical performance.

Chen et al. [74] fabricated inorganic hybrid fibers from GO and nanoclay via non-liquid-crystal spinning with additional chemical reduction, as shown in Figure 11f. The hybrid fibers possessed relatively ordered structure that accounted for improved mechanical properties, good affinity with electrolytes, and enhanced capacitive performance. Specifically, the assembled supercapacitor showed a specific capacitance of 230.9 F/cm^3 at a current density of 0.234 A/cm^3 , as shown in Figure 11g. Meanwhile, a high energy density of 6.14 mWh/cm^3 could be achieved at the power density of 28.33 mWh/cm^3 , which is even higher than that of rGO/MoS₂ supercapacitors.

5.5. Multiple Functional Materials/Graphene

In order to achieve further improvement in the electrochemical properties and supercapacitor device performance, more than one functional material has been integrated with graphene to fabricate composite fibers. For instance, a coaxial wet-spinning assembly strategy was proposed to prepare core-sheath fibers where a graphene/CNT mixture was wrapped by polyelectrolyte [21]. The aqueous solution of sodium carboxy methyl cellulose (CMC) was used as the outer spinning dope since CMC is an ionically conductive but electrically insulative polyelectrolyte. The consequent polymer sheath ensures fiber electrodes free of short circuits when intertwined together, while allowing ions to smoothly penetrate from the electrolyte matrix to electrodes. Then the coaxial fibers were directly assembled into two-ply intertwined yarn supercapacitors that showed ultra-high capacitances of 269 and 177 mF/cm^2 and energy densities of 5.91 and 3.84 mWh/cm^2 , respectively. Wang et al. [95] developed a one-step electrochemical deposition process to manufacture continuous fibers by integrating a variety of pseudocapacitive active materials such as GO, metal oxide, and conductive polymers with CNTs. The all-solid-state supercapacitor showed remarkable energy-storage capabilities. More recently, rGO fiber-based springs were fabricated as electrodes for stretchable and self-healable supercapacitors [123]. Therein, rGO was first mixed with multiwalled CNTs (MWCNTs) to produce composite fibers, which were subsequently wrapped by a thin layer of conductive PPy, to improve the conductivity and electrochemical performance. After being twisted into springs, polyurethane (PU) was coated on spring-like fiber electrodes to endow them with high stretchability and self-healing ability. As a result, the volumetric capacitance for composite fibers with PPy/rGO/MWCNTs showed the highest value of 25.9 F/cm^3 at the scan rate of 0.01 V/s compared to that of rGO (11.4 F/cm^3) and rGO/MWCNTs (10.8 F/cm^3). Similarly, electrodeposition of PANI on the surface of rGO/CNT composite fibers was applied to endow the fiber electrodes with good electrochemical characteristics, highest volumetric specific capacitance of 193.1 F/cm^3 at current density of 1 A/cm^3 , and excellent cyclic retention of 92.60% after 2000 CV cycles [124]. The resulting symmetric supercapacitor presented a volumetric capacitance of 36.7 F/cm^3 at current density of 0.2 A/cm^3 .

Table 2 compares in detail the mechanical properties and electrochemical performance of several graphene-based composite fibers, as previously reported.

Table 2. Brief summary of the mechanical and electrochemical performance of graphene-based composite fibers.

Electrodes	Electrolyte	WorkWindow (V)	Strength (MPa)	Electrical Conductivity (S/cm)	Specific Capacitance	Energy Density	Power Density	Cycling Stability	Ref.
Graphene + Carbon Allotropy									
rGO/CNT	PVA/KOH	0.8	78.4	133.3	60.75 F/cm ³	4.83 mWh/cm ³	18.1 mW/cm ³	94% (10,000 cycles)	[55]
SWNT/nitrogen-doped rGO	PVA/H ₃ PO ₄	1.0	84	102	300 F/cm ³	6.3 mWh/cm ³	1085 mW/cm ³	93% (10,000 cycles)	[78]
GO/CNT	PVA/H ₃ PO ₄	1.0	630	450	31.50 F/g	NA	NA	~100% (5000 cycles)	[93]
rGO/CNT	NA	1.2	46	153.6	559.9 F/cm ³	11.6 Wh/kg	NA	97.1% (5000 cycles)	[94]
rGO/CNT	PVA/H ₃ PO ₄	1.0	392.5	NA	68.4 F/cm ³	2.4 mWh/cm ³	18 mW/cm ³	~100% (10,000 cycles)	[95]
Graphene/active carbon	PVA/H ₃ PO ₄	0.8	22.7	185	27.6 F/cm ³	2.5 mWh/cm ³	5 mW/cm ³	90.4% (10,000 cycles)	[96]
rGO/active carbon	PVA/LiCl	1.0	4.2	47.3	145.1 mF/cm ²	5.04 µWh/cm ²	0.5 mW/cm ²	91.5% (10,000 cycles)	[97]
Graphene + Conductive Polymer									
rGO/PEDOT:PSS	PVA/H ₃ PO ₄	0.8	631	~42–47	143.3 F/cm ³	12.7 mWh/cm ³	66.5 µWh/cm ²	96% (10,000 cycles)	[98]
rGO/PEDOT:PSS	PVA/H ₂ SO ₄	1.0	NA	387.1	263.1 F/cm ³	~7.0 mWh/cm ³	NA	97.2% (20,000 cycles)	[99]
rGO/PANI	PVA/H ₂ SO ₄	1.0	NA	282.7	155.2 F/cm ³	~3.8 mWh/cm ³	NA	94.1% (20,000 cycles)	[99]
Graphene/PANI	PVA/H ₂ SO ₄	0.8	484	14	357.1 mF/cm ²	7.93 µWh/cm ²	0.23 mW/cm ²	96.2% (5000 cycles)	[49]
rGO/PPy	PVA/H ₂ SO ₄	1.0	NA	259.4	184.1 F/cm ³	~4.1 mWh/cm ³	NA	94.8% (20,000 cycles)	[99]
Graphene/PPy	PVA/H ₂ SO ₄	0.8	80	137–144	107.2 F/cm ³	6.6 µWh/cm ²	NA	98% (1000 cycles)	[100]
rGO/PANI	PVA/H ₂ SO ₄	0.8	140	NA	148 F/cm ³	8.8 mWh/cm ³	30.77 mW/cm ³	NA	[62]

Table 2. Cont.

Electrodes	Electrolyte	WorkWindow (V)	Strength (MPa)	Electrical Conductivity (S/cm)	Specific Capacitance	Energy Density	Power Density	Cycling Stability	Ref.
Graphene + Metal Oxide									
Graphene/MnO ₂	PVA/H ₃ PO ₄	1.8	NA	NA	26.9 F/cm ³	NA	NA	93% (1000 cycles)	[48]
rGO/MnO ₂	PVA/H ₃ PO ₄	0.8	117	25.2	66.1 F/cm ³	5.8 mWh/cm ³	0.51 mW/cm ³	96% (10,000 cycles)	[101]
Graphene/MnO ₂	PVA/H ₃ PO ₄	1.0	NA	172	42 F/cm ³	1.46 µWh/cm ²	2.9 mW/cm ²	92% (1000 cycles)	[102]
GO/MnO ₂	PVA/H ₃ PO ₄	0.8	NA	10	34-36 F/g	NA	NA	~100% (1000 cycles)	[103]
Graphene + Layered Materials									
rGO/MoS ₂	PVA/H ₂ SO ₄	0.8	NA	NA	189.73 mF/cm ²	6.5 mWh/cm ³	268.66 mW/cm ³	89.7% (5000 cycles)	[104]
rGO/MoS ₂	PVA/H ₂ SO ₄	0.8	181	NA	368 F/cm ³	NA	NA	80% (8000 cycles)	[105]
rGO/Mxene	PVA/H ₃ PO ₄	0.8	12.9	290	586.4 F/cm ³	13 mWh/cm ³	0.59 mW/cm ³	94% (3000 cycles)	[106]
rGO/Mxene	PVA/H ₂ SO ₄	0.8	NA	NA	253 mF/cm ²	27.1 µWh/cm ²	2.5 mW/cm ²	82% (1000 cycles)	[107]
rGO/Mxene	PVA/H ₂ SO ₄	0.8	110.7	743.1	342.6 mF/cm ²	9.85 mWh/cm ³	7.1 mW/cm ³	85% (10,000 cycles)	[108]
rGO/clay	PVA/H ₂ SO ₄	1.0	102.7	10.4	230.9 F/cm ³	6.14 mWh/cm ³	28 mW/cm ³	~100% (5000 cycles)	[74]

6. Conclusions and Perspectives

Supercapacitors feature numerous advantages of fast charge and discharge, high power density, and long cycle life. Electrode materials act as a key factor that determines the energy storage capability of supercapacitors. Research in recent years has demonstrated extensive application of graphene materials as electrode materials due to their high specific surface area, high conductivity, high flexibility and robustness. However, the creation of graphene fibers still presents difficulties in fabrication of continuous and highly ordered graphene sheets with strong interlayer interactions.

In this context, the combination of graphene and other materials affords an effective way to improve the electrochemical performance of fiber-based electrodes. The introduced guest molecules include carbon allotropes, conductive polymers, metal oxides and other materials (e.g., clay and other 2D materials). Our study discusses the complementary and synergistic contributions of graphene and other materials to the enhancement of electrochemical performance. Furthermore, the intercalation of the guest molecules increases the interlayer spacing or fills in the interlayer galleries between graphene layers, resulting in restriction of the aggregation and restacking of graphene sheets.

Although there are a number of preparation methods for graphene-based composite fibers, mixing the graphene and other complementary materials in spinning solutions represents the most efficient path to manufacture graphene-based composite fibers before the fiber production or deposition of graphene coating on as-prepared fibers. Other commonly used methods, including in situ polymerization, CVD growth, electrophoretic deposition, and direct coating, were also introduced here for comparison.

Research in recent years has demonstrated the microstructures and interfaces in composite fibers are key parameters defining the electrochemical performance of graphene-based composite fiber electrodes. This gives us an opportunity to design high-performance graphene-based composite fiber electrodes through the rationalized optimization of the microstructure design and surface modification. We elucidate the deep relationship of hierarchical porous structures to promote charge storage, increase ion transport, and improve the electrochemical performance of fiber-based supercapacitor. Another factor worthy of close scrutiny is the wrinkled structure that favors the flexibility as well as interfacial bonding of graphene-based composite fibers. Nevertheless, it should be noted that these voids and random wrinkles result in a reduction of the mechanical and durability performance of composite fibers. It is necessary to tune the wrinkled structure and porosity of graphene-based fibers in order to reach a balance between the mechanical degradation and electrochemical performance enhancement. Alternatively, adding functional groups or heteroatoms containing oxygen, nitrogen, and sulfur into graphene-based fibers without damaging the 3D order also contributes to their specific properties and extends their functionalities. Both approaches have proved effective in preventing the restacking of graphene sheets and increasing the specific surface area, eventually enhancing the electrochemical performance of hybrid graphene fiber electrodes.

It has now been clearly demonstrated that graphene-based fiber electrodes will promote the development of flexible supercapacitors. However, several important challenges still urgently need to be overcome: (1) Clarifying the effects of graphene and other functional materials on the electrochemical properties, as well as the relationship between energy storage and defects, layer number, sizes, and surface chemistry, is necessary. Future efforts can be concentrated on the control of the size, morphology, quality, quantity, and distribution of functional components. Rational design of the texture or microstructure of graphene-based hybrid materials can ensure reproducibility and better understanding of the structure–property relationships. (2) The controllability of the interactions between graphene and complementary materials is essentially important, especially for supercapacitor applications that involve charge transfer processes. Currently, most composite materials are synthesized by direct mixing, giving rise to relatively poor interfaces. A good understanding of the surface chemistry of graphene and other materials is critical for improving interfacial bonding between graphene and functional building blocks, hence

reaching a well-defined uniform structure. (3) New approaches to fabricate graphene-based composites have to involve a combined focus on new chemistry, controlled synthesis, and device-performance of novel composite materials with optimized properties and functionalities, which is essential to improve the electrochemical performance of graphene-based composite fiber electrodes, and to create novel graphene-based energy storage devices. (4) Besides conductivity and capacitance, the flexibility and stretchability are two crucial factors for making practical advanced flexible supercapacitors. A balance between the electrochemical and mechanical performance should be struck by optimization of the microstructures and interfaces. (5) In terms of the industrial implementation, the successful application of graphene-based composite fibers requires a comprehensive improvement in scalability, cost-effectiveness, stability, and environmental sustainability, not merely high performance of the composite electrodes. With continuous exploitation, it is believed that there may be breakthroughs in practical application of graphene-based composite fiber electrodes in wearable electronics in the near future.

Funding: This research was funded by the Anhui Provincial Key Natural Science Research Project (wjmkn [2017] No. 12 KJ2016A0510) and Anhui Provincial Quality Project—Massive Open Online Courses (MOOC) demonstration project: Modern spinning techniques (2018mooc007).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The author declare no conflict of interest.

References

1. Luo, Y.; Wang, M.; Wan, C.; Cai, P.; Loh, X.J.; Chen, X. Devising materials manufacturing toward lab-to-fab translation of flexible electronics. *Adv. Mater.* **2020**, *32*, e2001903. [\[CrossRef\]](#) [\[PubMed\]](#)
2. Rogers, J.A.; Someya, T.; Huang, Y. Materials and mechanics for stretchable electronics. *Science* **2010**, *327*, 1603–1607. [\[CrossRef\]](#)
3. Wang, L.; Fu, X.; He, J.; Shi, X.; Chen, T.; Chen, P.; Wang, B.; Peng, H. Application challenges in fiber and textile electronics. *Adv. Mater.* **2020**, *32*, e1901971. [\[CrossRef\]](#) [\[PubMed\]](#)
4. Weng, W.; Chen, P.; He, S.; Sun, X.; Peng, H. Smart electronic textiles. *Angew. Chem. Int. Ed. Engl.* **2016**, *55*, 6140–6169. [\[CrossRef\]](#) [\[PubMed\]](#)
5. Cherenack, K.; van Pieterse, L. Smart textiles: Challenges and opportunities. *J. Appl. Phys.* **2012**, *112*, 091301. [\[CrossRef\]](#)
6. Wang, G.; Zhang, L.; Zhang, J. A review of electrode materials for electrochemical supercapacitors. *Chem. Soc. Rev.* **2012**, *41*, 797–828. [\[CrossRef\]](#)
7. Chmiola, J.; Largeot, C.; Taberna, P.-L.; Simon, P.; Gogotsi, Y. Monolithic carbide-derived carbon films for micro-supercapacitors. *Science* **2010**, *328*, 480–483. [\[CrossRef\]](#)
8. Liu, C.; Yu, Z.; Neff, D.; Zhamu, A.; Jang, B.Z. Graphene-based supercapacitor with an ultrahigh energy density. *Nano Lett.* **2010**, *10*, 4863–4868. [\[CrossRef\]](#)
9. Zhang, L.L.; Zhao, X. Carbon-based materials as supercapacitor electrodes. *Chem. Soc. Rev.* **2009**, *38*, 2520–2531. [\[CrossRef\]](#)
10. Peng, Z.; Ye, R.; Mann, J.A.; Zakhidov, D.; Li, Y.; Smalley, P.R.; Lin, J.; Tour, J.M. Flexible Boron-doped laser-induced graphene microsupercapacitors. *ACS Nano* **2015**, *9*, 5675–5868. [\[CrossRef\]](#)
11. Frackowiak, E. Carbon materials for supercapacitor application. *Phys. Chem. Chem. Phys.* **2007**, *9*, 1774–1785. [\[CrossRef\]](#) [\[PubMed\]](#)
12. Wang, Y.; Song, Y.; Xia, Y. Electrochemical capacitors: Mechanism, materials, systems, characterization and applications. *Chem. Soc. Rev.* **2016**, *45*, 5925–5950. [\[CrossRef\]](#)
13. Yu, Z.; Tetard, L.; Zhai, L.; Thomas, J. Supercapacitor electrode materials: Nanostructures from 0 to 3 dimensions. *Energ. Environ. Sci.* **2015**, *8*, 702–730. [\[CrossRef\]](#)
14. Yang, Z.; Deng, J.; Chen, X.; Ren, J.; Peng, H. A highly stretchable, fiber-shaped supercapacitor. *Angew. Chem. Int. Ed. Engl.* **2013**, *52*, 13453–13457. [\[CrossRef\]](#) [\[PubMed\]](#)
15. Dong, L.; Xu, C.; Li, Y.; Huang, Z.-H.; Kang, F.; Yang, Q.-H.; Zhao, X. Flexible electrodes and supercapacitors for wearable energy storage: A review by category. *J. Mater. Chem. A* **2016**, *4*, 4659–4685. [\[CrossRef\]](#)
16. Choi, C.; Kim, S.H.; Sim, H.J.; Lee, J.A.; Choi, A.Y.; Kim, Y.T.; Lepró, X.; Spinks, G.M.; Baughman, R.H.; Kim, S.J. Stretchable, weavable coiled carbon nanotube/MnO₂/polymer fiber solid-state supercapacitors. *Sci. Rep.* **2015**, *5*, 1–6. [\[CrossRef\]](#)
17. Cai, Z.; Li, L.; Ren, J.; Qiu, L.; Lin, H.; Peng, H. Flexible, weavable and efficient microsupercapacitor wires based on polyaniline composite fibers incorporated with aligned carbon nanotubes. *J. Mater. Chem. A* **2013**, *1*, 258–261. [\[CrossRef\]](#)
18. Li, Z.; Shao, M.; Zhou, L.; Zhang, R.; Zhang, C.; Han, J.; Wei, M.; Evans, D.G.; Duan, X. A flexible all-solid-state micro-supercapacitor based on hierarchical CuO@layered double hydroxide core-shell nanoarrays. *Nano Energy* **2016**, *20*, 294–304.

19. Jiang, H.; Lee, P.S.; Li, C. 3D carbon based nanostructures for advanced supercapacitors. *Energ. Environ. Sci.* **2013**, *6*, 41–53. [[CrossRef](#)]
20. Chen, X.; Qiu, L.; Ren, J.; Guan, G.; Lin, H.; Zhang, Z.; Chen, P.; Wang, Y.; Peng, H. Novel electric double-layer capacitor with a coaxial fiber structure. *Adv. Mater.* **2013**, *25*, 6436–6441. [[CrossRef](#)]
21. Kou, L.; Huang, T.; Zheng, B.; Han, Y.; Zhao, X.; Gopalsamy, K.; Sun, H.; Gao, C. Coaxial wet-spun yarn supercapacitors for high-energy density and safe wearable electronics. *Nat. Commun.* **2014**, *5*, 1–10. [[CrossRef](#)]
22. Luo, J.; Jang, H.D.; Huang, J. Effect of sheet morphology on the scalability of graphene-based ultracapacitors. *ACS Nano* **2013**, *7*, 1464–1471. [[CrossRef](#)]
23. Stoller, M.D.; Park, S.; Zhu, Y.; An, J.; Ruoff, R.S. Graphene-based ultracapacitors. *Nano Lett.* **2008**, *8*, 3498–3502. [[CrossRef](#)]
24. Zhang, L.L.; Zhou, R.; Zhao, X. Graphene-based materials as supercapacitor electrodes. *J. Mater. Chem.* **2010**, *20*, 5983–5992. [[CrossRef](#)]
25. Huang, Y.; Liang, J.; Chen, Y. An overview of the applications of graphene-based materials in supercapacitors. *Small* **2012**, *8*, 1805–1834. [[CrossRef](#)]
26. Shao, Y.; El-Kady, M.F.; Wang, L.J.; Zhang, Q.; Li, Y.; Wang, H.; Mousavi, M.F.; Kaner, R.B. Graphene-based materials for flexible supercapacitors. *Chem. Soc. Rev.* **2015**, *44*, 3639–3665. [[CrossRef](#)]
27. Zheng, X.; Hu, Q.; Zhou, X.; Nie, W.; Li, C.; Yuan, N. Graphene-based fibers for the energy devices application: A comprehensive review. *Mater. Des.* **2021**, *201*, 109476. [[CrossRef](#)]
28. Wu, S.; Qureshi, T.; Wang, G. Application of graphene in fiber-reinforced cementitious composites: A review. *Energies* **2021**, *14*, 4614. [[CrossRef](#)]
29. Sun, P.Z.; Yang, Q.; Kuang, W.J.; Stebunov, Y.V.; Xiong, W.Q.; Yu, J.; Nair, R.R.; Katsnelson, M.I.; Yuan, S.J.; Grigorieva, I.V.; et al. Limits on gas impermeability of graphene. *Nature* **2020**, *579*, 229–232. [[CrossRef](#)] [[PubMed](#)]
30. Berry, V. Impermeability of graphene and its applications. *Carbon* **2013**, *62*, 1–10. [[CrossRef](#)]
31. Bolotin, K.I.; Sikes, K.J.; Jiang, Z.; Klima, M.; Fudenberg, G.; Hone, J.; Kim, P.; Stormer, H.L. Ultrahigh electron mobility in suspended graphene. *Solid State Commun.* **2008**, *146*, 351–355. [[CrossRef](#)]
32. Balandin, A.A.; Ghosh, S.; Bao, W.Z.; Calizo, I.; Teweldebrhan, D.; Miao, F.; Lau, C.N. Superior thermal conductivity of single-layer graphene. *Nano Lett.* **2008**, *8*, 902–907. [[CrossRef](#)]
33. Owais, M.; Zhao, J.; Imani, A.; Wang, G.; Zhang, H.; Zhang, Z. Synergetic effect of hybrid fillers of boron nitride, graphene nanoplatelets, and short carbon fibers for enhanced thermal conductivity and electrical resistivity of epoxy nanocomposites. *Compos. Part A Appl. Sci. Manuf.* **2019**, *117*, 11–22. [[CrossRef](#)]
34. Wang, K.; Qu, C.; Wang, J.; Quan, B.; Zheng, Q. Characterization of a microscale superlubric graphite interface. *Phys. Rev. Lett.* **2020**, *125*, 026101. [[CrossRef](#)] [[PubMed](#)]
35. Wang, G.; Dai, Z.; Wang, Y.; Tan, P.; Liu, L.; Xu, Z.; Wei, Y.; Huang, R.; Zhang, Z. Measuring interlayer shear stress in bilayer graphene. *Phys. Rev. Lett.* **2017**, *119*, 036101. [[CrossRef](#)]
36. Arif, T.; Wang, G.; Sodhi, R.N.S.; Colas, G.; Filleter, T. Role of chemical vs. physical interfacial interaction and adsorbed water on the tribology of ultrathin 2D-material/steel interfaces. *Tribol. Int.* **2021**, *163*, 107194. [[CrossRef](#)]
37. Lee, C.; Wei, X.; Kysar, J.W.; Hone, J. Measurement of the elastic properties and intrinsic strength of monolayer graphene. *Science* **2008**, *321*, 385–388. [[CrossRef](#)] [[PubMed](#)]
38. Wang, G.; Dai, Z.; Xiao, J.; Feng, S.; Weng, C.; Liu, L.; Xu, Z.; Huang, R.; Zhang, Z. Bending of multilayer van der Waals materials. *Phys. Rev. Lett.* **2019**, *123*, 116101. [[CrossRef](#)]
39. Xia, J.; Chen, F.; Li, J.; Tao, N. Measurement of the quantum capacitance of graphene. *Nat. Nanotechnol.* **2009**, *4*, 505–509. [[CrossRef](#)]
40. Wan, S.; Chen, Y.; Wang, Y.; Li, G.; Wang, G.; Liu, L.; Zhang, J.; Liu, Y.; Xu, Z.; Tomsia, A.P.; et al. Ultrastrong graphene films via long-chain π -bridging. *Matter* **2019**, *1*, 389–401. [[CrossRef](#)]
41. Cong, H.-P.; Chen, J.-F.; Yu, S.-H. Graphene-based macroscopic assemblies and architectures: An emerging material system. *Chem. Soc. Rev.* **2014**, *43*, 7295–7325. [[CrossRef](#)] [[PubMed](#)]
42. Zhang, Y.; Liu, L.; Sun, B.; Wang, G.; Zhang, Z. Preparation of lipophilic graphene oxide derivatives via a concise route and its mechanical reinforcement in thermoplastic polyurethane. *Compos. Sci. Technol.* **2016**, *134*, 36–42. [[CrossRef](#)]
43. Duan, F.; Li, W.; Wang, G.; Weng, C.; Jin, H.; Zhang, H.; Zhang, Z. Can insulating graphene oxide contribute the enhanced conductivity and durability of silver nanowire coating? *Nano Res.* **2019**, *12*, 1571–1577. [[CrossRef](#)]
44. Marcano, D.C.; Kosynkin, D.V.; Berlin, J.M.; Sinitskii, A.; Sun, Z.; Slesarev, A.; Alemany, L.B.; Lu, W.; Tour, J.M. Improved synthesis of graphene oxide. *ACS Nano* **2010**, *4*, 4806–4814. [[CrossRef](#)]
45. Xu, Z.; Liu, Y.; Zhao, X.; Peng, L.; Sun, H.; Xu, Y.; Ren, X.; Jin, C.; Xu, P.; Wang, M. Ultrastiff and strong graphene fibers via full-scale synergetic defect engineering. *Adv. Mater.* **2016**, *28*, 6449–6456. [[CrossRef](#)]
46. Liu, Y.; Xu, Z.; Zhan, J.; Li, P.; Gao, C. Superb electrically conductive graphene fibers via doping strategy. *Adv. Mater.* **2016**, *28*, 7941–7947. [[CrossRef](#)]
47. Xin, G.; Zhu, W.; Deng, Y.; Cheng, J.; Zhang, L.T.; Chung, A.J.; De, S.; Lian, J. Microfluidics-enabled orientation and microstructure control of macroscopic graphene fibres. *Nat. Nanotechnol.* **2019**, *14*, 168–175. [[CrossRef](#)]
48. Lim, L.; Liu, Y.; Liu, W.; Tjandra, R.; Rasenthiram, L.; Chen, Z.; Yu, A. All-in-one graphene based composite fiber: Toward wearable supercapacitor. *ACS Appl. Mater. Interfaces* **2017**, *9*, 39576–39583. [[CrossRef](#)]

49. Zheng, X.; Yao, L.; Qiu, Y.; Wang, S.; Zhang, K. Core-sheath porous polyaniline nanorods/graphene fiber-shaped supercapacitors with high specific capacitance and rate capability. *ACS Appl. Energy Mater.* **2019**, *2*, 4335–4344. [\[CrossRef\]](#)
50. Yu, G.-H.; Han, Q.; Qu, L.-T. Graphene Fibers: Advancing Applications in Sensor, Energy Storage and Conversion. *Chin. J. Polym. Sci.* **2019**, *37*, 535–547. [\[CrossRef\]](#)
51. Li, J.; Huang, X.; Cui, L.; Chen, N.; Qu, L. Preparation and supercapacitor performance of assembled graphene fiber and foam. *Prog. Nat. Sci. Mater. Int.* **2016**, *26*, 212–220. [\[CrossRef\]](#)
52. Fang, B.; Chang, D.; Xu, Z.; Gao, C. A review on graphene fibers: Expectations, advances, and prospects. *Adv. Mater.* **2020**, *32*, e1902664. [\[CrossRef\]](#) [\[PubMed\]](#)
53. Yu, D.; Qian, Q.; Wei, L.; Jiang, W.; Goh, K.; Wei, J.; Zhang, J.; Chen, Y. Emergence of fiber supercapacitors. *Chem. Soc. Rev.* **2015**, *44*, 647–662. [\[CrossRef\]](#)
54. Galhena, D.T.L.; Bayer, B.C.; Meyer, J.C.; Hofmann, S.; Amaratunga, G.A.J. Reduced graphene oxide as a monolithic multifunctional conductive binder for activated carbon supercapacitors. *ACS Omega* **2018**, *3*, 9246–9255. [\[CrossRef\]](#) [\[PubMed\]](#)
55. Park, H.; Ambade, R.B.; Noh, S.H.; Eom, W.; Koh, K.H.; Ambade, S.B.; Lee, W.J.; Kim, S.H.; Han, T.H. Porous graphene-carbon nanotube scaffolds for fiber supercapacitors. *ACS Appl. Mater. Interfaces* **2019**, *11*, 9011–9022. [\[CrossRef\]](#) [\[PubMed\]](#)
56. Beidaghi, M.; Wang, C. Micro-supercapacitors based on interdigital electrodes of reduced graphene oxide and carbon nanotube composites with ultrahigh power handling performance. *Adv. Funct. Mater.* **2012**, *22*, 4501–4510. [\[CrossRef\]](#)
57. Lu, Z.; Foroughi, J.; Wang, C.; Long, H.; Wallace, G.G. Superelastic hybrid CNT/graphene fibers for wearable energy storage. *Adv. Energy Mater.* **2018**, *8*, 1702047. [\[CrossRef\]](#)
58. Li, B.; Cheng, J.; Wang, Z.; Li, Y.; Ni, W.; Wang, B. Highly-wrinkled reduced graphene oxide-conductive polymer fibers for flexible fiber-shaped and interdigital-designed supercapacitors. *J. Power Sources* **2018**, *376*, 117–124. [\[CrossRef\]](#)
59. Meng, Y.; Zhao, Y.; Hu, C.; Cheng, H.; Hu, Y.; Zhang, Z.; Shi, G.; Qu, L. All-graphene core-sheath microfibers for all-solid-state, stretchable fibriform supercapacitors and wearable electronic textiles. *Adv. Mater.* **2013**, *25*, 2326–2331. [\[CrossRef\]](#)
60. Sha, Z.; Zhou, Y.; Huang, F.; Yang, W.; Yu, Y.; Zhang, J.; Wu, S.; Brown, S.A.; Peng, S.; Han, Z.; et al. Carbon fibre electrodes for ultra long cycle life pseudocapacitors by engineering the nano-structure of vertical graphene and manganese dioxides. *Carbon* **2021**, *177*, 260–270. [\[CrossRef\]](#)
61. Wu, G.; Yang, X.; Hou, C.; Li, Y.; Zhang, Q.; Wang, H. High volumetric energy density asymmetric fibrous supercapacitors with coaxial structure based on graphene/MnO₂ hybrid fibers. *ChemElectroChem* **2020**, *7*, 4641–4648. [\[CrossRef\]](#)
62. Li, P.; Jin, Z.; Peng, L.; Zhao, F.; Xiao, D.; Jin, Y.; Yu, G. Stretchable all-gel-state fiber-shaped supercapacitors enabled by macromolecularly interconnected 3D graphene/nanostructured conductive polymer hydrogels. *Adv. Mater.* **2018**, *30*, e1800124. [\[CrossRef\]](#)
63. Wu, Q.; Xu, Y.; Yao, Z.; Liu, A.; Shi, G. Supercapacitors based on flexible graphene/polyaniline nanofiber composite films. *ACS Nano* **2010**, *4*, 1963–1970. [\[CrossRef\]](#)
64. Huang, Y.; Tao, J.; Meng, W.; Zhu, M.; Huang, Y.; Fu, Y.; Gao, Y.; Zhi, C. Super-high rate stretchable polypyrrole-based supercapacitors with excellent cycling stability. *Nano Energy* **2015**, *11*, 518–525. [\[CrossRef\]](#)
65. Roberts, M.E.; Wheeler, D.R.; McKenzie, B.B.; Bunker, B.C. High specific capacitance conducting polymer supercapacitor electrodes based on poly (tris (thiophenylphenyl) amine). *J. Mater. Chem.* **2009**, *19*, 6977–6979. [\[CrossRef\]](#)
66. Song, Y.; Liu, T.Y.; Xu, X.X.; Feng, D.Y.; Li, Y.; Liu, X.X. Pushing the cycling stability limit of polypyrrole for supercapacitors. *Adv. Funct. Mater.* **2015**, *25*, 4626–4632. [\[CrossRef\]](#)
67. Xu, T.; Ding, X.; Liang, Y.; Zhao, Y.; Chen, N.; Qu, L. Direct spinning of fiber supercapacitor. *Nanoscale* **2016**, *8*, 12113–12117. [\[CrossRef\]](#)
68. Hu, X.; Rajendran, S.; Yao, Y.; Liu, Z.; Gopalsamy, K.; Peng, L.; Gao, C. A novel wet-spinning method of manufacturing continuous bio-inspired composites based on graphene oxide and sodium alginate. *Nano Res.* **2016**, *9*, 735–744. [\[CrossRef\]](#)
69. Zhang, Y.; Peng, J.; Li, M.; Saiz, E.; Wolf, S.E.; Cheng, Q. Bioinspired supertough graphene fiber through sequential interfacial interactions. *ACS Nano* **2018**, *12*, 8901–8908. [\[CrossRef\]](#)
70. Najafi, F.; Wang, G.; Mukherjee, S.; Cui, T.; Filleter, T.; Singh, C.V. Toughening of graphene-based polymer nanocomposites via tuning chemical functionalization. *Compos. Sci. Technol.* **2020**, *194*, 108140. [\[CrossRef\]](#)
71. Wang, G.; Dai, Z.; Liu, L.; Hu, H.; Dai, Q.; Zhang, Z. Tuning the interfacial mechanical behaviors of monolayer graphene/PMMA nanocomposites. *ACS Appl. Mater. Interfaces* **2016**, *8*, 22554–22562. [\[CrossRef\]](#)
72. Wu, Z.-S.; Ren, W.; Wang, D.-W.; Li, F.; Liu, B.; Cheng, H.-M. High-energy MnO₂ nanowire/graphene and graphene asymmetric electrochemical capacitors. *ACS Nano* **2010**, *4*, 5835–5842. [\[CrossRef\]](#)
73. Wu, Z.-S.; Zhou, G.; Yin, L.-C.; Ren, W.; Li, F.; Cheng, H.-M. Graphene/metal oxide composite electrode materials for energy storage. *Nano Energy* **2012**, *1*, 107–131. [\[CrossRef\]](#)
74. Chen, G.; Ai, Y.; Mugaanire, I.T.; Ma, W.; Hsiao, B.S.; Hou, K.; Zhu, M. A simple inorganic hybrids strategy for graphene fibers fabrication with excellent electrochemical performance. *J. Power Sources* **2020**, *450*, 227637. [\[CrossRef\]](#)
75. Ge, W.; Ma, Q.; Ai, Z.; Wang, W.; Jia, F.; Song, S. Three-dimensional reduced graphene oxide/montmorillonite nanosheet aerogels as electrode material for supercapacitor application. *Appl. Clay Sci.* **2021**, *206*, 106022. [\[CrossRef\]](#)
76. Xu, T.; Zhang, Z.; Qu, L. Graphene-based fibers: Recent advances in preparation and application. *Adv. Mater.* **2020**, *32*, e1901979. [\[CrossRef\]](#)

77. Zhang, G.; Han, Y.; Shao, C.; Chen, N.; Sun, G.; Jin, X.; Gao, J.; Ji, B.; Yang, H.; Qu, L. Processing and manufacturing of graphene-based microsupercapacitors. *Mater. Chem. Front.* **2018**, *2*, 1750–1764. [[CrossRef](#)]
78. Yu, D.; Goh, K.; Wang, H.; Wei, L.; Jiang, W.; Zhang, Q.; Dai, L.; Chen, Y. Scalable synthesis of hierarchically structured carbon nanotube–graphene fibres for capacitive energy storage. *Nat. Nanotechnol.* **2014**, *9*, 555–562. [[CrossRef](#)] [[PubMed](#)]
79. Tian, Q.; Xu, Z.; Liu, Y.; Fang, B.; Peng, L.; Xi, J.; Li, Z.; Gao, C. Dry spinning approach to continuous graphene fibers with high toughness. *Nanoscale* **2017**, *9*, 12335–12342. [[CrossRef](#)] [[PubMed](#)]
80. Li, X.; Zhao, T.; Wang, K.; Yang, Y.; Wei, J.; Kang, F.; Wu, D.; Zhu, H. Directly drawing self-assembled, porous, and monolithic graphene fiber from chemical vapor deposition grown graphene film and its electrochemical properties. *Langmuir* **2011**, *27*, 12164–12171. [[CrossRef](#)]
81. Carretero–González, J.; Castillo–Martínez, E.; Dias–Lima, M.; Acik, M.; Rogers, D.M.; Sovich, J.; Haines, C.S.; Lepró, X.; Kozlov, M.; Zhakidov, A. Oriented graphene nanoribbon yarn and sheet from aligned multi-walled carbon nanotube sheets. *Adv. Mater.* **2012**, *24*, 5695–5701. [[CrossRef](#)]
82. Jang, E.Y.; Carretero–González, J.; Choi, A.; Kim, W.J.; Kozlov, M.E.; Kim, T.; Kang, T.J.; Baek, S.J.; Kim, D.W.; Park, Y.W. Fibers of reduced graphene oxide nanoribbons. *Nanotechnology* **2012**, *23*, 235601. [[CrossRef](#)]
83. Al Faruque, M.A.; Syduzzaman, M.; Sarkar, J.; Bilisik, K.; Naebe, M. A review on the production methods and applications of graphene-based materials. *Nanomaterials* **2021**, *11*, 2414. [[CrossRef](#)] [[PubMed](#)]
84. Jiang, Z.; Li, Q.; Chen, M.; Li, J.; Li, J.; Huang, Y.; Besenbacher, F.; Dong, M. Mechanical reinforcement fibers produced by gel-spinning of poly-acrylic acid (PAA) and graphene oxide (GO) composites. *Nanoscale* **2013**, *5*, 6265–6269. [[CrossRef](#)] [[PubMed](#)]
85. Zhang, M.; Wang, X.; Yang, T.; Zhang, P.; Wei, X.; Zhang, L.; Li, H. Polyaniline/graphene hybrid fibers as electrodes for flexible supercapacitors. *Synth. Met.* **2020**, *268*, 116484. [[CrossRef](#)]
86. Ren, H.; Zheng, L.; Wang, G.; Gao, X.; Tan, Z.; Shan, J.; Cui, L.; Li, K.; Jian, M.; Zhu, L.; et al. Transfer-medium-free nanofiber-reinforced graphene film and applications in wearable transparent pressure sensors. *ACS Nano* **2019**, *13*, 5541–5548. [[CrossRef](#)] [[PubMed](#)]
87. Lin, L.; Deng, B.; Sun, J.; Peng, H.; Liu, Z. Bridging the gap between reality and ideal in chemical vapor deposition growth of graphene. *Chem. Rev.* **2018**, *118*, 9281–9343. [[CrossRef](#)]
88. Xiong, G.; Meng, C.; Reifengerger, R.G.; Irazoqui, P.P.; Fisher, T.S. Graphitic petal electrodes for all-solid-state flexible supercapacitors. *Adv. Energy Mater.* **2014**, *4*, 1300515. [[CrossRef](#)]
89. Zeng, J.; Ji, X.; Ma, Y.; Zhang, Z.; Wang, S.; Ren, Z.; Zhi, C.; Yu, J. 3D graphene fibers grown by thermal chemical vapor deposition. *Adv. Mater.* **2018**, *30*, e1705380. [[CrossRef](#)]
90. Wang, C.; Li, J.; Sun, S.; Li, X.; Zhao, F.; Jiang, B.; Huang, Y. Electrophoretic deposition of graphene oxide on continuous carbon fibers for reinforcement of both tensile and interfacial strength. *Compos. Sci. Technol.* **2016**, *135*, 46–53. [[CrossRef](#)]
91. Zhao, X.; Zheng, B.; Huang, T.; Gao, C. Graphene-based single fiber supercapacitor with a coaxial structure. *Nanoscale* **2015**, *7*, 9399–9404. [[CrossRef](#)]
92. Park, S.; Kim, S. Effect of carbon blacks filler addition on electrochemical behaviors of Co₃O₄/graphene nanosheets as a supercapacitor electrodes. *Electrochim. Acta* **2013**, *89*, 516–522. [[CrossRef](#)]
93. Sun, H.; You, X.; Deng, J.; Chen, X.; Yang, Z.; Ren, J.; Peng, H. Novel graphene/carbon nanotube composite fibers for efficient wire-shaped miniature energy devices. *Adv. Mater.* **2014**, *26*, 2868–2873. [[CrossRef](#)]
94. Jiang, N.; Huang, F.; Xia, W.; Wei, J.; Zhou, L.; Huo, Z.; Pang, Q. Facile fabrication of rGO/CNT hybrid fibers for high-performance flexible supercapacitors. *J. Mater. Sci. Mater. Electron.* **2017**, *28*, 12147–12157. [[CrossRef](#)]
95. Wang, B.; Fang, X.; Sun, H.; He, S.; Ren, J.; Zhang, Y.; Peng, H. Fabricating continuous supercapacitor fibers with high performances by integrating all building materials and steps into one process. *Adv. Mater.* **2015**, *27*, 7854–7860. [[CrossRef](#)] [[PubMed](#)]
96. Ma, W.; Chen, S.; Yang, S.; Chen, W.; Weng, W.; Zhu, M. Bottom-up fabrication of activated carbon fiber for all-solid-state supercapacitor with excellent electrochemical performance. *ACS Appl. Mater. Interfaces* **2016**, *8*, 14622–14627. [[CrossRef](#)] [[PubMed](#)]
97. Ho, B.T.; Lim, T.; Jeong, M.H.; Suk, J.W. Graphene fibers containing activated graphene for high-performance solid-state flexible supercapacitors. *ACS Appl. Energy Mater.* **2021**, *4*, 8883–8890. [[CrossRef](#)]
98. Qu, G.; Cheng, J.; Li, X.; Yuan, D.; Chen, P.; Chen, X.; Wang, B.; Peng, H. A fiber supercapacitor with high energy density based on hollow graphene/conducting polymer fiber electrode. *Adv. Mater.* **2016**, *28*, 3646–3652. [[CrossRef](#)] [[PubMed](#)]
99. PadmajanSasikala, S.; Lee, K.E.; Lim, J.; Lee, H.J.; Koo, S.H.; Kim, I.H.; Jung, H.J.; Kim, S.O. Interface-confined high crystalline growth of semiconducting polymers at graphene fibers for high-performance wearable supercapacitors. *ACS Nano* **2017**, *11*, 9424–9434. [[CrossRef](#)]
100. Ding, X.; Zhao, Y.; Hu, C.; Hu, Y.; Dong, Z.; Chen, N.; Zhang, Z.; Qu, L. Spinning fabrication of graphene/polypyrrole composite fibers for all-solid-state, flexible fibriform supercapacitors. *J. Mater. Chem. A* **2014**, *2*, 12355–12360. [[CrossRef](#)]
101. Ma, W.; Chen, S.; Yang, S.; Chen, W.; Cheng, Y.; Guo, Y.; Peng, S.; Ramakrishna, S.; Zhu, M. Hierarchical MnO₂ nanowire/graphene hybrid fibers with excellent electrochemical performance for flexible solid-state supercapacitors. *J. Power Sources* **2016**, *306*, 481–488. [[CrossRef](#)]
102. Li, X.; Zhao, T.; Chen, Q.; Li, P.; Wang, K.; Zhong, M.; Wei, J.; Wu, D.; Wei, B.; Zhu, H. Flexible all solid-state supercapacitors based on chemical vapor deposition derived graphene fibers. *Phys. Chem. Chem. Phys.* **2013**, *15*, 17752–17757. [[CrossRef](#)]

103. Chen, Q.; Meng, Y.; Hu, C.; Zhao, Y.; Shao, H.; Chen, N.; Qu, L. MnO₂-modified hierarchical graphene fiber electrochemical supercapacitor. *J. Power Sources* **2014**, *247*, 32–39. [\[CrossRef\]](#)
104. Tang, M.; Wu, Y.; Yang, J.; Xue, Y. Hierarchical core-shell fibers of graphene fiber/radially-aligned molybdenum disulfide nanosheet arrays for highly efficient energy storage. *J. Alloys Compd.* **2020**, *828*, 153622. [\[CrossRef\]](#)
105. Wang, B.; Wu, Q.; Sun, H.; Zhang, J.; Ren, J.; Luo, Y.; Wang, M.; Peng, H. An intercalated graphene/(molybdenum disulfide) hybrid fiber for capacitive energy storage. *J. Mater. Chem. A* **2017**, *5*, 925–930. [\[CrossRef\]](#)
106. Yang, Q.; Xu, Z.; Fang, B.; Huang, T.; Cai, S.; Chen, H.; Liu, Y.; Gopalsamy, K.; Gao, W.; Gao, C. MXene/graphene hybrid fibers for high performance flexible supercapacitors. *J. Mater. Chem. A* **2017**, *5*, 22113–22119. [\[CrossRef\]](#)
107. He, N.; Liao, J.; Zhao, F.; Gao, W. Dual-core supercapacitor yarns: An enhanced performance consistency and linear power density. *ACS Appl. Mater. Interfaces* **2020**, *12*, 15211–15219. [\[CrossRef\]](#)
108. He, N.; Patil, S.; Qu, J.; Liao, J.; Zhao, F.; Gao, W. Effects of electrolyte mediation and MXene size in fiber-shaped supercapacitors. *ACS Appl. Energy Mater.* **2020**, *3*, 2949–2958. [\[CrossRef\]](#)
109. Zhi, M.; Xiang, C.; Li, J.; Li, M.; Wu, N. Nanostructured carbon-metal oxide composite electrodes for supercapacitors: A review. *Nanoscale* **2013**, *5*, 72–88. [\[CrossRef\]](#)
110. Salanne, M.; Rotenberg, B.; Naoi, K.; Kaneko, K.; Taberna, P.-L.; Grey, C.P.; Dunn, B.; Simon, P. Efficient storage mechanisms for building better supercapacitors. *Nat Energy* **2016**, *1*, 1–10. [\[CrossRef\]](#)
111. Chmiola, J.; Yushin, G.; Gogotsi, Y.; Portet, C.; Simon, P.; Taberna, P.-L. Anomalous increase in carbon capacitance at pore sizes less than 1 nanometer. *Science* **2006**, *313*, 1760–1763. [\[CrossRef\]](#)
112. Largeot, C.; Portet, C.; Chmiola, J.; Taberna, P.-L.; Gogotsi, Y.; Simon, P. Relation between the ion size and pore size for an electric double-layer capacitor. *J. Am. Chem. Soc.* **2008**, *130*, 2730–2731. [\[CrossRef\]](#)
113. Zheng, X.; Zhang, K.; Yao, L.; Qiu, Y.; Wang, S. Hierarchically porous sheath-core graphene-based fiber-shaped supercapacitors with high energy density. *J. Mater. Chem. A* **2018**, *6*, 896–907. [\[CrossRef\]](#)
114. Zhang, X.; Wang, Q. Fibrous and flexible electrodes comprising hierarchical nanostructure graphene for supercapacitors. *Micro Nano Lett.* **2020**, *15*, 992–996. [\[CrossRef\]](#)
115. Wang, G.; Liu, L.; Zhang, Z. Interface mechanics in carbon nanomaterials-based nanocomposites. *Compos. Part A Appl. Sci. Manuf.* **2021**, *141*, 106212. [\[CrossRef\]](#)
116. Wu, G.; Tan, P.; Wu, X.; Peng, L.; Cheng, H.; Wang, C.F.; Chen, W.; Yu, Z.; Chen, S. High-performance wearable micro-supercapacitors based on microfluidic-directed nitrogen-doped graphene fiber electrodes. *Adv. Funct. Mater.* **2017**, *27*, 1702493. [\[CrossRef\]](#)
117. Chen, P.; Yang, J.-J.; Li, S.-S.; Wang, Z.; Xiao, T.-Y.; Qian, Y.-H.; Yu, S.-H. Hydrothermal synthesis of macroscopic nitrogen-doped graphene hydrogels for ultrafast supercapacitor. *Nano Energy* **2013**, *2*, 249–256. [\[CrossRef\]](#)
118. Zhang, Y.; Li, Y.; Ming, P.; Zhang, Q.; Liu, T.; Jiang, L.; Cheng, Q. Ultrastrong bioinspired graphene-based fibers via synergistic toughening. *Adv. Mater.* **2016**, *28*, 2834–2839. [\[CrossRef\]](#) [\[PubMed\]](#)
119. Ma, Y.; Li, P.; Sedloff, J.W.; Zhang, X.; Zhang, H.; Liu, J. Conductive graphene fibers for wire-shaped supercapacitors strengthened by unfunctionalized few-walled carbon nanotubes. *ACS Nano* **2015**, *9*, 1352–1359. [\[CrossRef\]](#)
120. Qu, Q.; Zhang, P.; Wang, B.; Chen, Y.; Tian, S.; Wu, Y.; Holze, R. Electrochemical performance of MnO₂ nanorods in neutral aqueous electrolytes as a cathode for asymmetric supercapacitors. *J. Phys. Chem. C* **2009**, *113*, 14020–14027. [\[CrossRef\]](#)
121. Xu, C.; Li, B.; Du, H.; Kang, F.; Zeng, Y. Supercapacitive studies on amorphous MnO₂ in mild solutions. *J. Power Sources* **2008**, *184*, 691–694. [\[CrossRef\]](#)
122. Yu, G.; Hu, L.; Vosgueritchian, M.; Wang, H.; Xie, X.; McDonough, J.R.; Cui, X.; Cui, Y.; Bao, Z. Solution-processed graphene/MnO₂ nanostructured textiles for high-performance electrochemical capacitors. *Nano Lett.* **2011**, *11*, 2905–2911. [\[CrossRef\]](#) [\[PubMed\]](#)
123. Wang, S.; Liu, N.; Su, J.; Li, L.; Long, F.; Zou, Z.; Jiang, X.; Gao, Y. Highly Stretchable and Self-Healable Supercapacitor with Reduced Graphene Oxide Based Fiber Springs. *ACS Nano* **2017**, *11*, 2066–2074. [\[CrossRef\]](#)
124. Liu, D.; Du, P.; Wei, W.; Wang, H.; Wang, Q.; Liu, P. Skeleton/skin structured (RGO/CNTs)@PANI composite fiber electrodes with excellent mechanical and electrochemical performance for all-solid-state symmetric supercapacitors. *J. Colloid Interface Sci.* **2018**, *513*, 295–303. [\[CrossRef\]](#) [\[PubMed\]](#)