



## Nanofiber technology: current status and emerging developments

Kenry<sup>a,b</sup>, Chwee Teck Lim<sup>b,c,\*</sup>

<sup>a</sup> NUS Graduate School for Integrative Sciences and Engineering, National University of Singapore, 117456, Singapore

<sup>b</sup> Department of Biomedical Engineering, National University of Singapore, 117575, Singapore

<sup>c</sup> Mechanobiology Institute, National University of Singapore, 117411, Singapore



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### ABSTRACT

Nanofibers have emerged as exciting one-dimensional nanomaterials for a broad spectrum of research and commercial applications owing to their unique physicochemical properties and characteristics. As a class of nanomaterials with cross-sectional diameters ranging from tens to hundreds of nanometers, nanofibers possess extremely high specific surface area and surface area-to-volume ratio. They are capable of forming networks of highly porous mesh with remarkable interconnectivity between their pores, making them an attractive choice for a host of advanced applications. In fact, the significant impact of nanofiber technology can be traced from the wide range of fundamental materials that can be used for the synthesis of nanofibers. These include natural polymers, synthetic polymers, carbon-based materials, semiconducting materials, and composite materials. Correspondingly, the emerging proof-of-concept applications of nanofibers spanning several important areas have been rapidly reported. This Review explores the current status and up-and-coming development of nanofiber technology, with an emphasis on its syntheses and applications. First, we highlight the current and emerging strategies used in synthesizing nanofibers. We briefly introduce the various established nanofiber synthesis techniques, especially the electrospinning method. We then focus on the emerging nanofiber synthesis strategies, such as solution blow spinning, centrifugal jet spinning, and electrohydrodynamic direct writing. Next, we discuss the emerging applications of nanofiber technology in various fields, specifically in three important areas of energy generation and storage, water treatment and environmental remediation, and healthcare and biomedical engineering. Despite all these advancements, there are still challenges to be addressed and overcome for nanofiber technology to move towards maturation. Nevertheless, we envision that with further progress in the development of nanofiber synthesis strategies and identification of “killer” applications of nanofibers, nanofiber technology will mature and move beyond its current state towards commercial realization and applications.

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\* Corresponding author at: Department of Biomedical Engineering, National University of Singapore, 117575, Singapore.

E-mail address: [ctlim@nus.edu.sg](mailto:ctlim@nus.edu.sg) (C.T. Lim).

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## 1. Introduction

The world of nanomaterials comprises a wide range of intriguing materials with outstanding physical and chemical properties and characteristics. These materials include zero-dimensional nanoparticles or quantum dots, one-dimensional nanowires, nanorods, nanofibers, and nanotubes, and two-dimensional nanosheets [1–3]. Widely regarded as nanomaterials with great potential applications, nanofibers stand out among the rest of the nanomaterials. One of the most striking features of nanofibers is their exceptionally high surface area-to-volume ratio and high porosity, making them a robust and attractive candidate for many advanced applications. In fact, the real testament to the importance of nanofibers can be witnessed from the many building blocks from which they can be synthesized to the range of applications in which they have been demonstrated to have significant impact. To date, nanofibers have been prepared from an assortment of materials, such as natural polymers [4], synthetic polymers [5,6], carbon-based nanomaterials [7], semiconducting nanomaterials [8,9], and composite nanomaterials [10–16]. Along with the rapid progress in the synthesis and characterization of nanofibers over the past few years, tremendous efforts have been focused on exploring the potential functional applications of nanofibers, including energy generation and storage, water and environmental treatment, and healthcare and biomedical engineering.

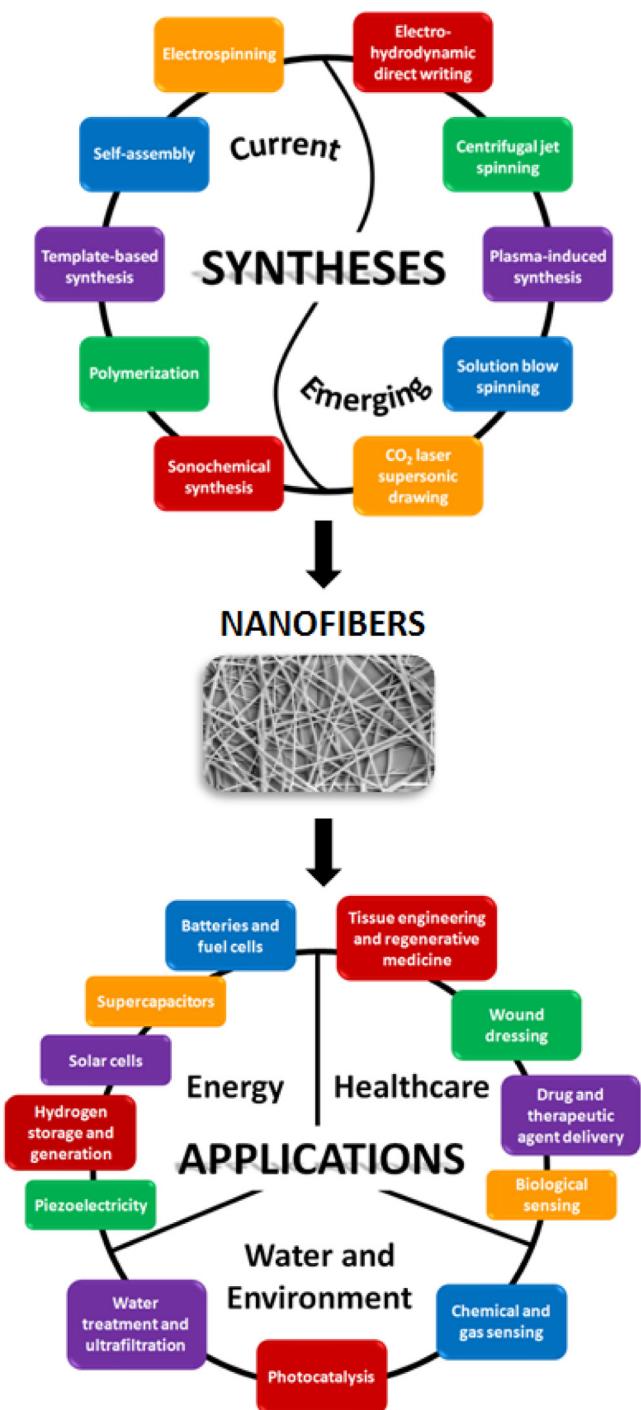
Here, we provide a review on the current status, challenges, and emerging development of nanofiber technology. In contrast to several excellent reviews that have detailed specific nanofiber synthesis techniques, particularly electrospinning, for certain applications, either in electronics, photonics, or regenerative medicine [17–19], this article aims to provide a broad overview of the various emerging nanofiber synthesis techniques coupled with their applications spanning three major themes of energy, water and environment, and healthcare, over the last several years. We start with an introduction to the current and emerging nanofiber fabrication techniques. This will be followed by discussion on the applications of nanofiber technology over a broad spectrum of areas encompassing energy generation and storage, water and environmental treatment, and healthcare and biomedical engineering (Fig. 1). We then present our perspectives and outlook on the current challenges facing the development and applications of nanofiber technology and highlight numerous future research directions in this field. An important question that we seek to address here is, with the potential it possesses, how

nanofiber technology can move from its current state in terms of fabrications and applications, to commercialization and implementation in everyday lives.

## 2. Current strategies for nanofiber fabrication

Of all the current strategies available for synthesizing one-dimensional nanofibers, electrospinning is one of the most established and widely adopted techniques [20–23]. In general, the electrospinning set-up consists of a syringe with a nozzle, an electric field source, a counter electrode or grounded target, and a pump. The electrospinning process is based on the principle of electrostatics in which the electrostatic repulsion forces in a high electrical field are used for nanofiber synthesis. The solution to be electrospun is held in a syringe nozzle and a large electrical field is generated between the nozzle and counter electrode. As the solution is ejected, the solution droplet at the nozzle adopts a cone-shaped deformation due to the potential difference between the nozzle and the grounded target. As the charged jet accelerates towards the counter electrode, the solvent in the solution evaporates, leading to the formation of solid continuous nanofibers on the grounded target. The physical properties of the electrospun nanofibers are heavily dependent on a multitude of parameters, such as solution properties (e.g., conductivity, viscoelasticity, and surface tension), environmental factors (e.g., processing temperature and humidity), and technical variables (e.g., tip-counter electrode distance, applied electrical potential, and flow rate). In fact, a wide range of fibrous nanostructures have been successfully prepared using electrospinning. For example, more recently, multifunctional colloidal polymer nanofibers have been prepared by electrospinning the aqueous blends of poly(vinyl alcohol-co-vinyl acetate)/octadecyl amine-montmorillonite (PVA/ODA-MMT) matrix nanocomposite and poly(maleic acid-*alt*-acrylic acid) (poly(Mac-*alt*-AA) copolymers [24].

Besides the conventional electrospinning technique, several variations of this method have been developed lately. These include the multineedle, needleless, and co-electrospinning or co-axial electrospinning. The multineedle and needleless electrospinning techniques are utilized to enhance the productivity of the conventional electrospinning. The co-axial electrospinning, on the other hand, is developed to synthesize core-shell and multilayer composite nanofibrous structures with additional functionalities and improved quality. In co-axial electrospinning, two distinct



**Fig. 1.** Syntheses and applications of nanofiber technology. Different strategies have been developed for the synthesis of nanofibers, ranging from current methods (e.g., electrospinning, self-assembly, and polymerization and template-based synthesis) to emerging strategies (e.g., solution blow spinning, centrifugal jet spinning, and electrohydrodynamic writing). Simultaneously, nanofiber technology has increasingly found applications in a wide range of areas, such as energy storage and generation, water treatment and environmental remediation, and healthcare and biomedical engineering.

nanofiber building blocks are supplied through different coaxial capillary channels and then integrated into core-shell composite nanofibers. In fact, the emergence of co-axial electrospinning has significantly contributed to the development of numerous novel functional nanomaterials in a large scale manner. For example, massive throughput preparation of two-layer core-shell polymer

nanofibers has been achieved via co-axial electrospinning [25]. Fe-doped oxide core-shell  $\text{In}_2\text{O}_3\text{-}\alpha\text{-Fe}_2\text{O}_3$  nanofibers with improved magnetic features have also been synthesized via co-axial electrospinning [26].

Co-electrospinning is generally used to generate single layer and bilayer nanofibers. Nevertheless, these nanofibrous structures have limited assembling configurations and functionalities. As such, by increasing the number of layers of nanofibers, the resultant connectivity of the composites and their functionalities can be enhanced. A recent study has shown that multifunctional nanofibers with more than two layers may be prepared via co-electrospinning [27]. It was reported that the facile preparation of a trilayer nanofibrous structure with alternating phases of  $\text{BaTiO}_3$  and  $\text{CoFe}_2\text{O}_4$  could be achieved through co-electrospinning [27]. Remarkably, the as-synthesized nanofibers displayed magnetoelectric coupling. Besides multilayer nanofibers, electrospinning can also be used to synthesize hierarchical nanofiber structures. This was shown in a study in which a hierarchical homoassembled polyacrylonitrile (PAN) nanofibrous mat decorated with ZnO nanostructures was prepared via electrospinning [28]. By following the conventional electrospinning with selective component removal, porous nanofibers with high specific surface area can be synthesized using the same method. This was demonstrated through the synthesis of pure mesoporous carbon and mesoporous Nafion nanofibers [29]. These porous nanofibers were obtained using the electrospinning of the polymer blends of Nafion-PAN continued with the specific removal of one of the components of the blends. Another intriguing variation of electrospinning is the sol-gel-based electrospinning method. Several novel nanofiber structures have recently been reported based on this technique. For example, the syntheses of ZrC nanofibers [30] and multiferroic BiFeO<sub>3</sub> and polymeric P(VDF-TrFE) composite nanofibers [31] have been achieved through a combination of electrospinning and sol-gel chemistry.

In addition to the electrospinning technique, nanofibers are currently synthesized through self-assembly in solution. Using the self-assembly technique, the preparation of natural or synthetic nanofibers may be achieved through the spontaneous organization of individual macromolecules into ordered and stable nanoscale supramolecular structures or patterns. For example, chitin nanofibers self-assembled to form networks on drying a squid pen  $\beta$ -chitin solution in a chitin nanofiber ink [4]. As compared to the electrospun nanofibers, the self-assembled nanofibers possess a much smaller diameter in the range of several nanometers. However, the self-assembly is a complex and low throughput method which requires elaborate set-up. In addition, sonochemical method (e.g., the sonochemical preparation of conductive PANI and cellulose-coated PANI nanofibers [32]) and polymerization and template-based synthesis (e.g., rapid chemical oxidative polymerization-based preparation of interconnected PANI nanofibers in a soft template [33] and synthesis of hybrid single-walled carbon nanotube-templated PANI nanofibers through in situ polymerization of aniline [34]) are also currently being used for the synthesis of nanofibers.

### 3. Emerging strategies for nanofiber fabrication

While most nanofibers are prepared using electrospinning, this technique suffers from several drawbacks, such as the requirement for specialized equipment, high electrical potential, and electrically conductive targets. Consequently, recent years have seen the increasing emergence of novel strategies in generating nanofibers in a larger scale and higher throughput manner, as summarized here.

### 3.1. CO<sub>2</sub> laser supersonic drawing

A CO<sub>2</sub> laser supersonic drawing technique is used to produce long nanofibers based on a single continuous process in the absence of chemical solvents. Using a CO<sub>2</sub> laser, original fibers with diameters between 100 and 200 μm are melted and then passed through a supersonic airflow to achieve the supersonic drawing of nanofibers based on the force of the air. Generally, this strategy is applicable to a wide range of thermoplastic polymers, including polylactic acid (PLLA), polyethylene terephthalate (PET), and polyglycolic acid (PGA) [35]. Further, a recent study has demonstrated, for the first time, the synthesis of nylon-66 nanofibers with high melting point near the equilibrium melting point using the CO<sub>2</sub> laser supersonic drawing [35]. This study showed that using this simple technique, the production of polymeric nanofibers with extended chains and improved mechanical properties could be achieved.

### 3.2. Solution blow spinning

Solution blow spinning technique has been developed to overcome the various restrictions conventional electrospinning technique possesses, such as the difficulty in *in situ* synthesis of nanofibers and the requirements for high electrical potential and conducting targets [5]. Requiring only a simple commercial airbrush, concentrated polymer solution, and a compressed gas source, the technique may potentially be utilized for *in situ* deposition of nanofiber mats and scaffolds for conformable coverage of non-conducting targets as well as for numerous tissue engineering and surgical applications. An example of the application of this synthesis method is the *in situ* deposition of conformal PLGA nanofiber mats or meshes on any substrate using only a painting airbrush and high pressure CO<sub>2</sub> gas (Fig. 2a–c) [5]. In the report, polymer nanofibers were synthesized from 10% PLGA solutions in acetone with two distinct viscosities corresponding to low and high molecular weights under CO<sub>2</sub> flow (Fig. 2d and e). The as-prepared nanofibers had an average diameter of 470 ± 260 nm. As it is challenging to translate the current electrospinning method into *in situ* setting, the simple solution blow spinning represents a viable alternative for directly generating adaptable and conformable nanofiber mats on various surfaces.

### 3.3. Plasma-induced synthesis

Using the plasma-induced synthesis method, nanofibers are prepared based on five distinct steps: (1) rapid and energetic bombardment of radicals onto the electrode surface, (2) atomic vapor deposition, (3) expansion of plasma, (4) condensation of solution medium, and (5) *in situ* reaction of oxygen and growth of nanofibers. Plasma is typically generated from the discharge between a pair of metal electrodes in solution by a pulse direct current. A recent example of the nanofiber synthesis utilizing the plasma-induced process is the preparation of CuO nanofibers with diameters between 15 and 25 nm in water [36].

### 3.4. Centrifugal jet spinning

The versatile centrifugal jet spinning has been developed for the synthesis of micro- or nanofibers in a highly efficient, low cost, and high-throughput fashion [37–39]. In principle, the thinning of solution filament into nanofibers using centrifugal jet spinning is achieved through the controlled manipulation of centrifugal force, viscoelasticity, and mass transfer characteristics of the spinning solutions. As such, the elasticity and evaporation rate of spinning solution and solvent, respectively, will heavily influence the eventual diameter of the as-prepared nanofiber [39]. In fact, different polymer-solvent combinations, such as polyvinylpyrrolidone

(PVP)-water, PVP-ethanol, PVP-dichloromethane (PVP-DCM), and PLLA-DCM, have been used as spinning solutions for the preparation of nanofibers through centrifugal jet spinning [39].

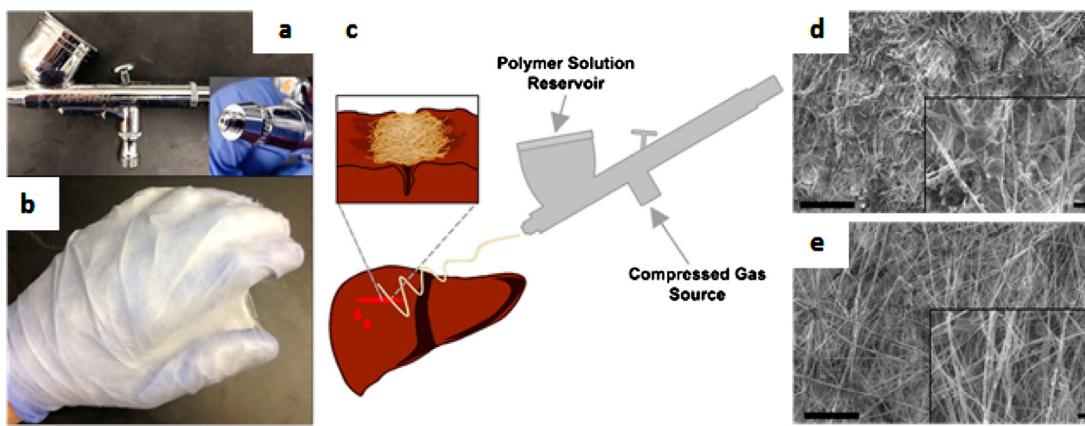
One of the most notable advantages of the centrifugal jet spinning technique lies in its exceptional throughput. Specifically, its productivity is estimated to be approximately 500 times higher than that of conventional electrospinning. This was illustrated in a recent study reporting the use of centrifugal jet spinning for the rapid preparation of customizable multilevel-structured silica micro- and nanofibers, based on the phase separation effect of silica sol-gel induced by non-solvent evaporation in the spinning solution [38]. The centrifugal jet spinning set-up in the study comprised a DC motor, a hollow spinning chamber, and several fiber-collecting posts (Fig. 3a). It was demonstrated that by utilizing thermal annealing and tuning the amount of non-solvent in the polyvinylpyrrolidone (PVP)-ethanol spinning solution, continuous silica nanofiber assembly with different internal structures and cross sections of porous (Fig. 3b and c), hollow (Fig. 3d and e), and solid (Fig. 3f and g) could be easily prepared.

### 3.5. Electrohydrodynamic direct writing

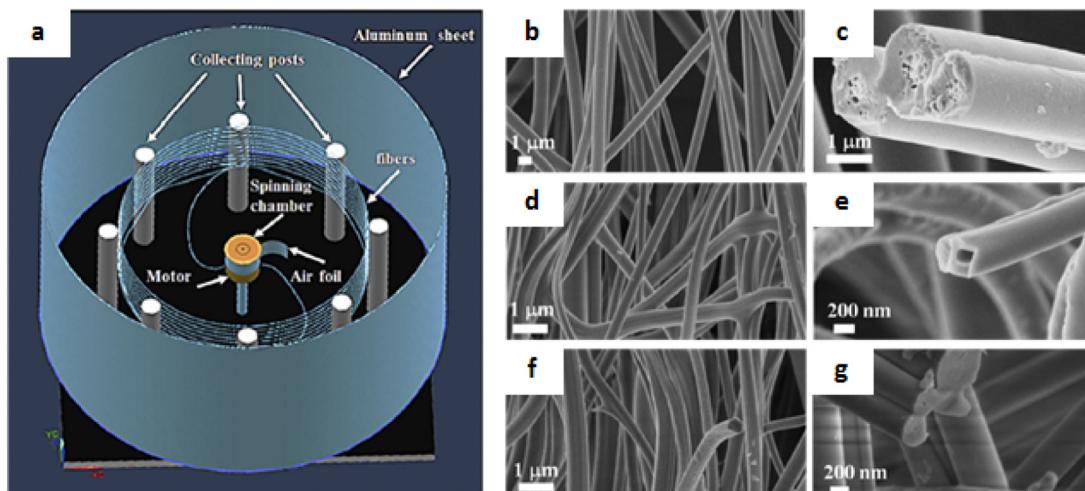
Electrohydrodynamic direct writing of micro-/nanofibers is a popular method of nanofiber synthesis due to its simplicity and high throughput. A kinetically controlled mechanoelectrospinning (MES) process for the continuous and programmable direct writing of hierarchical micro-/nanofibers in high resolution has been demonstrated [40]. This highly versatile and cost-effective MES technique combines both electrical and mechanical forces to drive the viscous ink for the large scale direct writing of solution-based materials.

In principle, the MES direct-writing technique possesses four unique operational features (Fig. 4a): (1) precise simultaneous manipulation of position, size, and morphology of every nanofiber through adjustment of both electrical field and mechanical drawing force, (2) customizable nozzle-to-substrate separation, (3) tunable applied voltage, and (4) digitally controlled motion stage on which the substrate rests. The operational process of the MES system can be divided into three steps (Fig. 4b): (1) filling of functional ink in the syringe nozzle, (2) application and increase of an external voltage followed by the stretching of jetting fiber from the nozzle, and (3) formation of a fine “jet chord” between the substrate surface and meniscus. By controlling the key processing parameters, several modes of the MES direct-writing process may be developed to generate distinct fiber structures (Fig. 4c–f): (1) the mapped direct-writing of linear nanofiber array structures (Fig. 4d), (2) the helix direct-writing of wavy or serpentine nanofiber structures (Fig. 4e), and (3) the leap direct-writing of bead-on-string structures (Fig. 4f). As a whole, on top of the common ink-jet method features like large area printing and tunable flexibility [41], the MES nanofiber synthesis technique presents several advantages, notably tunable printing resolution, simultaneous control over the position and morphology of the deposited nanofibers, and direct deposition of smooth hierarchical and complex nanofiber structures.

The electrohydrodynamic direct writing may also be integrated with other synthesis techniques to form novel functional structures. For example, based on the combination of electrohydrodynamic jet printing and self-assembly, three-dimensional block-copolymer films with hierarchical configurations may be generated [42]. With the ultrahigh resolution afforded by direct additive jet printing in patterning the poly(styrene-block-methyl methacrylate) (PS-b-PMMA) block-copolymers, coupled with their self-assembly upon thermal annealing, deterministically-defined structures with various hierarchical patterns with distinct sizes,



**Fig. 2.** Solution blow spinning of nanofibers. (a) Airbrush utilized for the deposition of nanofibers. (b) Nanofibers deposited on a gloved hand. (c) Schematic illustration showing the *in situ* application of the solution blow spun nanofibers on a liver injury. (d–e) Scanning electron microscopy (SEM) images of the polymer nanofibers obtained from 10% PLGA solutions in acetone with two different viscosities under a  $\text{CO}_2$  flow: (d) PLGA solution with low molecular weight. (e) PLGA solution with high molecular weight. Scale bars represent 100  $\mu\text{m}$  and 10  $\mu\text{m}$  (for insets). [5], Copyright 2014. Adapted with permission from the American Chemical Society.



**Fig. 3.** Centrifugal jet spinning of nanofibers. (a) Schematic illustration showing the experimental set-up of a centrifugal jet spinning system. (b–c) SEM images of the porous silica nanofibers prepared from 15 wt% PVP-ethanol spinning solution with a  $\text{H}_2\text{O}/\text{TEOS}$  ratio of 1.65. (d–e) SEM images of the hollow silica nanofibers prepared from 10 wt% PVP-ethanol spinning solution with a  $\text{H}_2\text{O}/\text{TEOS}$  ratio of 1.65. (f–g) SEM images of the solid silica nanofibers prepared from 10 wt% PVP-silica-ethanol solution with a  $\text{H}_2\text{O}/\text{TEOS}$  ratio of 2. TEOS (i.e., tetraethyl orthosilicate) served as the precursor of the silica sol-gel. [38], Copyright 2014. Adapted with permission from Elsevier Inc.

morphologies, periodicities, and length scales ranging from nanometers to centimeters may be realized.

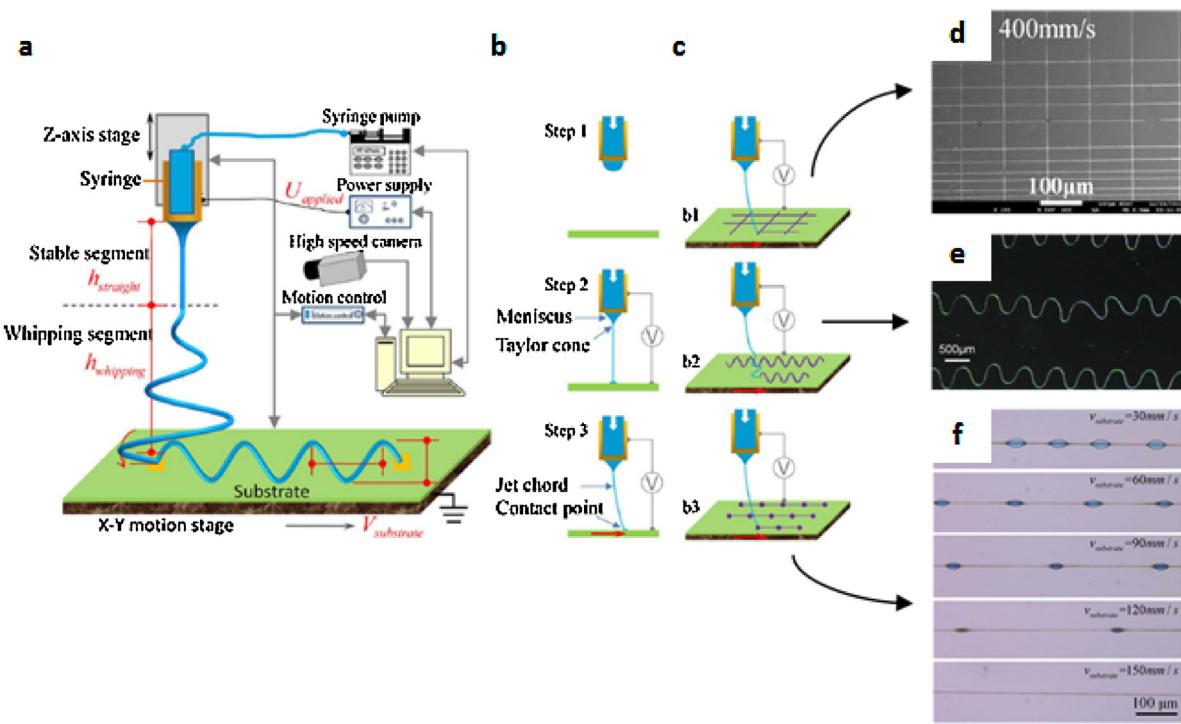
#### 4. Emerging applications in energy generation and storage

##### 4.1. Batteries and fuel cells

As one of the most promising energy storage technologies, lithium ion batteries (LiBs) have found applications in numerous portable and personal electronics. Nevertheless, the widespread use of LiBs, especially in large-scale energy storage devices, is still hampered by various factors, such as the limited capacity and efficiency of the anode and cathode materials, the low electrochemical performance of the electrodes, and their high material cost. Consequently, there is an increasing need for novel electrochemically active alternatives with high energy density and capacity, long cycle life, high electrochemical performance, and low cost. Nanofibers have been investigated as the potential electrode materials for energy generation devices, such as batteries and fuel cells, due to their large specific surface area and high porosity which may be utilized for storing electrolytes and supporting rapid and long term electron/ion transport. Over the last few years, highly porous

nanofiber networks have been synthesized from a wide range of materials to enhance the capacity, electrochemical properties, and cycling performance of LiBs. For examples, chamber-confined Si/C composite nanofibers have been synthesized for improving the cycling life and Coulombic efficiency of LiBs [43], composite Si/C/TiO<sub>2</sub> nanofibers have been synthesized as the LiBs anode through sol-gel-based electrospinning for increasing the specific capacity and cycling life of LiBs [10], and highly porous interwoven ZnMn<sub>2</sub>O<sub>4</sub> nanofibers have been electrospun as the electrode material of LiBs for enhancing their specific capacity and rate capability [44].

Apart from LiBs, the capability of nanofibers to form three-dimensional (3D) interconnected networks with uniform micropores distribution has also been utilized for lithium-sulfur (Li-S) battery applications. A flexible free-standing porous carbon nanofibers-carbon nanotubes-sulfur composite (S@PCNFs-CNT) has been prepared as the cathode material of Li-S battery for improved electrochemical performance of the battery [45]. The S@PCNFs-CNT was prepared based on electrospinning (Fig. 5a). More clearly, the initial PAN-CNT fibers were prepared via electrospinning, then stabilized at 280 °C, and carbonized under Ar gas at 800 °C to obtain the CNFs-CNT composite. The as-produced



**Fig. 4.** Electrohydrodynamic writing of nanofibers. (a) Schematic illustration demonstrating the MES direct-writing set-up and operational mechanism. (b) Operational process of the MES direct-writing system: Step 1—filling of functional ink in the syringe nozzle followed by the formation of a droplet at the nozzle end; Step 2—application of an external voltage followed by the jetting of droplet from the nozzle, leading to the formation of Taylor cone; Step 3—formation of a fine “jet chord” between the substrate contact point and meniscus upon the movement of substrate. (c) Three distinct operational modes of MES direct-writing process: the mapped direct-writing of linear nanofiber array structures, the helix direct-writing of wavy fiber structures, and the leap direct-writing of bead-on-string structures. (d) Linear fiber array structures directly written at a speed of 400 mm/s. Scale bar represents 100  $\mu\text{m}$ . (e) Serpentine or wavy fiber array structures. Scale bar represents 500  $\mu\text{m}$ . (f) Bead-on-string fiber structures directly written at various substrate speeds ranging from 5 to 150 mm/s. Scale bar represents 100  $\mu\text{m}$ . [40], Copyright 2014. Adapted with permission from the Nature Publishing Group.

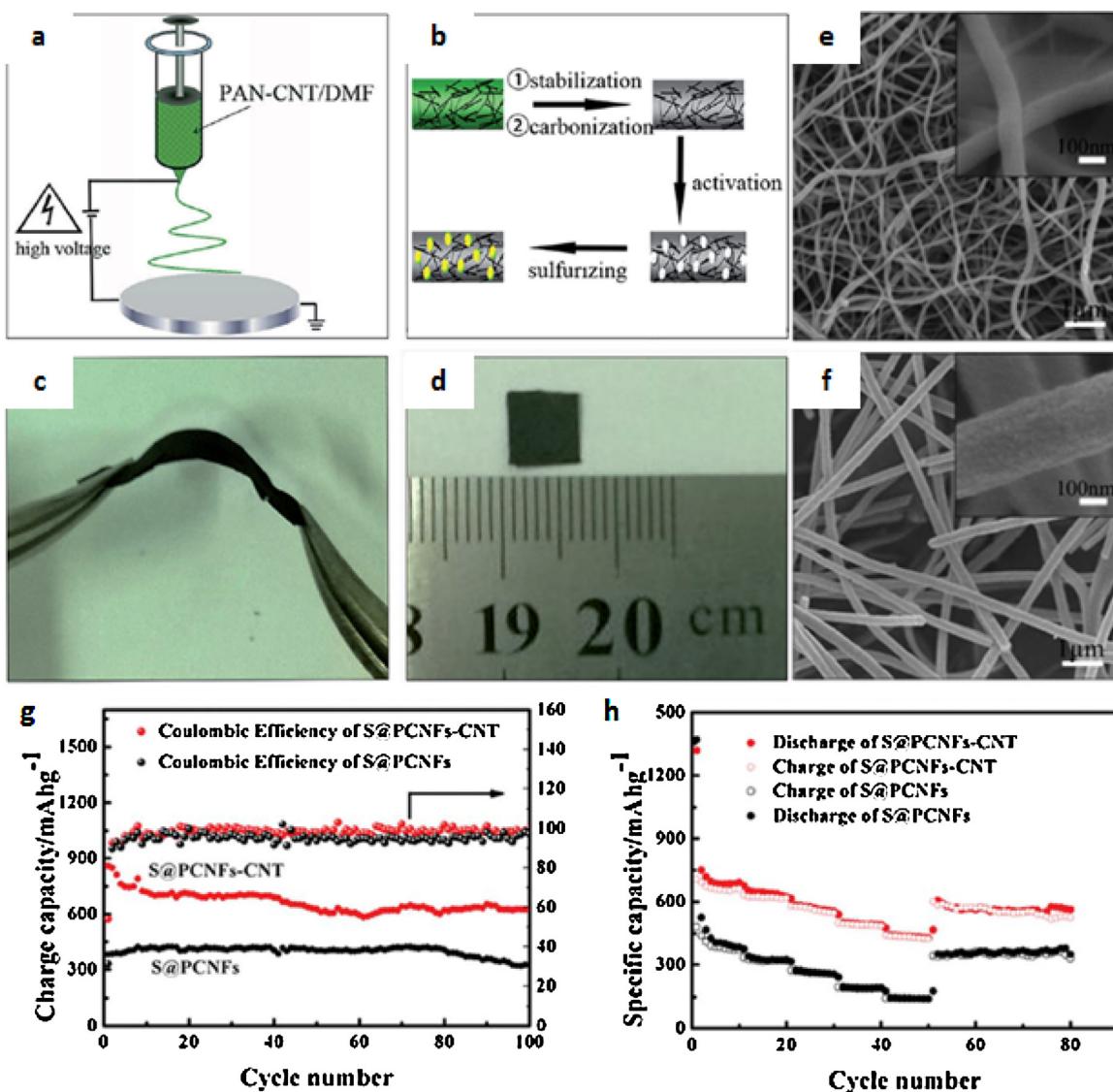
composite was next activated chemically with KOH to produce PCNFs-CNT. Eventually, S@PCNFs-CNT was formed through the heating of a mixture of S and PCNFs-CNT (Fig. 5b). A composite structure without the inclusion of CNTs (S@CNFs) was synthesized for comparison. The as-prepared composites were then cut and tested as the flexible free-standing Li-S battery cathode material (Fig. 5c and d). No significant change in the macromorphology was noted from the two composites (Fig. 5e and f). Subsequently, the cycling performance (Fig. 5g) and rate capabilities (Fig. 5h) of both S@PCNFs-CNT- and S@CNFs-based electrodes were examined. The S@PCNFs-CNT electrode displayed enhanced cycling and rate performances. In fact, it retained higher reversible capacity and rate capability as compared to the S@CNFs electrode. This suggests an excellent electrochemical performance of the flexible free-standing composite S@PCNFs-CNT as the cathode material of Li-S batteries. Interestingly, in addition to batteries, nanofibers have also been synthesized as the building blocks of microbial fuel cells. This was demonstrated in a latest study in which 3D activated nitrogen-doped carbon nanofiber networks were prepared as a cathode material for the enhancement of the current density and electron transfer of fuel cells [7].

#### 4.2. Supercapacitors

Solid-state flexible supercapacitors are promising energy storage devices which have attracted increasing interests in the last few years. As compared to batteries, supercapacitors are deemed to be more suitable to be utilized in electronics due to their unique advantages, such as faster charging/discharging capacity, longer cycle life, higher power density, and excellent safety. In fact, recent years have seen the increasing fabrication and utilization of the

lightweight, knittable, and wearable fiber-shaped supercapacitors. Composite nanomaterials based on cellulose nanofibers (CNFs), in particular, have been widely used as the building block of flexible supercapacitors. For example, solid-state CNFs-graphene hybrid aerogel-based flexible supercapacitors exhibit high capacitance, power, and energy density [46].

In another instance, CNFs have been integrated with single-walled carbon nanotubes (CNF/SWCNT) for the preparation of a novel hybrid non-woven macrofiber mat-based wearable supercapacitor [47]. The as-fabricated supercapacitors exhibited outstanding electrochemical properties and stability as well as excellent tailorability and damage reliability. In the study, the hybrid non-woven macrofiber mats were synthesized via controlling the extrusion patterns of the suspension of CNF/SWCNT in an ethanol coagulation bath (Fig. 6a) followed by air-drying (Fig. 6b). The individual macrofibers had a uniform diameter of about 50  $\mu\text{m}$  (Fig. 6c) and the as-prepared macrofiber-based structure was highly porous (Fig. 6d). In addition, the SWCNTs oriented preferentially along the axial or extrusion direction of the macrofiber (Fig. 6e and f). Intriguingly, the CNF/SWCNT hybrid supercapacitor displayed superior tailorability in which it could be divided into two parts easily (Fig. 6g and h). The electrochemical characterization of the supercapacitor performance revealed that the original supercapacitor and the two sub-supercapacitors displayed ideal capacitive behavior. This suggests that the electrochemical performance of the hybrid macrofiber mat was not significantly affected by tailoring (Fig. 6i). Further, under various degrees of damage (Fig. 6j), the non-woven mat showed outstanding damage reliability. After undergoing severe deformation, with its robust reliability, the CNF/SWCNT hybrid non-woven macrofiber-based



**Fig. 5.** Nanofibers for lithium ion battery application. **(a-b)** Schematic illustration showing the detailed preparation process of the flexible free-standing S@PCNFs-CNT composite-based electrode. **(c-d)** Optical photographs showing the actual prepared flexible free-standing porous carbon nanofibers (PCNFs)-based electrode. **(e-f)** Field-emission SEM (FESEM) images of the as-prepared S@PCNFs-CNT and S@PCNFs composites, respectively. Scale bars represent 1  $\mu\text{m}$ . Insets show the corresponding composites in high magnification. Scale bars represent 100 nm. **(g)** Charge capacity vs cycle number profiles of both the S@PCNFs-CNT and S@PCNFs electrodes recorded at 50  $\text{mA g}^{-1}$ . **(h)** Specific capacity vs cycle number profiles of both the S@PCNFs-CNT and S@PCNFs electrodes recorded at various current densities of the charge-discharge cycles, ranging from 0.05 to 1  $\text{A h g}^{-1}$ . [45]. Copyright 2014. Adapted with permission from the Royal Society of Chemistry.

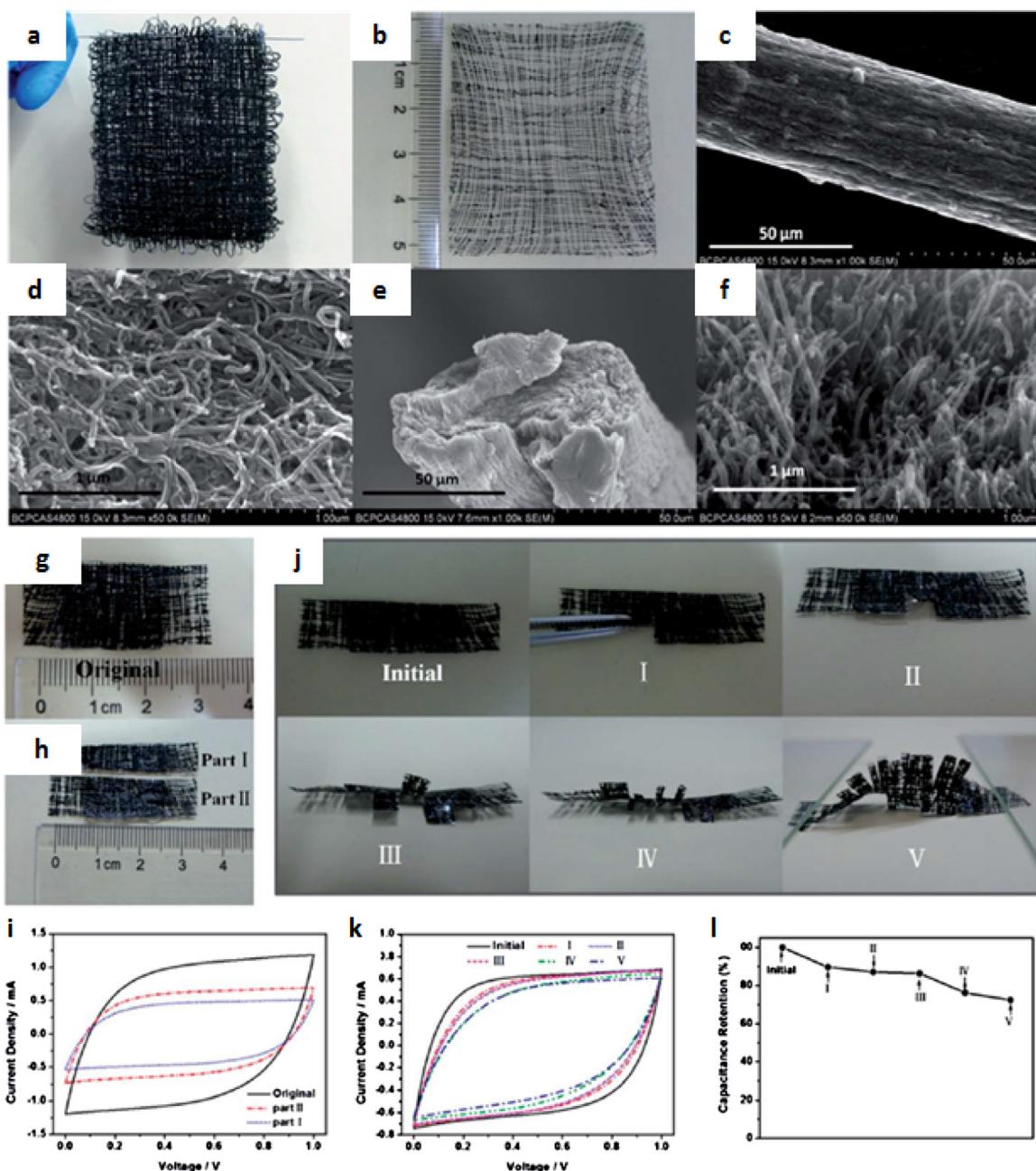
wearable supercapacitor still maintained an excellent capacitive behavior (Fig. 6k and l).

#### 4.3. Solar cells

First reported by O'Reagan and Gratzel in 1991 [48], dye-sensitized solar cells (DSSCs) have been seen as potential replacements to the conventional single-crystalline Si solar cells owing to their higher efficiency, simpler production process, lower material cost, and environmental-friendliness. One-dimensional nanofibers have been actively synthesized as the photoelectrode material of DSSCs as they provide a direct and short electron transport pathway which translates into superior charge transport properties. Among the semiconducting metal oxide-based nanofibers, TiO<sub>2</sub> with their excellent photoelectrochemical properties has been conventionally chosen as the primary DSSCs electrode material.

The energy conversion efficiency and photocatalytic activity of TiO<sub>2</sub> nanofiber-based photoelectrode may be significantly improved by increasing the specific surface area and enhancing the electron transport and light capture efficiency through the incorporation of other nanomaterials, such as ZnO nanoparticles [49] and CNT [50]. A study showed that composite photoanode films fabricated from hollow TiO<sub>2</sub> nanofibers blended into ZnO nanoparticles exhibited increased light scattering and suppressed electron recombination which, in turn, enhanced the energy conversion efficiency of DSSCs [49]. Similarly, in a separate report, the anode material prepared from the electrospun CNT/TiO<sub>2</sub> composite nanofibers was showed to increase the electron transfer, decrease charge recombination, and improve the power conversion efficiency of DSSCs as a whole [50].

In addition to DSSCs, more recently, the solution-processed organic photovoltaics (OPVs) have emerged as an attractive class of solar energy harvesting devices. For example, the sequential deposition-processed OPVs constructed from an inter-



**Fig. 6.** Nanofibers for supercapacitor application. **(a-b)** Optical photographs showing the actual hybrid CNF/SWCNT non-woven macrofiber mat under **(a)** wet and **(b)** dry conditions. **(c-d)** SEM images of the as-synthesized hybrid CNF/SWCNT macrofiber mat. Scale bars represent **(c)** 50  $\mu\text{m}$  and **(d)** 1  $\mu\text{m}$ . **(e-f)** Cross-sectional images of the as-prepared hybrid CNF/SWCNT macrofiber mat. Scale bars represent **(e)** 50  $\mu\text{m}$  and **(f)** 1  $\mu\text{m}$ . **(g-h)** Optical photographs showing the **(g)** original supercapacitor cut into **(h)** two sub-supercapacitors. **(i)** Cyclic voltammetry (CV) curves of the original supercapacitor (in black) and two sub-supercapacitors (in blue and red) recorded at 50  $\text{mV s}^{-1}$ . **(j)** Optical photographs illustrating the different degrees of damage experienced by the non-woven macrofiber mat-based wearable supercapacitor. **(k)** CV curves of the wearable supercapacitor undergoing the corresponding degrees of damage, as shown in **(j)**, recorded at 50  $\text{mV s}^{-1}$ . **(l)** Capacitance retention profile of the wearable supercapacitor undergoing different degrees of damage. [47]. Copyright 2014. Adapted with permission from the Royal Society of Chemistry. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

digitated bilayer of alkoxynaphthalene-based polymer (PONTBT) nanofiber/fullerene have been demonstrated [51]. In this work, a layer of dense polymer nanofibers with diameters between 30 and 50 nm was first prepared by spin-coating a polymer solution containing 1-chloronaphthalene. Subsequently, the sequential deposition of a fullerene-based (PCBM) layer onto the layer of polymer nanofibers resulted in an interdigitated bilayer, enabling a robust bulk heterojunction morphology. The as-fabricated OPV exhibited a remarkable photocurrent density and overall solar cell performance.

#### 4.4. Hydrogen storage and generation

With its high energy content and zero carbon dioxide emission, hydrogen is one of the most important alternative energy carriers for renewable fuels and other future energy generation sources. The use of hydrogen as an energy carrier, nonetheless, is still limited by the availability of efficient, reliable, sustainable, and economical hydrogen storage and generation. In the last few years, nanostructured hydrogen storage materials have been reported to display an enhanced energy storage capacity. In fact, nanostruc-

tured materials like nanofibers shorten the diffusion path lengths of hydrogen and active species as well as reduce the thickness of reactive interfaces during hydrogen absorption and desorption [52]. An interesting example shows that highly porous carbon-coated Li<sub>3</sub>N nanofibers were synthesized through a template-free electrospinning for improved hydrogen storage, in which the diffusion of hydrogen for reaction with active species was facilitated by the presence of different micropores, mesopores, and macropores on the carbon walls of the nanofibers [53].

In addition to hydrogen storage, nanofibers have also been actively pursued for renewable photoelectrochemical generation of hydrogen. Numerous nanofiber-based structures have been synthesized to enhance the energy conversion efficiency of hydrogen generation. For example, (1) a high-performance hydrogen generation system based on the hydrolysis of ammonia borane solution was built from the electrospun PAN/Ag/Pd composite nanofibers [54], (2) the hierarchical network structure of core-shell TiO<sub>2</sub>/CdSe nanofiber film was prepared to improve the photoelectrochemical generation of hydrogen through an increase in the number of active sites for oxidation reaction as well as a larger TiO<sub>2</sub>/CdSe interface area to improve the separation efficiency of photogenerated charges [11], (3) the ZnO- and Fe<sub>2</sub>O<sub>3</sub>-functionalized TiO<sub>2</sub> nanofibers were synthesized via electrospinning and used as effective photocatalysts for water splitting under visible light [55], and (4) the electrospun SrTiO<sub>3</sub> nanofibers showed an enhanced photocatalytic efficiency in hydrogen generation under UV light irradiation [56].

#### 4.5. Piezoelectricity

Piezoelectricity represents one of the most important alternative energy sources. Piezoelectric devices typically generate power by scavenging small mechanical forces, such as pressure, vibration, compression, stretching, and bending, from the environment and converting them into usable electrical energy. For devices with this specific functionality, piezoelectric polymers may serve as a promising building block owing to their structural flexibility and toughness, excellent chemical resistance, facile processing, simple device design and integration, and associated low cost [57]. Since they are deformable by small mechanical forces and capable of withstanding large mechanical deformations due to their high strain level, piezoelectric polymers are highly suitable for constructing self-powering flexible sources. Importantly, piezoelectric polymers are capable of withstanding high driving field due to their high operating field strength and dielectric breakdown.

Of all piezoelectric polymers, poly(vinylidenefluoride) (PVDF) and its copolymers are generating tremendous interests due to their outstanding mechanical-to-electrical energy conversion performance and overall piezoelectric properties, and high mechanical flexibility and stability [58–60]. In fact, their nanostructures, notably nanofibers, have exhibited distinct strengths in terms of their piezoelectric response and material functionality. Conventional electrospinning has been primarily used to produce PVDF nanofibers. For instance, near-field and far-field electrospinning have been utilized to fabricate single isolated strands of PVDF nanofibers and non-woven PVDF nanofibrous mats, respectively [58,59]. Aligned PVDF nanofiber arrays, in which individual nanofibers are separated from each other by a few microns, have also been electrospun and demonstrated to possess more superior piezoelectric performances as compared to individual nanofibers. Besides the conventional electrospinning techniques, lately, there have been active utilizations of needleless disc electrospinning for the fabrication of piezoelectric nanofibers. In one report, randomly oriented PVDF nanofiber webs were fabricated through needleless electrospinning and integrated into a mechanical-to-electrical energy harvesting device [60]. Impressively, the needleless electrospun PVDF nanofiber webs exhibited greatly enhanced energy

conversion yield as compared to the conventional needle-based electrospun nanofibers. As such, these needleless disc electrospun nanofibers could be used directly to construct piezoelectric power generators to drive a thermoelectric cooler.

In addition to PVDF, one of its copolymers, poly(vinylidene fluoride-co-trifluoroethylene) (PVDF-TrFE), has attracted interest in recent years [61–63]. As a multifunctional polymer with exceptional piezoelectric property, PVDF-TrFE displays pyroelectric, ferroelectric, and electrocooling effects too [61]. The nanofibrous structures of this polymer, in particular, have shown great potential for energy harvesting and sensor applications [62–64]. For example, a recent study reported that dense arrays of aligned PVDF-TrFE nanofibers (10<sup>7</sup> fibers/mm<sup>2</sup>) prepared through electrospinning displayed enhanced piezoelectric property and output power [62]. Interestingly, flexible and mechanically robust free-standing piezoelectric sheets could be formed from these high density arrays of aligned PVDF-TrFE nanofibers through electrospinning onto a rapid rotating collector. The as-fabricated piezoelectric textile could cover a large area of up to tens of cm<sup>2</sup> and could be bent or twisted without any crack or fracture. Importantly, with its excellent piezoelectric characteristic, the three-dimensional architecture of aligned PVDF-TrFE nanofibers could enable ultrahigh sensitivity for pressure measurement. Meanwhile, a separate study has demonstrated the fabrication of highly stretchable piezoelectric PVDF-TrFE polymeric yarns and coils through twisting the electrospun PVDF-TrFE nanofibers [63]. The as-prepared nanofibrous yarns and coils displayed enhanced failure strain, toughness, and overall strength.

Apart from individual PVDF and its copolymer PVDF-TrFE, the PVDF polymeric nanofiber may be integrated with other low-dimensional nanostructures to enhance its overall piezoelectric property. More lately, a study has reported the electrospinning of a uniaxially-aligned nanofibrous matrix consisting of PVDF nanofibers with a diameter of 200 nm, embedded with barium titanate (BaTiO<sub>3</sub>) nanoparticles [65]. The highly aligned BaTiO<sub>3</sub>-PVDF nanofibers displayed significantly enhanced piezoelectric characteristic. More clearly, the composite nanofibers generated much higher piezoelectric output voltage than bare PVDF nanofibers when subjected to similar mechanical deformations. By increasing the quantity of BaTiO<sub>3</sub> nanoparticles, a corresponding increase in the piezoelectric-induced voltage could be observed.

#### 4.6. What's next?

Nanofibers have demonstrated tremendous potential in various energy generation and storage applications. In fact, these low-dimensional nanostructures have shown great promise as the fundamental building blocks of batteries, supercapacitors, solar cells, hydrogen store and generation devices, and piezoelectric power generators. With outstanding physical features, notably high surface area-to-volume ratio and high porosity, nanofibers are capable of facilitating long-term electrolyte storage and rapid electron/ion transport. This results in a considerable enhancement in the performance of the nanofiber-based energy-related devices. Nonetheless, additional efforts are definitely needed to further maximize the potential of nanofibers for energy-based applications. For example, with flexible, lightweight, and wearable electronics and other related devices generating waves of interests in recent years, more stringent requirements will definitely be placed on energy storage and generation devices. To meet these demands, nanofibers must also possess significantly enhanced physicochemical characteristics. This may be achieved through an appropriate selection of the basic materials from which nanofibers will be fabricated as well as advanced synthesis of nanofiber networks with tunable porosity and outstanding durability. All these are necessary for constructing functional devices

with improved energy density, capacity, and cycle life, as well as sufficiently robust to withstand large mechanical deformations without fracture or crack. With this bright outlook, nanofibers and their functional structures are certainly poised to be increasingly exploited for energy generation and storage.

## 5. Emerging applications in water treatment and environmental remediation

### 5.1. Water treatment and ultrafiltration

As one of the safest nanomaterials, the long and highly porous nanofibers serve as a promising platform for numerous emerging environmental applications, in particular in liquid filtration and particulate separation for water treatment and environmental remediation, respectively. Both pristine and adsorbents- or catalysts-functionalized nanofibrous materials have been actively prepared for removing or separating sub-micrometer pollutants and contaminants from liquid and gas environments based on various physical and chemical techniques, notably adsorption [14] and ultrafiltration [13]. Utilization of nanofibrous structures as adsorbent or filtration materials has significantly enhanced the adsorption capacity and separation efficiency. This means better particulate removal capacity, higher separation flux, and lower operational energy. With their high surface-to-volume ratio, high specific surface area, and continuous matrix structure consisting of small pores, nanofibrous structures facilitate highly efficient separation process, particularly when the primary driving force for pollutant and contaminant separation is surface interaction, as in the case of air filtration. Numerous studies have been published more recently, illustrating the enormous potential of nanofibers as the building blocks of adsorption- and ultrafiltration-based fine particulate removal systems.

The hybrid MnO<sub>2</sub>-coated cellulose nanofibers were synthesized for the efficient removal of methylene blue [14]. The as-prepared hybrid nanofibers displayed high adsorption and oxidation efficiency in the decolorization of methylene blue. In another study, a heavy metal adsorbent was prepared from highly porous quaternary NH<sub>3</sub>-functionalized cellulose nanofiber-based aerogels [66]. With its large specific surface area, the nanofiber-based aerogel could remove the metallic ions of Cr(VI) from contaminated water rapidly and efficiently. Separately, the inorganic and organic toxic contaminants, such as As(V), Cr(VI), and Congo red dye, could be effectively and quickly removed from wastewater using the metallic Fe nanoparticle-loaded PANI composite nanofibers [67]. The adsorption and removal of oxidized organosulfur compounds, such as benzothiophene sulfone, on the other hand, could be achieved through the molecularly imprinted polybenzimidazole (PBI) nanofibers [68]. The polymeric PBI nanofibers exhibited high selectivity towards sulfone-containing compounds and excellent sulfur removal performance. Interestingly, lately, the composite polymeric nanofibers comprising the hydrophobic PET and hydrophilic PVA polymer-based interpenetrating network (HH-IPN-CNF) have been synthesized as a support layer of the forward osmosis membrane via electrospinning [69]. As a result of an increase in the content of the PVA nanofibers in the HH-IPN-CNF support layer, a significant improvement in the forward osmosis membrane flux could be observed. In addition to being used in the forward osmosis membrane, nanofibers have been synthesized for the electrically conducting ultrafiltration membrane application.

By blending the SWCNT/PANI composite nanofibers into a polysulfone matrix, an electrically conductive ultrafiltration membrane could be simply prepared [13]. The pure polysulfone and composite SWCNT/PANI-polysulfone membranes possessed a dense nanoporous top layer and a finger-like sub-layer with large

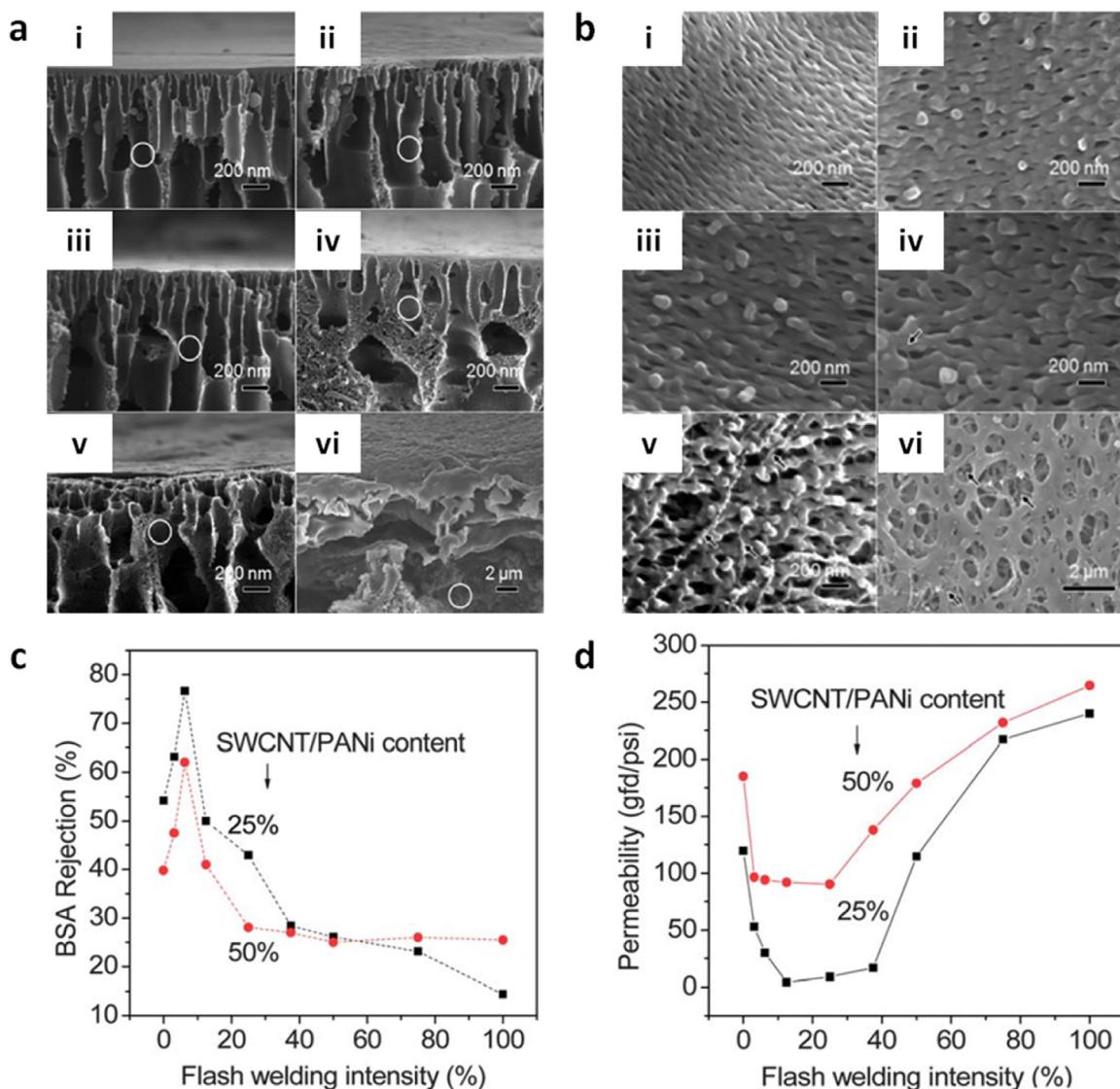
macropores (Fig. 7a). Intriguingly, with an increasing percentage of nanofibers, the finger-like structures in the membranes displayed higher interconnectivity and became more sponge-like morphologically. As the nanofibers were increasingly blended into the polysulfone, the SWCNT networks penetrated into the bulk membranes and could be clearly observed after flash welding (Fig. 7b). The ultrafiltration performance, specifically the selectivity and water permeability, of the as-fabricated membrane was subsequently evaluated. Ultrafiltration experiments revealed that by increasing the amount of SWCNT/PANI nanofibers in the membrane, the bovine serum albumin (BSA) nanoparticles were considerably rejected (Fig. 7c) while the water permeability was significantly enhanced (Fig. 7d). Further, by tuning the intensity of the flash welding, i.e., an externally applied electric potential, the pore sizes and the resultant membrane performance could be controlled. As the flash welding intensity increases, the BSA rejection profile exhibited an increase-decrease trend while a reverse pattern was observed from the permeability profile of the composite membrane. In short, by tuning the quantity of the composite SWCNT/PANI nanofibers and the intensity of flash welding, the selectivity and permeability of the ultrafiltration membrane could be easily manipulated.

### 5.2. Photocatalysis

"Green" and sustainable photocatalysis technology has gained considerable interest since the report on photoelectrochemical water splitting by Fujishima and Honda [70]. In addition to water splitting for hydrogen generation, nanofiber-based photocatalysis has been intensively investigated for the degradation of pollutants and various toxic environmental chemicals. With its high photocatalytic activity, high photochemical stability, and low toxicity, TiO<sub>2</sub> has emerged as one of the most efficient and widely employed photocatalysts. Various functionalized and composite TiO<sub>2</sub>-based nanofibers with high aspect ratio and improved photocatalytic performance have been reported in the past several years. For example, a multifunctional large-area flexible nanofibrous mat was realized from Ag nanoparticle-functionalized TiO<sub>2</sub> nanofibers for the photocatalytic degradation of Rhodamine B and phenol [8], highly porous composite SnO<sub>2</sub>/TiO<sub>2</sub> nanofibers were electrospun for an improved degradation of Rhodamine B under UV-vis light irradiation [12], and PANI-coated TiO<sub>2</sub>/SiO<sub>2</sub> nanofiber membranes were developed via electrospinning, calcinations, and in situ polymerization for an enhanced degradation of methyl orange under visible light [71].

### 5.3. Chemical and gas sensing

Over the last several years, nanofibers synthesized from metal oxide semiconductors have been actively explored in numerous chemical and gas sensing applications, including in the detection of air quality, inspection of toxic and inflammable gases, and monitoring of environment. These nanofibers are capable of detecting various reducing and oxidizing gases in real-time reliably with excellent selectivity, sensitivity, and stability. The large surface-to-volume ratio, specific surface area, and high porosity of one-dimensional nanofibers enhance the diffusion and mass transport of the gaseous species, leading to an improved sensing performance. To further increase the sensing capability and performance of these nanofibrous structures, two primary approaches may be adopted: (1) by increasing the active surface area of the nanofibers through grain size reduction and porous structure construction, notably, the hollow nanostructures, and (2) by functionalizing or doping the oxide semiconductor nanofibers with metallic nanoparticles, such as Au, Ag, and Pd, or other catalytic elements. Several studies have reported the validity of



**Fig. 7.** Nanofibers for ultrafiltration application. **(a)** SEM images showing the cross sections of the ultrafiltration membranes prepared using different SWCNT/PANI composite nanofiber contents: **i.** 0%, **ii.** 10%, **iii.** 15%, **iv.** 25%, **v.** 50%, and **vi.** membrane (**v**) underwent 100% flash welding. **(b)** SEM images showing the corresponding sub-structural circled regions of (a). Scale bars represent 200 nm (for **i** to **v**) and 2 μm (for **vi**). **(c)** Selectivity (i.e., BSA rejection) and **(d)** permeability (i.e., pure water flux) of the as-fabricated ultrafiltration membranes using 25% and 50% SWCNT/PANI composite nanofibers followed by flash welding with different intensities. [13], Copyright 2013. Adapted with permission from the Royal Society of Chemistry.

these approaches. For example, the *p*-type Cr<sub>2</sub>O<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub> oxide semiconductor-based nanofibers were synthesized for the rapid sensing of C<sub>2</sub>H<sub>5</sub>OH [72], the porous hollow SnO<sub>2</sub> nanofibers were electrospun for the selective and fast ethanol sensing [9], the Pr-doped SnO<sub>2</sub> hollow nanofibers were prepared via electrospinning and calcination for the fast and sensitive ethanol sensing [73], and the Au-doped SnO<sub>2</sub> nanofibers were prepared through sol-gel-based electrospinning for the sensing of CO in a highly sensitive and quick manner [74].

In addition to the metal oxide semiconductor-based nanofibers, wide band-gap semiconductors and polymers are also used for the synthesis of nanofibers for chemical and gas sensing applications. For example, porous GaN nanofibers were electrospun for the selective sensing of ethanol [75]. The as-prepared nanofiber sensor displayed high sensitivity and selectivity towards ethanol with fast response time. The composite interconnected polymeric chitosan/PANI nanofibers were prepared through *in situ* polymerization of aniline for the sensing of alcohols and amines in air with high sensitivity and reproducibility [15].

#### 5.4. What's next?

Considerable development has been demonstrated in the applications of nanofibers for water treatment and environmental remediation, notably in ultrafiltration, photocatalysis, and chemical sensing. Nanofibers and their network architectures are typically endowed with high porosity, which are advantageous for separating particulates for air and water purification. At the same time, with their long structure and high specific surface area, nanofibers possess high adsorption capacity for particulates, further enhancing the filtration efficiency and sensing performance of the nanofiber-based devices. With increasing harmful pollutions in recent years, the need for monitoring environmental quality as well as for access to clean air and water have increased correspondingly. To meet these surging demands, there has to be a dramatic improvement in the performance of nanofibers as a promising alternative for water treatment and environmental remediation. To achieve this, the fabrication and applications of nanofibers with tunable physicochemical properties and features are absolutely

required. Controlling the pore size of nanofibrous networks may be one of the fundamental keys to improve the filtration performance of nanofibers. In addition, integration with other nanostructures may be necessary to impart nanofibers with additional functionalities such that there will be substantial enhancement in their photocatalysis capability in degrading different pollutants and toxic environmental chemicals as well as in their sensing capability in monitoring water and environmental quality. Overall, an encouraging outlook is certainly awaiting the applications of nanofibers for water and environmental monitoring and treatment as various fabrication techniques develop further to produce nanofibers and related devices with excellent filtration, photocatalysis, and sensing performances.

## 6. Emerging applications in healthcare and biomedical engineering

### 6.1. Tissue engineering and regenerative medicine

As an interdisciplinary field combining various biological and engineering expertise, tissue engineering and regenerative medicine seek to restore or regenerate the normal tissue and organ functions using the three fundamental entities of cells, biomolecules, and biomaterials. As one of the most actively researched biomaterials, nanofiber-based scaffold emerges as a versatile alternative for tissue engineering and regenerative medicine applications. With their extremely high surface-to-volume ratio and porosity, nanofibers offer a high loading capacity for biological substances and active species. Furthermore, with their interconnected network of micropores mimicking the native *in vivo* topographic features of extracellular matrix (ECM), nanofibrous scaffolds present a favorable avenue for cellular growth, proliferation, and differentiation. For the particular application of tissue engineering, biodegradable and biocompatible natural or synthetic polymers are typically used as the nanofiber materials [76]. The specific selection of materials depends very much on the types and properties of the tissues to be regenerated as well as the duration of regeneration. An increasing number of studies on the applications of nanofibrous scaffolds for tissue engineering have been reported lately. Some examples are highlighted here.

First, self-assembled chitin nanofibers were synthesized for the fabrication of biodegradable and flexible substrates micropatterned through replica molding for engineering cell sheets [4]. On the substrates, the seeded fibroblast cells attached and aligned along the primary axis of the micropatterned features, leading to the formation of ultrathin and free-standing ordered cell sheets which were flexible and could be easily controlled for the construction of complex tissue structures. Second, aligned gelatin nanofibers-multiwalled CNTs composites were synthesized via electrospinning as the scaffolds for the growth of myoblast, specifically, for an improvement in the formation of aligned myotubes with enhanced contractility [77]. The activation of mechanotransduction-related genes was upregulated and the myotube maturation and contractions were improved through the presence of the hybrid scaffolds. Third, electrospun PLGA nanofibers were functionalized with adhesive peptides for cardiac tissue engineering application, specifically for improving the adhesion and contraction of cardiomyocytes [78]. Fourth, biodegradable electrospun PCL nanofiber-based scaffolds were coated with platelet-rich plasma (PRP-PCL nanofibers) to enhance the adhesion and proliferation of mesenchymal stem cells (MSCs) [79]. Fifth, multifunctional osteoinductive hybrid peptide nanofibers were synthesized based on the self-assembly of three bioactive peptide molecules and then utilized as an implant coating to promote bone-like mineralization on a medical grade tita-

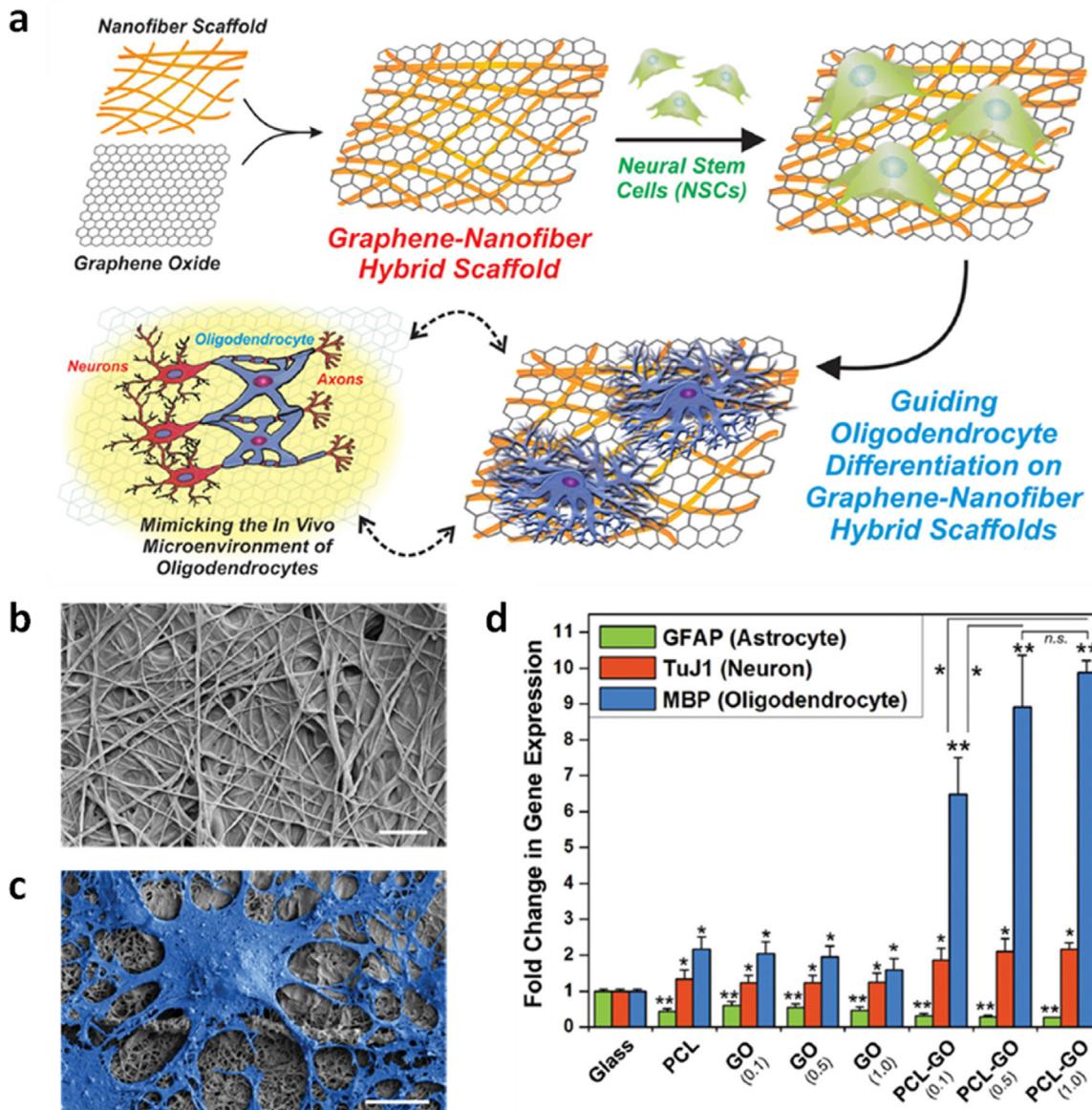
nium substrate surface [80]. The nanofibers were functionalized with osteoinductive collagen I-derived Asp-Gly-Glu-Ala peptide sequence to increase the adhesion, proliferation, and osteogenic differentiation of MSCs into mature osteoblast. Sixth, composite chitosan/silk fibroin nanofibrous membrane scaffolds were synthesized based on electrospinning for bone tissue engineering, in particular, for enhancing the proliferation and osteogenic differentiation of human MSCs [81]. Apart from that of MSCs, nanofibrous scaffolds are also used for supporting the differentiation of neural stem cells (NSCs). For example, collagen nanofibrous scaffolds were prepared for facilitating the presynaptic maturation of NSC-derived neurons towards the formation of neural network [82].

More recently, a unique hybrid polycaprolactone-graphene oxide (PCL-GO) nanofibrous scaffold has been demonstrated to provide instructive physical cues in guiding the specific differentiation of NSCs into mature oligodendrocytes in the absence of chemical inducers (Fig. 8a) [6]. In the study, biocompatible and biodegradable polymeric PCL nanofibers were synthesized through electrospinning, followed by oxygen plasma treatment. GO, the oxygenated derivative of graphene [83–87], was then uniformly coated on the hydrophilic surface of PCL nanofibers (Fig. 8b). NSCs cultured on the GO-coated PCL nanofibers exhibited extensive branching characteristic of oligodendrocytes (Fig. 8c). Further gene expression investigations revealed that cells grown on PCL-GO scaffolds exhibited significant increase in their MBP expression (i.e., mature oligodendrocyte marker) and slight increase in the TuJ1 expression (i.e., neuron marker) while their GFAP expression (i.e., astrocyte marker) decreased simultaneously (Fig. 8d). By increasing the concentration of GO, the MBP expression increased proportionately. This highlights the crucial role of GO in modulating oligodendrogenesis as well as the synergistic effect brought about by the hybrid PCL-GO nanofibrous composites in promoting the preferential NSC differentiation towards the oligodendrocyte lineage.

### 6.2. Wound dressing

Wound dressing plays a crucial role in the management of specific types of wounds, including thermal, chronic, and traumatic wounds, as well as in facilitating the regeneration of epidermal and dermal tissues in wound healing. An ideal wound dressing is expected to exhibit important dual properties: (1) the promotion of exudate absorption for rapid and enhanced epithelialization and wound healing and (2) the inhibition of external infectious microorganism growth, including that of antibiotic resistant bacteria. The past several years have increasingly seen the use of nanoscale biomaterial-based wound dressings in aiding wound healing. Latest advances in nanotechnology have enabled the synthesis of nanomaterials possessing architectural features and morphologies mimicking those of *in vivo* ECMs, notably the nanofibrous structures prepared through electrospinning. Electrospun nanofibrous scaffolds with their large surface area and highly porous configuration support the adhesion and proliferation of skin cells, such as fibroblasts and keratinocytes, and facilitate the secretion of critical ECM components like collagens and growth factors, for the synthesis of new natural ECMs and the subsequent repair of damaged tissues. Nanofibrous scaffolds have been prepared from a wide range of biomaterials. In particular, the biocompatible and biodegradable natural biopolymers, such as chitosan and sericin, are widely used for this purpose due to their excellent biocompatibility, biodegradability, and importantly, their broad spectrum of antibacterial activity coupled with low immunogenicity.

Applications of nanofibers with excellent antimicrobial activity in wound dressings have been actively reported in the last few years [16,88–90]. For example, continuous uniform polyurethane-dextran nanofibrous mats loaded with ciprofloxacin HCl drug



**Fig. 8.** Nanofibers for tissue engineering and regenerative medicine applications. **(a)** Schematic illustration demonstrating the synthesis and application of the hybrid PCL-GO nanofibrous scaffold in guiding and enhancing the specific differentiation of NSCs into mature oligodendrocyte lineage. **(b)** FESEM image showing the GO-coated PCL nanofibers using GO solution with a concentration of 1 mg/mL. Scale bar represents 2  $\mu$ m. **(c)** FESEM image showing the differentiated NSCs seeded on the hybrid PCL-GO nanofibrous scaffold. Scale bar represents 10  $\mu$ m. **(d)** The fold change in the gene expression of the different biomarkers indicative of astrocytes (GFAP), neurons (TuJ1), and oligodendrocytes (MBP), derived from the NSCs cultured on various substrates. The hybrid PCL-GO nanofibrous scaffold demonstrated the highest MBP expression. The \*, \*\*, and n.s represent  $p < 0.05$ ,  $p < 0.01$ , and no significance, respectively, evaluated based on the Student's unpaired *t*-test, as compared to the PLL-coated glass control or between various substrates. [6], Copyright 2014. Adapted with permission from Wiley-VCH Verlag GmbH & Co.

have been electrospun as a wound dressing material with antimicrobial property against both Gram-positive and Gram-negative bacteria [88]. At the same time, the cellular attachment and viability of the seeded fibroblast cells were enhanced with the use of the composite nanofibrous mats. Next, Ag nanoparticle (AgNP)-functionalized chitosan nanofibers were synthesized via electrospinning for wound dressing application [89]. The as-prepared composite nanofibers exhibited excellent antibacterial activity against Gram-negative *P. aeruginosa* and Gram-positive *S. aureus* bacteria, demonstrating the potential of these materials for topical antimicrobial treatment in wound care. In another report, antimicrobial wound dressing nanofibrous mats were fabricated by combining the colloidal dispersions of AgNPs embedded in chitosan with the polymer poly vinyl alcohol (PVA) [90]. The multi-component chitosan/AgNPs/PVA nanofibrous system showed good

antimicrobial performance against *E. coli*, one of the most prevalent infectious bacteria. Separately, based on two natural biopolymers, i.e., chitosan and sericin, the continuous uniform hybrid chitosan-sericin nanofibers were electrospun for wound dressing application [16]. The as-prepared non-woven composite nanofibers were biocompatible and non-toxic. They also enhanced cell proliferation and displayed excellent bactericidal property against both Gram-positive *B. subtilis* and Gram-negative *E. coli* bacteria. This was attributed to the synergistic biological effects presented by the two natural polymers. More recently, chitosan/polyethylene oxide/green tea extract (chitosan/PEO/GT) nanofibers with controllable diameter were prepared through electrospinning and investigated as a wound dressing scaffold [91]. The as-fabricated polymeric composite nanofibers exhibited antibacterial characteristic against both Gram-positive and Gram-negative bacteria. Also,

these nanofibers induced a more effective and improved rate of healing and wound recovery.

### 6.3. Drug and therapeutic agent delivery

Individual nanofibers and nanofibrous scaffolds serve as attractive vehicles for localized and targeted delivery of therapeutic agents. The large surface area and the microporous structure of nanofiber networks are advantageous for the encapsulation and direct incorporation of active biomolecules, including drugs and growth factors, into nanofibers for cellular function modulation. This renders nanofibers suitable as a carrier for drug and therapeutic agent delivery.

One of the latest groundbreaking examples in the application of nanofibers for drug delivery is the development of a nanofiber-based platform for the delivery of therapeutic peptides across the blood-brain barrier into the brain to stimulate a pharmacological response [92]. The peptide nanofibers were synthesized through the self-assembly of amphiphilic peptide in which the active peptide epitope firmly surrounded the nanofiber core. Interestingly, the nanofibrous configuration prevented peptide degradation while the amphiphilic nature of the peptide facilitated peptide transport across the barrier between blood and brain. Another example shows the development of gelatin nanofiber-based platform for the localized transient delivery of miRNA-based therapeutic agent, specifically, the miR-29a inhibitor, for the enhancement of ECM synthesis and deposition in cells [93]. By inhibiting the activity of miR-29, the cellular production of ECM might be increased. The miRNA inhibitor was continuously released over 72 h and the pre-osteoblastic cells grown on the miR-29a inhibitor-functionalized nanofibers exhibited enhanced synthesis of osteonectin, suggesting an efficient delivery of the inhibitor.

In a separate work, it was shown that the localized delivery of antibiotic ciprofloxacin could be achieved via the functionalization of the antibiotic on the hydrophilic and biodegradable PVA-sodium alginate composite nanofiber-based transdermal patch [94]. In another study, biocompatible core-shell nanofibers were prepared for emerging application in tumor therapy against ovary cancer [95]. Polymeric core-shell nanofibers were prepared as a carrier for drug delivery based on co-axial electrospinning using two water-soluble polymers, i.e., PVA and chitosan. The anticancer agent doxorubicin (DOX) was incorporated into the nanofiber core for targeting SKOV3 human ovary cancer cells. In vitro release experiments demonstrated that the loaded DOX could be delivered into the cellular nucleus of SKOV3 and the release rate of the anticancer drug could be simply controlled through the adjustment of the PVA-chitosan feed ratio. Significantly, the DOX-loaded PVA-chitosan core-shell nanofibers inhibited the attachment and proliferation of the ovary cancer cells, underlining the potential application of the core-shell nanofibers for ovary cancer chemotherapy.

### 6.4. Biological sensing

Similar to their applications in chemical sensing, nanofibers have also found application in biological sensing due to the abundant immobilization sites for biomolecules and active species brought about by their large specific surface area. In addition, nanofibers possess excellent electrocatalytic activity and rapid electron transfer characteristic, resulting in higher redox species diffusion. These properties underscore the advantages of using nanofiber-based sensors for the detection of various biological analytes with high specificity, sensitivity, and fast response. Nanofibers have, in fact, been actively utilized for biosensing applications [96–98]. For example, a stable biofunctionalized mesoporous TiO<sub>2</sub> nanofiber mat-based biosensing platform was prepared through electrospinning for the rapid and sensitive electrochemical detec-

tion of esterified cholesterol [97]. In this work, aligned TiO<sub>2</sub> nanofibers were covalently immobilized with cholesterol esterase (ChEt) and cholesterol oxidase (ChOx) biomolecules. The ChEt-ChOx-functionalized TiO<sub>2</sub> nanofiber-based biosensor displayed a higher signal-to-noise ratio and superior voltammetric and catalytic performances, leading to an improved detection limit or higher sensitivity with high reproducibility. This was ascribed to the stable and enhanced loading of biomolecules and improved charge transfer due to the high aspect ratio and porous structure of TiO<sub>2</sub> nanofibers.

In another study, a versatile biosensor was prepared using an electrospun CNT-PMMA composite nanofibers for inducing stable and active electrochemiluminescent emission from peroxydisulfate [98]. Based on the immobilization of the specific recognition biomolecule on the composite nanofibers via the physisorption electrostatic interaction, a label-free and highly sensitive amplified electrochemiluminescent immunosensor was fabricated. The developed platform was capable of detecting α-fetoprotein with a wide dynamic response and high reproducibility. The amplified peroxydisulfate electrochemiluminescence and enhanced analytical performances were attributed to the highly conductive nature, larger active surface, and enhanced electron transfer kinetics of the CNT-functionalized PMMA nanofibers. In a separate work, biocompatible polycarbonate-polycaprolactone (PC-PCL) core-shell polymer nanofibers were fabricated through co-axial electrospinning and developed as oxygen sensors for investigating tumor hypoxia [99]. An oxygen-sensitive luminescence probe made of transition-metal porphyrin complexes (i.e., Pd(II) meso-tetra(pentafluorophenyl) porphine) was embedded in optically clear, highly stable, and gas permeable PC core. Owing to its high sensitivity and rapid response, the nanofiber-based biosensor was capable of locating and imaging hypoxic areas around glioblastoma cell aggregates.

### 6.5. What's next?

Nanofibers have been widely utilized for numerous applications in healthcare and biomedical engineering, such as tissue engineering and regenerative medicine, wound dressing, drug and therapeutic agent delivery, and biological sensing, owing to their unique structural architecture and physicochemical properties. For example, the interconnected networks of nanofibers with high density of micropores are capable of mimicking the *in vivo* native topographical features of ECM. As such, they are highly suitable as scaffolds for cell growth and proliferation, promoting their applications in tissue engineering and wound dressing. Furthermore, the high porosity and large specific surface area of nanofibrous networks are highly attractive for immobilizing various biomolecules and active species. Consequently, this high molecular loading capacity of nanofibers renders them desirable for drug delivery and biological sensing applications. Nevertheless, despite these encouraging attributes, there are still challenges facing the practical applications of nanofibers in healthcare and biomedical engineering. For example, to further enhance the applicability of nanofibers for bioapplications, various physical characteristics of nanofibers and their network structures, such as size, orientation, arrangement, and porosity, need to be carefully controlled and optimized as these factors will heavily influence numerous biological events taking place in the presence of nanofibers, notably, biomolecule adsorption, cell adhesion, and cell proliferation. Moreover, it is necessary to endow nanofibers with additional characteristics, such as antibacterial feature essential for wound dressing, through functionalization with other polymeric or inorganic nanostructures. Finally, systematic and thorough assessment of the *in vitro* and *in vivo* biocompatibility, nanotoxicity, and biodegradability of nanofibers for specific bioapplications are important for the

translation of nanofibers into practical healthcare and biomedical engineering applications.

## 7. Perspectives and outlook

### 7.1. Transformative change potential

The transformative change potential of one-dimensional nanofibers has been highlighted in this review. As discussed, individual nanofibers and nanofiber-based composite structures have been actively prepared using different synthesis strategies. Simultaneously, this class of nanomaterials has been anticipated to play a major role in a wide array of applications, notably in energy generation and storage (e.g., batteries and fuel cells, supercapacitors, solar cells, hydrogen storage and generation, and piezoelectricity), water treatment and environmental remediation (e.g., water treatment and ultrafiltration, photocatalysis, and chemical and gas sensing), and healthcare and biomedical engineering (e.g., tissue engineering and regenerative medicine, wound dressing, drug and therapeutic agent delivery, and biological sensing).

With their attractive and revolutionary physical features, specifically their high surface area-to-volume ratio, large specific surface area, and unique porous structure, nanofibers have continuously transformed numerous fields disruptively and demonstrated how nanotechnology as a whole is capable of contributing to a better day-to-day life. Nonetheless, it is important to note that a large number of the demonstrated preparations and applications of the nanofibers-based structures are still confined within the academic and research environments. In fact, there still exists a notable gap which hinders the translation of nanofiber technology from academia to industry. In order to realize its commercial applications, extensive works are needed to be carried out.

### 7.2. Future research directions

Academic studies and research on one-dimensional nanofibers are moving ahead at an incredibly fast pace. Novel synthesis techniques and applications of nanofibers are being reported in the literature at an ever increasing rate and there is no sign of slowing down. However, to move beyond the current state of nanofiber syntheses and applications towards realization in commercial and industrial settings, several challenges need to be addressed and overcome. None of these challenges are trivial, but they are not insurmountable.

Firstly, it is imperative to develop novel nanofiber synthesis methods capable of integrating the best features of all current and emerging strategies to produce high quality nanofibers with a large industrial scale throughput. Most nanofibers and nanofiber-based composite structures are still synthesized based on the established electrospinning method. However, as pointed out in this Review, electrospinning suffers from several drawbacks, such as low throughput, requirement for specialized equipment, high voltage, and conducting targets, and difficulty in achieving *in situ* deposition of nanofibers. Concurrently, the electrospun nanofiber networks typically possess low mechanical strength due to their low crystallinity and random alignment and orientation of nanofibers. As such, it is necessary to move beyond the current electrospinning method. To increase the throughput of the nanofiber synthesis, innovative variations of the conventional electrospinning, such as multi-needle and needleless electrospinning, may be further developed. To introduce the desired functionalities and complexities into nanofibers as well as to enhance their physical properties for more intricate and specific applications, selection of suitable materials coupled with novel approaches in manipulating nanofiber structures, including smaller fiber dimension, interfiber

adhesion, and fiber surface functionalization, are necessary. More advanced nanofiber configurations, such as core-shell, multilayer, and multicomponent nanofibers, may be prepared through methods like co-axial electrospinning. Combining nanofiber synthesis with other techniques, such as heat treatment, plasma treatment, chemical grafting, and control of fiber arrangement, is attractive to further improve the physicochemical properties of nanofibers. Eventually, integrated nanofiber synthesis strategies which are able to offer the best attributes, such as advanced nanofiber structures of co-axial electrospinning, high throughput of centrifugal jet spinning, *in situ* nanofiber deposition of solution blow spinning, etc., are highly desirable and should be the ultimate goal in the pursuit of nanofiber fabrication techniques.

Secondly, moving beyond nanofiber synthesis, the next challenge lies in the identification of “killer” applications, of which nanofibers are capable of revolutionizing. We have summarized the emerging applications of nanofibers in three important fields: energy, water and environment, and healthcare and biomedical engineering, although most of them are still at the early proof-of-concept stage. Consequently, numerous challenges lie ahead. Take the energy storage application for example. Despite the fact that nanofiber-based energy storage devices have demonstrated enhanced electrochemical properties and cycling performance, the potential of nanofiber-based structures has not been fully exploited. Definitely, there is still room for improvement in this area. It is important to note that the energy storage capacity of the nanofiber-based devices is strongly dependent on the porosity of the nanofibers. As such, it is necessary to synthesize nanofiber networks with controlled and optimized porosity and pore distance such that a higher number of ions can be stored while the whole nanofiber-based electrode can be highly conductive with an enhanced voltammetric energy and power density.

Another example which is of immense interest is the emerging applications of nanofiber technology in tissue engineering and wound dressing. Nanofibrous scaffolds serve as one of the most exciting alternatives for facilitating the regeneration of many types of cells and tissues. Although the relationships between a wide range of nanofibrous scaffolds and cells have been investigated, the majority of these studies are still limited to qualitative proof-of-concept investigations of the cytocompatibility of the nanofibrous scaffolds in terms of cellular adhesion, proliferation, and differentiation. Consequently, more attentions should be focused on the quantitative analyses of the changes in cellular functions as influenced by the topographical cues provided by the nanofibrous scaffolds. At the same time, we note that most of the preliminary studies were still conducted *in vitro* and nanofiber technology has yet to make a real impact in *in vivo* applications. Encouraging results have been demonstrated in numerous *in vitro* assays and in a small number of *in vivo* studies, particularly on animal models, with different categories and degrees of tissue injuries. Clearly, more extensive *in vivo* studies, possibly on human, and clinical trials are needed to evaluate the real impacts and significance of nanofiber technology in healthcare and biomedical engineering.

In conclusion, we believe that nanofibers are at the forefront of nanotechnology. With regard to this exciting technology, we foresee and anticipate that by overcoming all the challenges ahead, we will be able to make significant breakthroughs in moving beyond the current state of the nanofiber technology towards commercial viability and implementation in our everyday lives.

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