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Review

A Mini-Review on Preparation of Functional Composite Fibers and Their Based Devices

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Abstract: Composite fibers are composed of two or more different components by functionating, coating or direct spinning, enabling unique characteristics, such as design ability, high strength, and high- and low-temperature resistance. Due to their ability to be directly woven into or stitched onto textiles to prepare flexible electronic devices, stretchable composite fibers have drawn great attention, enabling better wearability and integrality to wearable devices. Fiber or fiber-based electronic film or textiles represent a significant component in wearable technology, providing the possibility for portable and wearable electronics in the future. Herein, we introduce the composite fiber together with its preparation and devices. With the advancement of preparation technology, the as-prepared composite fibers exhibit good performance in various applications closely related to human life. Moreover, a simple discussion will be provided based on recent basic and advanced progress on composite fibers used in various devices.

Keywords: fiber; composite; preparation; application

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1. Introduction

Fibers are an indispensable part of people's lives, and ordinary fibers can no longer meet the development of social technology [1–3]. Therefore, composite fibers are gradually assuming an essential role as an alternative and improved option. Composite fibers are composed of two or more different components, and advanced preparation technology has allowed optimization of the various properties [4–8]. The interaction of each component provides it with excellent comprehensive properties, which enables good performance in various applications closely related to human life [9–11]. The developed composite fiber has been applied in the field of environment, energy and devices owing to several advantages when compared with ordinary fiber: (1) Composite fibers have a higher specific strength and electron transmission along with the fiber [12]. Such composite fibers possess excellent wearability and are widely used to design wearable electronic devices [13,14]. (2) Composite fibers are related to the components' various unique properties and applications, such as in energy devices, microelectronics, optics, catalytic, sensors devices, etc. [15,16]. (3) The composite fibers' structure and properties can be designable [17,18]. The designed composite fiber can meet various requirements by controlling the structures via different preparation processes [19–21]. Due to its advantages, such as being lightweight, long-lasting, flexible, and conformable, composite fibers are highly desirable for wearable electronic devices [22].

The use of mature and affordable textile processing technologies has allowed the manufacture of many fibrous structures to design intelligent wearable devices, such as sensors, environmental and energy devices [23]. Herein, we introduce the basic preparation methods of composite fibers, including surface coating and direct preparation, and their applications in sensors, environments, and energy will be described according to the representative literature. A simple discussion will also be provided based on recent basic and advanced progress in various applications of composite fibers. Lastly, the challenges and opportunities of composite fibers are proposed at the end of the paper.

2. Preparation of Functional Composite Fiber

With advanced nanotechnology, it is possible to build electronic devices directly inside single fibers' or on their surfaces. Thus, the functional composite fibers can be obtained either from the functionalization of the original fiber or direct preparation. Appropriate preparation technology could meet the various requirements for various applications.

2.1. Functionalization of Fiber

To functionalize fibers and preserve fiber enhancement, it is feasible to coat a secondary material to a functional group on the surface, which could improve their thermal, electrical or mechanical properties. We briefly present the methods for fiber's functionalization in Figure 1, which will obtain the composite fiber through functionalizing the original fiber. Carbonization is the thermal decomposition of pre-prepared fibers under high temperatures, which removes the unstable parts and gains high pure carbon-based composite fiber to enhance the electroconductivity, chemical stability, and mechanical strength [24]. Hydroxylation is a chemical reaction where hydroxyl groups are coated on the fibers' surface [25]. Surface hydroxyl groups play an important role in the catalytic process as active centers. Vulcanization is often performed in a vulcanizing boiler at $\leq$180 °C by heating fibers with sulfur [26]. Vulcanized fibers are a durable, hard, chemically pure cellulose product without resin or bonding agents, enabling the fiber to exhibit more flexibility, high tear strength, impact resistance, smooth and abrasion-resistant surface. Plasma treatment and anodic oxidation can introduce more chemical bonds into or onto the fiber, positively affecting the composite fiber's interfacial strength [27]. Dipping, chemical vapor deposition, spraying or sputtering are used to form new functional coatings on the fibers, bringing unique properties [28–31]. It should be noted that Figure 1 could not cover all methods for preparing composite fiber by functionalization, and there are some other surface modification or fiber functionalization methods not listed here.

2.2. Direct Preparation of Composite Fibers

In some cases, the composite fiber can be obtained by direct preparation from the solution using a template or direct spinning. As shown in Figure 2, the dispersion of composite precursors was injected into a capillary tube directly in a template method. The solvent was subsequently removed by thermal treatment and left a fiber product [32].

The spinning methods can normally be divided into melt spinning and solution spinning. Melt spinning is an effective technique for manufacturing polymer fibers [33,34]. As shown in Figure 2, the melted polymer was extruded through a spinneret. A monofilament or multifilament yarn was obtained after solidification by cooling. It should be noted here that other materials (such as chemicals or nanoparticles) could be melted into the melted polymer for complex applications.

Solution spinning often includes wet spinning, dry spinning and electrospinning. For dry spinning and wet spinning: A certain proportion of polymer is dissolved in a certain solvent and obtains a specific viscosity for spinning. The spinning solution can also be prepared by direct polymerization of a homogeneous solution. Then, the spinning solution is extruded from a syringe with a spinneret into a warm air chamber (dry spinning) or a coagulation bath (wet spinning), where the solvent evaporates, and the fine filaments are obtained after solidifying [35,36]. For some polymers, it is ineffective to extrude the spinning solution into the coagulation bath directly. Therefore, the schematic diagram in Figure 2 shows that dry-jet wet spinning has been developed in that the spinning solution was extruded through a spinneret on an air gap and then transferred into a coagulation bath for solidification [37,38]. Electrospinning draws charged threads from polymer solutions/melts the fiber with an electric force, thus preparing large-scale nanofibers directly and continuously [39,40]. The melted polymer or solution is extruded through a spinneret under a high-voltage electric field. The fiber or fiber-based melt is obtained after solidifying or coagulating. It should be noted that the electrospinning process should be operated inside a closed chamber with an air environment to control the temperature and relative humidity. Moreover, other materials (such as chemicals or nanoparticles) could be mixed into the spinning solution to prepare composite fibers [41].

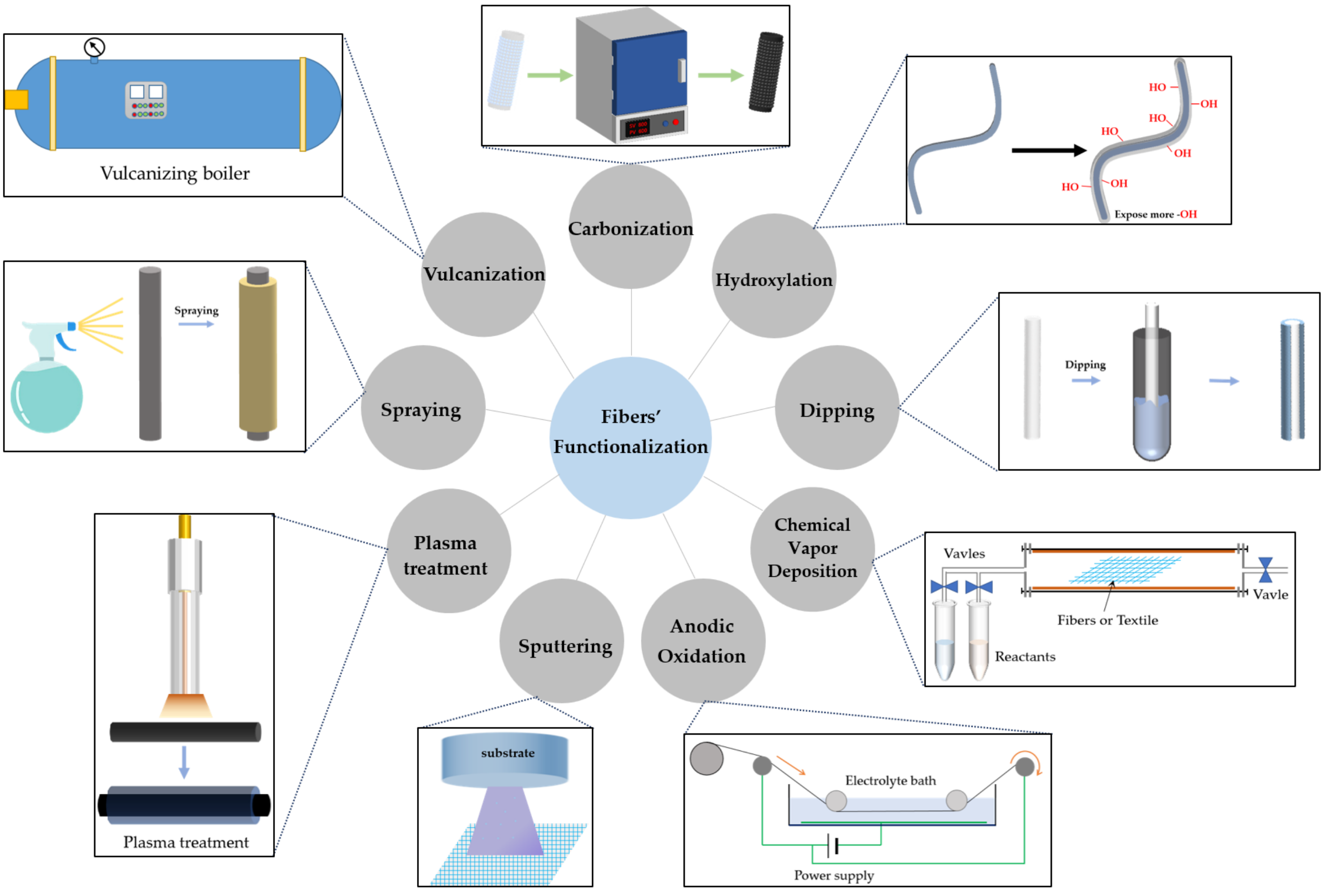

Figure 1. Methods for fiber functionalization to prepare composite fibers.

The development of nanofiber technology allows the original fibers to form a core-shell structure [42], such a structured fiber can control the thickness or structure of the core or shell layer to control the material properties, controlling the optical, electrical, magnetic and other properties of the obtained composite fiber. The core-shell fiber can be fabricated easily using coaxial electrospinning or wet spinning technology [43–46]. In Figure 2, we showed the model of coaxial electrospinning and wet spinning methods. The principle of coaxial spinning is similar to that of ordinary spinning. The core and shell layer material solutions are in different syringes and extruded through the composite spinneret. The shell layer solution flows out from the annular gap between the inner and outer spinneret, and the core solution flows out from the inner spinneret, retaining the coaxial and resulting in a coaxial fiber.

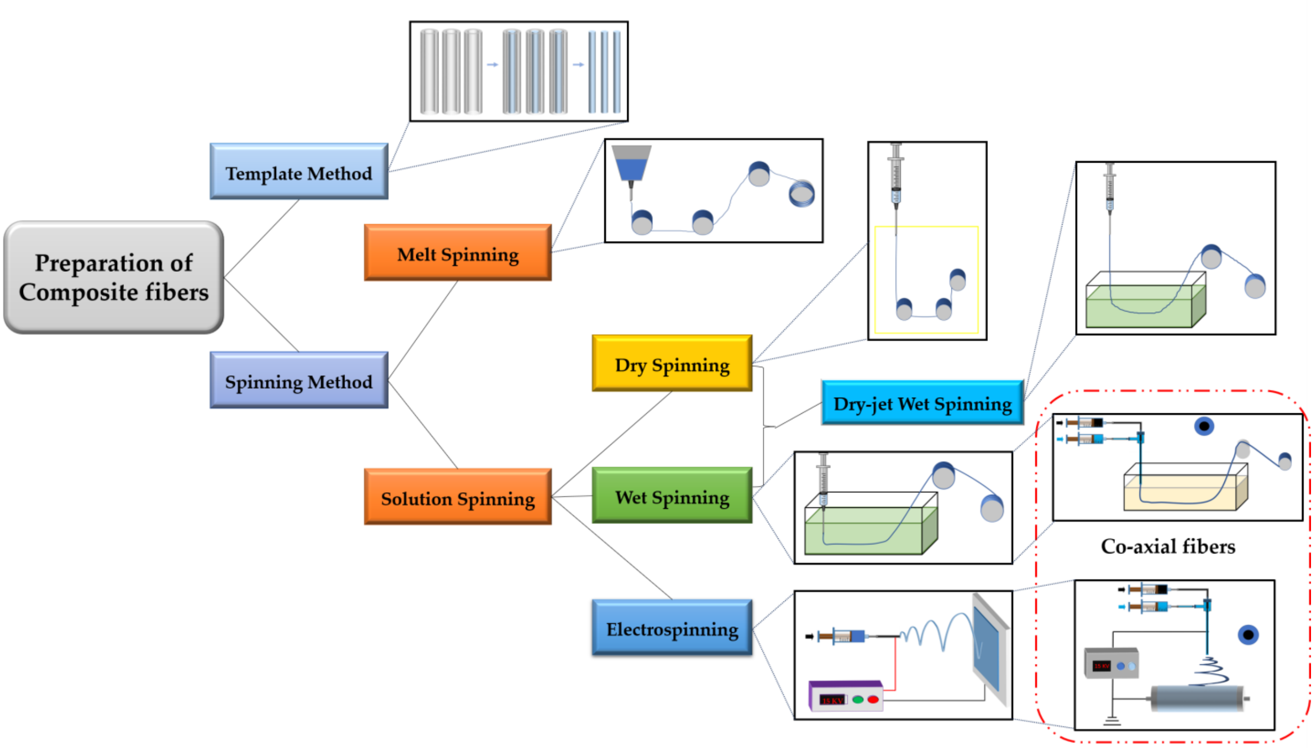

Figure 2. Methods for direct preparation of composite fibers.

3. Functionalized Composite Fiber-Based Devices

Composite fibers are composed of two or more different components, and advanced preparation technology optimizes the interaction of components making excellent comprehensive properties, which enables good performances in various applications closely related to human life. Thus, composite fibers have been used in many different applications, such as sensors, photo/electrocatalytic devices and other energy devices. This section will introduce the applications of composite fibers in different applications.

3.1. Sensing Devices

As shown in Figure 3, composite fibers have been applied in many sensors for different purposes, such as sensing gas, pollutants, ultraviolet radiation, temperature, humidity, pressure, and strain [47–52].

3.1.1. Gas Sensor

Similar to the classic film or bulk type gas sensors (Figure 3a), the fiber gas sensors have shown outstanding sensitivity with reversibility and good long-term device stability. Moreover, the as-fabricated fiber gas sensors exhibited excellent wearable functionality with flexible fiber shapes allowing excellent washability and an outstanding mechanical bending ability. For practical applications, optimization of the device structure, sensing elements, and surface coatings will further improve the sensing performance of the intelligent wearable fiber or textile.

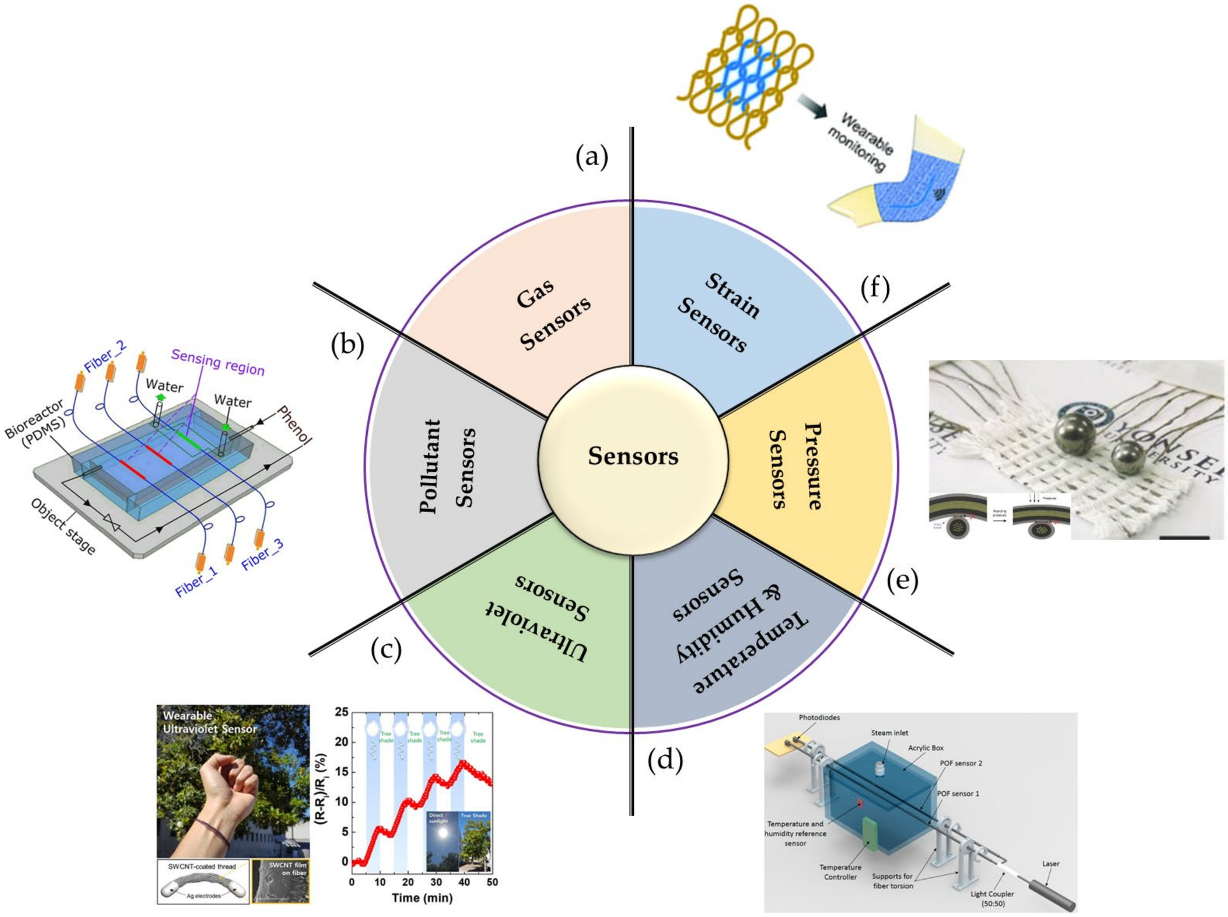

Figure 3. The different kinds of sensors assembled by composite fiber: (**a**) Gas sensor, Reproduced with permission from [47], Copyright 2019, American Chemical Society; (**b**) Pollutant sensor, Reproduced with permission from [48], Copyright 2019, American Chemical Society; (**c**) Ultraviolet sensor, Reproduced with permission from [49], Copyright 2018, American Chemical Society; (**d**) Temperature & Humidity sensor, Reproduced with permission from [50], Copyright 2018, MDPI; (**e**) Pressure sensor, Reproduced with permission from [51], Copyright 2015, Wiley-VCH; (**f**) Strain sensors, Reproduced with permission from [52], Copyright 2019, Royal Society of Chemistry.

3.1.2. Pollution Sensor

Environmental monitoring has efficiently dealt with environmental changes and detected pollution in our surroundings, which is equally important as pollution removal [48]. It is a promising scheme to utilize fiber pollution sensors for environmental monitoring due to advantages including a high transmission rate along with fiber axial, lightweight, small size, and flexibility. As shown in Figure 3b, pollution content could be determined when pollutants were injected into the sensor. The fiber pollution sensors with functionalized coatings were explored to detect many different kinds of pollution, such as volatile organic compounds (VOCs), heavy metal ions, persistent organic pollutants (POPs), antibiotic pollutants, and other industrial pollutants.

3.1.3. Ultraviolet Sensor

The ultraviolet (UV) sensors are photosensors that use the photo responded material as a sensing element. The photoresponses of two terminals of the composite fiber were measured upon exposure to ultraviolet light, which could detect the intensity, wavelength, portion and on/off cycles of the ultraviolet light based on sensor response. As shown in Figure 3c, a fabric-compatible UV sensor using a cellulose-based thread coated with single-wall carbon nanotube ink exhibit high UV sensing performance for wearable applications.

The UV sensor based on composite fibers could be stitched onto clothes for practical usability under direct sunlight, which shows potential as a wearable sensor compared to conventional bulk detectors.

3.1.4. Temperature and Humidity Sensor

Temperature and humidity are indispensable parts of production and daily life. These sensors (Figure 3d) were used to measure temperature or humidity changes in the ambient air. Composite fiber temperature sensors could possess real-time temperature-sensing capacities based on fiber interferometric or Bragg grating. In addition, an integrated smart cloth could measure the body temperature and track large-scale movements of human physiological signals. Humidity sensors typically convert these measurements into an electronic signal, which could indicate the humidity of the environment. Furthermore, composited fibers enhance the temperature and humidity sensors in various shapes and functionalities for various applications.

3.1.5. Pressure Sensor

A pressure sensor could convert sensing pressure into an electric signal from variations in the contact area between conductors upon compressive deformation depending on the pressure applied [53]. As for the nanostructured pressure sensor shown in Figure 3e, the structure changed with applied pressure resulting in the contact area changing, which means the composite fiber should possess porous structure and flexibility. The fiber or fiber-based textile pressure sensor allows smart clothes to use multifunctional non-contact intelligent human-machine systems.

3.1.6. Strain Sensor

Conductive composite fibers with inherent stretchability could be integrated onto human skin or cloth to detect strain in the desired direction as shown in Figure 3f. A fiber strain sensor could also convert sensing strain into an electric signal from variations in the connections among conductive fillers in the composite fiber in response to an applied strain. The development of wearable strain sensors with high sensitivity, excellent stability and an extensive workable strain range remains highly challenging.

3.2. Environmental Devices

This section mainly describes the composite fiber or fiber-based textile with catalytic activity to solve environmental issues, as shown in Figure 4 [54–59]. As well known, fiber-based textiles or fabrics could be designed for filtering/absorbing and self-cleaning with their superhydrophobic surface and unique physical properties [60]. Moreover, the fiber-based film or cloth could be used in smart device fabrication for cleaning air or organic pollution degradation. For example, high-efficiency textiles/metal-organic framework composites (MOFs@textiles) can be used as air filters as shown in Figure 4a and function excellent in removing particulate matter (PM) [54]. As shown in Figure 4b, SiO_2–TiO_2 porous nanofibrous membranes (STPNMs) can simultaneously realize highly efficient oil/water separation and the removal of heavy metal ions from wastewater, making them ideal candidates for practical applications in industrial wastewater purification [55]. The nanostructured photo/electrocatalyst functionalized composite fiber, fiber-based film, or textile will possess catalytic activity. The photocatalytic devices could be used for photocatalytic self-cleaning to degrade organic pollutants into CO_2 and H_2O see Figure 4c. The composite fibers with photo-sensitive inorganic nanoparticle coatings reflect the super degradation of heavy metals, making it possible to be used in protective garments and medical and military uniform systems [56]. In addition, the carbon fiber cloth (CFC), coated with TiO_2/Ag_3PO_4, has shown successful degradation capability of pollution as present in Figure 4d in static and flowing wastewater [57]. As shown in Figure 4e, Sn nanoparticles coated on carbon nanotubes (CNTs) in a hollow fiber promote high selective CO production from electrochemical CO_2 reduction [58]. A unique functional electrode comprised of hierarchal Ni–Mo–S nanosheets with abundantly exposed edges anchored on conductive and flexible carbon fiber cloth, exhibited a sizeable cathodic current and a low onset potential for hydrogen evolution reaction in a neutral electrolyte as shown in Figure 4f, and the incorporation of Ni atoms in Mo–S created substantial defect sites as well as modified the morphology of Ni-Mo-S network at the atomic scale, resulting in an impressive enhancement in the catalytic activity [59]. Notably, such functionalized composite fibers, fiber-based films, or textiles could be used for organic pollution removal, CO_2 reduction and H_2 production, which opens a new avenue to realize the separation and recovery of nanostructured photocatalysts from solutions in practical applications [61].

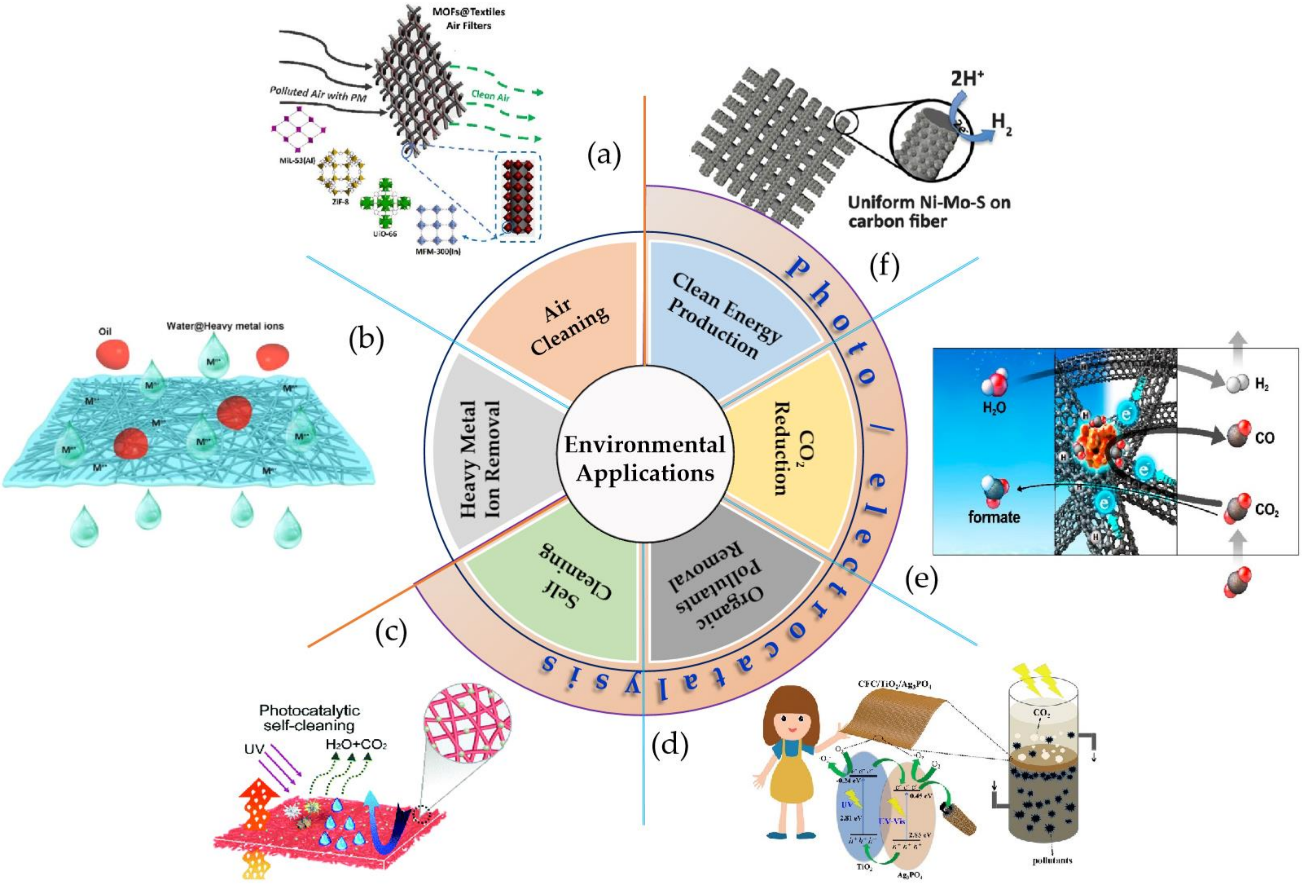

Figure 4. Schematic illustration of the composite fibers used for photo/electrocatalysis to solve the environmental issues. (**a**) Air Cleaning, Reproduced with permission from [54], Copyright 2019, American Chemical Society; (**b**) Heavy metal ion removal, Reproduced with permission from [55], Copyright 2019, American Chemical Society; (**c**) Self-cleaning, Reproduced with permission from [56], Copyright 2019, Royal Society of Chemistry; (**d**) Organic pollutants removal, Reproduced with permission from [57], Copyright 2020, Elsevier Inc.; (**e**) CO_2 reduction, Reproduced with permission from [58], Copyright 2020, American Chemical Society; (**f**) Clean energy production, Reproduced with permission from [59], Copyright 2015, American Association for the Advancement of Science.

3.3. Energy Devices

Recently, there has been significant interest in designing wearable and stretchable energy generation and storage devices utilizing composite fiber and fiber-based textiles as shown in Figure 5 [62–65]. For example, aligned MWCNT/MnO_2 composite fibers could be used to produce excellent lithium-ion batteries and wire-shaped supercapacitors as shown in Figure 5a [62]. A CNT-based rubber fiber and spring-like Ti wire as two electrodes in flexible perovskite solar cells showed high photovoltaic performances as shown in Figure 5b [63]. Assembled in fiber-shaped dye-sensitized solar cells (FDSSCs), in situ grown highly crystalline metal (Co, Ni) selenium on metal (Co, Ni) fibers have exhibited outstanding power conversion efficiency (Co–$Co_{0.85}Se$ 6.55% and Ni–$Ni_{0.85}Se$ 7.07%) and efficient electrochemical catalytic activity [66]. As shown in Figure 5c, a highly stretchable, fiber-convolving-fiber structured nanogenerator could produce a maximum short circuit charge transfer (Q_{SC}) of 61 nC and a maximum VOC of 142.8 V per stretching cycle, showing splendid stability and durability [64]. Similarly, based on buckled MnO_2/oxidized carbon nanotube (CNT) fiber electrodes, the stretchable fiber supercapacitor (SC) exhibited specific volumetric capacitance up to 409.4 F cm^{-3} with outstanding stability and repeatability(Figure 5d) [65]. In addition, coaxial fiber-like electrodes have been used for designing solar cells, supercapacitors, triboelectric nanogenerators and lithium-ion batteries [67–70]. These successes demonstrate the full incorporation of wearable energy devices based on functionalized fibers or fabrics. It is easy to scale up the fiber to meet the power, energy, and flexibility requirements of energy devices, and one fiber will provide a fundamental building block of large-scale devices.

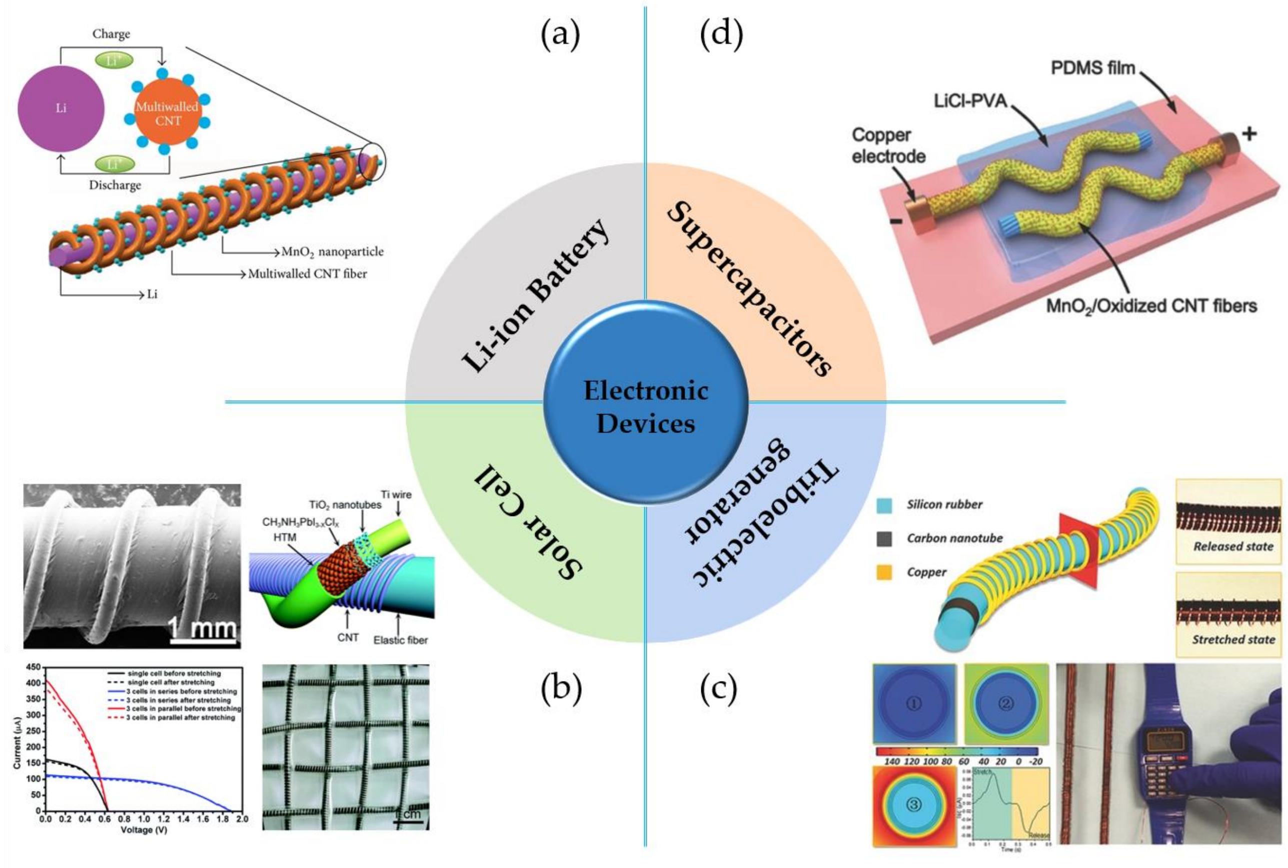

Figure 5. Schematic illustration of the composite fibers and fiber-based textile used for energy applications: (**a**) Li-ion battery, Reproduced with permission from [62], Copyright 2013, Wiley-VCH; (**b**) Solar cell, Reproduced with permission from [63], Copyright 2015, Royal Society of Chemistry; (**c**) Triboelectric generator, Reproduced with permission from [64], Copyright 2017, Wiley-VCH; (**d**) Supercapacitors, Reproduced with permission from [65], Copyright 2017, Wiley-VCH.

4. Conclusions and Outlooks

As described in this mini-review, composite fibers with various functions and a tunable structure could be obtained through controllable synthesis, fulfilling the various requirements concerning environmental and energy applications. Moreover, to develop high-performance fiber devices, numerous opportunities and challenges remain in the following aspects:

(1) For composite fiber preparation: Composite fibers remain a relatively expensive material used in specific special applications. Developing low-cost fiber preparation technology is significant for large-scale practical daily life applications.
(2) For the design of functional composite fibers: Flexibility of fiber-based devices is essential for improving their performance and exhibiting reliability and stability for target applications. Novel composite fibers need to be designed to obtain high-performance, multifunctional, and stable flexible devices to fulfill various requirements.
(3) For fiber-based devices: There are plentiful opportunities to diversify flexible devices with reconfigurable sizes, shapes, and properties. Advanced preparation technologies, structure and device designs, and device assembly methods need to be developed to prepare more fantastic functional composite fibers to fulfill various requirements in environmental and energy applications, such as different wearable sensors, pollution removal, air and water filtration, lithium-ion batteries, wire-shaped supercapacitors, self-powered devices and solar cells.

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