Industrial Upscaling of Electrospinning and Applications of Polymer Nanofibers: A Review

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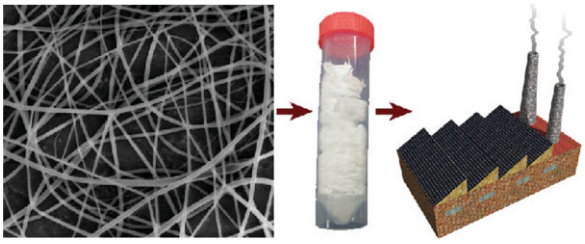
Electrospun nanofibers are extensively studied and their potential applications are largely demonstrated. Today, electrospinning equipment and technological solutions, and electrospun materials are rapidly moving to commercialization. Dedicated companies supply laboratory and industrial-scale components and apparatus for electrospinning, and others commercialize electrospun products. This paper focuses on relevant technological approaches developed by research, which show perspectives for scaling-up and for fulfilling requirements of industrial production in terms of throughput, accuracy, and functionality of the realized nanofibers. A critical analysis is provided about technological weakness and strength points in combination with expected challenges from the market.



1. Introduction

In the last years, one-dimensional (1D) nanostructured organic materials have gained a continuously growing scientific, technological, and industrial interest, with possible applications spreading in different fields such as air and water filtration,[1] drug delivery,[2] tissue engineering and regenerative medicine,[3] besides many others involving active materials for photonics or electronics.[4] Several fabrication and synthesis methods are currently available, which work well at laboratory scale for the production of 1D organic nanostructures and polymer fibers, such as polymerization against porous templates,[5] self-assembly,[6] melt-blowing,[7] and various patterning approaches belonging to soft lithographies.[8] However, the electrostatic spinning or electrospinning[9] is a unique technology not only for its unequalled operational simplicity, but also because it can be effectively up-scaled, opening actual perspectives for industrial production. At laboratory scale, for instance, electrospinning allows the processing of up to several liters of polymer solution under continuous runs, although the most of experiments in academic research are still performed by spinning volumes in the range of milliliters. Today, leading electrospinning research toward industrial applications has special interest since the nanofibrous media have shown great potential in different application fields thanks to the intriguing peculiarities of electrospun nanofibers which include their in-principle extreme length (up to km),[10] high surface-area and tunable porosity,[11] intrinsic three-dimensional (3D) topography,[12] and functional properties.[13]

Several reviews[14–17] and books[18] are available about electrospinning. The process is based on the uniaxial

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elongation of a jet, ejected from the surface of a charged polymer solution possessing sufficient molecular entanglements, in the presence of an intense electric field (typically 10^5–10^6 $V \cdot m^{-1}$) which is applied between the spinneret and a conductive collector. Electrospinning comprises therefore various, sequential stages involving the extruded polymer jet, all of which have been the subject of extensive experimental and modeling[19] works, in an effort to rationalize the underlying physical mechanisms and to improve the capability of predicting the key features of the resulting nanofiber morphologies depending on the processing parameters. Once formed because of the application of an electrostatic potential (≈5–30 kV), the jet undergoes substantial stretching and whipping processes induced by Coulombic repulsion among surface charges, and concomitant solvent evaporation. During the jet flight, the stream cross-section can be reduced up to six orders of magnitude. Finally, polymer nanofibers are collected on target electrodes. Once sufficient throughput and process stability and reliability are accomplished, fibers are then available to be used in technical applications.

Examination of past research allows the appreciation that many fundamental studies and, at a later stage, important issued patents, have contributed to lay the foundation of today's electrospinning technologies.[20] In 1600 the English physician W. Gilbert noticed that a water drop sitting on a dry surface is deformed into a conical shape when a piece of rubbed amber is held in its proximity. This was the first experimental observation of deformed liquid–air interfaces under the influence of an external electric field,[21] followed in 1749 by Nollet who studied how a charged water jet rapidly generates separated drops.[22] About 150 years later, the commercialization potential of electric-field-induced spinning processes was recognized, and the first related patents were deposited by Cooley[23] and Morton.[24] In Morton's device, for instance, fibers are spun and collected onto a negatively charged metallic chain. Zeleny studied the discharge processes from electrified liquid surfaces by a needle/capillary apparatus,[25] and Formhals in 1930s was the first to file patents about electrospinning of plastics in the United States, based on a needleless set-up equipped with a rotating collector.[26] However, none of these early patents could be finalized by actual industrial application, likely because of the complete lack of characterization equipment suitable to investigate the sub-μm features of the physical processes involved and of the fibrous structures generated. Developments in the USSR advanced much faster toward applications.

In late 1930s, I. V. Petryanov-Sokolov and collaborators carried out experiments that rapidly led to the first industrial facility for production of electrospun fibrous materials (Petryanov filters) for gas masks.[27] During the 1950–1960s the factory production capacity reached an equivalent of 6.5 $kg \cdot h^{-1}$.[17,28] It has been pointed out that reports on the scientific activity and technologies related to the production of these filters never circulated outside USSR because they were considered as military secrets in view of their possible use for protection against radioactive aerosols.[27] The first commercial products based on sub-μm fibers were introduced in the early 1980s in the United States by Donaldson Co., Inc.[29] In 1989, microdenier fibers were spun by DuPont.[30] In 1995, Reneker and co-workers finally rediscovered electrospinning, definitely evidencing its nanoscale nature and the high added-value of the resulting organic nanomaterials,[9,31] which is at the origin of the great success of the method still used today.

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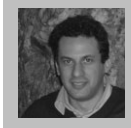

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Currently electrospinning research is as vibrant as ever, as demonstrated by the constantly increasing rate of published scientific contributions. More than 2500 articles have been published about polymer electrospun nanofibers in the last decade, reaching a current peak of more than 1.4×10^4 citations per year.[32] The number of publications in 2011 was approximately ten times more than that in 2003 (Figure 1a).[32] Research is widespread to many countries with USA, China, and South Korea holding about 70% of published items, followed by Japan, Germany, and Singapore (Figure 1b). Importantly, different from most nanotechnology fabrication approaches, many developing countries participate in this huge research effort, thus further confirming the absence of significant barriers to entering this field of technology.

Different geometrical modifications of the basic set-up equipment or post-processing treatments have been proposed, for achieving improved electric-field uniformity and enhanced control over inter-fiber positional ordering and intra-fiber molecular alignment.[33] An enormous variety of materials and solvents have been combined in order to tailor specific properties and functionalities of

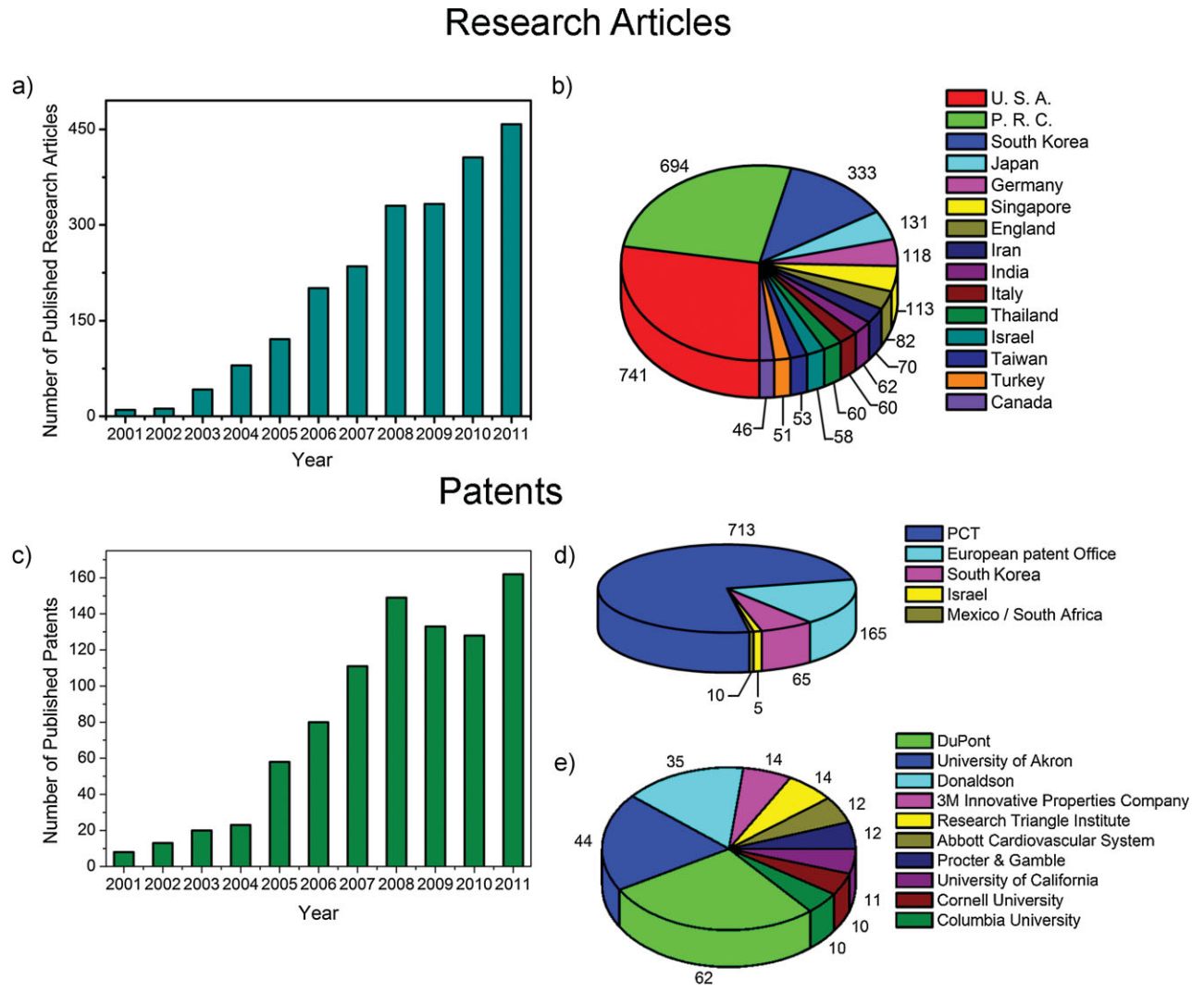

Figure 1. (a, b) Statistics of published research articles about electrospun polymer nanofibers (keywords:"polymer", "nanofibers" and "electrospinning", from 2001 to 2012, July, 24th, Web of Science Database). Source: Thomson Reuters Web of Knowledge.[32] (a) Number of items published yearly. In 2012, about 300 articles have been published before July, 24th. (b) Number of published articles per country/territory (Top-15 results reported). (c–e) Statistics of published patents on polymer nanofibers made by electrospinning (keywords: "polymer", "nanofibers," and "electrospinning", from 2001 to 2012, July, 9th), as provided by WIPO-PATENTSCOPE.[35] (c) Number of items published yearly. In 2012, about 70 patents have been published before July, 9th. (d) Geographical distribution of published patents. (e) Published patents per main applicant company or institution (e). Top-10 results reported.

electrospun products.[10,34] However, not all these achievements are easily transferable to industrial production.

On one hand, the number of issued patents has hugely increased, as shown in Figure 1c (more than 160 patents have been issued in 2011). Of 960 patents published in the last decade,[35] 75% are international applications (Patent Cooperation Treaty, PCT), whereas the remaining are mainly European (17%) and South Korean (7%) (Figure 1d). The top patent owners include both companies such as DuPont (6%) and Donaldson (4%), and universities (Figure 1e), with a major focus of the overall patent portfolio on the development of filtration media, methods, and apparatus.

On the other hand, the process scale-up is still largely an issue even for electrospinning technologies, with a lot of space for further improvements. For many classes of materials, the achievable length of electrospun nanofibers still ranges from hundreds of micrometers to millimeters, which is useless for most technical applications. In these cases, the method often exhibits poor performances in terms of reproducibility and accuracy in the production stage. These aspects are easily understandable given the general reliability issues inherent to most of nanofabrication approaches dealing with soft materials and organic solutions, and which are affected, in the case of electrospinning, by the complex physical behavior of electrified jets and by the plethora of solution-, equipment-, and ambient-dependent process parameters. Many polymer systems are difficult to optimize with electrospinning, due to their poor viscoelastic behavior, lack of sufficient molecular entanglements, limited solubility, and, more generally, because only a few processing parameters can be chosen directly. In addition, some of the involved parameters are either highly interdependent or derive from the properties of the used polymer solution. Industrially produced electrospun nanofibers reach a dimensional spread of the order of ten percentage points or worse among nominally identical samples. Therefore, a main challenge related with the mass production of nanofiber fabrics is the implementation of methods allowing increase of the process and product reproducibility and to extend the classes of utilizable materials.

This paper provides an overview on electrospinning technologies with focus on those approaches that show large-scale capability. In addition it aims to present a picture of the industrial background related to fabrication equipment and nanofiber-based products. Many companies supplying either laboratory and large-scale electrospinning equipment, or nanofibrous products (mainly for filtration) already exist and possess well-defined market segments. New interesting perspectives can emerge for nanofibers in the fields of renewable energy sources, such as in photovoltaic devices, and in energy storage and management, such as in battery separators, and many small and multi-national companies are testing nanofibrous products for biomedical applications. Overall, a tighter interaction between the academic and the industrial communities and a critical assessment of the weakness and strength points of electrospinning technologies for industrial processes can certainly be useful to stimulate future developments.

2. Spinning Technologies

Spinning technologies for fibers manufacturing are based on a spinneret extrusion process which allows the continuous production of single or multi-filament materials. The resulting product exhibits different properties depending on the specific process and parameters adopted. In particular, with regard to the state of the material to spin, such methods can be classified as melt spinning, solution spinning, and emulsion spinning. From a manufacturing point of view, polymer melt processing offers unique advantages in terms of high-throughput rate and process safety, whereas solvent-based methods are advantageous in terms of the large variety of materials that can be spun, lower energy consumption, and frequently superior mechanical, optical, and electrical properties of the resulting fibers. Emulsion spinning is a method of choice for processing polymers exhibiting high melting point, e.g., for the production of flame-retardant fibers. With respect to traditional spinning methods, electrospinning of melts, solutions or emulsions has unique advantages, such as the capability to encapsulate functional dopants, light-emitting dyes, drug and biomolecules and to induce high alignment of both polymer and nanocomposite fibers. The diameter range and peculiar morphology of electrospun fibers mimic those of the extracellular matrix thus making them particularly suitable for bio-scaffolds, and are ideal for filtration and catalysis applications. Finally, electrospinning is an especially flexible process, that can be carried out through needleless systems, thus overcoming limits imposed by the spinneret. In the following paragraphs we briefly overview traditional and contemporary fiber-forming spinning methods. Poly(lactide) (PLA) is among the most widely used and studied prototypical polymer, allowing comparison of spinning techniques and obtained fiber properties (Table 1).[36–45]

2.1. Melt Spinning

In conventional melt spinning a polymeric system in the melt state is extruded through a spinneret. The diameter of fibers is reduced by mechanically drawing the continuous flow at the wind-up and fibers solidification is achieved by rapid cooling.[46] The structural properties of the extruded filaments are mainly dependent on take-up speed, drawing temperature and draw ratio (which is a measure of the amount of stretching undergone by

Table 1. Processing conditions and properties of PLA fibers.

Spinning method	Molecular weight (pre-spinning) ($\times 10^3$)	Take-up/ collection speed [$m \cdot min^{-1}$]	Draw ratio	Draw temperature [°C]	Applied potential [kV]	Fiber diameter [μm]	Crystallinity [%]	Young's modulus [GPa]	Tensile strength [GPa]	Ref.
Melt	57–131	–	1–8	–	–	–	35	3.1	0.4	[36]
Melt	148	2 000–5 000	–	–	–	–	56	–	–	[37]
Melt	–	–	8	80	–	160	–	5	1	[38]
Centrifugal	–	[a)]	2400–111 000	–	–	0.25–2.2	–	–	–	[39]
Dry	910	3	12–14	190	–	17–28	–	–	2.2	[40]
Dry-jet	–	10	2–10	90	–	>50	65	8.2	0.6	[41]
Electrospinning	300	–	–	RT	12	0.1–0.3	54	4.8	0.2	[42]
Electrospinning	100	–	–	–	10	0.9	–	–	0.005	[43]
Electrospinning	100	–	21 000	–	25	1.4	–	0.005	–	[44]
Electrospinning	150–270	–	8 000	–	15	0.75	Amorphous	–	–	[45]

[a)]In centrifugal spinning, the reservoir rotation speed ranges between 4000 and 12 000 rpm.
RT: room temperature.

the material during drawing). Both the molecular chain orientation along the fiber axis and the overall crystallinity of melt-spun fibers increase upon increasing the draw ratio[36] and the take-up speed.[37] Post-annealing processes can further increase the crystallinity and/or local segmental orientation in the amorphous phase, thus resulting in earlier onset of strain hardening.[47] Among companies involved in the field, Hills Inc. produces fibers from a variety of both bi-component and homopolymers melts[48] and Teijin Fibers Ltd.[49] produces different kinds of textiles based on proprietary polyester fibers technology.[50] The main industrial advantage of melt spinning technology relies on the capability to easily spin multi-component systems and on the absence of solvents during processing, improving environmental safety and enabling a wider variety of biomedical applications. The large spinning speed achievable during the process (thousands of $m \cdot min^{-1}$) provides high throughput, however drawing instabilities can cause nonuniformity in the fiber diameters and the high viscosity of the melt required for spinning makes it very difficult to generate mechanical forces strong enough to reduce fiber diameters to or less than 1 μm. To reach such scales, suitable methods to spin polymer melts are melt blowing[51] and centrifugal spinning,[52] which combine the capability to fabricate nonwoven mats with fiber diameters as low as 100 nm and with good throughput. For instance, the ForceSpinning technology[53] is based on using centrifugal forces and multiple configurations of spinnerets, and is applicable to both polymer melts and solutions, achieving homogeneous fibers with diameters of few hundreds of nm in a variety of assemblies such as webs (Figure 2c) or free standing nonwoven mats (Figure 2d). FibeRio Technology Corporation can produce fibers of polycaprolactone (PCL) with average diameter of 220 nm[54] and supply both basic-research and industrial equipments.[55] Badrossamay et al.[39] have developed a similar technology, namely rotary-jet spinning, based on high-speed rotation of a polymer jet delivered in form of melt, solution, emulsion, or suspension. In this way, 3D scaffolds made of PLA continuous aligned fibers exhibiting diameters in the range of 0.05–3.5 μm have been demonstrated (Figure 2g and h).

2.2. Solution Spinning

Solution spinning is particularly suitable for polymeric systems which are thermally unstable and degrade while melting. In general, the higher amount of chain entanglements of polymers in the melt state results in fibers exhibiting inferior mechanical properties than solution-spun fibers. With regard to the solvent removal process, solution spinning methods can be classified as either dry or wet. In dry spinning, solvent evaporation and fiber solidification are achieved by blowing hot air or an inert gas on the extruded filament. In fact, one of the most important parameters affecting the morphology of dry-spun fibers is the solvent composition. A binary solvent system composed of chloroform/toluene has been used to produce high-strength PLA fibers (2.3 GPa) in a dry spinning process, followed by hot-drawing.[40] Highly aligned arrays of polystyrene (PS) fibers with diameters as low as 50 nm have been demonstrated by Nain et al. by using both planar and nonplanar rotating collectors.[56] Examples of materials used in commercial, dry-spun fibers include cellulose acetate, acrylic compounds (e.g., Orlon),[57] polyvinylchloride, and polyurethane (e.g., Lycra).[58]

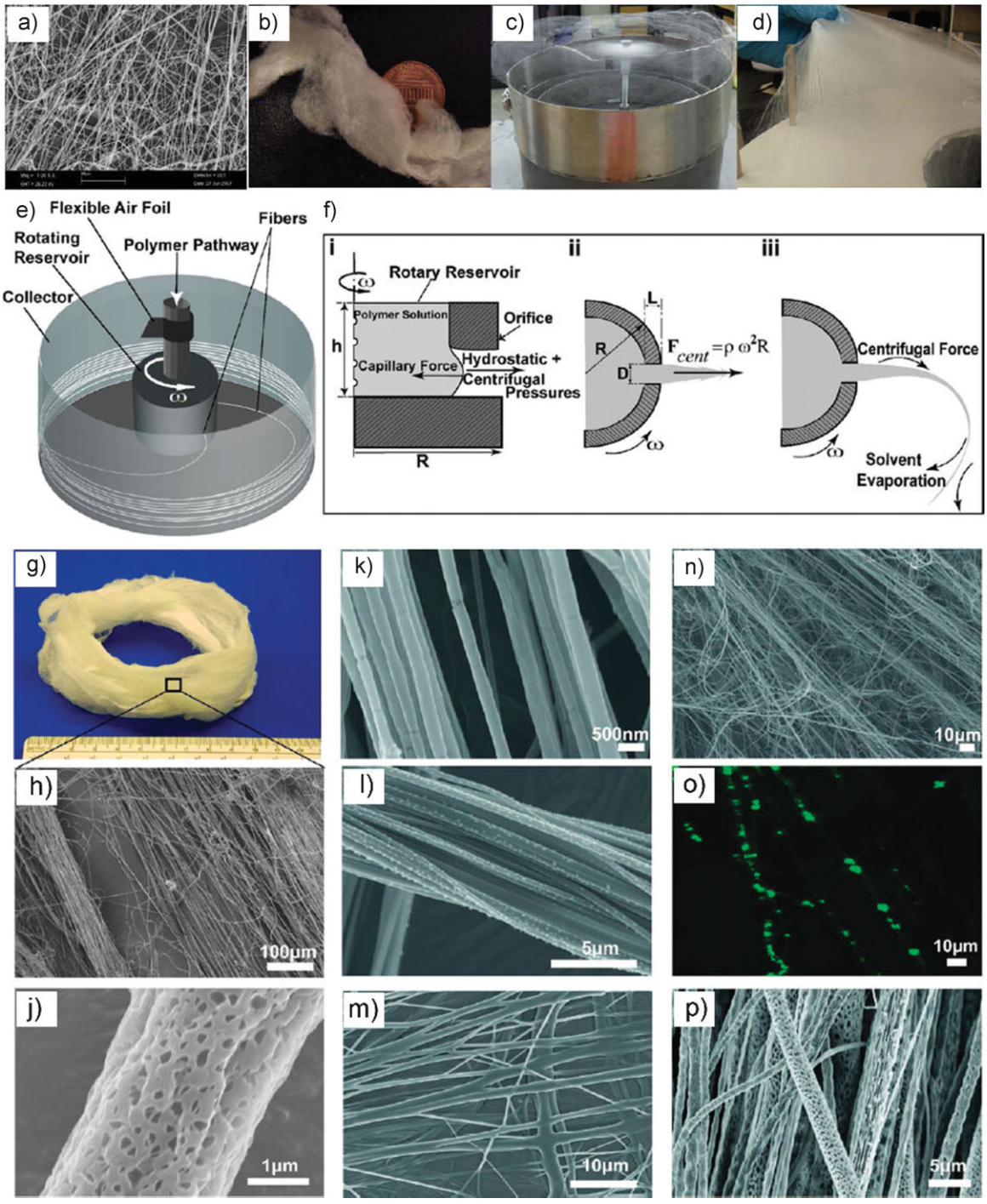

Figure 2. (a) SEM micrograph of PEO fibers made by solution Force-spinning; (b) PS mats, (c) nanofibers web, and (d) free-standing nonwoven mats realized by the Force-spinning technology. Reproduced with permission.[53] Copyright 2010, Elsevier (e)-(f) Schematic illustrations of the rotary-jet spinning; (g)-(h) Images of a 3D scaffold made of PLA continuously aligned fibers; (j) SEM micrograph of rotary-jet spun fibers made of PLA and produced under conditions of expedited solvent evaporation and high humidity; (k) PEO; (l)-(m) poly(acrylic acid); (n) gelatin fibers; (o) Laser scanning confocal image of PS beads encapsulated within PEO fibers; (p) SEM micrograph of gelatin/PLA fibers made by emulsion Rotary-jet Spinning. Reproduced with permission.[39] Copyright 2010, American Chemical Society.

In wet spinning, the polymer solution is extruded in a viscous coagulation bath consisting of a liquid which is miscible with the spinning solvent, but is a nonsolvent for the polymer. Exchange between solvent and nonsolvent causes phase separation which leads to solvent removal from the spun filaments, and fibers solidify while precipitation occurs. The solidification involves mass transfer through the polymeric solution–nonsolvent interface, which can lead to defects, such as voids and cross shape irregularities.[46] The formation of such defects can be limited by introducing an air-gap (3–5 mm) between the end of the spinneret and the coagulation bath. In this approach, named dry-jet or air-gap wet spinning, the filaments are firstly extruded through the air-gap, which allows stress relaxation of polymer chains, and then quenched in the bath.[46] An extensive study on PLA fibers, carried out by varying dry-jet spinning parameters, demonstrates high tensile strength (0.6 GPa) and high Young's modulus (8.2 GPa).[41] In 2008, Velev and Alargova[59] have patented a method based on the application of a shear force in wet spinning. In this way, during precipitation polymer filaments are tightly stretched, and nanofibers with high aspect ratios (100 or higher) and average diameter ranging from 100 nm to 5 μm can be obtained.[60] On a pilot commercial machine, Xanofi demonstrate continuous production of fibers at rates exceeding 60 $g \cdot min^{-1}$.[61]

2.3. Emulsion Spinning

This technique is usually employed to spin insoluble and non-melting compounds. Such materials are typically finely ground and mixed with solutions made of different polymers. Catalysts and emulsifier agents are also added. The emulsion is then extruded into a coagulation bath, similarly to wet spinning, or in air, similarly to dry spinning. The method allows the production of fibers made of fluorocarbons exhibiting high melting point,[62] inorganic materials such as ceramics[63] and blends with flame-retardant properties.[64]

3. Electrospinning Production Technologies

The basic laboratory equipment for electrospinning consists of three major components, i.e., (i) a high-voltage power supply, (ii) a spinneret (a metallic needle), and (iii) a metallic collector. A high-voltage direct current (DC) power is supplied to the spinneret, whose fluidics are usually connected to a syringe pump injecting the polymer solution to be spun, while the collector is usually ground- or negatively biased. When a high voltage is applied, a pendent drop of the polymer solution experiences forces due to surface tension and to the external field, together with stresses related to electrostatic repulsion between surface charges that deform the liquid–air interface into a conical shape (Taylor cone).[65] When the electrostatic force acting on the surface of the liquid overcomes the surface tension, a charged liquid jet is pulled from the Taylor cone and ejected toward the target electrode. Polymer nanofibers are normally deposited on the collector in form of nonwovens. Specific modifications to the basic experimental set-up have been introduced for improving the quality of nanofibers and for tuning their properties according to requirements of different applications. In particular, in view of large-scale production and of applications that clearly show significant commercial potential, in the next paragraphs we analyze some technological improvements targeting the fields of environment and energy, photonics and electronics, filtration, and biomedicine (in turn including tissue engineering, wound healing, and drug delivery).

3.1. Uniaxial Alignment of Nanofibers

The uniaxial alignment of nanofibers within ordered array is demonstrated to be important for different applications, thus becoming an important prerequisite to be taken into account in scaling-up the electrospinning production capability. In the field of tissue regeneration addressed to muscles, bone and cartilage meniscus, and neural cells, several groups show that cell cultures on uniaxially aligned nanofibrous scaffolds preferentially elongate along the fiber longitudinal axis.[66] In the field of photonics, mats of uniaxially aligned nanofibers can be used as optical polarizers[33d] and for decoupling sample emission and excitation signals in lab-on-chip devices,[12d] whereas composite samples containing aligned sulfonated polyimide nanofibers can be employed in proton-exchange membrane fuel cells for converting chemical energy to electrical energy with high efficiency and low emission of pollutants.[67] Due to such high added value of uniaxially aligned nanofiber yarns, many modifications of the electrospinning collector geometry have been made, specifically aimed to improve and control nanofiber orientation. Figure 3 sketches some proposed collector geometries. Pioneering alignment experiments[33d,68] have been carried out by using two static collecting stripes separated by a well-defined gap (Figure 3b) or frame electrodes, where, assisted by electrostatic interactions, nanofibers are stretched across the gap to form a parallel array. Polyvinyl pyrrolidone (PVP) nanofibers aligned in this way are shown in Figure 4. Optical and scanning electron microscopy (SEM) micrographs clearly indicate that the nanofibers across the gap have their longitudinal axes oriented perpendicular to the conductive edges (Figure 4a, b), very differently from nonwovens collected on continuous conductive planar surfaces (Figure 4c, d). The

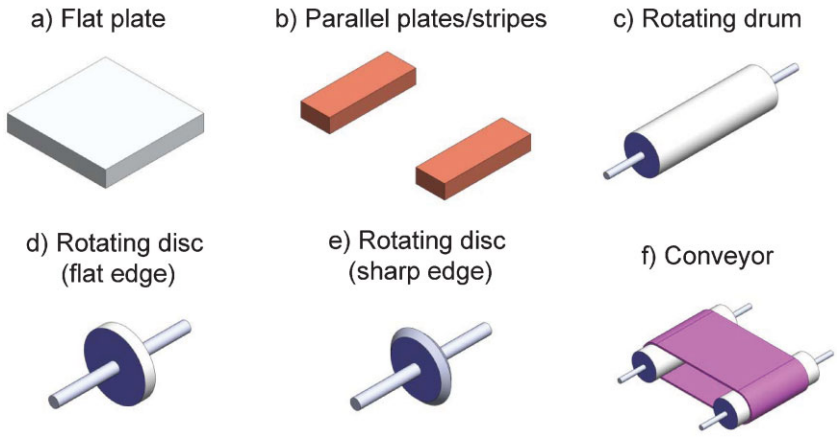

Figure 3. Sketches of the main possible geometries of electrospinning collectors.

principle behind this approach is elegant and general,[69] but unfortunately the ability to scale-up this method for producing large samples is poor even when using arrays of parallel electrodes,[70] and the capability to obtain a high degree of orientation and stacking density critically depends on the width and dielectric properties of the insulating gap[71] and on residual charges on the mats.[72] Higher scalability and material flexibility, as well as improved conformability of the realized, highly aligned fibrous samples, can be achieved by using rotating drums, mandrels, and disks which may have different collecting geometries (with solid or frame cylinders) and various edge morphologies (Figure 3c–e).[73] In such cases, the realization of complex 3D architectures such as yarns[74] and tubes for vascular graft applications,[75] and large-area depositions are made possible. Figure 5a and d show schematic illustrations of the collecting process using cylindrical collectors with different shapes and surface patterns.[76] The corresponding electrospun fibrous tubes (Figure 5b, e) exhibit specific microscale patterned architectures (Figure 5c, f, g). In particular, different patterns can be transferred on the same tube (Figure 5f, g) by designing appropriate collector templates. In general, the rotation speed of the mandrel has a strong influence on the degree of order of nanofibers, yielding better alignment when the linear speed of the mandrel surface is close to the jet velocity,[77] and also on mechanical properties[78] and crystallinity. This approach often allows a limited sample thickness to be reached,[33b] which can be a drawback for continuous operation runs. Jafari et al.[79] have proposed a potentially scalable method consisting of a three-pole configuration with a blade-cage collector set exhibiting an accurate control over the fibers diameters and alignment degree. This approach takes advantage of the combination of different factors, such as (i) a sharp electrode provided by the blade, (ii) parallel electrodes realized by parallel cage frames, and (iii) absence of a circumferential surface on the drum, in addition to the usual dynamic effect provided by the collector rotation, and may have good potential for industrial production.

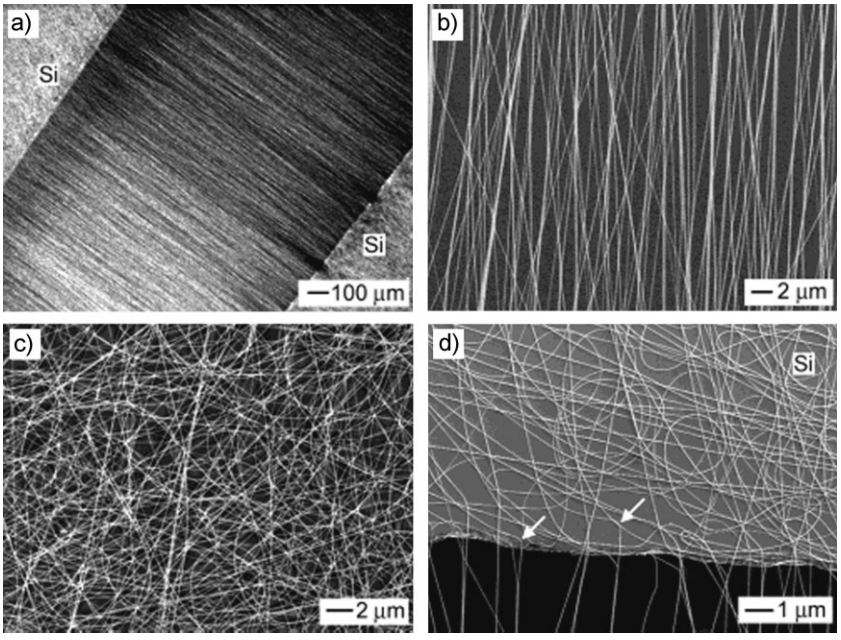

Figure 4. (a) Optical micrograph of PVP nanofibers collected on top of a gap between two silicon stripes. SEM micrographs of the same sample across the gap (b) and on top of a silicon stripe (c). (d) SEM micrograph of a region close to the edge of the gap from another sample. Reproduced with permission.[33d] Copyright 2003, American Chemical Society.

An alternative to static and rotating collectors, is represented by conveyor belts (Figure 3f) made of insulating[80] or metallic materials sliding on grounded metallic guides that, in addition to fiber alignment, offer significant possibilities of scaling up the material production. The integration of motorized conveyor guides can indeed allow continuous operation processing over different substrates.[81]

Of particular interest from the industrial point of view is the peculiar capability of electrospinning to realize

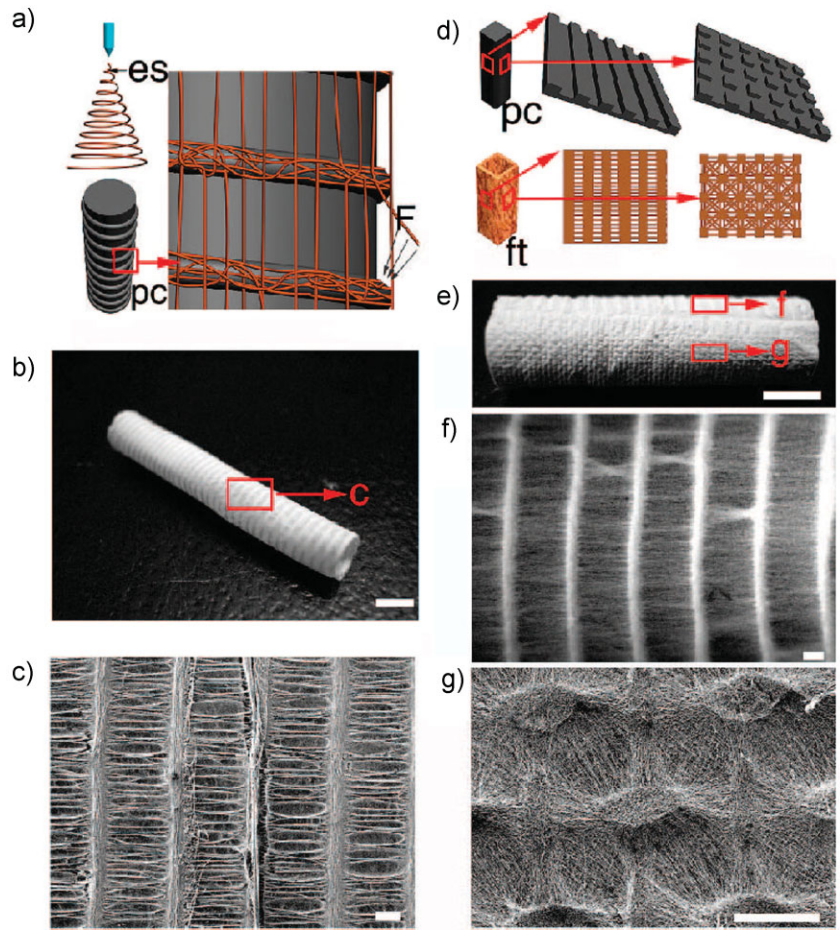

Figure 5. (a) Scheme of specialized nanofibers collection processes during electrospinning (es), by using a cylindrical collector with equally spaced circular protrusions (pc, patterned collector). (b) An electrospun fibrous tube with patterned architectures (scale bar = 5 mm). (c) Magnified micrograph of a portion of the same tube in (b). Scale bar = 200 μm. (d) Scheme of a patterned collector (pc) and a fibrous tube (ft) exhibiting two different surface patterns. (e) An electrospun fibrous tube with two different surface patterns (scale bar = 5 mm). (f) and (g) are magnified images of two different portions of the same tube in (e). Scale bars = 200 μm. Reproduced with permission.[76] Copyright 2008, American Chemical Society.

complex bi- and tri-dimensional architectures in a single run, and engineering the collector geometry is strategic in this respect. Yarns, two-dimensional meshes and tubes can exhibit interesting properties for prosthetic implant devices[82] and for blood vessel reconstruction,[83] thus being attractive for pharmaceutical companies. Zhang and Chang have reported on a method to fabricate 3D fibrous tubes with multiple micropatterns composed of electrospun nanofibers.[76] Micro- and macroscale tubes (diameter 500 μm–5 mm) with different shapes, structures, patterns, and T-shape interconnections have been prepared.

Finally, a very high degree of order can be achieved by coupling the application of additional centrifugal forces to the jet with electrostatic forces. Electrospinning experiments have been performed both under high operating voltage (≥ 5 kV) and rotational speed (1 800 rpm) for the fabrication of PLA fibers exhibiting improved mechanical properties,[84] and under low operating voltage (2.8 kV) and speed (390 rpm) for the fabrication of PS, polymethyl methacrylate (PMMA) and PVP fibers exhibiting (95.5 ± 2.9)% of fibers with mutual alignment within 5°.[85]

3.2. Scaling Volumes Through Injection Systems

Another important issue concerning process up-scaling for commercial purposes is related to the production capacity of the set-up. High volumes are especially desirable for biomedical applications such as tissue engineering, design of wound-healing materials, drug-delivery for air/liquid filtration, and for textile applications.

In the framework of tissue engineering, electrospinning is particularly suitable for the fabrication of 3D scaffolds since the final products fit most of requirements in terms of material porosity (defined as the number of 3D, unfilled voids among nanofibers[11c]), large surface-area-to-volume ratio, and tunable mechanical properties.[86]

For wound healing, electrospun, interconnected porous structures are advantageous for oozing fluids, controlling drainage and facilitating oxygen permeation, and in addition the flexibility of the electrospinning process allows the addition of drugs in the nanofibers, for medical treatment and antibacterial purposes. Figure 6a shows a prototype of scaffold, made of PCL/gelatin nanofibers directly electrospun onto polyurethane for wound dressing.[87] SEM micrographs of this construct (Figure 6b) show randomly interconnected structures with fiber diameters in the range 300–600 nm.

The potentiality of nanofibers in drug delivery has been investigated by several chemical drugs,[88] proteins,[89] and macromolecules such as DNA[90] with clear advantages over bulk materials due to the large specific surface and short diffusion path lengths. In particular, taking these scaffolds close to the market has to pass through in vivo studies before clinical validations. The volume of related

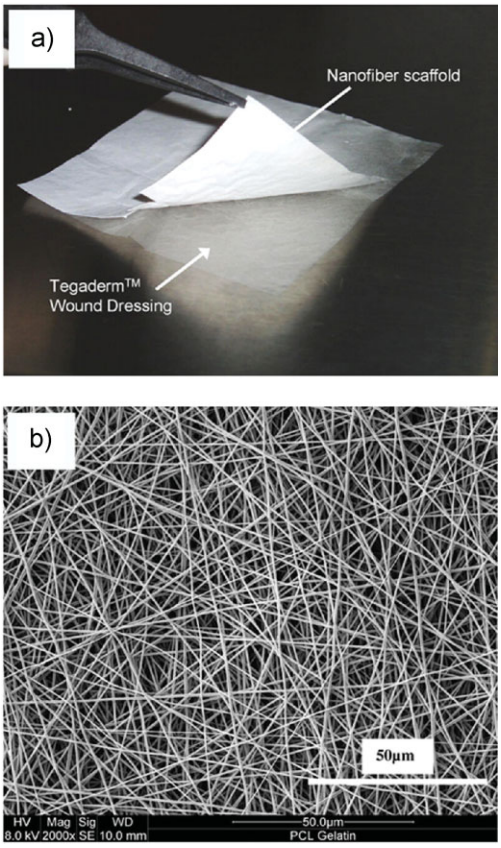

Figure 6. (a) Photograph of a scaffold made of PCL/gelatin nanofibers electrospun onto polyurethane (Tegaderm, 3M Medical) for wound dressing. (b) SEM micrograph of the scaffold. Reproduced with permission.[87] Copyright 2007, Elsevier.

literature to this field today is now huge.[91,92] However, all the applications mentioned above deserve further investigation, and extensive experimental campaigns are needed before making products fully ready for commercialization. In this respect the capacity of high volume production is critically important.

Within the environment protection area, filtration, and purification materials based on nanofiber mats are undoubtedly the currently most industrially advanced products, with a worldwide distribution of supplying companies as better detailed in the following Section 4.

Finally, textiles in general can benefit from embedding high-tech nanofibrous features for controlling surface properties. In these sectors, increased production volumes are even more important for fulfilling industrial requirements.

The most relevant technological advances that have, to date, been explored to increase the volume of production are mainly based on the modification of the polymer injection system and consist of: (i) the introduction of multi-spinneret components that allows parallel multi-processing, and (ii) the development of free surface electrospinning methods. Multi-jet electrospinning based on multi-spinneret components can be arranged in a uniaxial configuration or in a circular geometry (schematics in Figure 7). These approaches can be useful for increasing the overall set-up throughput and the thickness of resulting mats[26] and can also be applied for large area deposition and for mixing fibers made of different materials.[93]

A long-studied drawback of the multi-spinneret method is related to the alteration of the electric field profile induced by the presence of other electrospinning jets nearby.[94] To overcome this problem, an additional auxiliary electrode with charge of either the same polarity as the electrospinning jet or with opposite polarity can be used[95] or, alternatively, a secondary electrode has been proven to help to obtain high production rates with a five-nozzle spinning system.[96] Varesano et al. have reported on a systematic study about the effects of different multi-jet electrospinning configurations on nanofibers morphology.[93c] The number of jets has been varied from 2 to 16, investigating both negative and positive applied bias, and inter-jet repulsion estimated by measuring divergence angles. Large area depositions have been accomplished, with maximum collector dimension of 50 cm × 50 cm. Varabhas et al. have shown that 20 holes of 500 μm diameter drilled along two rows into the wall of a 130 mm long plastic tube, can produce 0.3–0.5 $g \cdot h^{-1}$ of fibers, and proposed that such production rate can be further increased by using longer tubes and a higher number of spinning holes.[97] Among commercially available industrial-scale electrospinning set-up, Inovenso Ltd. supplies an apparatus producing fibers with diameter down to 50 nm with a throughput area up to 5000 m^2 daily or to production rates up to about 200 $g \cdot h^{-1}$ for nanofiber coatings.[98] Various electrospinning industrial plants, some with production capability up to several $kg \cdot h^{-1}$ have been reported in the literature.[99a,17]

The traditional "needle-type" electrospinning method is, in principle, subject to problems related to polymer

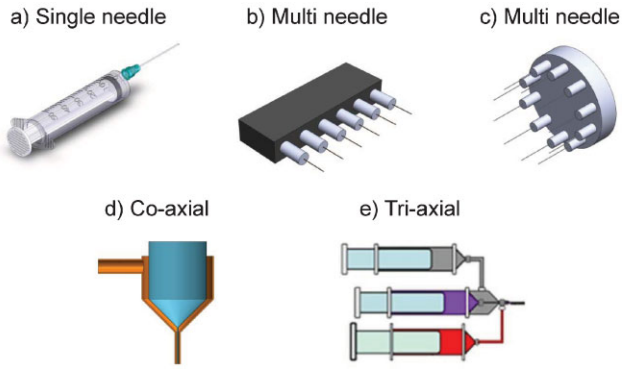

Figure 7. Sketches of the possible geometries of the electrospinning spinneret.

clogging at the spinneret nozzle, which may limit the achievable throughput of continuous production processes. Such clogging events can occur because of the fineness of the needle, and become more frequent for high solution concentrations or when spinning composite blends embedding nanoparticles. In this respect, "free-surface" (needleless) electrospinning techniques possess greater up-scaling potentialities. These processes are based on the formation of an electrospinning jet from the free surface of a liquid, without using needles or nozzles. Free-surface electrospinning may in principle produce micrometer-sized droplets resulting in defects deposited on the collector target, and significant variation of fiber diameter and limited configurability of the fabricated fiber assembly (e.g., general lack of fiber alignment, impracticability of core–shell fiber structures, etc.). Specific free-surface electrospinning equipment has to be designed to overcome some of these issues and to meet industrial requirements for functional nanofibers in the different application fields.

The Nanospider, developed by the Czech company Elmarco, can produce nonwovens made by fibers of various polymers including polyvinyl alcohol (PVA), exhibiting mean fiber diameters of 200 nm (standard deviation of 30%) with an annual throughput up to 50 million $\cdot$ m^2.[100] This technology couples needleless electrospinning with a rotating cylinder as the nanofiber generator.[101,102] The cylinder is partially immersed into the target polymer solution and rotated. Upon the application of a high voltage an enormous number of liquid jets is generated from the cylinder surface and is upward oriented.

A centrifuge electrospinning unit with three spin heads, supplied by Dienes Apparatebau, has been recently proposed.[103] This system is able to produce nanofibers exhibiting diameters as low as 80 nm, with throughout potentially 1000 times higher than conventional nozzle electrospinning using 25 rows of 1250 spinning jets.[104]

3.3. Fabrication of Functional Materials

The possibility to select and properly combine solution components and adjust their ratio allows one to effectively tailor the properties of electrospun fibers to obtain new and desired morphologies and functionalities. A well-known example is given by the formation of specific surface topologies on electrospun fibers, such as pores or pits in the 100 nm range (Figure 8a), which are induced by rapid phase separation due to solvent evaporation and subsequent rapid solidification.[11c] The resulting, enhanced surface to volume or surface to weight ratio of such fibers may be of relevant interest for sensing and filtration. For obtaining biofunctional nanomaterials, many kinds of biomolecules, copolymers, and polymer blends, such as fibroin in water-soluble polymers,[105] PCL/gelatin,[106]

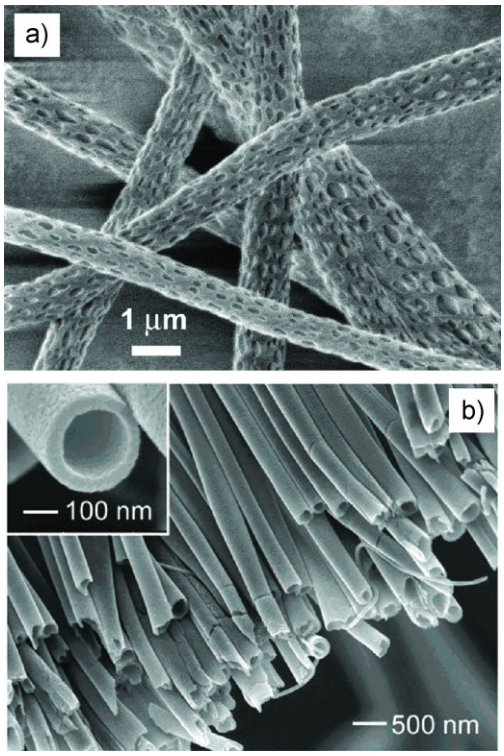

Figure 8. (a) Porous poly-L-lactide electrospun fibers. Reproduced with permission.[11c] Copyright 2001, John Wiley and Sons. (b) Uniaxially aligned TiO_2 hollow nanofibers. These fibers have been intentionally fractured using a razor blade to expose their cross-sections. Inset: high magnification micrograph of the same sample. Reproduced with permission.[111] Copyright 2004, American Chemical Society.

mixtures of collagen with elastin,[107] poly(L-lactide acid)/gelatin,[108] mixtures of chitosan with poly(ethylene oxide) (PEO),[109] and many others, have been electrospun and the properties of the resulting scaffolds for promoting cells proliferation have been demonstrated.

In such context, multi-axial (coaxial/triaxial) electrospinning, consisting of spinneret components (Figure 7d, e) which enable the simultaneous spinning of different liquids, deserve particular attention and are widely applied for the fabrication of functional nanofibers. In fact, the separate control toward the injection of fluids, either in multi-axial or uniaxial configurations, allows the realization of composites core/shell nanofibers,[110] of hollow tubes,[111] and the surface functionalization by various coatings.[112] For instance, using a conductive organic material as core and an insulating polymer as sheath, nanofibers can become intriguing building blocks for nanoelectronics and sensing applications. Polyacrylonitrile (PAN) and PS nanowire-in-microtube structures have been already demonstrated, which can be useful as optical waveguides and nanocables.[113]

Coaxial electrospinning is also useful for the encapsulation of nonspinnable materials such as nanoparticles or conjugated polymers exhibiting a poor thermoplastic behavior,[114] enzymes, protein, and cells.[115] It has been exploited to encapsulate self-healing materials (dicyclopentadiene and isophorone diisocyanate),[116] the complex hydride ammonia which find application for hydrogen storage,[117] and several drugs within polymers. In particular, core–shell fibers provide a release pattern different from bi-component monolithic fibers.[118] Additionally, coaxial electrospinning offers the possibility to combine product multi-functionality with good production volumes by exploiting multi-coaxial systems, analogously to the multi-needle configurations described above.

Coaxial electrospinning was first reported by Sun et al. in 2003.[119] In these early experiments, homopolymer core–shell nanofibers as well as double-polymer fibers were fabricated by a specifically engineered tip of concentric capillaries (scheme in Figure 7d). The core–shell fiber morphology is initiated by a structured Taylor cone formed at the exit of the coaxial tubes. A liquid jet emerges simultaneously from the vertices of the outer and inner meniscus, forming a co-flowing jet. A stable jet is generally formed if at least one of the involved polymer is electrospinnable. The method has been adapted to prepare hollow tubular nanofibers by using an extractable liquid as core material and a sol–gel precursor as shell to make a stronger inorganic sheath.[111,120] Hollow fibers made by Li and Xia with PVP blended with titanium isopropoxide and successive calcination are shown in Figure 8b.[111]

Other coaxial systems are based on pumping two independent polymer solutions into two concentric capillaries, with the inner capillary tube which also acts as an electrode for the spinning dopes, being positively biased with respect to the collector.[121] Reznik et al. have showed that the jetting effect at the tip of the shell nozzle does not necessarily cause entrainment of the core fluid and in such a case, core–shell nanofibers are not formed.[122] They have suggested that co-electrospinning is greatly facilitated by extending the core nozzle outside the shell outlet by about half the radius of the latter. Bazilevsky et al. have demonstrated that electrospinning of core–shell polymer nanofibers is even possible in an ordinary single-nozzle set-up by using an emulsion of the two polymer solutions. The continuous phase experiences very strong stretching forces leading to the formation of a core–shell jet.[123] Multifluidic coaxial electrospinning has been recently developed by three coaxial capillaries and a chemically inert middle fluid that works as spacer between the outer and inner fluids.[124] Finally, combining co-electrospinning with a high speed gas jet allows the fabrication of core–shell PMMA/PAN nanofibers that, after carbonization, yield carbon tubes with inner diameter 50–150 nm and outer diameter 400–600 nm.[125]

3.4. High-Precision Deposition of Fibers

The evaluation of the degree of accuracy achievable in nanomaterial manufacturing processes such as nanofibers and nanotubes production is a key issue for the application of nanostructures in high-tech industrial fields, and particularly in nanoelectronics and nanophotonics. To this end, near-field electrospinning (NFES) was introduced in 2006 by Lin and co-workers[126,127] to overcome the intrinsic limitations of electrospinning in terms of precise deposition, which are due to the jet instabilities. The key feature of NFES is the exploitation of the stable, linear region of the polymer jet trajectory by utilizing a short needle-to-collector distance (typically of the order of mm). Both individual fibers and patterns of fibers with almost arbitrary geometry can be deposited on specific areas by moving the substrate in the plane perpendicular to the polymer jet. Therefore, different from conventional electrospinning, the NFES is a direct-write serial deposition method, having the main advantage of producing fibers with uniform diameter and of precisely depositing the nanofiber on the target substrate. By this method nanofibers of PEO,[126–128] PCL,[129] and sugar-PCL core–shell fibers[129] have been produced. 3D ordered structures of nanofibers have also been demonstrated.[130] Fibers with diameters down to 16 nm have been realized by low-voltage NFES, a variant of the method that further disfavors the onset of instabilities in the polymer jet, allowing tiny and carefully positioned fibers to be obtained, even on 3D substrates.[128] Moreover, SnO_2 nanofibers with average diameter of 100 nm have been obtained by NFES of a PVA/$SnCl_4 \cdot 5H_2O$ solution, followed by an annealing process.[131] Analogous procedures have been developed to fabricate ordered arrayed of TiO_2 fibers with typical diameters of about 200 nm.[132] Chang et al. have reported the fabrication of poly(vinylidene fluoride) nanofibers with piezoelectric properties, onto flexible substrates.[133] The strong electric field characteristic of NFES (of the order of 10^7 $V \cdot m^{-1}$) and the stretching of the polymer solution during the process is reported to align the dipoles along the fiber axis, thus providing in situ electrical poling.[133]

The applicability of NFES to large-scale production is of course debated. Different from electrospinning, standard NFES methods allow the deposition nanofibers on small areas (mm^2–cm^2). This can be advantageous, however, for performing highly precise deposition, and enough to produce a large variety of active devices, such as gas microsensors.[131] In the nanoelectronic field, outstanding results concerning the realization of highly conductive organic nanofibers on large areas, by means of electrohydrodynamic printing processes with short nozzle-substrate distances and assisted by motorized stages, have been presented at the 2nd "International Conference of Electrospinning" held in Jeju Island, South Korea in 2012.[134]

4. Electrospinning: From Laboratories to Industry

Though the benefits of electrospinning technologies have been largely demonstrated for many application fields where polymer nanofibers can be used, there is still a strong need to implement the production in the most efficient way, in order to address the pressing issues concerning: (i) large volume processing, (ii) accuracy and reproducibility in all the fabrication stages, and (iii) safety and environmental attributes of electrospinning.

The scaling capability of the process and the technological issues explored to date evidence that free-surface methods exhibit high up-scaling potentialities in terms of production volumes. Also centrifugal electrospinning may in principle become widespread industrially, and the capability of this approach to achieve nanofiber diameters down to 100 nm has been demonstrated.[103] On the other side, higher flexibility toward materials and processing and consequently more various functionalities of the resulting nanofibers can be achieved by co-axial and multi-axial technologies, that also offer possibility for scale-up if multi-needle approaches are adopted together with suitable methods to reduce multi-jet related instabilities.

Many advanced applications and active polymer materials are still limited due to the lack of reliable and affordable electrospinning approaches which can guarantee the very high needed accuracy and reproducibility of the fabrication process, and the convergence between theoretical modeling and real-time control over the involved parameters which would be useful in this respect to offer new processing solutions extending the variety of usable compounds. Finally, it is largely demonstrated that ambient conditions strongly influence the properties of electrified jets and of resulting electrospun materials, and even small environmental perturbations can cause significant variations of the fiber properties. To address this issue, many providers of commercial set-ups have developed proprietary climate-controlled electrospinning systems guaranteeing temperature and humidity control within certain ranges. For example, IME Technologies supplies a laboratory-scale system consisting of an electrospinning chamber and a control cabinet that houses the air conditioning, water filtration and control system. They guarantee $\pm 0.5\,^{\circ}C$ accuracy in the control of temperature (for the working range 20–45 °C) and $\pm 1\%$ in the control of relative humidity (for the working range: 10–90%).[135]

Another important concern regards process environmental issues about solvent-electrospun materials. This aspect is very important not only for safety reasons during processing, but also for final products since solvent residues could be trapped inside the produced nanofibers. Solvent-based electrospinning with high control over fiber morphology and functionality could be safely used in nontextile applications where production volumes are moderate (e.g., nanoelectronics), whereas an accurate control over solvent residuals become crucial for biomedical and pharmaceutical applications. Novel formulations of electrospinning materials processable by aqueous solutions should therefore be developed, possibly also including active and conjugated polymers, to reduce as much as possible the consumption of volatile organic solvents.

4.1. Electrospinning Apparatus at Laboratory and Industrial Scale

From the commercial viewpoint, the rising interest in electrospinning has already produced increased competition among laboratory-scale equipment suppliers. To gain more market shares, companies offer different spinning and collecting-electrode devices and accessories. A wide selection of laboratory-scale electrospinning equipment is, therefore, available in the market. A few key players on the industrial-scale equipment market also exist, and these companies can be distinguished on the basis of equipment types and applications. A list of representative companies supplying electrospinning equipments includes: Elmarco (www.elmarco.com), NaBond (www.electro-spinning.com), Holmarc Opto-Mechatronics (www.holmarc.com), E-Spin Nanotech (www.espinnanotech.com), Linari Engineering (www.linaribiomedical.com), Kato Tech (www.keskato.co.jp), Mecc Co. (www.mecc.co.jp), Toptec (www.toptec.co.kr), Electrospinz (www.electrospinz.co.nz), Electrospunra (www.electrospunra.com), IME Technologies (www.imetechnologies.nl), Yflow (www.yflow.com), and Inovenso (www.inovenso.com). Most of the laboratory-scale equipment is based on needle-type electrospinning, with production rates relatively low, but definitely adequate to implement applied research. Concerning accessories and components, many different spinning and collecting electrode systems are available, particularly for laboratory-scale apparatus, including controllers and high-speed cameras. In industrial systems, nanofibers are mainly collected on a rotating drum or on substrates by using winding–unwinding systems.

For commercial systems targeting academic research, achieving multi-functionality and flexibility is very important for an equipment to be capable of carrying out different research projects. Key requirements to be fulfilled include: (i) price reduction, since most customers are from academia and governmental institutions, (ii) multi-functional set-up, which is often challenging, given the difficulty to offer "all-in-one" set-ups to meet different requirements from the customer, and (iii) compactness, which is critically important for equipment to be installed in laboratories with limited space. A few representative laboratory-

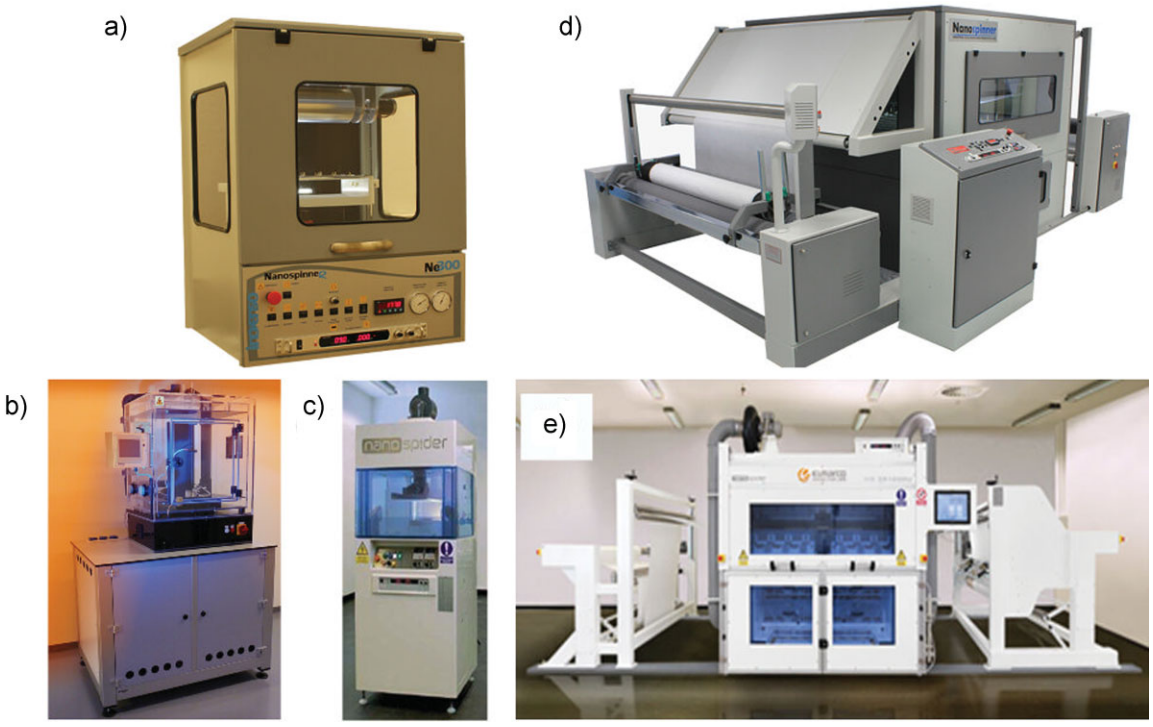

Figure 9. (a–c) Commercial, laboratory-scale electrospinning apparatus. Reproduced with permission, courtesy of (a) Inovenso Ltd.,[98] (b) IME Technologies,[130] and (c) Elmarco.[100] (d) Industrial-scale electrospinning system, Nanospinner416 produced by Inovenso Ltd. Reproduced with permission, courtesy of Inovenso Ltd.[98] (e) Industrial-scale, free-surface electrospinning system, Nanospider produced by Elmarco. Reproduced with permission, courtesy of Elmarco.[100]

scale commercial electrospinning apparatus are shown in Figure 9a–c.

For industrial-scale equipment, the main issues to be addressed are: (i) productivity, throughput still being below what is needed by industry demand in many sectors as described above, (ii) know-how, with multi-disciplinary knowledge being required for successful manufacturing and often needed by customers, (iii) well-established capacity of process monitoring, since there is still often a lack of control over solution and process parameters during production, and (iv) quality control, possibly through in-line systems which need to be developed for the produced nanofiber materials. Representative pictures of an industrial-scale apparatus by Inovenso Ltd. and of the free-surface Nanospider system by Elmarco are shown in Figure 9d and e, respectively.

4.2. Product Industrialization

As discussed above, filtration and purification materials and components constitute the most developed field where the peculiarities of nanofibers have been fruitfully transferred to industrial products. These nanostructures can indeed determine higher filtration efficiency and lower pressure drop than conventional air-filter media. In addition, nanofiber media are easy to clean, enabling customers to significantly extend the life of filters, thus reducing maintenance costs. The nanofiber air-filter market has grown very fast. In the short and medium term, potential products ready to market are those related to liquid filtration (waste-water treatment and desalination) and energy storage (battery separator). In particular, following the news release by DuPont[136] regarding the new nanofiber battery separator (Energain), which improves performance and battery life, there has been strong interest in considering the future and market size of electric vehicles. Applications in the biomedical area are expected to be ready for industry in the medium-long term periods, also considering longer times which are required to get international validations and authorizations to bring products on the market. Many emerging companies in this field are small enterprises belonging to academic spin-offs, or pharmaceutical companies which are developing proprietary products.

Representative companies supplying electrospun products for different fields of application include: Donaldson (www.donaldson.com), DuPont (www.dupont.com), Ahlstrom Corporation (www.ahlstrom.com), Espin Technologies (www.espintechnologies.com), Esfil Tehno AS (www.esfiltehno.ee), Finetex Technology (www.finetextech.com), Hemcon Medical Technologies, Inc (www.hemcon.com), Hollingsworth and Vose Company (www.hollingsworth-

vose.com), Japan Vilene Company (www.vilene.co.jp), Johns Manville (www.jm.com), Kertak Nanotechnology (www.kertaknanotechnology.com), Nanofiber Solutions (www.nanofibersolutions.com), Nano109 (www.nano109.com), NanoSpun (www.nanospuntech.com), Yflow (www.yflow.com), Polynanotec (www.polynanotec.com), Soft Materials and Technologies s.r.l (www.smtnano.com), and SNS NanoFiber Technology (www.snsnano.com).

5. Conclusion and Outlook

The market of electrospinning equipment, both for laboratory research and for industrial production, is expected to grow significantly due to the many advantages of nanofibers and their application in a wide range of industrial fields including environment, energy, electronics, automotive, biotechnology, pharmaceutics, and cosmetics. The continuous, still vibrant development of electrospinning technologies driven by research can undoubtedly both stimulate sustained demand for such equipment, and highlight novel strategic applications for electrospun nanofibers in the near future, thus opening further commercialization perspectives for nanomaterials. Many technological solutions are already being transferred out of the laboratories, and exhibit clear industrialization perspectives as here reviewed. Several companies are active as providers of electrospinning specialized equipment as well as of nanofiber-based products. To date, electrospinning is a success story, one of the very few belonging to the broad area of nanotechnologies which hold so great, unprecedented promises. Notwithstanding some process criticalities as discussed above, this manufacturing process is offering actual opportunities of technology transfer, economic development, and ultimately employment which is especially important in the present unfavorable socio-economic situation. Specific applications are already in the most advanced phase of commercialization. However, some significant issues still need to be addressed. Continuing research efforts in the near future will certainly allow improvements in available technological alternatives and eventually transfer forthcoming electrospinning processes and products toward commercialization.

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