Multi-functional electrospun nanofibres for advances in tissue regeneration, energy conversion & storage, and water treatment

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Tissue regeneration, energy conversion & storage, and water treatment are some of the most critical challenges facing humanity in the 21st century. In order to address such challenges, one-dimensional (1D) materials are projected to play a key role in developing emerging solutions for the increasingly complex problems. Eletrospinning technology has been demonstrated to be a simple, versatile, and cost-effective method in fabricating a rich variety of materials with 1D nanostructures. These include polymers, composites, and inorganic materials with unique chemical and physical properties. In this tutorial review, we first give a brief introduction to electrospun materials with a special emphasis on the design, fabrication, and modification of 1D functional materials. Adopting the perspective of chemists and materials scientists, we then focus on the recent significant progress made in the domains of tissue regeneration (*e.g.*, skin, nerve, heart and bone) and conversion & storage of clean energy (*e.g.*, solar cells, fuel cells, batteries, and supercapacitors), where nanofibres have been used as active nanomaterials. Furthermore, this review's scope also includes the advances in the use of electrospun materials for the removal of heavy metal ions, organic pollutants, gas and bacteria in water treatment applications. Finally a conclusion and perspective is provided, in which we discuss the remaining challenges for 1D electrospun nanomaterials in tissue regeneration, energy conversion & storage, and water treatment.

Key learning points

(1) Fundamental principles of typical electrospinning.
(2) General introduction to tissue regeneration, energy conversion & storage, and water treatment.
(3) Discussion of the relationship between the functional properties and the structures.
(4) Overview of the recent advances of electrospun materials in tissue regeneration, energy conversion & storage, and water treatment.
(5) Perspectives on the opportunities and challenges facing electrospun materials.

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1. Introduction

Tissue regeneration, energy conversion & storage, and water treatment are three technological frontiers of great concern to our society in the immediate future. With regard to tissue regeneration, it is well established that damage to tissue (such as skin, nerve, heart and bone) can lead to significant pain, functional impairment, and disability to a patient due to the lack of regenerative capability in most adult tissues. Therefore, the clinical need for improved therapies to aid in the repair and regeneration of damaged tissue is critical. Related to the field of energy conversion and storage, fossil fuels are presently the primary resources used to meet the energy demands of humanity. However, these resources are limited. Furthermore, continued

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reliance on non-renewable energy sources brings into sharp relief another major global issue that needs to be taken into consideration: the impact of greenhouse gas emissions on the environment. Hence, reducing our dependence on fossil fuels by augmenting them with supplies from cleaner, renewable sources of energy is of paramount urgency. With respect to the subject of water treatment, the twin problems of water pollution and water scarcity are approaching crisis levels due to the rapid development of industries and the expansion of the global population. The issue of water scarcity is of tremendous significance, and poses an enormous threat to global health, economic growth, sustainability, and social progress. Thus, a cost-effective water purification technology is highly sought after today as a means to secure the future of humanity.

With the emergence of nanotechnology over the past three decades, there has been an increasing number of studies on nanofibres and their potential applications, largely owing to the unique properties they possess such as large surface area and

engineered high porosity. Compared to other methods of nano-fibre production, electrospinning is one of the simplest and most effective technologies that can be scaled-up to produce a wide range of nanomaterials at an industrial scale.[1] Electrospun 1D nanostructures with a high degree of functional performance and flexible, tuneable properties are considered potential candidates as materials to improve the performance of advanced functional devices such as extracellular matrices, neural networks, advanced electrode materials, photocatalysts, and filters.[2] The rapid development of the electrospinning technique is indicative of the potential that electrospun materials have in the domains of tissue regeneration, energy conversion & storage, and water treatment, as illustrated from the steady growth of nanofibres related publications since 2008 (Fig. 1).

Nanofibrous scaffolds are ideal for the purpose of tissue regeneration because they have similar dimensions to the components of the native extracellular matrix (ECM) and mimic its protein fibres (such as fibrillar collagen and elastin).[3]

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interest is to enhance the performance of energy storage devices such as lithium ion batteries, supercapacitors and advanced batteries.
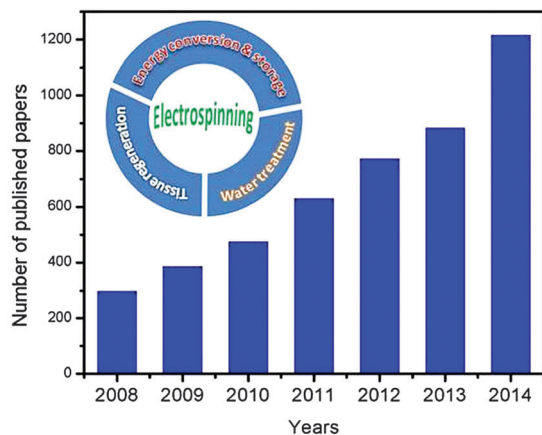
Fig. 1 Research articles published on electrospun nanofibres in tissue regeneration, energy conversion & storage, and water treatment (data are from source SciFinder).

These nanofibrous proteins not only provide architectural and mechanical support for cellular interactions, but also have specific biological functions in cellular processes in terms of cell migration, proliferation, differentiation, and paracrine signalling. As a result, artificial fibrous scaffolds capable of mimicking the fibrous structure of ECM have been intensively studied to aid in tissue regeneration. What is noteworthy is that the electrospinning process possesses advantages in terms of ease of production, robustness, versatility, and the flexibility in allowing for the fabrication of scaffolds composed of a variety of materials with controlled shapes and sizes. The merits of electrospinning enable its capability to fabricate desired fibrous scaffolds to meet different demands of tissues with distinct criteria for scaffold functionality.

With regard to clean energy, significant advances in energy conversion & storage technologies are urgently needed to make sustainable energy resources more economically viable. Typical energy devices include solar cells, fuel cells, batteries (especially Li-ion batteries), and supercapacitors. As primary conversion devices, solar cells and fuel cells can, respectively, convert solar energy and chemical energy directly into electrical energy with little pollution. Once generated, electricity must be efficiently stored for further utilization on demand. Conventionally, the primary conversion systems are connected to storage devices like batteries or supercapacitors to store the energy, making these storage devices critical aspects of the modern power infrastructure. To meet the requirements of integrating future electrochemical power sources into the market, the development of highly efficient solar cells, high energy/power batteries, and highly efficient supercapacitors is imperative. The process of energy conversion and storage can be considered to comprise charge generation, transport, and collection, as well as diffusion. Electrospun nanofibres can shorten the path of carrier transportation and enhance the carrier collection ability by functioning as an electron expressway in the axial direction.[2] Other unique characteristics of the nanofibres include high electrical conductivity, optical transparency, high specific surface area, low cost, and good mechanical flexibility/strength. The combination of these characteristics gives these materials great potential to be applied in the next generation of energy conversion and storage devices with high energy/power density, transparency, portability, and flexibility.

With regard to water treatment, one avenue to overcome the shortage of water is to treat alternative sources of water such as seawater, rainwater, and wastewater. Contaminants and pollutants such as heavy metals, organic pollutants, gas, and bacteria can be highly toxic and carcinogenic in nature, and have to be removed before the water can be fit for use. Electrospun materials have been used as nanoabsorbents and adopted for the removal of heavy metals as a result of their high

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cells and solar cells. He has published over 230 papers in international journals, edited 8 books on energy chemistry and advanced batteries, and been awarded 30 (CN, US, and EU) patents. He is a FRSC, a member of the Editorial Board of Materials Horizons, Nano Research, Solid State Sciences, and J. Energy Chemistry.

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surface areas.[4] Electrospun photocatalysts can chemically break down the organic contaminants and self-regenerate, allowing for continual and repeated use.[5] Furthermore, when electrospun into mats, these nanofibres can act as filters and membranes composed of different nanomaterials and architectures such as carbon, dendrimers, nanoporous ceramics, zeolites, and nanosponges.[6] These electrospun materials offer high porosity, a large number of active sites for metal binding, small sizes, regeneration, and faster removal of contaminants.

The progress made in electrospun nanofibres has been scattered in several reviews either with a focus on specific materials such as inorganic materials or polymers, or on specific applications in biology, energy, or environment. However, a holistic view of electrospun materials from general methods of preparation, to the use of different materials (polymers, composites, and inorganic materials), and their application to tissue regeneration, energy conversion & storage and water treatment is still lacking. In this tutorial review, we highlight the unique chemical and physical properties of electrospun nanofibres enabling their applications in these three important domains. We first give a brief description of the electrospinning process, which is followed by a discussion of the unique properties of the electrospun nanofibres. Then, we review the recent progress of 1D materials fabricated by electrospinning combined with other chemical and physical processes, in the respective applications in tissue regeneration (skin, nerve, heart and bone), energy conversion & storage (solar cells, fuel cells, batteries, and supercapacitors), and water treatment (adsorption, photocatalysis, and membrane filtration) areas. Finally, a conclusion and perspective on the future challenges and opportunities in electrospun 1D materials is provided to conclude this review.

2. Principles of electrospinning

Electrospinning is an effective and simple method of fabricating nanofibres of polymers, composites, and inorganic materials including oxides, carbides, nitrides, metal nanofibres and hybrid composites, and is usually followed by post-treatment processing. The electrospinning technique utilizes electrostatic forces to produce nanofibres from a polymer solution.[7] A typical electrospinning setup contains three main components with a high voltage power supply, a spinneret, and a conductive collector, as shown in Fig. 2. In the electrospinning process, a potential (typically in the kV range) is applied between the spinneret and the collector, both of which are electrically conducting and separated at an optimum distance. When the applied electric field overcomes the surface tension of the droplet, a charged jet of polymer solution is ejected from the tip of the needle. The jet extends through spiralling loops with the loop diameter increasing as the jet grows longer and thinner, resulting in the solidification of the polymer as the solvent evaporates. The solidified nanofibres are then collected on the target.

In general, there are two types of electrospun nanofibre assemblies, namely random and aligned nanofibres.[7] Electrospinning using a simple plate collector produces nonwoven and
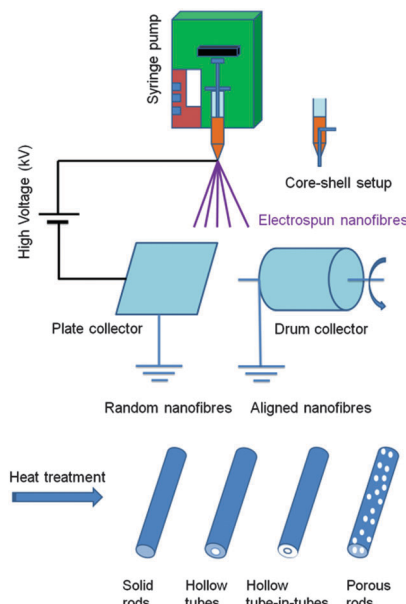

Fig. 2 Schematic of an electrospinning setup to obtain random, aligned nanofibres and nanofibres with various structures, which are influenced by the properties of precursor polymers, electrospinning parameters, and post-treatment.

random nanofibre mats. When a disc or cylinder rotating at a high speed is used as the collector, aligned nanofibre mats or uniaxial fibre bundles can be produced, respectively, along the direction of rotation. In addition to these advantages, electrospun nanofibres possess unique characteristics, such as high surface-to-volume ratios, controllable fibre diameters and surface morphologies (dense, hollow, and porous), and fibrous structures, which can be obtained by varying the following parameters: (i) the system parameters such as the molecular weight of polymers and the polymer solution properties (viscosity, conductivity, dielectric constant, and surface tension).[8,9] (ii) The processing parameters such as the electric potential, flow rate, feeding rate, distance between the capillary and collection, as well as using coaxial or triaxial needles for hollow, core–shell or multi-sheathed structures. (iii) With regard to inorganic materials, controlled post processing parameters such as heating rates and heating temperatures can produce desirable nanostructures.[10]

3. Tissue regeneration

Regenerative medicine is a multidisciplinary approach that incorporates biology, materials science, and engineering, to emerge as a promising therapy for patients with damaged tissues or organs. The ultimate goal in regenerative medicine or tissue regeneration is to reconstruct the cellular microenvironment that processes a wide range of signals such as chemical, physical, and mechanical cues, which can provide guidance of cell behaviors and functions. Electrospun nanofibrous scaffolds (NFS) are of great interest in regenerative medicine because of their structural similarity to that found in a native extracellular matrix (ECM). Moreover, electrospun nanofibres with

interconnected pores and large surface area to volume ratios can provide more structural space for the accommodation of cells, and support their behaviors such as migration, proliferation, and differentiation. The dynamic interactions between cells and the surrounding microenvironments happen all the time during tissue homeostasis. Thus, understanding the biophysical and biochemical interactions between cells and the ECM is fundamental to guiding cellular behaviors for efficient tissue regeneration. Therefore, knowledge of electrospun nanofibres' features in terms of surface chemistry, fibre tomography, mechanical, and physical properties will provide a reliable way of fine tuning the nanofibres for use as suitable grafts in targeted tissue regeneration.

3.1 Skin tissue regeneration

Skin is the largest organ in the human body, acting as a barrier which protects the human body against the invasion of pathogens and excessive water loss. However, when the skin is damaged, it loses the integrity and barrier function. Clinically, skin autografts still represent the gold standard treatment for large surface skin wounds. However, the lack of suitable donor sites for autografting complicates wound closure, which can compromise recovery, increase the risk of invasive wound infection and even mortality. Tissue regeneration combining scaffolds, cells, and bioactive molecules has burgeoned as a new and promising field for the treatment of skin lesions. Tissue-engineered skin grafts such as Epicel®, Dermagraft® and Apligraf® are currently available in the market. However, the drawbacks for these commercially available skin grafts include short self-life, high cost, and poor mechanical properties to withstand handling, and still need to be addressed.[11]

Electrospun nanofibres with continuous and interconnected structures, high surface area-to-volume ratios, and porous properties can facilitate nutrient transport, cellular migration, and waste elimination so as to promote tissue regeneration. Both synthetic polymers and naturally occurring proteins have been successfully electrospun into nanofibres with tunable architectures and suitable mechanical and chemical properties for targeted tissue regeneration. Commonly used biodegradable synthetic polymers in electrospinning include poly(L-lactic acid) (PLLA), poly(lactic-co-glycolic acid) (PLGA), and poly-(ε-caprolactone) (PCL), all of which have been approved by U.S. Food and Drug Administration for biomedical applications. Naturally occurring proteins such as collagen, fibronectin, laminin, and silk have also been electrospun into nanofibres either neat, or blended with synthetic polymers depending on the mechanical properties required. Electrospun nanofibrous scaffolds of synthetic polymers (such as PCL, PLLA and PLGA) have been evaluated as skin grafts *in vitro*. However, the hydrophobic surfaces hinder their interactions with cells and lead to poor cell adhesion. Hence, surface modification with proteins found in native ECM such as collagen and fibronectin has become a common technique to improve cell interaction of scaffolds with lower affinity for cell adhesion. Polymer solution blending is ostensibly the most commonly used method to introduce bioactive molecules in electrospun nanofibres as it does not require any additional setup or equipment. Electrospun nanofibres fabricated from polymer solutions blended with native proteins (such as collagen, gelatin, fibronectin and chitosan) have been applied as potential tissue-engineered grafts for skin regeneration. Typically, the electrospun nanofibre scaffolds which have undergone native protein incorporation are imbued with improved bioactivity and enhanced cellular attachment, spreading, viability, and accelerated wound closure *in vivo*.[3] In addition to improving the biocompatibility, tuning the alignment of electrospun nanofibres has also showed great promise in skin regeneration. Uniaxially aligned nanofibres have showed a stronger propensity to guide cell migration as compared to random fibres. However, the uniaxially aligned nanofibres are not ideal scaffolds for wound healing applications due to the irregular shape of the wound. With this consideration, radially aligned nanofibre sheets have been developed *via* a ring type collector with a point electrode in the center. The radially aligned nanofibres were found to encourage cells to migrate from the peripheral healthy tissue toward the central injured site, which improves wound healing by providing contact guidance for cell migration.[12]

3.2 Neural tissue regeneration

Severe injuries to nerves will cause axonal degeneration in the peripheral nervous system (PNS) that will eventually lead to disability. Currently, the gold standard in clinical practice for bridging large nerve gaps is the nerve autograft, which is restricted by limited availability and donor site deficits. To this end, various tissue engineered nerve grafts have been developed by using a combination of stem cells and biomaterials to realize nerve therapy, yielding promising results. Among the diverse forms of biomaterials that are being applied in nerve regeneration, electrospun nanofibres that are more physiologically similar to the fibrous structures of neural tissue native ECM have been intensively studied and found to provide contact guidance for directed neurite extension. Generally, there are three ways to obtain aligned nanofibres including rotating mandrel collection, conductive substrates, and magnetic substrates, both with air gap collection systems.

The obtained aligned nanofibres applied in regenerative medicine present a simple, scalable, and straightforward strategy to induce stem cell alignment and introduce directional contact guidance of cell behaviors such as neurite outgrowth and alignment. Nevertheless, the mechanisms by which they influence these cells are still unclear. To this concern, thin films in the form of electrospun aligned nanofibres or solvent cast smooth films were fabricated from the same polymer and used to investigate the potential role of differential protein adsorption on topography-dependent neural cell responses. It was found that the extremely high surface area to volume ratio enabled electrospun nanofibres to have higher protein absorption and more efficient presentation of biomolecules to cells, which translated into the modulation of cell behavior.[13] Despite the existing large body of work demonstrating how electrospun aligned nanofibres can promote neurite outgrowth and differentiation of neural stem cells (NSCs) *in vitro*, at the time of writing, there has been little follow-up which delves into possible mechanistic explanations from an intracellular point

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of view of the observed phenomena. In this contribution, the topographical influence of electrospun aligned NFS on the differentiation of NSCs was assessed and compared with randomly patterned or planar unpatterned substrates. Electrospun aligned nanofibres were found to induce NSC elongation and alignment leading to an increased efficiency of neuronal differentiation. This effect was due to the combined effect of aligned nanofibres selectively supporting the survival and viability of neuronal progenitors derived from NSCs, as well as a substrate-mediated increase in canonical Wnt/β-catenin signaling, that led to the accumulation of cytosolic β-catenin, followed by translocation to the nucleus. Nuclear β-catenin binds to the TCF/LEF promoter region to activate gene expression and induce neuronal differentiation of NSCs.[14]

The aforementioned results clearly indicate that cells are capable of detecting biomechanical properties of the underlying substrate, and alter their morphology accordingly *via* rearrangement of cytoskeletal components such as actin structures and focal adhesion complexes, thus facilitating a conversion of the extrinsic mechanical signal into initiation of intracellular signaling. Instead of just guiding the neurites to extend along the direction of aligned nanofibres, the influence of aligned nanofibres on cell behavior could be far more complex and intricate, depending on the contact cues such as the density and the protein deposition of the aligned nanofibres. It has been demonstrated that the neurites could not only project along the nanofibres, but also be directed to grow along a direction perpendicular to the aligned nanofibres if the density of aligned nanofibres is relatively low or the interaction between the neurites and fibres is much weaker than the interaction between neuritis (Fig. 3). These findings offer new
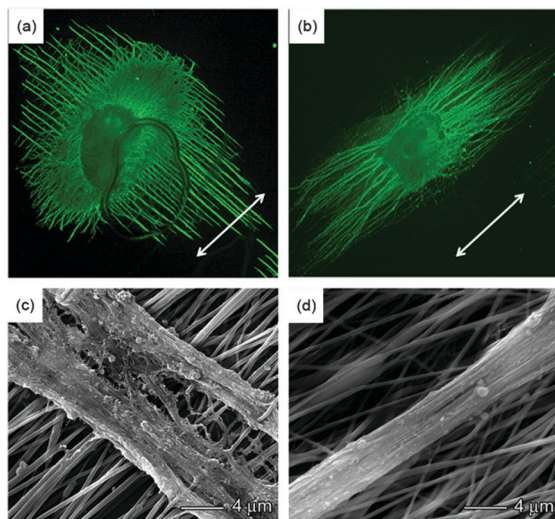

Fig. 3 (a and c) Fluorescence micrograph and SEM image showing neurite growth along a direction perpendicular to the aligned nanofibres that were deposited on glass coverslips pre-coated with polyethylene glycol (PEG) due to the weak interaction between neurites and aligned nanofibres because of the repelling effect of the PEG. (b and d) Fluorescence micrograph and SEM image showing Neurites growing along the direction of the aligned nanofibres coated with laminin. Reproduced with permission from ref. 15, Copyright 2014 American Chemical Society.
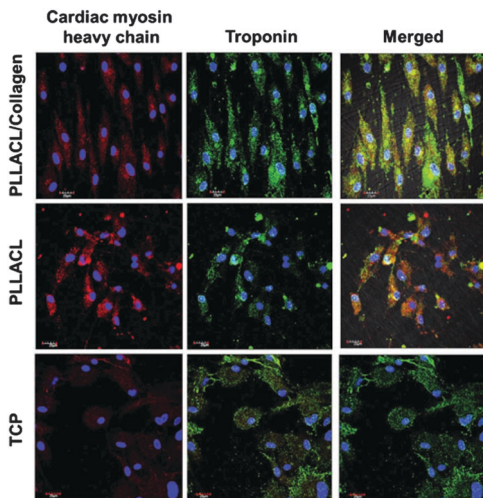
insights into the design of nanofibre-based scaffolds for nerve injury repair and provide new guidelines for the construction of well-defined neuronal network architectures.[15]

Similar to the mechanical and chemical cues in guiding stem cell fate, electrical stimulation from conductive materials has also been applied in neural tissue regeneration to assist neural tissue recovery and regeneration. The aligned core–sheath nanofibres with the incorporation of a nerve growth factor (NGF) in the core and a conductive polymer polyaniline (PANi) in the shell were prepared by coaxial electrospinning. A constant voltage of 100 mV cm^{-1} was applied across the wires and along the fibre direction to study the effect of electrical stimulation, fibre tomography and NGF on neurite outgrowth of pheochromocytoma 12 (PC12) cells, which are able to differentiate into neuron-like cells with ease. The scaffolds loaded with NGFs under electrical stimulation could effectively support PC12 neurite outgrowth and increase the percentage of neurite-bearing cells as well as the median neurite length. More importantly, the NGF release from the conductive core–shell nanofibre could be increased by electrical stimulation. These promising results demonstrated the synergistic effects of electrical stimulation and NGF on neurite outgrowth of PC12 cells.[16]

3.3 Cardiac and vascular tissue regeneration

Myocardial infarction (MI), the main cause of heart failure, leads to a loss of cardiac tissue, followed by the formation of cardiac fibrosis that may cause cardiac dysfunction, due to the lack of regenerative ability. To address this, tissue engineered cardiac patches for improving cardiac function after MI have been intensively studied, with electrospun NFS being explored as a promising tool for the control of regenerated cardiac tissue architecture, owing to their tunable physicochemical properties. In the native cardiac ECM, collagen plays a major role in consistently coordinating the contractility and maintenance of cardiac shape and size as well as the function of the cardiomyocytes. Collagen blended electrospun PLLACL/collagen nanofibres have therefore been fabricated and investigated for cardiac tissue regeneration. Tissue constructs obtained from a rabbit heart were cultured on the electrospun NFS displayed anisotropic rearrangement of cells, characteristic of the native cardiac tissue.[17] By providing both topographical and biochemical cues, electrospun PLLACL/collagen nanofibres showed superior support for the attachment and growth of adult cardiac cells favoring native myocardium-like alignment of newly seeded cardiac cells compared to their purely synthetic PLLACL counterparts (Fig. 4).

Since the native myocardial tissue is subjected to constant and cyclical deformation, the bioengineered scaffold should be flexible enough to allow the contraction of the growing cells. Hence, materials with elastomeric properties and long-term elasticity are highly desired in fabricating tissue-engineered cardiac patches. With this consideration, an elastomer-like poly (glycerol sebacate) (PGS) was encapsulated within core/shell structured electrospun gelatin nanofibres to mimic the softness and elasticity of native myocardial tissue. The PGS incorporated NFS provided the required mechanical strength to support seeded mesenchymal stem cell (MSCs) differentiation into cardiomyocytes

Fig. 4 Immunofluorescence shows cardiomyocytes on electrospun random NFS of PLLACL/collagen, PLLACL and TCP stained for cardiac specific protein cardiac myosin heavy chain – Alexa Fluor 594 and troponin T – Alexa Fluor 488 show colocalized expression, with PLLACL/collagen showing the strongest expression. Reproduced with permission from ref. 17, Copyright 2011 Wiley-VCH.

Fig. 5 Water contact angle and actin expression on unmodified and PDA-coated PCL nanofibres, respectively. In the presence of a PDA ad-layer, cells positively expressed actin. Reproduced with permission from ref. 19, Copyright 2010 Elsevier.

for the regeneration of cardiac tissue with improved cardiac function in the form of improved ejection fraction and a reduction in the left ventricle volume dimensions.[18] Despite the aforementioned promising outcomes, isolated cardiac cell cultures cannot match the functionality of the native tissue (without contraction), due to the lack of proper environmental factors that allow cardiomyocytes to respond morphologically, mechanically, and physiologically as they do in the native tissue. Therefore, substrates that can deliver electrophysiological cues to cardiomyocytes in an efficient way are highly desirable. Electrospinning, which can easily incorporate various materials, specifically conductive polymers, is a prime candidate for developing advanced tissue-engineered cardiac patches.

Heart diseases such as MI are most often caused by damaged or weakened coronary arteries. Hence, there is an urgent clinical need for tissue engineered blood vessels that could be used to replace or bypass damaged arteries. Electrospun fibrous scaffolds have been widely investigated for vascular graft replacement due to their ease of fabrication and compatibility with many natural and synthetic polymers. However, thrombosis (static aggregation of blood factors) is the major issue that hinders the success of small-diameter synthetic vascular grafts. One approach to reduce thrombosis is the establishment of a confluent and stable endothelial cell layer in the lumen of vascular grafts for long-term patency of small-diameter vascular grafts. To this end, the surface of electrospun PCL nanofibres was functionalized with poly (dopamine) (PDA) ad-layer to change the hydrophobic surface of PCL nanofibres to a hydrophilic one, thereby enhancing the attachment and proliferation of endothelial cells (Fig. 5). This approach holds great promise in vascular tissue regeneration. When PDA-coated PCL nanofibres were compared to unmodified and gelatin-coated nanofibres, human umbilical vein endothelial cells exhibited highly enhanced adhesion and
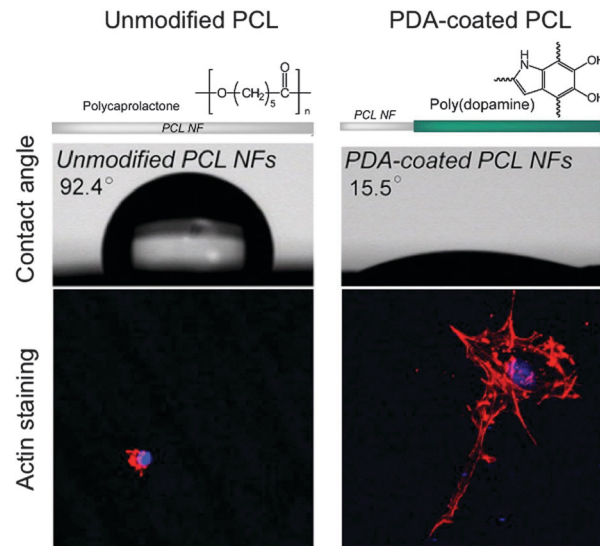
viability, increased stress fibre formation, and positive expression of endothelial cell markers. This successful endothelialization of electrospun NFS could be an effective strategy to improve the effectiveness of small-diameter vascular grafts *in vivo*.[19]

3.4 Bone tissue regeneration

Electrospun NFS with nano-scaled fibrous structure and large surface to volume ratios has been extensively studied in bone tissue regeneration due to the ease of tailoring the mechanical, physical, and chemical properties of electrospun NFS. Studies in the field of bone tissue regeneration have shown that mechanical stimulation alone, without exogenous growth factors, was capable of guiding the fate of stem cells. Generally, the comparatively rigid matrices that mimic collagenous bone will improve stem cell osteogenic differentiation, while matrices with lower stiffness mimic muscle and promote stem cell myogenic differentiation. Therefore, fine-tuning the stiffness of electrospun nanofibrous scaffold will advance the regeneration of targeted tissue.

Compared to the strain changes induced by the beats in cardiac tissue, tendon tissue has to absorb more strain to buffer mechanical loads generated by the attached muscles or bones. To mimic the nonlinear stiffening behavior of crimped collagen fibrils that provide mechanical support, as well as the highly anisotropic structure of tendon tissue, an aligned electrospun nanofibre bundle with a crimped structure was developed by treating the aligned nanofibres collected from rotating mandrel with ethanol. The crimped nanofibres exhibited many of the mechanical characteristics of native tendon tissues. Specifically, the crimped nanofibres obtained by ethanol treatment have a yield strain comparable to native tendon, and may therefore be a better choice for tendon and soft connective tissue repair.[20] However, limited cell infiltration is still a challenge that hinders the widespread application of electrospun aligned nanofibres in regenerative medicine.

Aligned nanofibres with dense fibre packing are more likely to have very lower porosity compared to the random nanofibres. In order to obtain aligned nanofibres with ideal pore sizes sufficient to allow cell penetration and the formation of blood vessels, the electrospun aligned PCL and polyethylene oxide (PEO) nanofibres were simultaneously fabricated using a dual spinneret system, followed by removing the water soluble PEO nanofibres by immersion in water.[21] The remaining aligned PCL nanofibres provided sufficient cues to align cells and direct the formation of a highly organized ECM across multiple length scales, nearly matching native tissue of the knee meniscus. Another approach to increasing the porosity is by fabricating a cotton-like scaffold using a spherical dish embedded with metal array as the collector for nanofibre deposition during electrospinning. The obtained cotton ball-like scaffold consists of electrospun nanofibres with a similar diameter but larger pores and a less dense structure compared to traditional electrospun scaffolds.[22]

Remodeling in adult bone tissue involves an initial assembly of collagen fibres with entrapped cells, followed by calcium salt precipitation on the collagen fibres to form bone. Therefore, by incorporating bone-like minerals, such as hydroxyapatite, electrospun composite nanofibrous scaffolds that structurally mimic the bone tissue, ECM can improve cell adhesion, stem cell differentiation, and bone tissue formation. To accomplish this, hydroxyapatite mineralized electrospun PLLA/collagen nanofibres were successfully fabricated by dipping nanofibres in a series of calcium and phosphorous solutions. These nanocomposites were then used to induce osteogenic differentiation of MSCs. The *in situ* bone mineral production was observed from MSCs grown on these nanocomposites even in the absence of osteogenic supplements in the cell-culture medium. Moreover, after subcutaneous transplantation of the nanocomposite scaffold enriched with human MSCs into nude mice, the formation of the bone matrix can be achieved within only one week.[23] The results of this study showed that the biomimetic method could successfully be used to coat electrospun nanofibrous scaffolds with a hydroxyapatite layer, to improve the *in vivo* bioactivity of the polymer.

In the body, almost all cells reside in a three-dimensional (3D) environment where cell–cell and cell–matrix interactions provide the guidance for cellular responses. The 3D matrix acts as a novel platform that guides cell fate in a controllable and accurate way, enabling advanced biomedical applications. Different from other tissue types, bone often tends to experience greater compressive forces. Electrospun nanofibres, including the cotton-like 3D nanofibrous scaffold, however, lack the appropriate mechanical performance under compression. To improve the capability of electrospun NFS in bearing compressive loads, as well as to replicate the lamellar structural hierarchy of native bone, electrospun nanofibre based biomimetic scaffolds can be generated by orienting single layers of nanofibres (~250 μm thickness) in a concentric manner with an open central cavity. These scaffolds exhibited a similar compressive modulus and stress/strain behavior to that of native bone. The biomimetic scaffolds with cells were able to maintain their mechanical properties, whereas the control scaffolds without cells showed a

significant decrease in compressive modulus after 28 days of culture due to hydrolytic degradation. In addition, results from the alkaline phosphatase activity and mineralization studies confirmed the progression of calcium deposition and primary cell maturation resulting from the interactions between cells and the nanofibre-based biomimetic scaffolds.[24]

Besides providing mechanical, chemical, and topographical cues in guiding cellular behavior, the ECM also serves as a reservoir of signaling molecules, comprising both adhesion molecules and growth factors, to instruct cell decision processes. However, direct blending of bioactive molecules within electrospun NFS usually suffers from rupturing and fast release, which lead to a reduction in the therapeutic effect of these bioactive molecules. Another extraordinary feature of electrospinning NFS is the ability to incorporate materials of different forms (such as particles) to construct composite scaffolds. To realize the dual delivery of bone morphogenetic protein-2 (BMP-2) and dexamethasone (DEX) in a finely controlled way, BMP-2 loaded bovine serum albumin (BSA) nanoparticles were embedded within electrospun nanofibres blended with DEX for the efficient repair of critically-sized rat calvarial defects. The bioactivity of DEX and BMP-2 was preserved in the dual-drug-loaded NFS, and the sequential release of DEX and BMP-2 was achieved. The dual-drug-loaded NFS manifested superior calvarial repair efficacy *in vivo* compared to those obtained with the blank materials due to a synergistic effect between BMP-2 and DEX (Fig. 6).[25] The results demonstrated that hybrid constructs mimicking the
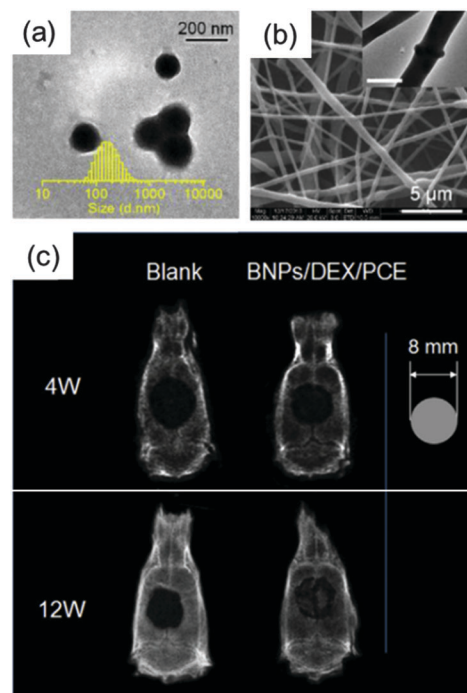

Fig. 6 (a) Morphology characterization of BSA nanoparticles and (b) electrospun particle-embedded nanofibres, the inset is a TEM image of the nanoparticle-embedded nanofibres. (c) Radiograms of the X-ray detection after implanted *in vivo* for 4 and 12 weeks. Reproduced with permission from ref. 25, Copyright 2014 Elsevier.

structure of native ECMs, together with the incorporation of multiple components found within the native bone matrix, can enhance the overall performance in cell viability, proliferation, *in vitro* differentiation, and *in vivo* tissue formation. The concept in developing hybrid constructs based on electrospun nanofibres can be equally applied to any tissue, including skin, nerve, and heart.

4. Energy conversion and storage

As the performance of energy devices depends significantly upon the functional materials, the characteristics of 1D electrospun nanofibres, especially the calcined nanofibres and as-electrospun mats, are being intensively explored as a new class of promising building blocks for fabricating energy devices. This is attributed to their low cost and easy processing routes, which are possible for industrial scale fabrication. All these advantages can potentially unlock many advanced applications in the development of energy technologies. With this in mind, this section is devoted to summarizing recent developments in electrospun materials for energy conversion and storage, ranging from solar cells, fuel cells, batteries, and supercapacitors.

4.1 Sensitized solar cells

While many advances have been achieved in photovoltaic devices, efforts still need to be made to dramatically improve the conversion efficiency of solar cells. As a new class of solar cells, sensitized solar cells, consisting dye-sensitized solar cells (DSSCs) and quantum dot-sensitized solar cells (QDSCs) have emerged as the archetype third generation of photovoltaic devices due to their low cost, easy fabrication, and high power conversion efficiency. Of the approaches to improve the efficiencies of these devices, one promising strategy is the introduction of novel structured materials like electrospun nanofibre materials.[26] Significant strides have been made concerning the photoanodes, counter electrodes, and electrolytes based on electrospun nanofibres, with much work focused on improving the performance of these solar cells.

Electrospun metal oxide nanofibres coated on the conductive substrate as the photoanode have been a hot research topic due to their high specific surface area and 1D fibrous morphology.[26] The high specific surface area can enhance the absorption of photosensitizing dye. In contrast to sintered nanoparticles, the 1D fibrous morphology, with lower grain boundaries, has better interconnectivity and higher surface areas, which lead to better charge conduction and reduced charge-carrier recombination. In addition, the large and controllable pore sizes of nanofibres contribute to the penetration of the viscous polymer gel electrolyte. Furthermore, nanofibres provide an open structure which allows better pore-filling with the electrolyte compared to conventional nanoparticle-based electrodes, leading to enhanced energy conversion efficiency.

Exploring this concept, several recent studies reported 1D electrospun photoanode materials with enhanced performance, including TiO_2, ZnO, and SnO_2.[27–29] The retained electrospun
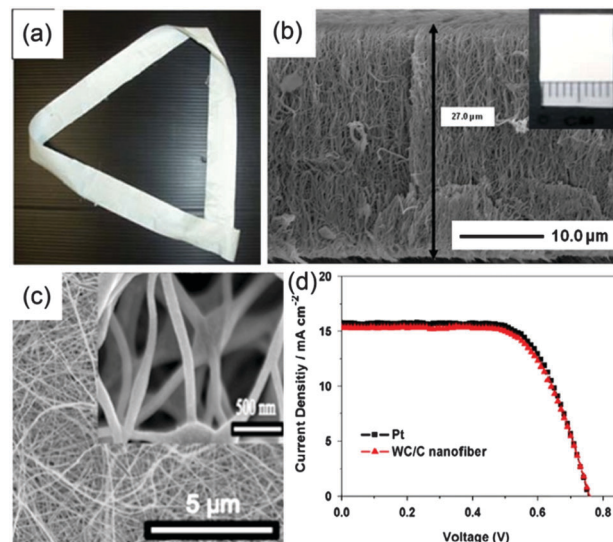

Fig. 7 (a) Photo image of horizontally aligned electrospun TiO_2 nanofibrous ribbon. (b) SEM image of vertically aligned electrospun TiO_2 nanowires. The inset is the photo image of the aligned nanofibrous film indicating size reduction after sintering. Reproduced with permission from ref. 27. Copyright 2011, The Royal Society of Chemistry. (c) SEM image of electrospun WC/C composite. (d) Photocurrent–photovoltage characteristics for QDSCs with different materials as the counter electrodes. Reproduced with permission from ref. 30. Copyright 2014 Elsevier.

TiO_2 nanofibre network apparently provided a solution for the infiltration of the electrolyte into the pores of inorganic nanostructures. Apart from that, electrospun nanofibres can also be applied as a novel light-scattering nanocrystalline film to enhance photovoltaic efficiency.[29] All these advantages lead to superior conversion efficiencies in photovoltaic devices. Mimicking the vertical architecture in electronic devices which can directly and effectively transport electrons, horizontally aligned TiO_2 nanofibres were first produced by using a modified electrospinning setup and then erected to form vertical nanowires on a conductive substrate after a post-treatment process, as shown in Fig. 7a and b.[27] The sintered vertical TiO_2 nanowire film presents a thickness of 27 μm with an average diameter of 90 nm for the ceramic fibres and a fabrication area of 60 cm × 2 cm. Although the anatase phase TiO_2 vertical nanowires achieved a relatively low efficiency in DSSCs, this method provides a facile and expeditious route towards the fabrication of vertically-standing TiO_2 nanowires in DSSCs.

Carbon has been touted as a cheap, alternative material to replace the commonly used Pt electrode. Activated carbon nanofibres are very suitable for the reduction of triiodide ions into iodide and for facile ion transfer by increasing the contact area between carbon and the liquid electrolyte, leading to high efficiency. Tungsten carbide/carbon (WC/C) composite nanofibres for DSSCs were successfully prepared through electrospinning, as shown in Fig. 7c and d.[30] The interconnected WC/C nanofibre structure was formed by fusing the nanofibres together. This structure may further improve the catalytic activity of the fibres, providing an efficient charge transport network. As a result, the WC/C composite demonstrated good

performance in QDSCs, corresponding to 96% that of conventional Pt counter electrodes.

As electrospun polymers can provide three-dimensional network structures, high porosity, large electrolyte solution uptake, and adequate mechanical properties, several polymers have been electrospun into membranes for polymer electrolytes in quasi-solid-state dye-sensitized solar cells, including PVDF-HFP, PEO, PAN, *etc.* Among them, PVDF-HFP showed relatively high ionic conductivities at room temperature, and demonstrated stability in the presence of TiO_2 and Pt nanoparticles. The PVDF-HFP mat exhibited high conductivity and transport abilities due to the high degree of crystallinity. These unique characteristics endowed the PVDF-HFP membrane with a high conversion efficiency and good stability in quasi-solid-state DSSCs.

4.2 Fuel cells

Fuel cells are energy devices that can convert chemical energy into electrical energy through a redox reaction between the anode and the cathode in the presence of catalysts. They are presently receiving considerable attention as an alternative energy source because of their high efficiency without the emission of pollutants. Among the common types of fuel cells, direct methanol fuel cells (DMFCs) and proton exchange membrane fuel cells (PEMFCs) are widely considered to be the most promising for use in portable devices such as cellular phones, laptops, and personal digital assistants due to their high power density and low operating temperature. Novel designs have incorporated electrospun nanofibres to act as anodes, cathodes, or proton conductive membranes in these fuel cells.

Traditionally, nanomaterials consisting of platinum and its alloys have been used as catalysts in fuel cells in view of their high catalytic activity. However, the high cost of the catalyst is one of main impediments to the commercialization of DMFCs. It is therefore one of the major endeavours of scientists to increase the catalytic efficiency of platinum while decreasing the amount of catalyst needed simultaneously. One method is to use a supporting material to improve the performance of the anode catalyst. When applied in fuel cells, the catalytic supporting materials must be stable and dispersed uniformly. In recent years, researchers found that novel nanostructured carbon materials can be used as superior catalyst-supports in fuel cells due to their good electric conductivity and low cost.[31] In particular, electrospun carbon nanofibres (CNFs) have been demonstrated to be superior catalyst-supporting materials with the better overall electrode performance attributed to their higher porosity and larger specific surface areas, which favour the uniform dispersion of noble metal nanoparticles.

Because carbon monoxide (CO) poisoning, commonly associated with Pt catalysts, limits the practical application of Pt catalysts, some alloys and non-precious metal substitutes have been incorporated with CNFs to form composite electrocatalysts to investigate their oxygen reduction reaction (ORR) activity. In one instance, Pd–Co alloy nanoparticles were found to be uniformly dispersed in the carbon nanofibre matrix.[32] In such a structure, the ECF serves not only as a conductive carbon support but also as a solid barrier to prevent nanoparticles
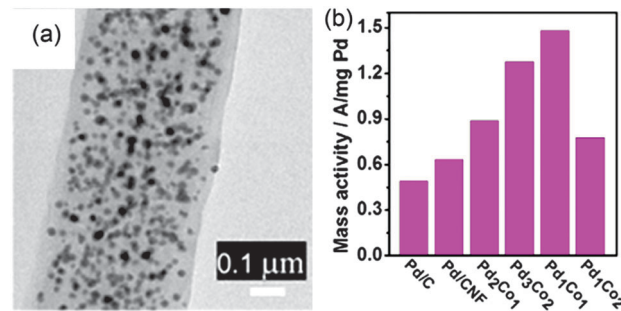

Fig. 8 (a) HRTEM of Pd_xCo_y/ECF nanocomposite. (b) Mass activity of Pd-based electro-catalysts for formic acid oxidation. Reproduced with permission from ref. 32. Copyright 2014, American Chemical Society.

from aggregation, as shown in Fig. 8. The Pd_xCo_y/CNF nanocomposites exhibited much higher electrocatalytic activity and stability in formic acid and methanol oxidation reactions than Pd/C and other state-of-the-art Pd- or Pt-based catalysts.

With regard to PEMFCs, one of the most important issues faced has been to develop a proton exchange membrane that is able to achieve high proton conductivity, low gas permeability of the fuel and oxidant, and sufficient chemical stability. Electrospun PEMs have demonstrated efficient proton conduction to positively influence the performance of DMFCs. At present, Nafion is the most commonly used commercial polymer electrolyte membrane, exhibiting relatively high proton conductivity derived from its unique chemical structure. As Nafion alone is hard to electrospin, it should be blended with high molecular weight polymers such as polyvinyl alcohol (PVA) and polyethylene glycol (PEG) to form composite membranes. The incorporation of PVA nanofibres not only enhances the DMFC performance, but also reinforces the mechanical properties and decreases the proportion of Nafion required. In addition, the ionic morphology of the polymer membrane is an important characteristic that influences proton conductivity and methanol permeability. High-purity aligned nafion nanofibres were successfully collected between two grounded parallel metallic wires during electrospinning with the use of only 0.1 wt% PEO.[33] The electrospun fibre had a diameter of 400 nm and exhibited proton conductivities as high as 1.5 S cm^{-1} – an order of magnitude higher than the bulk film properties ($\sim$0.1 S cm^{-1}). This is largely attributed to the preferential alignment of interconnected ionic aggregates along the fibre axis direction as evidenced by X-ray scattering. In addition to the combination and morphologies, some inorganic fillers including micro- or nano-particles have been incorporated into polymer matrices to enhance water retention and thermal stability, thereby improving the barrier properties for methanol crossover when dispersed into acidic membranes.

4.3 Battery

Among various secondary batteries, lithium ion batteries (LIBs) have attractive advantages, such as high energy density, low maintenance, and relatively low self-discharge. A LIB consists of an anode and a cathode separated by an electrolyte containing

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dissociated lithium salts, which enables the transfer of lithium ions between the two electrodes. To obtain high-performance LIBs with high capacity, high charging efficiency, and long cycling life, it is necessary to design and develop novel electrode materials with superior lithium storage behaviour.[34,35] Electrospinning is one favourable technique that can be adopted to design component materials (anodes, cathodes, and separators) for LIBs. Recent studies show that electrospun component materials for LIBs present several advantages, including a short Li-ion insertion/extraction distance, facile strain relaxation upon electrochemical cycling, and very large surface area contact with the electrolyte, all of which can improve performance in terms of power, charge/discharge properties, and capacity retention.[31]

4.3.1 Anode. Anode materials can influence the cycle life, rate capability, and lithium storage capacity of full LIBs. Extensive research is required in the area of anode materials to enhance the performance of anodes. An ideal anode should be able to accommodate a large amount of Li ions per formula unit, have a potential as high as Li metal, be stable to generate high capacity, and be economical and environmentally friendly. To meet these requirements, electrospun carbon, carbon composites, and various oxides have been investigated for LIB applications.

Carbon nanofibre (CNF) is an interesting candidate among carbonaceous anode materials due to its 1D nanostructure, good electronic conductivity, and free-standing characteristics. To improve LIB performance, it is often necessary to incorporate another high Li$^+$ storage capacity component into the carbon matrix such as silicon (Si) or tin (Sn). Si@C composite core–shell structures in 1D fibres have been created by a single electrospinning setup using a dual nozzle.[36] As shown in Fig. 9, the commercially available Si nanoparticles were indeed encapsulated within the carbon shell. The unique core–shell structure

resolved various limitations of a Si anode operation, such as pulverization, vulnerable contacts between Si and carbon conductors, and an unstable solid–electrolyte interphase, thereby resulting in outstanding cell performance. This includes a gravimetric capacity as high as 1384 mA h g^{-1}, a 5 min discharging rate capability while retaining 721 mA h g^{-1}, and a cycle life of 300 cycles with almost no capacity loss.

Metal oxides that undergo displacement reactions have also been found to exhibit high capacities. Compared to simple metal oxides, composites composed of an electrochemically inactive/active matrix such as MO_x (M = Zn, Sr, Mn, Co, Ca *etc.*) have been proposed, where the uniformly distributed matrix not only buffers the volume changes during cycling, but also prevents the aggregation of active materials, eventually leading to improved cycling stability.[37,38] For example, novel eggroll-like $CaSnO_3$ (CSO) nanotubes have been prepared by a single spinneret electrospinning method and investigated in LIBs, as shown in Fig. 9. It can be observed that the CSO-NR possessed a channel-like morphology with a high surface area, leading to a reversible capacity of 648 mA h g^{-1} after 50 cycles, higher than the nanorod structure. The enhanced electrochemical performance can be attributed to the unique interior hollow structures and channel-like morphology, which provides sufficient space to buffer the volume change and also facilitates fast lithium ion diffusion during lithiation/delithiation.

4.3.2 Cathode. Lithium containing metal oxides (*i.e.* $LiFePO_4$, $LiMn_2O_4$, and $LiCoO_2$) are widely used as cathode materials for LIBs, due to their lower insertion potential (<0.1 V *vs.* Li), appreciable theoretical capacity, low-cost, and being environmentally friendly. Although $LiFePO_4$ was demonstrated as a promising cathode material, it was severely limited as a result of its poor conductivity and lithium ion diffusion. One way to address this inadequacy is to decrease the particle size and apply a coating of an electronically conductive matrix (*e.g.*, carbon). For example, electrospinning can produce *in situ* carbon-coated single-crystalline $LiFePO_4$ nanowires with diameters of around 100 nm.[39] This unique structure leads to good rate performance (169 (0.1C), 162 (0.5C), 150 (1C), 114 (5C), 93 mA h g^{-1} (10C)) and excellent cycling stability at elevated temperatures (98% capacity retention after 100 cycles at 60 °C). From the cost and environmental perspective, $LiMn_2O_4$ is another noteworthy contender. Porous $LiMn_2O_4$ hollow nanofibres were fabricated by electrospinning followed by calcination.[40] As shown in Fig. 10, the hollow nanofibres were 3–10 mm in length and 500 nm in diameter, while the thickness of the $LiMn_2O_4$ layer in the hollow structure was found to be ∼65 to 85 nm. This unique hollow structure retained 87% of the initial reversible capacity of 119 mA h g^{-1} after 1250 cycles at the 1C rate. When assembled into a full battery with electrospun PVdF-HFP and TiO_2 as the separator and the anode, respectively, the full-cell $LiMn_2O_4$|gelled PVdF-HFP|TiO_2 delivered good capacity characteristics and excellent cyclability (capacity retention of 90% after 70 cycles at 150 mA h g^{-1}) with an operating potential of 2.2 V at a current density of 150 mA h g^{-1}.

Vanadium pentoxide has a high theoretical capacity of ∼400 mA h g^{-1} and possesses certain advantages over the
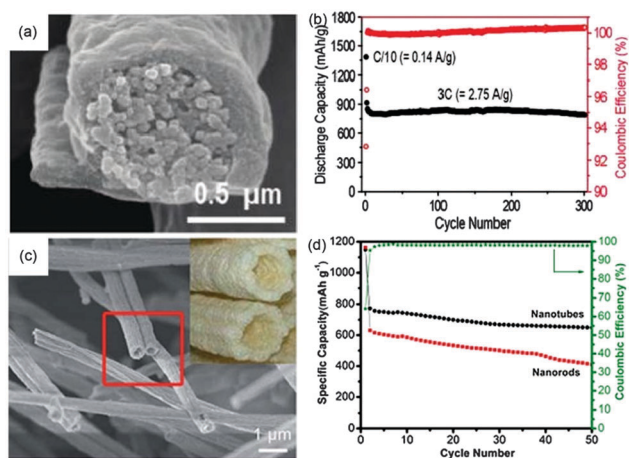

Fig. 9 (a) A cross-sectional SEM view of a single Si nanoparticles@C indicating that the core full of Si nanoparticles is wrapped by carbon shell. (b) Cycling performance of Si nanoparticles@C measured at 3C rate (2.748 A g^{-1}), and the right axes are Coulombic efficiencies. Reproduced with permission from ref. 36. Copyright 2012, American Chemical Society. (c) FESEM image of $CaSnO_3$ nanotubes. The inset in (d) is a photograph of egg-roll. (d) Cycling performance of CSO-NT and CSO-NR at a current density of 60 mA g^{-1}. Reproduced with permission from ref. 37. Copyright 2013, The Royal Society of Chemistry.
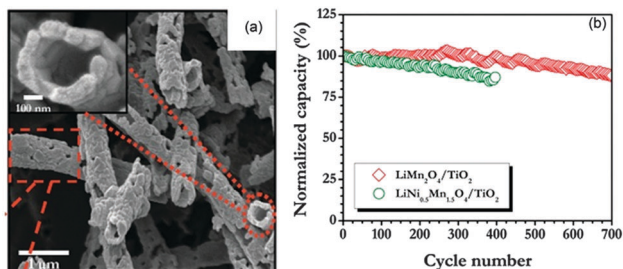
Fig. 10 (a) FESEM image of LiMn$_2$O$_4$ nanofibres. Inset: magnified view of nanofibres indicating a hollow structure. (b) Normalized capacity of LiMn$_2$O$_4$/TiO$_2$ (at a current density of 300 mA g^{-1}) and LiNi$_{0.5}$Mn$_{1.5}$O$_4$/TiO$_2$ (at a current density of 150 mA g^{-1}) full cells. Reproduced with permission from ref. 40. Copyright 2015, The Royal Society of Chemistry.

above mentioned cathodes, however, it suffers from severe capacity fading and poor rate capability. To mitigate these issues, several approaches have been adopted such as reducing Li-ion diffusion pathways by fine-tuning the morphology of V$_2$O$_5$ by creating 1D and 3D nanostructured networks.[41] When carbon was coated on the electrospun V$_2$O$_5$ using a plasma enhanced chemical vapour deposition method, the carbon-coated VNF showed an initial discharge capacity of 300 mA h g^{-1} with an improved capacity retention of 65% after 50 cycles at 0.1C rate. This study highlighted the importance of the electro-spun fibre network morphology to increase the Li-ion diffusion and prevent undesired side reactions, thereby improving the overall efficiency of LIBs.

4.3.3 Separator. The separator is a membrane placed between the positive electrode (cathode) and the negative electrode (anode) to prevent direct contact while allowing the transportation of ions between the electrodes. Electrospun fibrous membranes have high porosities, large specific surface areas, and interconnected porous structures. As a result, they are able to take up large amounts of liquid electrolyte and offer effective conduction channels. This in turn leads to high ionic conductivities and good electrochemical properties. Among the nanofibre-based polymer nonwoven separator materials, PVDF has attracted significant attention because of its good thermal and electrochemical stabilities, and excellent affinity with electrolyte solutions.[42] Furthermore, several other methods were developed to enhance the mechanical properties of PVDF, including heat treatment and the incorporation of nanoparticles. The heat-treated PVDF mat showed higher tensile strength and tensile modulus than the untreated PVDF, while PVDF/SiO$_2$ nonwoven membranes showed high ionic conductivity, high level of porosity, and electrolyte uptake, leading to excellent performance in LIBs.

4.4. Metal–air batteries

In metal–air batteries, a metal anode (Li, Zn, Al, *etc.*) is coupled with an air-breathing porous cathode. These types of batteries have attracted much attention because of their very high theoretical specific energy,[43] but unfortunately, most metal–air batteries suffer from sluggish catalytic kinetics and thus display very poor cycling life and poor power capability, leaving them far
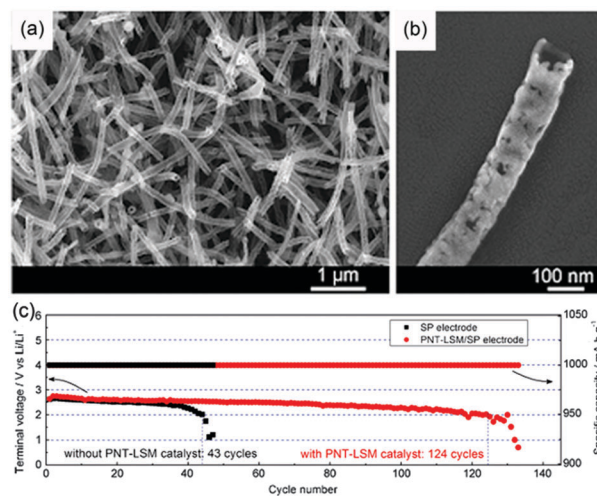

Fig. 11 (a and b) PNT-LSM after calcination at 650 °C for 3 h. (c) Voltage of the terminal discharge *vs.* the cycle number for Li–O$_2$ cells with and without a PNT-LSM catalyst at 0.15 mA cm^{-2}. Reproduced with permission from ref. 44. Copyright 2013, Wiley-VCH Verlag GmbH & Co.

from realizing commercial application. Recently, intense scientific activity has been directed towards carbonaceous materials and non-precious metal oxides in developing advanced catalysts for metal–air batteries. 1D fibrous nanomaterials exhibit unique properties that make them suitable for use as catalysts, for instance, high surface area-to-volume ratios, short lengths for charge transport/diffusion in the radial direction, and low resistance to the flow of gas and liquid through fibre bundles and/or porous fibres. For example, perovskite-based porous La$_{0.75}$Sr$_{0.25}$MnO$_3$ nanotubes (PNT-LSM) were electrospun as highly efficient electrocatalysts for rechargeable Li–O$_2$ batteries.[44] As shown in Fig. 11, the electrospun composite nanotubes presented a diameter of about 100 nm and the wall thickness of about 15 nm. When applied in Li–O$_2$ batteries, this ideal design for a unique porous tubular structure possessed several advantages. First, the 1D tubular structure facilitated electron transport. Second, the open porous morphology provided short diffusion distances for O$_2$ and the electrolyte, ensuring fast and uniform O$_2$ and electrolyte distribution inside the electrode. Third, the porous and hollow structure could provide a large electrode–electrolyte contact area to ensure consistently high availability of the catalytic active sites. All these favourable characteristics resulted in excellent cyclic performance for PNT-LSM, achieving a 1000 mA h g^{-1} capacity limit for over 124 cycles, among the best cycling performance of Li–O$_2$ cells.

4.5. Supercapacitors

Similar to LIBs, supercapacitors (SCs) are also among the most popular types of energy storage devices. They allow for high energy density, high rates of charge–discharge, and long cycle life, which bridge the gap between traditional capacitors and secondary batteries. SCs can be divided into two main types, electrical double layer capacitance (EDLC) and pseudocapacitors. In general, EDLCs are typically made with high surface area materials that work by accumulating electrostatic charges on

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the electrode/electrolyte interface, while the pseudocapacitors are based on redox active electrode materials, thus rendering an increased energy density, at the expense of inferior power density and cycle life compared to EDLCs. However, the practical applications of SCs are limited by their energy and power densities, and thus the demand for electrode materials with high capacity is extremely high. Generally, the performance of electrode materials for SCs is intimately dependent on both the accessible specific surface area and the pore structure.

Transition metal oxides as pseudocapacitor electrode materials exhibit higher capacitances due to the reversible Faradic redox reaction as compared to EDLC materials. Among various metal oxides, spinel nickel cobaltite ($NiCo_2O_4$) is considered a promising electrode material for SCs. More significantly, $NiCo_2O_4$ possesses better electrical conductivity and higher electrochemical activity than the two single component oxides, namely nickel oxide and cobalt oxide.[45] The various precursor concentrations and heating rates can be tuned to produce many various desired ternary mixed metal oxides with tube-in-tube, nanotube, and 1D solid nanostructures, including $CoMn_2O_4$, $NiCo_2O_4$, $CoFe_2O_4$, $NiMn_2O_4$, and $ZnMn_2O_4$, all using a single-nozzle electrospinning technique (Fig. 12).[10] When applied in SCs, tube-in-tube $NiCo_2O_4$ shows a specific capacitance of 1756 F g^{-1} at 5 A g^{-1}, higher than the other two structures. The superior electrochemical performance of tube-in-tube $NiCo_2O_4$ could probably be attributed to the unique porous, hollow morphology and relatively high specific surface area.

In another regard, growing demand for flexible electronics in our daily life drives much research toward high-performance, light-weight, and flexible SCs. The self-supporting nature of these flexible SCs eschews the use of binders and the tedious preparation processes for fabricating typical electrodes. Electrospun CNFs have been investigated as highly porous, free-standing, flexible mats in SCs due to their relatively simple fabrication process, high surface areas, and high conductivity. The electrochemical performance in SCs is closely related to their surface areas, with high surface areas responsible for accelerating ion transport, accommodating large quantities of ions, as well as improving rate capability. Other aspects of the carbon materials, including pore size distribution, shape, and structure, can also influence the performance to a large extent. Therefore, an activation step to optimize the porosity is required to improve their electrochemical performance. These include physical activation with steam or chemical activation by $ZnCl_2$, KOH, or SiO_2. A bamboo-like graphitic carbon nanofibre with well-balanced macro-, meso-, and microporosities can be obtained by etching SiO_2 in an aqueous HF solution (Fig. 13a and b).[46] The CNF web can be bent to an angle of 180°, demonstrating that the structure of bamboo-like nanofibres is retained without suffering any damage. The mechanically robust membrane electrode recovered its initial state easily even after being manipulated into being folded thrice. Additionally, these electrodes displayed an extraordinarily high stability with ∼100% of the initial capacitance after 5000 cycles tested at 10 A g^{-1} (Fig. 13c).

To further increase the energy and power densities of electrospun CNFs, transitional metal oxides have been deposited on the CNF web to leverage their pseudocapacitance. For example, a flexible and efficient electrode based on an electrospun carbon fibre substrate with elaborately designed hierarchical porous V_2O_5 nanosheets (V_2O_5/CNF) was prepared by a simple solvothermal method.[47] As shown in Fig. 13d and e, the 3D network configuration appeared unchanged after thermal treatment, benefiting from the robust support of CNFs. This unique electrode possessed several advantageous hybrid features including the good electrochemical performance of V_2O_5, and high conductivity, ease of handling, low cost, and mechanical robustness of CNFs. Flexible solid state SCs assembled from these
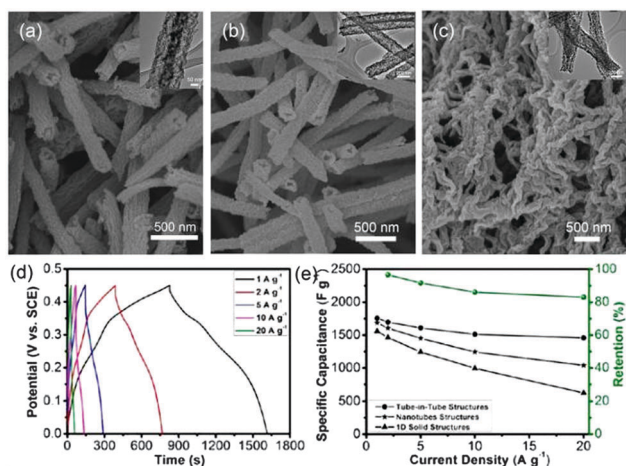

Fig. 12 (a–c) SEM images of $NiCo_2O_4$ tube-in-tubes, nanotubes and solid 1D nanostructures. The insets are their corresponding HRTEM images. (d) Galvanostatic charge/discharge profiles of $NiCo_2O_4$ tube-in-tube nanostructures at various current densities in a 2.0 M KOH electrolyte. (e) The specific capacitance at various current density of $NiCo_2O_4$ tube-in-tube, nanotube, and 1D solid nanostructures. Reproduced with permission from ref. 10. Copyright 2015, American Chemical Society.
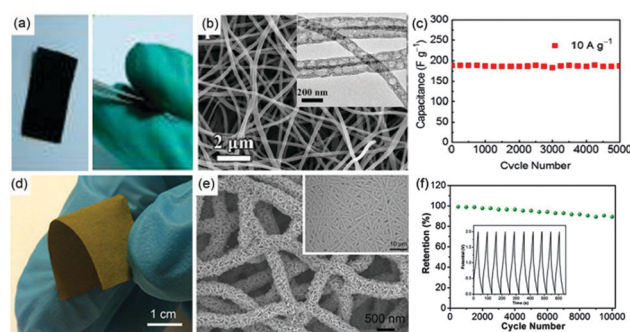

Fig. 13 (a) Photograph of electrospun carbon nanofibres (left) and the folded state (right). (b) SEM and HRTEM images (inset) of the carbon nanofibres. (c) Cyclic stability of a carbon electrode at a current density of 10 A g^{-1}. Reproduced with permission from ref. 46. Copyright 2015, American Chemical Society. (d) Photograph of the flexible V_2O_5/CNF film. (b) Low magnified and high magnified SEM (inset) of V_2O_5/CNF film. (e) The specific capacitance of V_2O_5/CNF at various current densities. (f) Cycling stability of the flexible V_2O_5/CNF//CNF solid SC device at a current density of 1.2 A g^{-1}. The inset shows galvanostatic charge–discharge voltage curves for the last ten cycles. Reproduced with permission from ref. 47. Copyright 2015, Wiley-VCH Verlag GmbH & Co.

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integrated electrodes manifested enhanced energy storage and power delivery (a maximum energy density of 22.3 W h kg^{-1} and a power density of 1500 W kg^{-1}), and outstanding cycling stability (10.7% decay in specific capacitance after 10 000 cycles) (Fig. 13f). Encouragingly, the superior electrochemical performance of the device could be maintained even after 200 bending cycles.

5. Water treatment

In today's world, increasing demand and shortage of clean water sources due to rapid industrialisation, population growth, and persistent drought conditions have become critical global issues. As far as the environment is concerned, the reuse and recycling of wastewater is necessary to augment the limited fresh water supply and to meet the growing strain on water resources in the long run. During the past few decades, a variety of practical strategies and solutions have been proposed and applied to develop viable wastewater treatment technologies.[4] As shown in Fig. 14, electrospun materials have been demonstrated as promising candidates for heavy ion adsorbents and photo-catalysis of organic pollutants in water treatment, due to their high porosity, interconnectivity, and a large surface-to-volume ratio. Especially benefitting from the interconnectivity, microscale interstitial space, mat characteristics, and nonwoven electrospun nanofibre mats can be used as water filtration membranes for water treatment.

Heavy metal ions including Pd, Hg, and Cr are major pollutants not only in the industrial sector, but also in our living environment, which can cause severe public health problems. Several technologies have been developed for the removal of heavy metal

Fig. 14 Schematic of water treatment from three major types of pollutants through absorption, photocatalysis, or filtration processes.

ions from water. Compared to other treatment methods, adsorption is simple, economical, and effective. Electrospun nanofibre sorbents possess a large surface area, which facilitates the attachment of target molecules, requiring reduced sorbent amounts, and smaller sample and eluent volumes. Taking lead ions for example, electrospun polystyrene functionalized with dithizone (DZ) as the absorbent can absorb lead(II) at pH 8.5 and desorb it by three times under acidic conditions, recording a breakthrough capacity of 16 μg mg^{-1}.[48]

Photocatalysis has been considered as one of the most appealing options for wastewater treatment, owing to its great potential and high efficiency by using sunlight to remove organic pollutants and harmful bacteria with the aid of solid photocatalysts. With regard to powder photocatalysts, the post treatment removal of the powder after photocatalytic reaction can be a time consuming and costly process, hindering its large-scale adoption in the industry. One promising method to assuage this limitation is to immobilize the photocatalysts on electrospun polymer webs to form recycled mats for pollutant degradation. As electrospun mats are usually porous, the construction of an open three-dimensional network is possible, which not only results in a high surface area, but also permits the permeation of water, a favourable feature in water purification. TiO$_2$ and ZnO are typical semiconductor photocatalysts that have been deposited on polyacrylamide (PAN) or other polymers through the hydrothermal method. These materials showed almost no decay in their catalytic activity when reused. A novel multifunctional nanofibrous mat based on TiO$_2$ nano-cables functionalized by Ag nanoparticles, and coated with a thin graphitic shell was obtained through electrospinning, and had photodegradation capabilities.[49] In this mat, each component served a unique function: the carbon coating acted as both an adsorption material for absorbing pollutants and as a charge-transfer material, the Ag nanoparticles acted as a visible-light sensitizing agent and also as a charge-transfer material, finally the TiO$_2$ flexible mat acted as a UV sensitive photocatalytic matrix. This multifuctional mat exhibited excellent photocatalytic activity for the degradation of rhodamine (RhB) and phenol, which provides new insight into the design and preparation of advanced and scalable photocatalytic composite membrane materials.

Filtration systems can offer another potential solution for water treatment.[6] Compared to other techniques, electrospun nanofibre membranes act as very specific filters that will efficiently allow the passage of water, while rejecting suspended solids and other substances, due to their high tuneable porosities, interconnected pore structures, and relatively high strength. In general, membrane filtration is a process of removing suspended particulates from water by applying a pressure to drive water through a porous media. Currently, almost all the membranes manufactured for drinking water production are made of polymeric materials such as polysulfone, poly(acrylonitrile), poly(vinylidenefluoride), and poly(acrylonitrile)–poly(vinyl chloride) copolymers, since they are significantly less expensive than membranes constructed of other materials. In most cases, electrospun nanofibres should be surface functionalized with
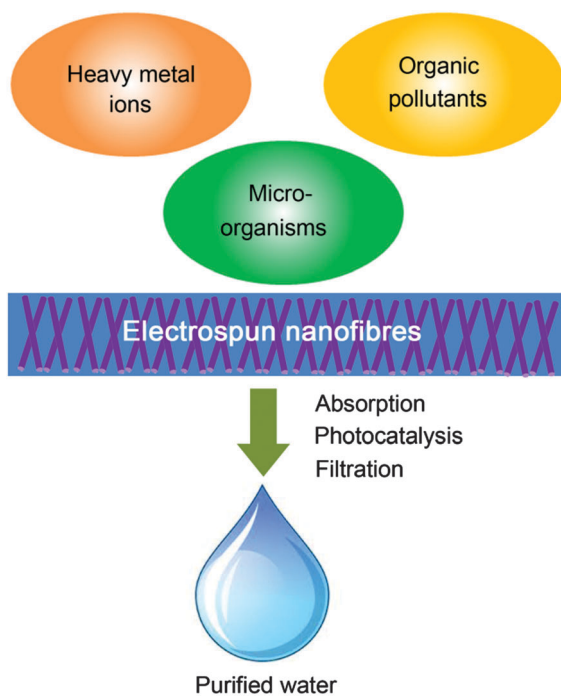
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ligands to improve the performance of selectivity and permeability. Cellulose nanofibre membranes have been surface functionalized with cibacron blue for the purification of albumin.[50] Cellulose nanofibre membranes functionalized with protein A/G show a significant ability to capture IgG molecules with a capacity of $\sim$134 μg cm^{-2}, higher than that of commercial membranes ($\sim$80 μg cm^{-2}).

6. Conclusion and perspective

In this tutorial review, we have described significant progress in the fabrication of electrospun nanofibres and their applications in the domains of tissue regeneration, energy conversion & storage, and water treatment, which are the important issues and challenges in the 21st century. Through a combination of calcination, hydro/solvothermal reactions and other chemical or physical methods, the capability of electrospinning has been successfully extended to fabricating various types of nanofibres with well-defined, controllable structures, including polymers, carbon, carbon composites, and oxides. Due to their large surface areas, high porosity, and unique mat structure, electrospun nanofibres have demonstrated many advantages and great potential in the fields of tissue regeneration (skin, nerve, heart, and bone), energy conversion & storage (solar cells, fuel cells, and batteries), and water treatment (adsorption, photocatalysis, and filtration) in the last decade. The current advances in electrospinning technology are milestones demonstrating important evidence of the promising future applications of this technique in these areas.

While electrospun nanofibres offer exciting opportunities for the development in tissue regeneration, energy conversion & storage and water treatment, with their development reaching unprecedented levels of success, it should be pointed out that several key points remain to be addressed. First, the fabrication of electrospun nanomaterials with high and uniform quality is a basic requirement but remains relatively challenging, as high performance devices strongly depend on high quality nanofibres. At present researchers have encountered difficulties in the following aspects: (1) one drawback of electrospinning is the difficulty in obtaining uniform nanofibres with diameters below 50 nm. (2) Controllable patterns such as uniaxially aligned nanofibres or twisted yarns are ideal structures for devices and can be fabricated by deliberately designing and controlling the electrospinning setup. (3) Compared to the polymer counterparts, electrospinning of inorganic materials is more challenging as it involves the preparation of precursor solutions followed by subsequent critical heat treatments. These post processing treatments require great attention and care, needing well defined strategies to be laid out for the whole fabrication process to get ideal products. (4) As composites can synergistically combine the properties of its constituents and even possess novel hybrid characteristics, they hold tremendous potential in various applications. It is therefore essential to understand the properties of the components used for modifying and developing advanced electrospinning techniques to obtain the ideal composite. In addition, different morphologies of the nanofibres could have important implications in developing novel properties of an electrospun material.

Second, despite the promising progress that has been achieved by using electrospun nanofibres for regenerative medicine, issues such as the low cell infiltration rate still exist, and remain a major challenge yet to be overcome before its widespread adoption in *in vivo* systems. Although incorporating a sacrificial component can increase the porosity of a nanofibre-based scaffold, it is usually accompanied by compromised mechanical properties and integrity of the scaffold. Meanwhile, shrinkage of nanofibres in aqueous environment would compromise the enlarged porosity in the electrospun cotton-like scaffold. Although the adhesive gradient has been created within electrospun nanofibres to increase cell infiltration, the rate of migration of cells from surface into the electrospun nanofibres is still far from ideal.

Third, although electrospun materials are used as active materials for charge collection and transport in electronic devices, there are still numerous critical problems requiring in-depth understanding for the improvement in their quality and function. These include the morphology, defects, surface functional groups, and assembly behaviour in composites. Although electrospun nanomaterials have been applied as flexible electrodes in batteries and supercapacitors, much effort should be focused on separators in batteries to make full use of the mat property.

Fourth, with regard to photocatalysis in water treatment, although the currently available photocatalytic materials are shown to be effective in removing many pollutants from aqueous solutions, the photocatalytic mechanism should be thoroughly understood for the development of new photocatalysts. As recyclability without loss of efficiency is an important parameter to be considered for economically large scale commercial application, a simple and low-cost technique of renewing photocatalysts after several successive reuses needs to be developed.

Fifth, the research into understanding the relationship between electrospun nanomaterials and improved performance is still at an early stage, which hinders the development and design of effective functional electrospun materials. Interesting properties have also been explored by controlling the size, shape, composition, and microstructure. We predict that the application of these materials in environmental and energy fields will benefit from fundamental research in the design and fabrication of nanostructured semiconductor materials.

Sixth, most experiments for electrospinning are conducted at a laboratory scale. Developing the ability to scale the technologies to a pilot plant or real scenario is essential for their commercial application. At present, world-renowned companies such as Nicast, DuPont, and SePRO Corporation are actively involved in producing nanofibrous products such as vascular access graft (AVflo™), nanofibre battery separators (Energain), and ultrafiltration membranes (Sepro UF, PES10) for improved performance in tissue engineering, energy, and water treatment. Furthermore, many other companies such as Hills Inc., Johnson & Johnson, Donaldson, Teijin Fibres Ltd,

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Esfil Tehno AS, eSpin Tech, *etc.* also take an active part in these fields. However, for electrospinning technology to progress further, engineers should develop equipment with suitable characteristics in scale and function, with the technologies having an adequate cost-benefit outcome.

In conclusion, electrospun materials have been playing an increasingly important role in materials science and engineering, offering exciting opportunities for development in tissue regeneration, energy and water treatment applications. On the other hand, the major challenges outlined above provide new opportunities and avenues for the collaboration of the electrospinning research communities around the world. Electrospinning will continue to contribute towards the development in these areas and also in opening up more frontiers and new applications in the near future.

Acknowledgements

Notes and references

1 Z. M. Huang, Y. Z. Zhang, M. Kotaki and S. Ramakrishna, *Compos. Sci. Technol.*, 2003, **63**, 2223–2253.

2 V. Thavasi, G. Singh and S. Ramakrishna, *Energy Environ. Sci.*, 2008, **1**, 205–221.

3 R. J. Wade and J. A. Burdick, *Nano Today*, 2014, **9**, 722–742.

4 M. M. Khin, A. S. Nair, V. J. Babu, R. Murugan and S. Ramakrishna, *Energy Environ. Sci.*, 2012, **5**, 8075–8109.

5 R. Das, M. E. Ali, S. B. Abd Hamid, S. Ramakrishna and Z. Z. Chowdhury, *Desalination*, 2014, **336**, 97–109.

6 S. Kaur, R. Gopal, W. J. Ng, S. Ramakrishna and T. Matsuura, *MRS Bull.*, 2008, **33**, 21–26.

7 R. Sridhar, R. Lakshminarayanan, K. Madhaiyan, V. Amutha Barathi, K. H. C. Lim and S. Ramakrishna, *Chem. Soc. Rev.*, 2015, **44**, 790–814.

8 C. Niu, J. Meng, X. Wang, C. Han, M. Yan, K. Zhao, X. Xu, W. Ren, Y. Zhao, L. Xu, Q. Zhang, D. Zhao and L. Mai, *Nat. Commun.*, 2015, **6**, 7402.

9 H. Hou, L. Wang, F. Gao, G. Wei, B. Tang, W. Yang and T. Wu, *J. Am. Chem. Soc.*, 2014, **136**, 16716–16719.

10 S. Peng, L. Li, Y. Hu, M. Srinivasan, F. Cheng, J. Chen and S. Ramakrishna, *ACS Nano*, 2015, **9**, 1945–1954.

11 F. Groeber, M. Holeiter, M. Hampel, S. Hinderer and K. Schenke-Layland, *Adv. Drug Delivery Rev.*, 2011, **63**, 352–366.

12 J. Xie, M. R. MacEwan, W. Z. Ray, W. Liu, D. Y. Siewe and Y. Xia, *ACS Nano*, 2010, **4**, 5027–5036.

13 V. J. Mukhatyar, M. Salmerón-Sánchez, S. Rudra, S. Mukhopadaya, T. H. Barker, A. J. García and R. V. Bellamkonda, *Biomaterials*, 2011, **32**, 3958–3968.

14 S. H. Lim, X. Y. Liu, H. Song, K. J. Yarema and H.-Q. Mao, *Biomaterials*, 2010, **31**, 9031–9039.

15 J. Xie, W. Liu, M. R. MacEwan, P. C. Bridgman and Y. Xia, *ACS Nano*, 2014, **8**, 1878–1885.

16 J. Zhang, K. Qiu, B. Sun, J. Fang, K. Zhang, H. Ei-Hamshary, S. S. Al-Deyab and X. Mo, *J. Mater. Chem. B*, 2014, **2**, 7945–7954.

17 S. Mukherjee, J. Reddy Venugopal, R. Ravichandran, S. Ramakrishna and M. Raghunath, *Adv. Funct. Mater.*, 2011, **21**, 2291–2300.

18 R. Ravichandran, J. R. Venugopal, S. Mukherjee, S. Sundarrajan and S. Ramakrishna, *Tissue Eng., Part A*, 2015, **21**, 1288–1298.

19 S. H. Ku and C. B. Park, *Biomaterials*, 2010, **31**, 9431–9437.

20 W. Liu, J. Lipner, C. H. Moran, L. Feng, X. Li, S. Thomopoulos and Y. Xia, *Adv. Mater.*, 2015, **27**, 2583–2588.

21 B. M. Baker, R. P. Shah, A. M. Silverstein, J. L. Esterhai, J. A. Burdick and R. L. Mauck, *Proc. Natl. Acad. Sci. U. S. A.*, 2012, **109**, 14176–14181.

22 B. A. Blakeney, A. Tambralli, J. M. Anderson, A. Andukuri, D. J. Lim, D. R. Dean and H. W. Jun, *Biomaterials*, 2011, **32**, 1583–1590.

23 S. Liao, L. T. H. Nguyen, M. Ngiam, C. Wang, Z. Cheng, C. K. Chan and S. Ramakrishna, *Adv. Healthcare Mater.*, 2014, **3**, 737–751.

24 M. Deng, S. G. Kumbar, L. S. Nair, A. L. Weikel, H. R. Allcock and C. T. Laurencin, *Adv. Funct. Mater.*, 2011, **21**, 2641–2651.

25 L. Li, G. Zhou, Y. Wang, G. Yang, S. Ding and S. Zhou, *Biomaterials*, 2015, **37**, 218–229.

26 P. S. Kumar, J. Sundaramurthy, S. Sundarrajan, V. J. Babu, G. Singh, S. I. Allakhverdiev and S. Ramakrishna, *Energy Environ. Sci.*, 2014, **7**, 3192–3222.

27 T. Krishnamoorthy, V. Thavasi, M. G. Subodh and S. Ramakrishna, *Energy Environ. Sci.*, 2011, **4**, 2807–2812.

28 E. N. Kumar, R. Jose, P. S. Archana, C. Vijila, M. M. Yusoff and S. Ramakrishna, *Energy Environ. Sci.*, 2012, **5**, 5401–5407.

29 J. J. Wu, Y. R. Chen, W. P. Liao, C. T. Wu and C. Y. Chen, *ACS Nano*, 2010, **4**, 5679–5684.

30 I. Jeong, J. Lee, K. L. Vincent Joseph, H. I. Lee, J. K. Kim, S. Yoon and J. Lee, *Nano Energy*, 2014, **9**, 392–400.

31 Z. Dong, S. J. Kennedy and Y. Wu, *J. Power Sources*, 2011, **196**, 4886–4904.

32 D. Liu, Q. Guo, H. Hou, O. Niwa and T. You, *ACS Catal.*, 2014, **4**, 1825–1829.

33 B. Dong, L. Gwee, D. Salas-de la Cruz, K. I. Winey and Y. A. Elabd, *Nano Lett.*, 2010, **10**, 3785–3790.

34 J. Chen and F. Cheng, *Acc. Chem. Res.*, 2009, **42**, 713–723.

35 F. Cheng, J. Liang, Z. Tao and J. Chen, *Adv. Mater.*, 2011, **23**, 1695–1715.

36 T. H. Hwang, Y. M. Lee, B. S. Kong, J. S. Seo and J. W. Choi, *Nano Lett.*, 2012, **12**, 802–807.

37 L. Li, S. Peng, Y. L. Cheah, J. Wang, P. Teh, Y. Ko, C. Wong and M. Srinivasan, *Nanoscale*, 2013, **5**, 134–138.

38 L. Li, S. Peng, Y. Cheah, Y. Ko, P. Teh, G. Wee, C. Wong and M. Srinivasan, *Chem. – Eur. J.*, 2013, **19**, 14823–14830.

39 C. Zhu, Y. Yu, L. Gu, K. Weichert and J. Maier, *Angew. Chem., Int. Ed.*, 2011, **50**, 6278–6282.

40 V. Aravindan, J. Sundaramurthy, P. S. Kumar, Y.-S. Lee, S. Ramakrishna and S. Madhavi, *Chem. Commun.*, 2015, **51**, 2225–2234.

1240 | *Chem. Soc. Rev.*, 2016, **45**, 1225–1241

This journal is © The Royal Society of Chemistry 2016

41 Y. L. Cheah, R. von Hagen, V. Aravindan, R. Fiz, S. Mathur and S. Madhavi, *Nano Energy*, 2013, **2**, 57–64.

42 F. Croce, M. L. Focarete, J. Hassoun, I. Meschini and B. Scrosati, *Energy Environ. Sci.*, 2011, **4**, 921–927.

43 F. Cheng and J. Chen, *Chem. Soc. Rev.*, 2012, **41**, 2172–2192.

44 J. J. Xu, D. Xu, Z. L. Wang, H. G. Wang, L. L. Zhang and X. B. Zhang, *Angew. Chem., Int. Ed.*, 2013, **52**, 3887–3890.

45 L. Li, S. Peng, Y. Cheah, P. Teh, J. Wang, G. Wee, Y. Ko, C. Wong and M. Srinivasan, *Chem. – Eur. J.*, 2013, **19**, 5892–5898.

46 Y. Sun, R. B. Sills, X. Hu, Z. W. Seh, X. Xiao, H. Xui, W. Luo, H. Jin, Y. Xin, T. Li, Z. Zhang, J. Zhou, W. Cai, Y. Huang and Y. Cui, *Nano Lett.*, 2015, **15**, 3899–3906.

47 L. Li, S. Peng, H. B. Wu, L. Yu, S. Madhavi and X. W. Lou, *Adv. Energy Mater.*, 2015, **5**, 1500753.

48 J. Deng, X. Kang, L. Chen, Y. Wang, Z. Gu and Z. Lu, *J. Hazard. Mater.*, 2011, **196**, 187–193.

49 M. Shang, W. Wang, S. Sun, E. Gao, Z. Zhang, L. Zhang and R. O'Hayre, *Nanoscale*, 2013, **5**, 5036–5042.

50 Z. Ma, M. Kotaki and S. Ramakrishna, *J. Membr. Sci.*, 2005, **265**, 115–123.