Electrospinning of Fluorinated Polymers: Current State of the Art on Processes and Applications

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Abstract

Electrospinning is a unique and versatile technique to produce fine submicrometric fibers and nanofibrous membranes from polymer solution or melt. In the last decade, fluorinated polymers (particularly polyvinylidene fluoride, PVDF, VDF copolymers and polytetrafluoroethylene, PTFE) have attracted significant attention in electrospinning processes. Fluoropolymers are extraordinary specialty materials characterized by outstanding properties, such as high chemical resistance, high thermostability, low surface energy, and electroactivity. Interestingly, electrospinning can further maximize their properties, thus allowing to fabricate advanced and fascinating nanostructured materials. Electrospun fluoropolymers show a tremendous potential for exciting applications in several areas, from filtration to environmental and energy fields (e.g., Li-ion batteries), chemical and biological sensing, electroactive applications, superhydrophobic coatings, textile and sport wear, and biomedical applications. This review presents the recent advances in the use of the wide family of fluoropolymers in electrospinning, describing the processes for the preparation of the fibrous materials, their properties, and their applications in several fields.

Keywords: electrospinning; fluoropolymers; membranes; PVDF; nanofibers

1. Introduction

Fluorinated polymers are unique specialty materials involved in many high-tech applications, and endowed with outstanding properties, such as high thermostability, chemical resistance, low surface energy, low friction coefficient, and electroactivity (e.g., piezoelectricity).[1–4] They exhibit low cohesive and surface energy, due to their low

intra- and inter-molecular interactions. The small van der Waals radius (1.32 Å) and high electronegativity of a fluorine atom play the crucial roles in strong C-F bond (485 kJ/mol) and low polarizability.[5, 6] In general, fluoropolymers can be categorized into:[1] i) fluoropolymers with fluorinated groups within the backbone, such as homopolymers of vinylidene fluoride (VDF), tetrafluoroethylene (TFE) and chlorotrifluoroethylene (CTFE), and ii) fluoropolymers with a pendant fluorinated group such as poly(acrylate)s with (per)fluorinated side chains.[7, 8]

Because of their extraordinary properties, fluoropolymers (particularly polyvinylidene fluoride, PVDF, VDF copolymers and polytetrafluoroethylene, PTFE) have attracted significant attention in electrospinning processes for the fabrication of advanced nanostructured materials. Electrospinning is a unique and relevant technique to produce fine submicrometric fibers and nanofibrous membranes from polymer solution or melt as will be discussed below. During the electrospinning process, an electrified jet of polymer solution or melt is generated from the liquid droplet, is consecutively stretched and elongated under the applied electric field, and finally solidifies as a fine fiber. The technique is rather easy to employ and cost-efficient; moreover, by modifying the experimental set-up and controlling the properties of the polymer solution/melt, fibers of different structures can be obtained. Because of this feature, electrospun nanofibers find applications in well-established technologies, as well as in new fields of scientific and industrial interest. Indeed, fluorinated nanomaterials prepared by electrospinning are fascinating, showing a tremendous potential for exciting applications in several areas, from filtration to environmental and energy fields (e.g., fuel cell membranes, solid electrolytes for Li-ion batteries (LIBs), photocatalytic devices), chemical and biological sensors, superhydrophobic coatings, textile and sport wear, and biomedical applications (e.g., wound dressing and tissue engineering).

Actually, in the last few decades, extensive research has been conducted in such a field, as demonstrated by the continuous growing of the number of publications (Figure 1). However, no reviews have been published, except for a few works specifically devoted to electrospun PVDF-based piezoelectric systems.[9–11] Thus, it is of interest to provide a review on the recent advances in the applications of the wide family of fluorinated polymers in electrospinning, describing the processes for the preparation of the fibrous materials, their properties, and their applications in several fields. Although a wide and relevant industrial work has been conducted on the topic, also leading to many patents, this review focuses on literature scientific articles.

The review starts with an introduction on the fundamental aspects of the electrospinning process. Then, specific sections are devoted to the electrospinning of different classes of fluoropolymers, i.e., PVDF, PTFE, perfluorosulfonic acid polymers (e.g., Nafion^{TM}), poly(fluorinated acrylic) polymers, fluorinated polyurethanes, and fluorinated polyimides, and to the surface modification of electrospun membranes by fluorinated compounds. Relevant applications of the fluorinated materials obtained by electrospinning are presented. In particular, their use as membranes for filtration systems, superhydrophobic coatings, energy and sensing devices, textile and sport wear, biomedical applications, and carrier for photocatalytic materials are reported. Finally, the environmental issues related to fluorinated electrospun membranes are considered.

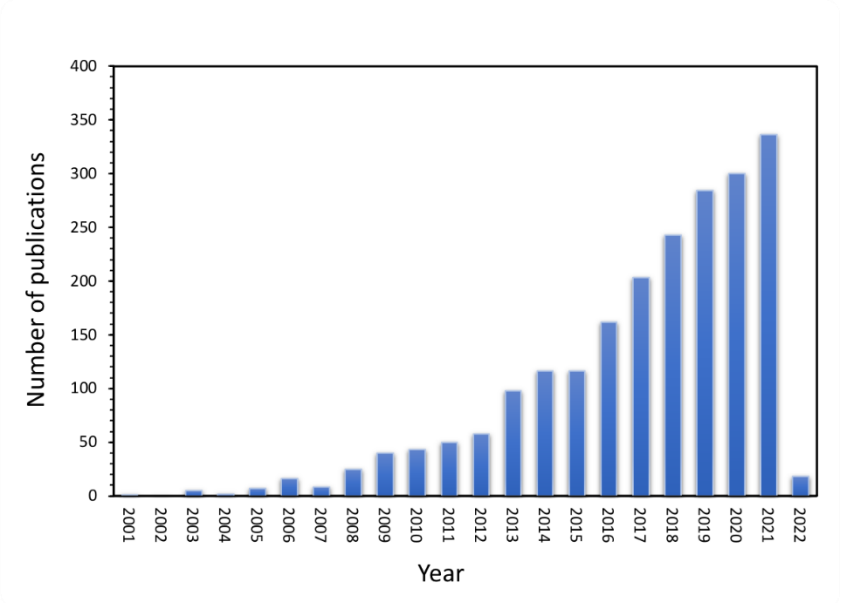

Figure 1. Number of publications on electrospinning of fluoropolymers per year (source: Scopus, Jan 2022; searched keywords: "electrospinning & fluoropolymer", "electrospinning & PVDF", "electrospinning & PTFE", "electrospinning & fluorine").

2. Basics on electrospinning process

Electrospinning is a unique technique to produce fine fibers from polymer solution or melt through the application of high electrostatic forces. In the recent decades, it has been gaining momentum in a variety of applications, from filtration to environmental and energy fields, chemical and biological sensing, and wound dressing. Electrospinning can be applied to a large set of polymers, both natural and synthetic, in the form of solution (i.e., solution electrospinning) or melt (i.e., melt electrospinning, suited for poorly soluble polymers). An electrospinning set-up consists of three main components (Figure 2a): a high voltage power supply, an electrically conducting spinneret and a grounded collector placed at a defined distance from the spinneret (i.e., working distance). During the process, a high voltage is applied to the spinneret containing the polymer solution or melt. The surface of the liquid droplet at the tip of the needle gets electrostatically charged, and the droplet elongates forming a conical shape, known as Taylor cone (Figure 2b). At a certain intensity of the electrical field, the electrical repulsive forces overcome the surface

tension holding the droplets, and thus a continuous jet of polymer solution or melt is generated. It initially extends along a straight line and subsequently undergoes whipping motion due to the growth of bending instabilities. For solution electrospinning, the process continues with the solvent evaporation, and the solidification and deposition of the solid jet as fibers on the collector, forming a nonwoven mat (Figure 2c).[12] In melt electrospinning, the polymer should be in its molten state in the spinneret, thus a heating device (e.g., electrical heating tape, circulating fluid) is needed. The molten jet ejected from the spinneret cools down while reaching the collector, solidifies and is collected as a solid fiber. In general, the whipping instability in melt electrospinning is suppressed, basically due to the lower electrical conductivity and higher viscosity of a polymer melt in comparison with a polymer solution. This, together with the absence of solvent, leads to larger fibers. By excluding the solvent from the process, melt electrospinning is advantageous over solution electrospinning. However, the complicated set-ups and the larger fiber diameters obtained are restricting its wide application. To further develop it, particular configurations can be used: for instance, the polymer can be locally melted with a CO_2 laser beam.[13, 14]

Electrospinning can be conducted in both far-field mode and near-field mode. As the polymer jet undergoes several stages (e.g., straight-line regime, stretching regime, whipping regime) before deposition on the collector, the selected working distance determines in which regime fibers are collected. Typically, electrospinning is carried out in far-field mode, with a working distance higher than 5 cm; consequently, fibers are deposited on the collector as nonwoven mat. Conversely, near-field electrospinning is performed when the fiber jet is still in the straight-line segment (the working distance is generally in the range 500 μm–5 cm). In this case, the lower supply voltage and the control

over the fiber deposition location are advantageous, and the latter makes this process a tool for direct-writing deposition of nanofibers.[15]

Many factors influence the outcome of the electrospinning process, as extensively reviewed.[12, 16, 17] In general, electrospinning parameters are classified as: solution (i.e., viscosity, conductivity, polymer molar mass, and surface tension), process (i.e., applied electric field, tip-to-collector distance and feeding or flow rate), and ambient (i.e., humidity and temperature) parameters. They allow tuning the morphology, primarily affecting the generation of smooth and bead-free electrospun fibers (the undesired formation of beads or beaded nanofibers is the most common defect in electrospinning process).

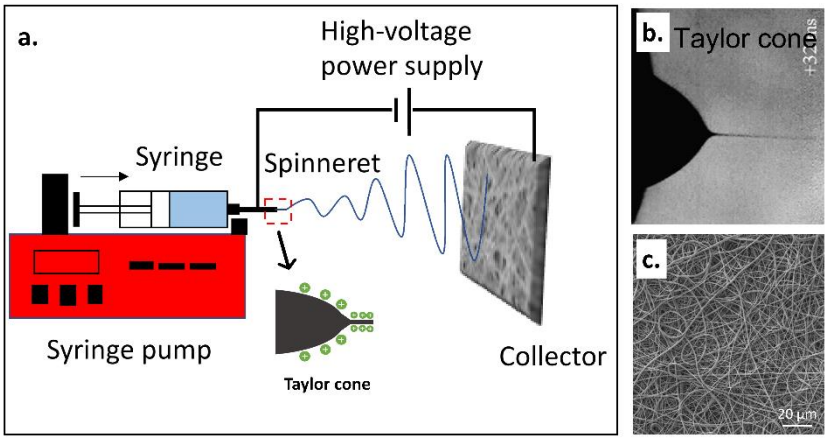

Figure 2. a. Schematic representation of the simple electrospinning set-up. b. Taylor cone formation during the electrospinning process. Adapted with permission from ref [18]. c. Example of a P(VDF-*co*-TrFE) electrospun fibrous membrane by scanning electron microscopy (SEM).

Moreover, peculiar fiber morphologies, including aligned, porous, core-shell, beaded and hollow fibers, can also be achieved by tuning the above-mentioned parameters and modifying the electrospinning configuration with innovative spinnerets (e.g., co-axial spinneret and needleless electrospinning) and collectors (e.g., rotating drum, disc, airgap, liquid bath collector, eventually equipped with a heating device).[12, 19, 20] In addition, it is possible to obtain multicomponent fibers and tune their composition by processing

polymer blends or incorporating fillers such as nanoparticles. Finally, electrospun membranes can be subjected to physical and chemical post-modifications (e.g., surface coating, mechanical drawing, thermal treatment, UV curing, vapor deposition) for further improvement of their properties.[19]

As proved by the huge number of papers (ca. 1900) and patents (ca. 6100) on the subject, the electrospinning technique is versatile and has the potential for further technical improvement.

3. Electrospinning of fluoropolymers: process and material properties

Fluoropolymers are characterized by extraordinary properties and have been extensively applied in electrospinning processes for the fabrication of advanced nanofibrous materials. Since their first discovery (especially of polychlorotrifluoroethylene in 1934,[21, 22] followed by that of PTFE in 1938 [23, 24]), their synthesis is usually achieved by conventional/free radical polymerization. In the late 70ies, the Daikin company pioneered the concept of iodine transfer polymerization (ITP), recently called "reversible deactivation radical polymerization" (RDRP), of fluoroalkenes [25, 26] as the first technique of controlled radical polymerization. ITP evidences the possibility to design original fluoropolymers with predicted controlled molar masses and narrow dispersities, as well as further obtaining block copolymers. The ITP process, which is regarded as a *quasi* living technique, was industrially scaled up in the 90ies to produce various thermoplastics, elastomers and thermoplastic elastomers. It has then been completed by reversible addition fragmentation transfer (RAFT)[27] and Cobalt mediated radical polymerization of fluoromonomers, mainly VDF and, to a lesser extent, CTFE and TFE.[28–30] Indeed, as the focus of the present review deals with electrospinning of fluoropolymers, two recent reviews on RDRP of fluoroalkenes and the design of well-defined fluorinated (co)polymers are suggested for the readers.[2, 31]

In the following sections, the electrospinning process applied to different fluoropolymers is described in detail, highlighting the practical conditions and the properties of the obtained electrospun materials.

3.1 Electrospinning of PVDF

PVDF with its fascinating physico-chemical and electrical characteristics [32] has been extensively studied and reported for electrospinning. PVDF is a semi-crystalline specialty polymer and consists of $–CF_2–CH_2–$ repeating unit. It is inert to many solvents (except for specific solvents, e.g., dimethylformamide (DMF), dimethylacetamide (DMAc) and dimethyl sulfoxide (DMSO)), acids and oils and has low permeability to gases and liquids, though its electrospun fibrous form is porous and permeable.[33] PVDF is not so hydrophobic as expected for a fluoropolymer, but its surface energy is reduced when the polymer is in fibrous nanostructure form (with superior surface roughness). The melting temperature (T_m) of PVDF depends on the crystallinity state and the structural characteristics (molar mass, VDF-VDF chain defects) of the polymer, and is in the range 155–192 °C;[32] whereas its glass transition temperature (T_g) is between -40 and -30 °C.[34]

Among all properties, piezoelectric, pyroelectrical, and ferroelectric characteristics of PVDF have received much interest, especially for electrospun materials. Depending on the chain conformation, this polymer can exhibit five distinct crystalline polymorphs, namely α, β, γ, δ and ε, where the first three are the most studied (Figure 3). Polymorphism of PVDF arises from the slight difference between the van der Waals radius of the fluorine and the hydrogen atoms (1.32 Å vs. 1.20 Å, respectively).[34–36] Crystalline forms depend on the chain conformation: for instance, α-PVDF has a nonpolar trans-gauche configuration (TGTG’), where fluorine and hydrogen atoms repeat alternatively in both sides of the backbone, while the β form is the most intriguing phase because of its zigzag

conformation (all trans TTTT), leading to a strong dipole and generating the extraordinary piezo-, pyro- and ferro-electric properties.[34, 37]

Several techniques can be used to induce the PVDF β-phase during the material forming process, such as uniaxial or biaxial mechanical stretching, heat treatment/annealing,[38] high electrical poling, and surface charging.[39] Correspondingly, electrospinning can lead to the β-phase formation directly during the fabrication of the nanofibers, due to the application of strong electrostatic forces.[40] Nonetheless, other mechanical forces, such as the shear force when the jet is ejected towards the collector and the stretching caused by a rotating drum or a XY-stage collector, can affect the fiber crystalline phase.[41]

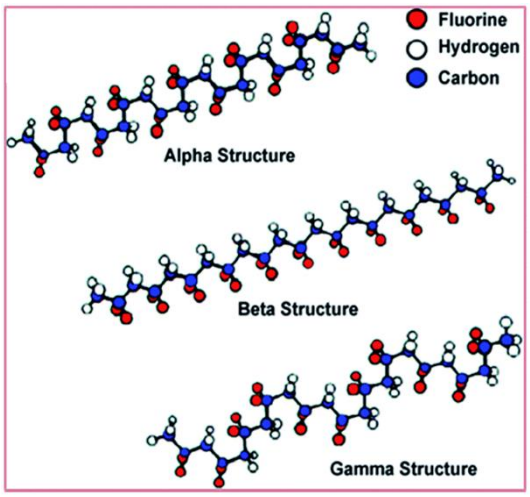

Figure 3. Main polymorphs of PVDF, where the blue, white, and red spheres represent carbon, hydrogen, and fluorine atoms, respectively. Adapted with permission from ref [34].

PVDF has been largely used in electrospinning to obtain nanofibers and nanostructured membranes. Both solution and melt electrospinning processes have been investigated. Figure 4 reports some examples of PVDF electrospun fibers, with different dimensions and surface morphology.[42-44]

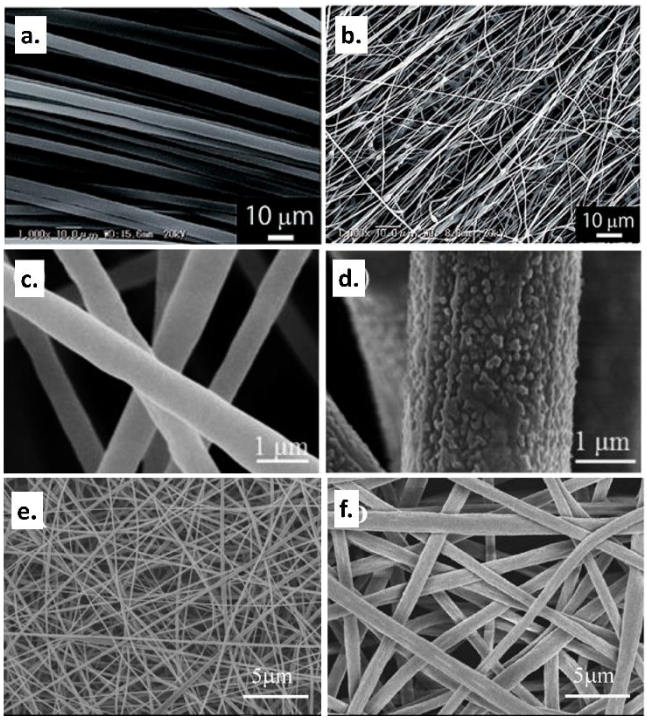

Figure 4. PVDF electrospun fibers with different morphologies and diameters. SEM images of aligned electrospun fibers of PVDF obtained by: a. melt electrospinning (voltage of 10 kV, rotating collector at 300 rpm), and b. solution electrospinning (voltage of 10 kV, rotating collector at 2000 rpm). Adapted with permission from ref [42]. SEM images of electrospun fibers of PVDF obtained at different relative humidity (RH): c. RH=2%, and d. RH=62%. Adapted with permission from ref [43]. SEM images of randomly oriented PVDF fibers obtained at different solvent composition, which resulted in different fibers diameter: e. DMF/acetone 8/2, and f. DMF/acetone 3/7. Adapted with permission from ref [44].

Table 1 summarizes the typical electrospinning parameters (i.e., solution, working distance, voltage, feed rate, collector type) for solution electrospinning of PVDF and VDF copolymers, as used in different literature works. For generating PVDF smooth and bead-free fibers, a proper combination of solvents should be employed.[45–47] Generally, a high boiling temperature solvent and a highly volatile solvent are used together. Actually, DMF, DMAc and DMSO, with quite high boiling point (153 °C, 165 °C, 189 °C, respectively) and slow evaporation rate, permit the stretching of the jet, while the volatile portion of the solvent system (e.g., acetone, Ac) prevents the bead formation during the electrospinning process.[48, 49] In this way, fibers with diameters from around 300 nm to few micrometers can be obtained.

Table 1. Parameters used for solution electrospinning of PVDF and VDF copolymers, together with the average fibers size obtained and the proposed application.

Polymer	Solvent	Concentration (wt.%)[1]	Working distance (cm)	Voltage (kV)	Feed rate (ml/h)	Collector type	Average fiber diameter (nm)	Application	Reference
PVDF	DMF:Ac	12	10–16	10–15	0.7–0.8	Rotating drum, 250 rpm	415 ± 139		[45]
	DMSO:Ac	10	18	11.5	0.8	Rotating drum, 250 rpm	625 ± 113		[45]
	DMAc:Ac	15	15	15	2	Plate	380 ± 106	Filtration membrane	[46]
	DMAc:toluene (18:7)		15	15	1.5	Plate	-	Anti-corrosive coating	[47]
P(VDF-*co*-HFP)	DMAc:Ac (3:2)	10, 12, 15	25	7	0.9	Plate	2250 ± 190		[50]
P(VDF-*co*-TrFE)	DMF:Ac (3:2)	21	10	12	1–1.5	Rotating drum, 2500 rpm	400–500		[51]
	MEK	12–18 (w/v%)		15–35		Plate	970 ± 480	Tissue engineering	[52]
P(VDF-*co*-CTFE)	DMF	20	25	12		Plate	300–400		[53]
P(VDF-*ter*-TrFE-*ter*-CTFE)	Ac:DMF (55:45)	30	14	26	0.8	Rotating drum, 2430 rpm	400–500	Soft actuator	[54]

[1]Except when stated differently

In the literature, PVDF fibers have been electrospun both as randomly oriented fibers and uniaxially aligned fibers. The aligned fibers can be obtained by using rotating drum collectors [55] or airgap collectors (magnetically collectors).[56] The rotating speed of

the drum can be varied from a few tens of rpm up to thousands of rpm, and a higher rotating speed results in a higher alignment of the fibers and a decreased mat porosity.[55] Zheng et al.[44] comprehensively investigated the polymorphism of PVDF fibers as a function of electrospinning parameters. At low electrospinning temperature, β- or γ-phase-PVDF fibers are more probable to be formed. The decrease in feeding rate results in more β-phase content, whereas the increase in working distance induces a reduction of α-phase content.[44] Regarding the effect of the solvent on the formation of a specific PVDF phase, in the literature, there are some contradictions. For instance, Zheng et al.[44] reported that the use of a solvent with lower boiling point, such as acetone, favors the transformation from α- to β-phase, while Damaraju et al.[57] claimed that the inclusion of a solvent with a higher boiling point is the reason of β-phase formation. However, tuning the electrospinning parameters can favor the formation of the electroactive β-phase, while it does not significantly influence the total crystalline faction of the material.[58]

Also by changing the relative humidity (RH) during the electrospinning process, different PVDF fibrous morphologies could be formed:[43] at low humidity (RH=2%), a smooth fibrous morphology with smaller fiber diameters was obtained, while by increasing the humidity (RH up to 62%), rougher fiber surfaces with interior pores and larger fiber diameters were produced, leading to higher hydrophobicity. Moreover, the β-phase content was enhanced by increasing the RH.

PVDF polymer can also be subjected to melt electrospinning, in which the solvent is completely excluded from the process. For instance, Damaraju et al.[57] compared the results of melt and solution electrospinning of PVDF, while Asai et al.[42] produced PVDF fibers through an innovative melt electrospinning set-up (shown in Figure 5a) that requires a CO_2 laser beam to locally melt the polymer. Both works revealed that the β-

phase content in the fibers produced by melt electrospinning was lower compared to that from solution electrospinning, and that an obvious presence of the α-phase was obtained. PVDF has also been subjected to peculiar electrospinning configurations, such as needleless electrospinning (Figure 5b)[59] and near-field electrospinning (NFES) (Figure 5c and d).[60][61] In the former, the nanofibers are directly formed from an open liquid surface, highly increasing the fiber rate formation due to multiple jets,[62] while in the latter, the needle-to-collector distance is reduced in order to control the location of the fiber deposition and thus the membrane porosity.

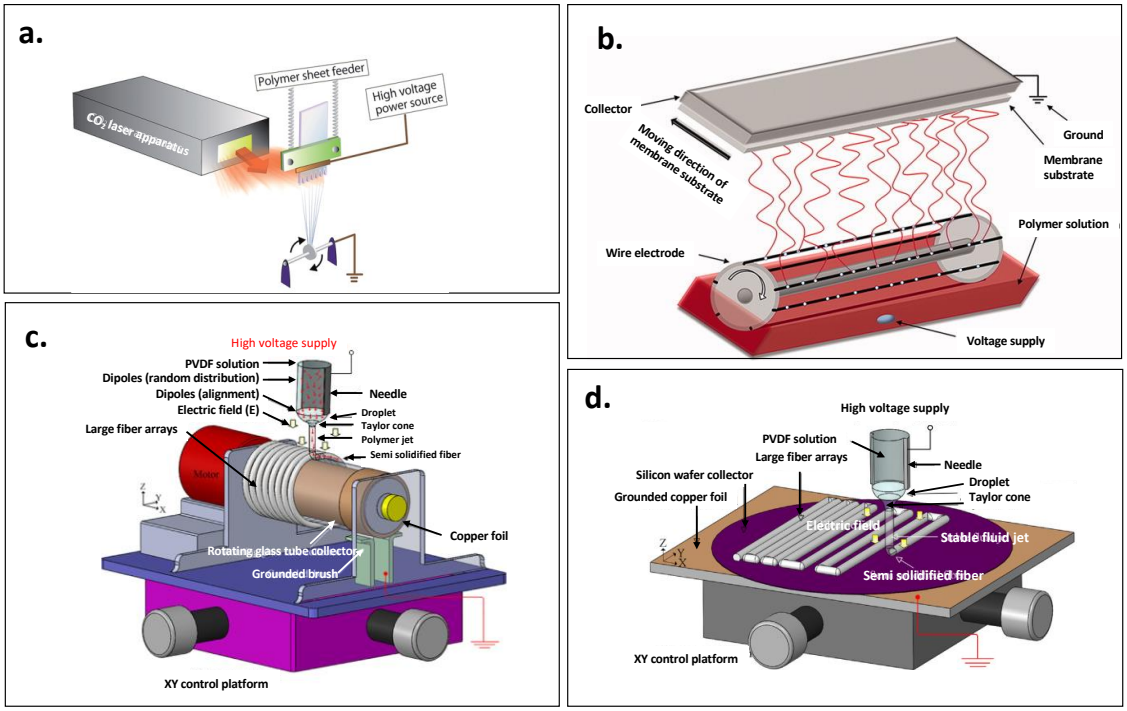

Figure 5. Schematic representations of peculiar set-ups for PVDF electrospinning. a. Melt electrospinning configuration using a CO_2 laser system. Adapted with permission from ref [42]. b. Needleless electrospinning set-up. Adapted with permission from ref [63]. c. and d. Near-field electrospinning (NFES) by drum-like collector (c) and XY stage (d). Adapted with permission from ref [61].

In conclusion, by tuning the electrospinning configuration and the process parameters, it is possible to fabricate different PVDF-based nanofibrous materials, with optimized morphology and properties for specific applications (as will be detailed in Section 5). It

is also possible to change the materials properties using VDF-based copolymers, PVDF-based blends or VDF-based composites, as illustrated below.

3.1.1 VDF-based copolymers

Three common VDF copolymers, used in electrospinning, are P(VDF-*co*-HFP), P(VDF-*co*-TrFE) and P(VDF-*co*-CTFE) copolymers, which are obtained by copolymerizing VDF with hexafluoropropylene (HFP), trifluoroethylene (TrFE) and CTFE, respectively (Figure 6). Table 1 lists the representative solution electrospinning parameters applied to VDF-based copolymers.

A wide range of P(VDF-*co*-HFP) copolymers can be produced, and they are either thermoplastic or elastomeric based on the HFP content.[32, 34] They show high thermostability and can exhibit improved mechanical properties and chemical resistance in hostile environment by crosslinking.[64] P(VDF-*co*-HFP) copolymers have several applications (e.g., for membrane distillation and in the energy harvesting area, such as rechargeable LIBs [32] and dye sensitized solar cells, DSSCs), mainly due to their appealing properties including high dielectric constant (ε=2–10), low crystallinity and T_g.[17] Thanks to these features, they are also broadly used to fabricate fibrous membranes by electrospinning.[50, 65]

The incorporation of TrFE units into PVDF induces the β-phase formation readily from the polymer melt, without a post-processing step,[66] due to a steric hindrance effect that prevents the α-polymorph formation. Thus, generally electrospun P(VDF-*co*-TrFE) fibers are mainly in their crystalline β-phase.[51, 52] Moreover, TrFE induces the appearance of ferroelectric to paraelectric (F-P) phase transition below the T_m, which is related to the crystalline phase change from the polar phase (β-PVDF) to the nonpolar phase (α-PVDF).[66]

Compared to P(VDF-*co*-HFP) and P(VDF-*co*-TrFE), P(VDF-*co*-CTFE) copolymers are less studied for electrospinning.[53, 62, 63, 67] They are either thermoplastics or elastomers,[68] with unique characteristics such as high electromechanical and strain response [68] and cold impact resistance. Furthermore, CTFE-based copolymers are excellent fire-retardant materials and resistant to chemicals, oxidations and heat. Therefore, P(VDF-*co*-CTFE) electrospun membranes are proposed as stable separators for LIBs.[68]

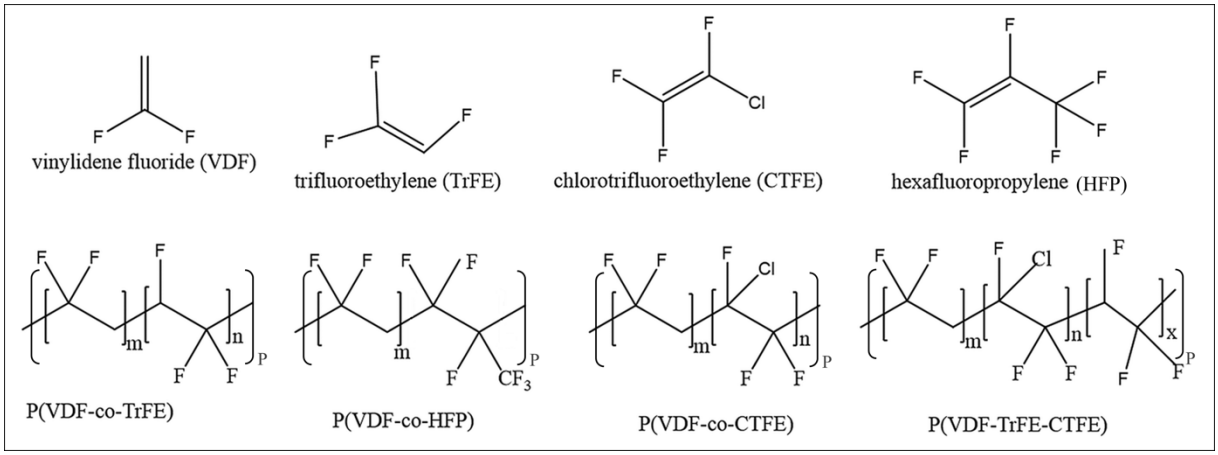

Figure 6. Molecular structures of VDF copolymers used in electrospinning. Adapted with permission from ref [69].

3.1.2 PVDF-based blends

The main purpose of preparing polymer blends is to optimize the properties of the final product, compared to parent (co)polymers, as well as to facilitate the processability and versatility. One principle requirement for blends is that the different components have to be fully or partly miscible.[34] In the case of PVDF, generally, the aims of using a blend for electrospinning are to: i) modify the fiber morphology, diameter and membrane porosity; ii) tune the membrane wettability (for example, blends with hydrophilic acrylic polymers can be used to obtain superhydrophilic [70] or superoleophilic membranes with superior anti-fouling properties);[71] iii) increase the electrospinnability of other

polymers, or serve as template/carrier for non-electrospinnable polymers;[72] iv) decrease the crystallinity, enhancing the ionic conductivity (for example, by blending with an amorphous polymer such as polyvinyl chloride, PVC);[73] v) modify the mechanical properties (for example, by forming a crosslinked network);[74] vi) enhance the piezoelectricity.

Table 2 summarizes the PVDF-based blends reported in the literature for solution electrospinning, together with the used electrospinning parameters and their potential applications.

Table 2. PVDF-based blend systems used for electrospinning: blend composition, process parameters, fibers size and applications.

Fluorinated polymer blend	**Concentration (wt.%)[1]**	**Solvent**	**Working distance (cm)**	**Voltage (kV)**	**Feed rate (ml/h)**	**Collector type**	**Average diameter (nm)**	**Application**	**Reference**
PVDF/FCP (P(MMA-*r*-FDMA))[2]	20 (w/v%)	DMAc:Ac (1:1)	15	20	2	Rotating drum, 1 rpm	400–2000	Oil/water separation	[71]
PVDF/poly(MAA-*co*-TFA)[3] (85/15)	12	DMF	15	25	1	Plate	-	TiO_2 carrier for photocatalytic activity	[75]
PVDF/PVC (8/2)	15	DMF:THF (7:3)	20	25	3	Plate	385–875	Electrolyte for Li-ion batteries	[73]
CA[4]/PVDF (9/1)	16	DMAc:Ac (2:1)	6	16	0.36	Rotating drum, 200 rpm	400	Filtration membrane	[72]
CA[4]/PVDF (75/25)	15		18	21–24	2	Rotating drum	789 ± 326	Osmosis membrane distillation	[76]
PVDF/PEO[5]		DMF	15	15–17	0.2	Rotating drum, 150 rpm	-	Electrolyte for Li-ion batteries	[77]

PVDF/PDA[6]		DMF:Ac (6:4)	25	22	0.5		-	Sensing	[78]
PVDF/PVP[7]		DMF:Ac (8:2)	15	15	0.5	Plate	100–600	Wound healing	[79]
PVDF/starch (2/1 and 1/2)	5 (w/v%)	DMSO: DMF (7:3)					30–180	Tissue engineering	[80]
PVDF/PU[8]	12 (w/v%)	THF:DMF (1:1)	15–20	12–18	0.8–1	Plate	1410 ± 320	Wound healing	[81]
P(VDF-*co*-HFP)/PU[8]	14.5 (w/v%)	DMF	20	9	0.6	Plate	400–2100	Biomedical application	[82]
P(VDF-*co*-HFP)/PEG[9]/ PEGDMA[10]	16 (PVDF)	Ac:DMAc (7:3)	12	11		Rotating drum	419 ± 160 – 738 ± 462	Separator for Li-ion batteries	[74]
P(VDF-*co*-HFP)/PS[11] (3/1)	15	Ac:DMAc (2:1)	13–21	8–14	2–5		800–1000	Dye-sensitized solar cells	[83]

[1]Except when stated differently
[2]FCP (P(MMA-*r*-FDMA)): fluorinated random copolymer of poly(methyl methacrylate-*random*-perfluorodecyl methacrylate)
[3]Poly(MAA-*co*-TFA): poly(methyl methacrylate-*co*-trifluoroethyl acrylate) copolymer
[4]CA: cellulose acetate
[5]PEO: polyethylene oxide
[6]PDA: polydiacetylene
[7]PVP: polyvinylpyrrolidone
[8]PU: polyurethane
[9]PEG: polyethylene glycol
[10]PEGDMA: polyethylene glycol dimethacrylate
[11]PS: polystyrene

Bicomponent fibers with a combination of properties of both components can also be fabricated by a side-by-side electrospinning set-up, as designed by Gupta et al.[84], in which two polymer solutions (e.g., PVC and PVDF solutions) are simultaneously electrospun from a single syringe divided into two compartments. Each solution receives the specific required voltage, the two polymers come in contact at the tip of the needle, and a single bicomponent jet or two separate jets can be formed depending on the working distance.

3.1.3 Composite fibers

Composite electrospun fibers formed by a matrix of PVDF, VDF-based copolymers or

PVDF-based blends and inorganic or organic nanofillers have been extensively investigated. In general, fabricating a PVDF composite with well-distributed nanoparticles is indeed challenging. Electrospinning can improve the uniformly distribution of the filler into the fluorinated fibrous matrix. As a matter of fact, PVDF and the nanofillers can exchange a reciprocal role in a composite fibrous structure.

Firstly, nanoparticles can enhance the physico-chemical properties of the PVDF-based fibrous membranes. Accordingly, to enhance the piezoelectric coefficients, many studies have been devoted to the incorporation of different nanoparticles, such as carbon nanotubes (CNTs), graphene oxide (GO), cellulose nanocrystals (CNC) and polyhedral oligomeric silsesquioxane (POSS). Moreover, PVDF fibrous membranes mainly suffer from insufficient mechanical properties and high thermal shrinkage, limiting their application in different fields. In this respect, many works are dedicated to the use of ceramic and natural fillers, such as SiO_2, TiO_2, ZnO, $BaTiO_3$,[85] montmorillonite (MMT)[86] and cellulose fibers, which can improve the mechanical, electrochemical, and thermal properties of the polymer material.[85]

Secondly, the PVDF-based electrospun membranes can act as suitable substrate for the nanoparticles, in order to prevent their agglomeration and degradation (e.g., by immobilization, crosslinking on surface, precipitation), while maintaining their characteristic features and activities. For instance, He et al.[75] reported that TiO_2 nanoparticles, which are highly prone to agglomerate, preserved their photocatalytic activity after the immobilization on a PVDF-based electrospun membrane. As another example, electrospun nanofiber membranes with sufficient surface area seem to be suitable substrates for the immobilization of CNTs, whereas stand-alone membranes of CNTs likely tend to collapse.[87] Also, Zhao et al.[88] reported of PVDF doped with negative ion powders (for instance composed of Al_2O_3, SiO_2, B_2O_3 and Fe_2O_3). The high

electronegativity of PVDF fibers played an active role in the releasing of the negative ions from the surface, useful for air filtration applications. Furthermore, PVDF/nanofillers composites can serve as substrate or template for other polymers suffering from poor mechanical properties and challenging processability, such as polypyrrole.[89]

Although PVDF is a slightly hydrophobic polymer and its hydrophobicity is enhanced by the surface roughness of the electrospun systems, it does not often provide suitable surface properties for applications in which the wettability matters. Hence, nanofillers (e.g., epoxy-siloxane modified SiO_2 [90] and CNT)[87] can be added to tune the wettability of PVDF, for example to improve its hydrophobicity.

The nanoparticles can also be incorporated into PVDF-based electrospun membranes with other purposes, such as imparting antibacterial [91] or anti-fouling properties.[92]

In addition to conventional nanoparticles, the use of fillers modified with fluorinated groups in PVDF-based electrospun membranes is also reported. For instance, Gebrekrstos et al.[93] prepared GO derivatives functionalized with fluorinated groups (Figure 7a). Interestingly, such fillers significantly enhanced the piezoelectricity of PVDF (piezoelectric coefficient of 63 pm/V,[93] while that of neat PVDF fibers is ~30 pm/V)[94] as well as the energy density and dielectric permittivity of the electrospun membrane, mainly due to the high electronegativity of extra fluorine atoms that leads to a higher amount of β-phase content in comparison to the systems with non-fluorinated fillers. In another work, Ganesh et al.[95] prepared an electrospun material of P(VDF-*co*-HFP) filled with a fluorinated POSS,[96] whose structure is reported in Figure 7b, and which is an excellent water repellent compound. Such material was used as coating for glass substrates, exhibiting transparency and superhydrophobic characteristics.

Table 3 summarizes some of the studies focusing on the incorporation of the above-

mentioned fillers in electrospun PVDF-based matrices.

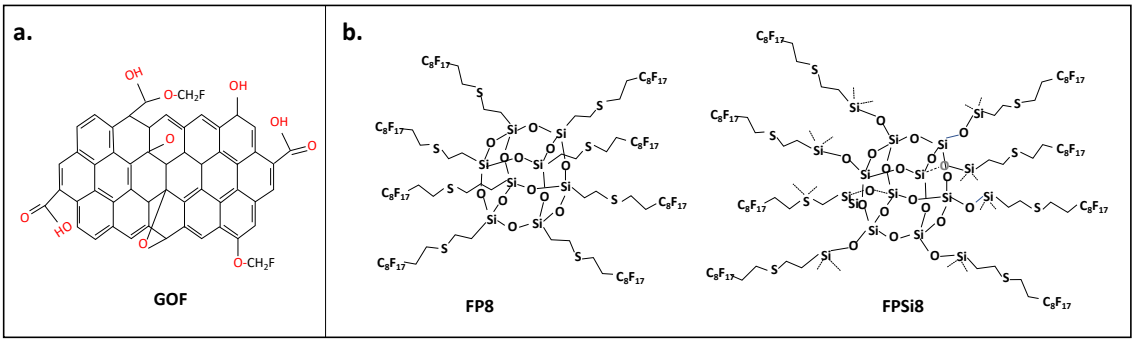

Figure 7. Fluorinated fillers used for PVDF-based composite materials. a. Molecular structure of a fluorine-doped graphene oxide. Adapted with permission from ref [93]. b. Molecular structures of two fluoro-POSS (fluorinated polyhedral oligomeric silsesquioxanes). Adapted with permission from ref [95].

Table 3. Filled PVDF-based composite systems used for electrospinning: composition and applications.

Additive	Polymer matrix	Application	Reference
SiO_2	PVDF	Superhydrophobic surfaces	[90]
	PVDF	Membrane distillation	[97]
	P(VDF-*co*-HFP)/PET/P(VDF-*co*-HFP)	Li-ion batteries	[98]
TiO_2	PVDF	Self-charging/self-cleaning surfaces	[99]
	PVDF	Dye-sensitized solar cells	[100]
	P(VDF-*co*-HFP)	Membrane distillation	[101, 102]
	Poly(MAA-*co*-TFA)/PVDF	Photo catalytic activity	[75]
Al_2O_3	PVDF	Oil/water separation	[103]
Ag/Al_2O_3	PVDF	Air filtration	[91]
$BaTiO_3$	PVDF	Wearable smart textiles and implantable biosensors	[104]
	PVDF	Piezoelectrodes	[105]
Fe_3O_4	PS/PVDF	Oil/water separation	[106]
ZnO	PVDF	Anti-corrosive coating	[47]
	PVDF	Oil/water separation	[107]
	PVDF and P(VDF-*co*-HFP)	Antibacterial, biomedical application	[108]
	PAN/PVDF	Antibacterial sport textile	[109]
MMT	PVDF	Li-ion batteries	[110]
	P(VDF-*co*-HFP)	Li-ion batteries	[111]

Nanoclay – Cloisite® 20A	PVDF	Membrane distillation	[150]
Zeolite	PVDF	Biomedical application	[112]
	PVDF	Water filtration	[113]
ZnS	Poly(MAA-*co*-TFA)/PVDF	Photo catalytic activity	[114]
$ZnIn_2S_4$	Poly(HFBA-*co*-MAA)/PVDF	Water splitting	[115]
$BiFeO_3$	P(VDF-*co*-TrFE)	Information storage, magnetic recording media, multiple-state memories, spintronics devices and sensors	[116]
GO	PVDF	Energy storage devices	[93]
	Sulfonated-PVDF/PVDF	Oil removal	[92]
	PAN/PVDF	Proton exchange membrane fuel cells	[117]
	PVDF/PMMA		[118]
Graphene	PVDF	Nanogenerator	[119]
	PVDF	Sound absorbing	[120]
Nanoscale graphite platelets (NGP)	PVDF	Air filtration	[121]
CNT	PVDF	Micro-actuator applications	[122]
	P(VDF-*co*-TrFE)	Li-ion batteries	[123]
	P(VDF-*co*-HFP)	Membrane distillation	[87]
MWCNT	PVDF	Wearable sensor/electromechanical actuators	[124]
Carbon black	PVDF/PVP	Energy storage devices	[125]
CNC	PVDF	Power generator	[126]
Cellulose fibers	PVDF	Energy storage application	[41]
Cu nanowire	PVDF	Flexible dielectric materials	[127]
Pt nanoparticle	PVDF	Wearable tactile sensor	[128]

As mentioned above, electrospun composite nanofibers can be subjected to post-processing techniques, such as UV irradiation and annealing, improving their piezoelectric, dielectric and mechanical properties.[125, 129–131]

3.1.4 Core-shell systems and hollow fibers

As already stated, by selecting the proper electrospinning set-up (specifically spinnerets with special designs), it is possible to produce nanofibers in different forms, such as core-shell or hollow fibers.

Electrospun membranes composed of core-shell fibers of PVDF and another polymer, conventionally obtained by co-axial electrospinning, have been investigated by several groups. For instance, Huang et al.[132] prepared cellulose acetate/P(VDF-*co*-HFP) core-shell fibrous membranes to be applied as separator in LIBs. In another work,[133] PEG/PVDF core-shell electrospun fibers were produced by co-axial electrospinning of a double spinneret set-up combining melt and solution electrospinning (Figure 8a-c), in which the melted PEG (core) and the PVDF solution (shell) compartments were separated. The PVDF fiber shell was used to encapsulate the PEG, almost without altering its thermal properties. The fabricated fibrous mat was proposed for heat energy storage applications and thermo-regulating textiles.[133]

Hollow nanofibers are usually produced by two different methods, namely the chemical vapor deposition (CVD) and the direct co-axial spinning. For the latter, two different solutions for the shell and the core are used (Figure 8d), and then the core material is dissolved with a selective solvent, leaving hollow fibers (Figure 8e and f). Halaui et al.[134] fabricated P(VDF-*co*-HFP) hollow fibers by dissolution of the PVP core, and proposed them for application in water filtration.

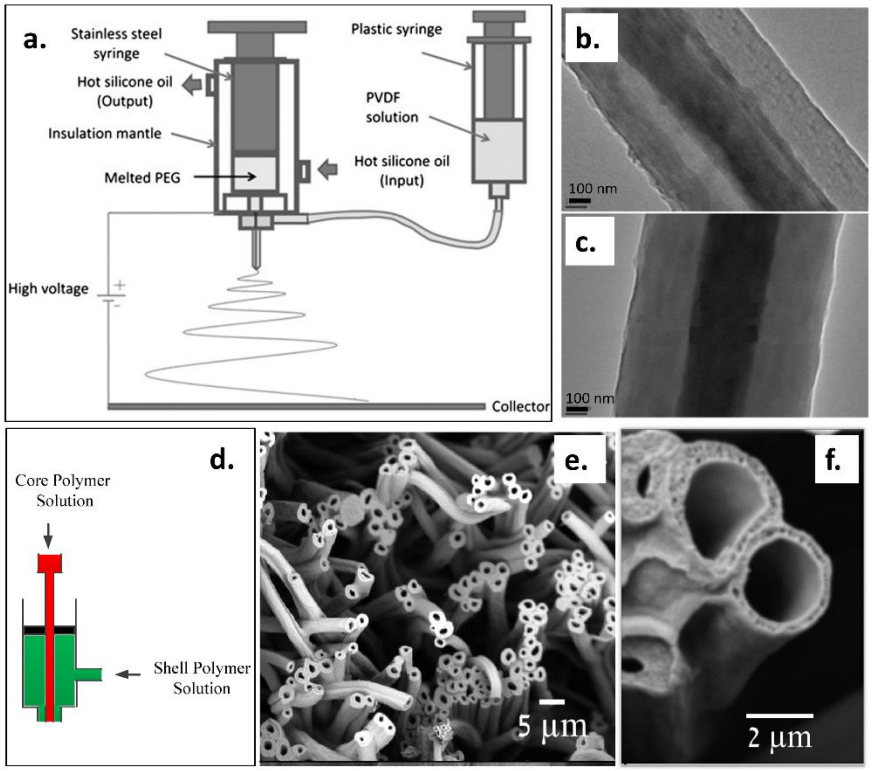

Figure 8. Core-shell and hollow PVDF-based fibers. a. Illustration of co-axial electrospinning set-up with a double spinneret (for concomitant melt and solution electrospinning); b and c. TEM images of core-shell electrospun PEG/PVDF fibers. Adapted with permission from ref [133]. d. Schematic representation of co-axial electrospinning set-up; e. and f. SEM images of the cross-section of P(VDF-*co*-HFP) hollow fibers, after PVP core removal. Adapted with permission from ref [134].

3.1.5 Sandwich structures

Electrospun membranes can be used to form sandwich structures: the different layers (each made of one material) are consecutively electrospun. As an example, Angulakshmi et al.[135] fabricated a tri-layer fibrous membrane of P(VDF-*co*-HFP)/PVC/P(VDF-*co*-HFP) with the aim of imitating commercially available Celgard® membrane separator (PP/PE/PP) for LIBs. Indeed, the adhesion among the layers has to be controlled to obtain acceptable mechanical properties. Similarly, Xiao et al.[136] fabricated a PVDF/poly(methyl methacrylate) (PMMA)/PVDF tri-layer structure, in which a cast film of PMMA was sandwiched between two PVDF electrospun membranes. Also in this case, the fabricated membrane was proposed for application in LIBs as polymer electrolyte.

3.2 Electrospinning of PTFE

Polytetrafluoroethylene (PTFE), repeating unit $–CF_2–CF_2–$, whose commonly known brand name is Teflon™ (by Chemours™), is synthesized from TFE monomer (Figure 9).[24] PTFE is a semi-crystalline thermoplastic polymer (T_m≈327 °C) with a high molar mass and a backbone covered by an electron cloud of fluorine atoms arranged in a helical conformation due to their strong repellence. This uniform fluorine coverage of backbone and the strong C-F bonds make the PTFE quite crystalline (up to 98%) and inert to nearly all chemicals. Because of a high chemical resistance and an excellent thermal stability, PTFE paved its way for a variety of applications.[24, 137–139]

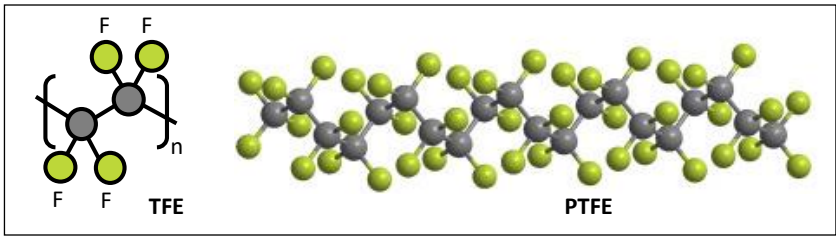

Figure 9. Molecular structure of TFE and PTFE. Adapted with permission from ref [139].

As expected, applying the electrospinning process to PTFE is indeed challenging due to its high chemical resistance, insolubility in any common solvent (except for its monomer), thermal stability, and molar mass. Therefore, it is widely accepted that the direct solution electrospinning of PTFE is impossible. Moreover, melt electrospinning of PTFE demands very high temperature and complex set-ups due to the polymer high T_m and viscoelastic properties.[140]

Therefore, driven by the outstanding properties of PTFE, other strategies have been developed to successfully obtain electrospun fibers and membranes. Emulsion electrospinning, using an emulsion formed by PTFE, an electrospinnable carrier polymer, such as polyvinyl alcohol (PVA)[141] or polyethylene oxide (PEO),[140, 142] and a

surfactant, is a suitable approach. Then, the fibrous structure of the carrier with dispersed PTFE is formed by electrospinning. The electrospinning process is followed by a sintering step: the membrane is heated, the carrier polymer completely decomposes, while PTFE particles undergo melting. As a result, a PTFE fibrous structure is produced (Figure 10a).[141–144] As shown in Figure 10b-e, the sintering duration has a strong effect on the fibers morphology.[141] The electrospinning conditions employed in the literature to obtain PTFE fibers are summarized in Table 4.

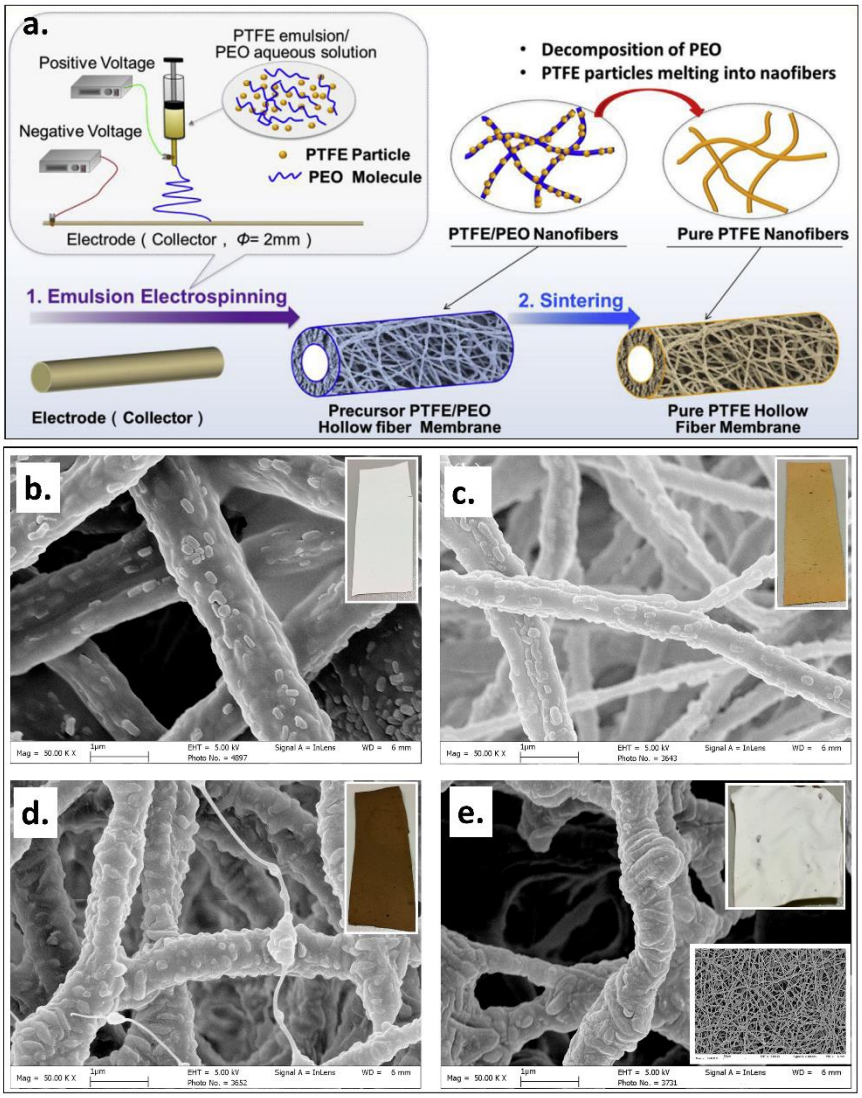

Figure 10. PTFE electrospun fibers by emulsion electrospinning in the presence of a carrier polymer and subsequent sintering. a. Schematic representation of the PTFE emulsion electrospinning with PEO as carrier and sintering process for PTFE nanofibrous membrane preparation. Adapted with permission from ref [142]. b-e. SEM images of PTFE/PVA electrospun fibrous membrane with varied sintering time (b: 0 h, c: 0.5 h, d: 2 h, e: 8 h); insets are photos of membranes after sintering. Adapted with permission from ref [141].

Emulsion electrospinning, followed by sintering, can also be applied to the NFES configuration. As an example, PTFE/PVA fibers were deposited layer-by-layer by direct write technique, forming porous structures with different pore geometry and size. After electrospinning, the porous membranes were sintered at 380 °C, and the fluorinated filters proposed for application in oil/water separation.[145]

PTFE-based composite fibrous membranes can also be fabricated by emulsion electrospinning and sintering, with the addition of nanoparticles as filler in the starting emulsion/solution to be processed. For instance, vinyl-terminated POSS [146] and ZnO [147] were introduced in PTFE fibers.

TFE-based copolymers, which are melt processable,[1, 3] have also been electrospun. In particular, amorphous Teflon™ AFs, which are copolymers of TFE and 2,2-bistrifluoromethyl-4,5-difluoro-1,3 dioxole (Figure 11a),[1] are a unique family of amorphous fluoropolymers, characterized by high fractional free volume, arising from the cyclic dioxole unit, as well as high mechanical properties, low surface energy, high permeability and optical transparency, which make them suitable for application in optical fibers, sensors and separators. They are only soluble in perfluorinated solvents,[148] thus the electrospinning process is mostly carried out through the co-axial set-up (see details in Table 4).

For instance, Han and Steckl [149] produced polycaprolactone (PCL)/Teflon™ AF core/shell fibers by co-axial electrospinning (Figure 11b and c). The core solution of PCL carries the non-electrospinnable shell solution of the fluoropolymer (in FC-75® as fluorinated solvent) towards the collector, and the shell solution does not interfere with the process due to its immiscibility with the solvent. The produced membrane exhibits superhydrophobic characteristics (WCA > 155 °), owing to the low surface energy of the fluorinated copolymer and to the high surface roughness of the electrospun fibers (Figure

11d).

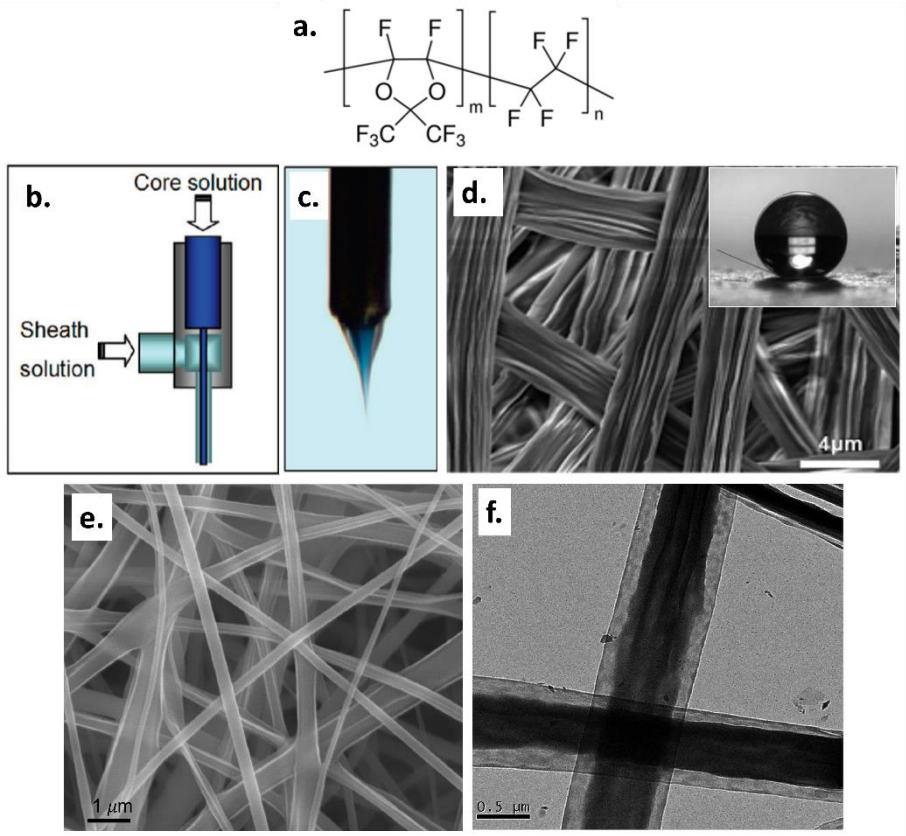

Figure 11. Teflon™ AFs electrospinning. a. Molecular structure of poly[4,5-difluoro-2,2-bis(trifluoromethyl)-1,3-dioxole-*co*-tetrafluoroethylene] copolymer. b. Schematic representation of the co-axial electrospinning set-up; c. Taylor cone formation for PCL/Teflon™ AF core-sheath droplet; d. morphology of core-shell PCL/Teflon™ AF fibers obtained with PCL concentration of 10 wt.% and 1.5 ml/h feed rate, and Teflon™ AF concentration of 1 wt.% and 1 ml/h feed rate. Adapted with permission from ref [149]. e. and f. SEM and TEM micrographs of core-shell PVDF/Teflon™ AF electrospun fibers (PVDF solution concentration of 15 wt.% with feed rate of 0.25 ml/h; Teflon™ AF solution concentration of 1 wt.% with feed rate 0.23 ml/h). Adapted with permission from ref [150].

Similarly, Teflon™ AF was successfully used in co-axial electrospinning together with PVDF,[150] which served as an electrospinning carrier both in core and shell conformation (Figure 11e and f).

A random terpolymer based on TFE, HFP and VDF, showing outstanding properties such as chemical resistance, optical clarity, low processing temperature and acceptable solubility in some organic solvents, was also employed in electrospinning,[151] using

ethyl acetate as the solvent The electrospun fibers exhibited a beaded morphology, and the membrane showed a very high hydrophobicity with a WCA of 145 °.[152]

Table 4. Parameters used for electrospinning of PTFE, both by emulsion electrospinning and co-axial electrospinning., together with the application of the membrane

Polymer system	**PTFE:carrier ratio (w/w)**	**Working distance (cm)**	**Voltage (kV)**	**Feed rate (ml/h)**	**Sintering temp (°C)**	**Application**	**Reference**
Emulsion electrospinning/sintering							
PTFE/PVA	90:10, 80:20, 70:30, 60:40, 50:50	15	7-15	0.01	390 (3 min)	Filtration	[143]
PTFE/PVA	14:1	15	16	0.40	380 (30 min and 8 h)	Oil/water separation	[141]
PTFE/PVA	4:1, 6:1, 8:1, 10:1	4 NFES	2.85	0.25	380 (5 h)	Oil/water separation	[145]
PTFE/PEO	6:0.3, 6:0.2, 6:0.6, 4.3:0.5	15	15	0.50	350, 360, 370 (15 min)	Triboelectric nanogenerators sensors	[140]
PTFE/PEO	98:2, 96:4, 94:6, 92:8	12	10	0.1	340, 360, 380, 400 (10 min)	Membrane distillation	[142]
Co-axial electrospinning							
Teflon™ AF/PCL	Core:shell PCL 10 wt.%: Teflon™ AF 1wt.%	25	12.5	1.5:1		Superhydrophobic and oleophobic membranes	[149]
Teflon™ AF/PVDF	Core: shell PVDF 7 wt.%: Teflon™ AF 1 wt.% PVDF 15 wt.%: Teflon™ AF 1wt.%	10 15	10-20	0.5:0.4 0.25:0.23		Li-air batteries	[150]

	Teflon™ AF 1 wt.%: PVDF 7wt.%	10		0.4:0.4			

3.3 Electrospinning of perfluorosulfonic acid polymers (PFSA)

Sulfonated TFE-based copolymers (commercialized as Nafion™, Aquivion™, Fumion™, Flemion™, 3M™ Membranes) represent an interesting class of fluoropolymers composed of statistically distributed side chains of perfluoroether bearing sulfonic acid end group along the backbone chain (Figure 12a), and commercially available as solution cast film, dispersion in water/alcohol solutions, or pellets. Due to their excellent thermal, chemical and mechanical properties, as well as high proton conductivity (~0.1 S/cm), these copolymers are used in fuel cells as proton exchange membrane (PEM).[153–158] NafionTM has also been utilized in water electrolysis, chlor-alkali electrolysis, sensors, and as a superacid catalyst.[159]

Table 5 summarizes the electrospinning process parameters used to obtain electrospun PFSA polymer fibers and mats. To be processed by electrospinning, Nafion™ is typically blended with a carrier electrospinnable polymer (e.g., PEO, polyacrylic acid PAA, PVP, PVA), as the insufficient chain entanglement in the fluoropolymer solution and the formation of aggregates prohibits defect-free fiber formation of pure Nafion™.[160, 161] Generally, a water/alcohol (e.g., isopropyl alcohol) solvent system is used, but also DMAc can be employed.[162] It was demonstrated that the addition of PAA provides sufficient chain entanglement and suitable solution properties for Nafion™ electrospinning and hinders the fluoropolymer aggregation (Figure 12b-e). Moreover, at low concentration, Nafion™ can improve the fiber formation of PAA (generally pure PAA in similar conditions is not electrospinnable), and thus a mutual and synergic effect in blend electrospinning was observed for both polymers.[160] A similar outcome was

also obtained by using high molar mass PEO (8000 kg/mol) as carrier polymer,[155] which is not usually electrospinnable,[163] yielding a gel-like behavior when in solution. Whereas, when Nafion™ is added to the PEO solution, a successful electrospinnable system is achieved.[155] Therefore, on the one hand, the fluoropolymer prevents the gel-like behavior of PEO counterpart in the Nafion™/PEO mixture solution, and, on the other hand, PEO lowers the fluorinated aggregate size (Figure 12f-i). This electrospinning process was used to produce high-purity Nafion™ electrospun nanofibers (99.9 wt.% Nafion™) exhibiting much higher proton conductivity (up to 1.5 S/cm) compared to bulk films (0.1 S/cm).[155]

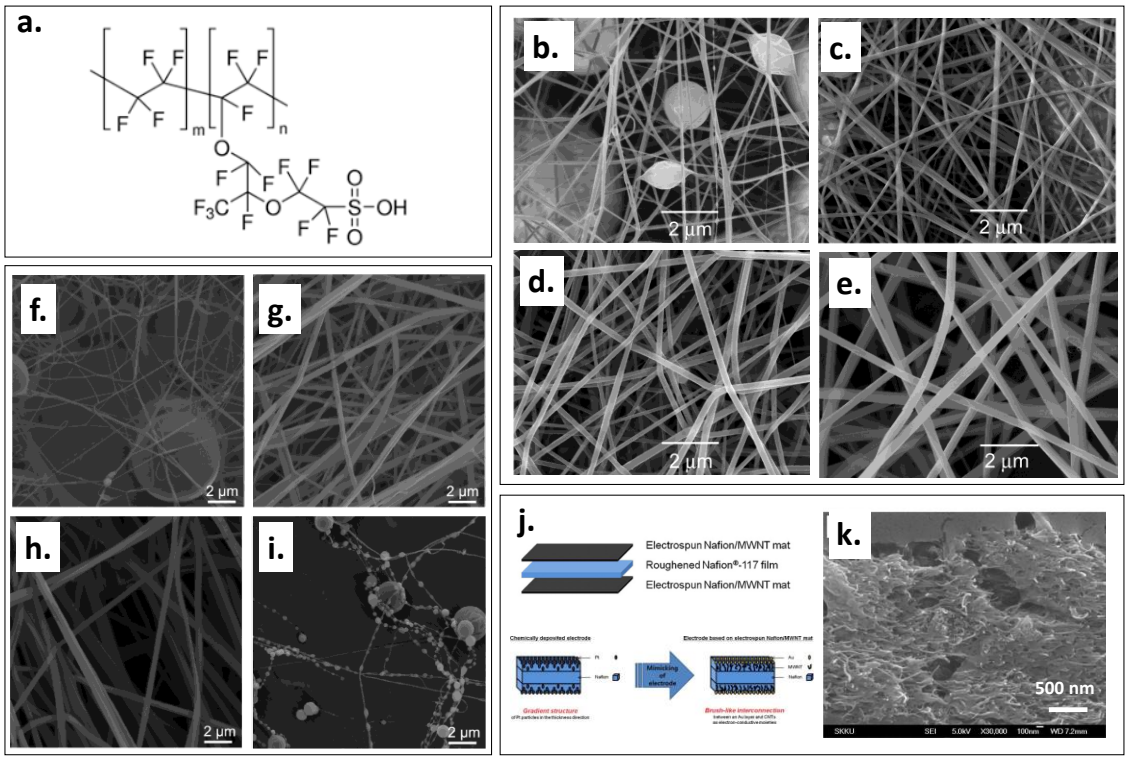

Figure 12. Examples of Nafion™ electrospinning. a. Molecular structure of Nafion™. b-e. SEM images of electrospun fibers of Nafion™/PAA with PAA content of 8 % (b), 12 % (c), 25 % (d), 66 % (e). Adapted with permission from ref [160]. f-h. SEM images of high-purity Nafion™ nanofibers, electrospun with high molar mass PEO (Mw = 8000 kg/mol) at fiber compositions of 98 (f), 99 (g), 99.9 (h) wt. % Nafion™; i. solutions with lower molar mass PEO (Mw = 400 kg/mol) produced beaded fibers at 99.9 wt. % Nafion™. Adapted with permission from ref [155].j. Schematic representation of the fabrication of multilayer composite membrane actuators; k. SEM image of cross-section of the fabricated actuator. Adapted with permission from ref [164].

PFSA polymers can also be used in electrospinning processes for the fabrication of composite fibers. For instance, an electrospun Nafion™/MWCNT layer was used to coat a commercially available Nafion®-117 membrane. For the electrospinning, a Nafion™/PEO solution in propanol/water containing 0–12 wt.% MWCNT (per Nafion™ wt.) was employed. Afterwards, the electrospun coatings on both sides of the membrane were sputter-coated by Au followed by hot-pressing (Figure 12j and k). This composite membrane was assessed for application as flexible polymer actuator.[164] In an another study,[165] composite membranes made of PFSA ionomer and PVDF containing sulfonic (sol-gel sulfonated) silica network were fabricated through a dual-syringe electrospinning set-up. The co-electrospun membranes were investigated for the proton conductivity at low humidity. PVDF was used to improve mechanical properties, while the proton-conducting sulfonated silica increased the water retention and the conductivity of the composite membrane at low RH.

Table 5. Parameters used for electrospinning of Nafion™ with a carrier polymer by solution blend electrospinning, and the proposed applications for the resulting electrospun membranes.

Polymer system	**Solution concentration (wt.%)**	**Nafion™/polymer carrier ratio (w:w)**	**Working distance (cm)**	**Voltage (kV)**	**Feed rate (ml/h)**	**Application**	**Reference**
Nafion™/PAA	5	0:100, 34:66, 50:50, 75:25, 84:16, 88:12, 92:8	18–28	10–18	0.5–5	Fuel cells	[160]
Nafion™/PEO	15–25	99:1, 98:2	5–6	4–7	0.2–0.6	Fuel cell membranes	[161]
Nafion™/PEO/ MWCNT	5.9	5:1	10	10–13.5	0.2	IPMC[1] actuators	[164]
Nafion™/PVA	8–9.5	90:10, 80:20, 70:30, 60:40	18–20	15	0.8	Heavy metal ions adsorption	[162]

[1]IPMC: ionic polymer–metal composite

3.4 Electrospinning of fluorinated acrylic polymers

The processing of fluoropolymers by direct electrospinning can be challenging, mainly due to their insolubility in common solvents, their low dielectric constant, and their high thermal properties. In terms of processability and practical cost, partially fluorinated polymers (e.g., fluorinated block-copolymers or homopolymers terminated with a fluorinated end-group) can address such issues. Considering the tendency of fluorinated compounds/polymer segments to spontaneously segregate at the surface minimizing the surface free energy of the material, these partially fluorinated polymers can display similar surface properties of analogue fluoropolymers due to the enrichment of the surface by fluorine.[166–168] Fluorinated acrylic copolymers are good examples of this kind of structures. At the same time, the acrylic part improves the solubility of the fluoropolymers, facilitating their processing and providing the proper viscosity for electrospinning.[167]

For instance, Choi et al.[168] fabricated electrospun membranes of poly(2,2,2-trifluoroethyl methacrylate) (PTFEMA), thus bearing short CF_3 side groups only, with superamphiphobic properties (i.e., both water and hexadecane contact angles >150 °) (Figure 13a-d).[168] It is worth noting that the high hexadecane contact angle on electrospun membranes can be attributed to the high level of surface strong "robustness" against droplet infiltration, which depends on the size and uniformity of the fibers, and on the gap distance between the fibers.

In another work, Deitzel et al.[166] synthesized random copolymers based on MMA with varying tetrahydroperfuorooctyl acrylate content (0−10%). The electrospun fibers (as well as thin spin-casted films) exhibited a surface fluorine enrichment, compared with the bulk polymer. In another work, an amphiphilic graft poly(MMA-*r*-hydroxypropyl acrylate)-*g*-poly(dodecafluoroheptyl methacrylate) copolymer was synthesized and

subsequently subjected to electrospinning. The fibrous membrane was demonstrated to be superhydrophobic, due to the fluorine rich surface, as the presence of both hydrophobic and hydrophilic groups in the graft-copolymer synergically enhanced the surface and bulk segregations.[169]

In another study, fluorinated electrospun membranes were prepared from a blend of PVDF and poly(dodecafluoroheptyl methacrylate–*co*–methacrylic acid) copolymer (PVDF/P(DFMA-*co*-MMA)), and proposed as photocatalyst carriers.[115] The results demonstrated that the electrospinnability of the copolymer depends on the MMA content: the lower the MMA content, the more difficult the electrospinning process. PDFMA was also used to prepare two block copolymers based on PS and PMMA and terminated by aminopropyl triethoxysilane (APTES) (i.e., APTES-PS-*b*-PDFMA and APTES-PMMA-*b*-PDFMA), then subjected to electrospinning (Figure 13e).[170] The authors discovered that for the APTES-PS-*b*-PDFMA block copolymer, thanks to negatively charged PS sequence migrating towards the core under electric field upon electrospinning, the surface segregation of fluorinated groups was more pronounced.

In a different work, Mao et al.[171] prepared high fluorine content platinum porphyrin-grafted poly(isobutyl methacrylate-*co*-DFMA) copolymers for application in optical oxygen sensors.[172] The high specific surface provided by electrospun fibers enhances the sensor sensitivity by promoting the oxygen diffusion (Figure 13f-i).

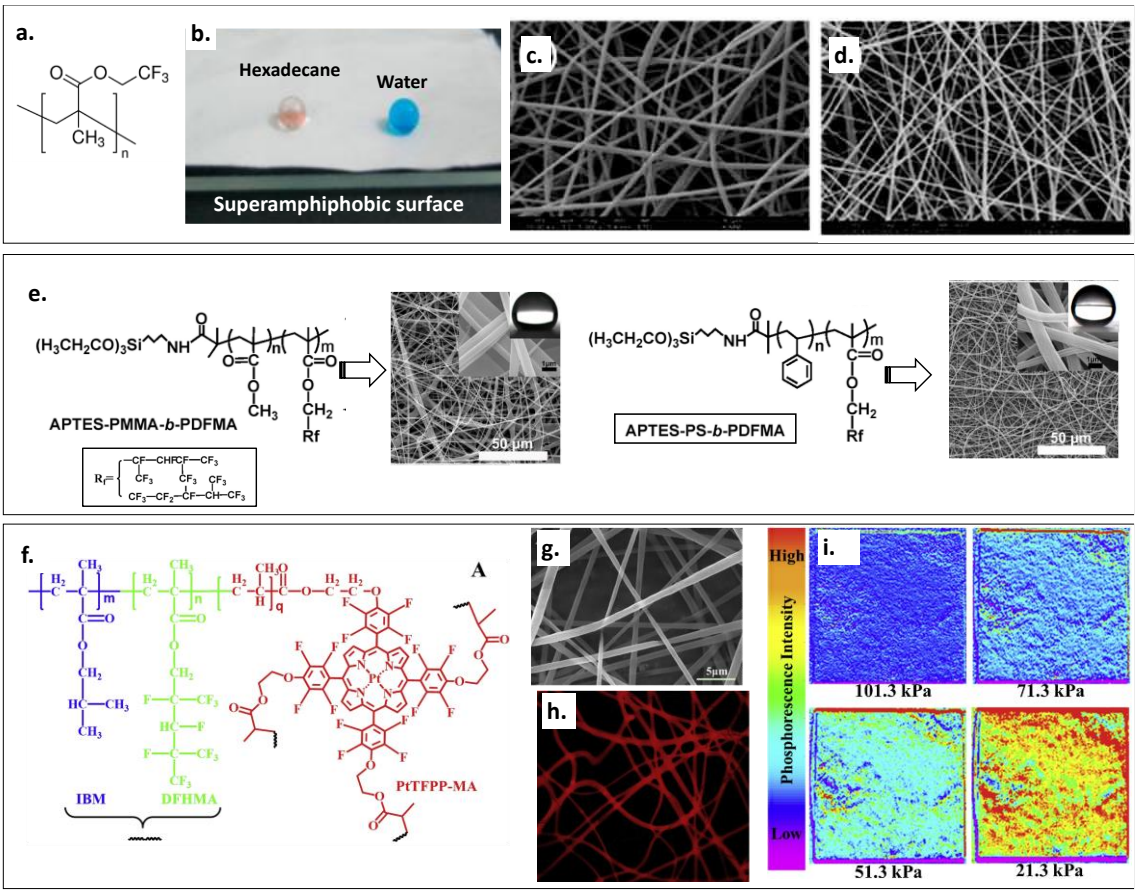

Figure 13. Electrospinning of fluoropolymers with acrylic groups. a. Chemical structure of PTFEMA; b. electrospun membrane of PTFEMA with superamphiphobicity characteristics; c. and d. SEM images of the PTFEMA fibers prepared by solution concentration of 30 wt.% and 26 wt.%, respectively. Adapted with permission from ref [168] e. Chemical structure of APTES-PMMA-*b*-PDFMA and APTES-PS-*b*-PDFMA, and SEM images of their electrospun fibers. Adapted with permission from ref [170]. f. Chemical structure of platinum porphyrin-grafted poly(isobutyl methacrylate-*co*-DFMA) (PtTFPP-p(IBM-*co*-DFHMA) copolymer; g. SEM image and h. phosphorescence micrograph image of PtTFPP-p(IBM-*co*-DFHMA); i. CCD images of excited PtTFPP-p(IBM-*co*-DFHMA) under different air pressure. Adapted with permission from ref [171].

3.5 Electrospinning of fluorinated polyurethanes

Superhydrophobic fluorinated polyurethanes (FPUs) have drawn great attention in recent years thank to their potential applications in anti-fouling coatings, surface modification of implantable devices, and separation membranes.[173] Wu et al.[174] synthesized polyurethanes (PUs) containing perfluoropolyether (PFPE) segments, fabricated electrospun membranes both of PU and FPU, and obtained uniform fibers or beaded fibers by varying the concentration of electrospinning solution. They evaluated the effect

of morphology and roughness on WCA and surface energy: the higher contact angles of FPU electrospun membranes rely on both the microstructure and the low surface energy provided by the fluorinated segments. The electrospun membranes showed higher hydrophobicity compared with solvent cast PU and FPU films. The bead-thread membrane had the highest WCA value, followed by the fibrous membrane and then by the cast film. Moreover, the WCA of FPU electrospun materials was higher than that of PU in similar surface morphology and microstructure.[174]

The electrospinning process has to be finely optimized when FPUs are used, especially regarding the choice of a suitable solvent, otherwise peculiar phenomena (e.g., phase separation) can occur. For example, Zheng et al.[173] synthesized and subsequently electrospun hyperbranched FPUs with two different fluorinated chain lengths (Figure 14). Especially the hyperbranched long-chain fluorinated PUs were not completely soluble in the utilized solvent, and during the electrospinning phase separation took place. As the solvent evaporated very fast, the jet of polymer solidified before sufficient stretching, and the deposited fibers showed wider diameters and larger pore size. The WCAs were found 149.6 ° and 159.7 ° for the fluoropolymer with short and long fluorinated chains, respectively. Moreover, the polymers with longer ones displayed a higher water adhesion ("petal effect", i.e., when a water droplet on the surface of a material appears spherical in shape but cannot roll off even when it is turned upside down), as depicted in Figure 14e, due to the particular surface microstructure of the membranes that can trap the water drop (Wenzel state)[175] and prevent it to roll off.

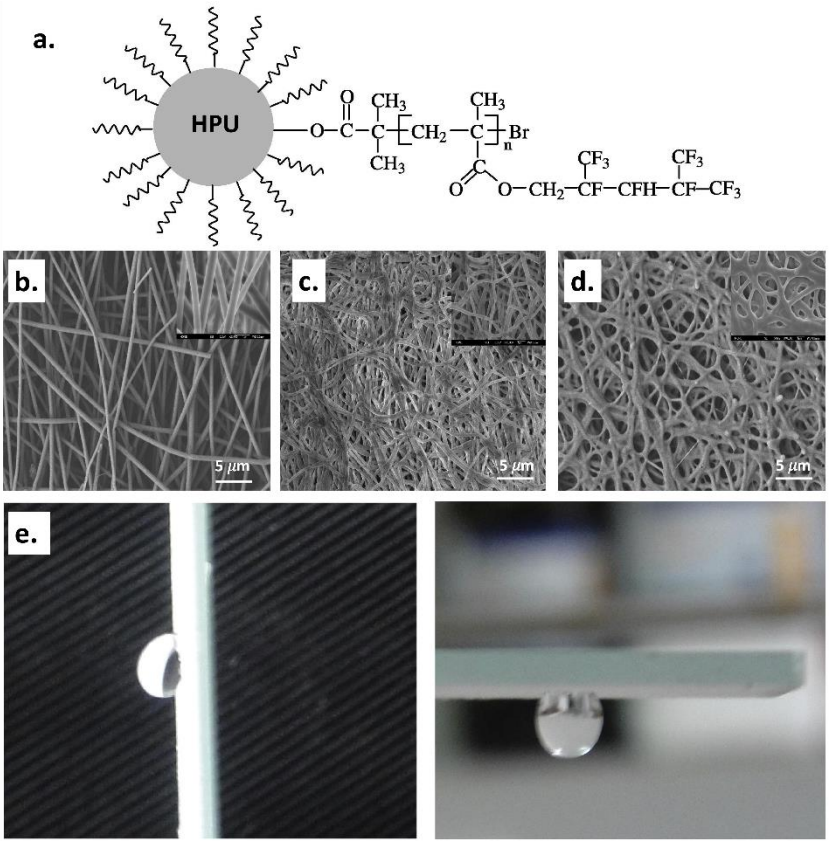

Figure 14. Electrospinning of fluorinated polyurethanes. a. Schematic illustration of fluorinated hyperbranched polyurethane (HPU); SEM images of electrospun fibers of: b. HPU, c. HPU with short grafted fluorinated chain, d. HPU with long grafted fluorinated chain; e. photographs of water droplet adhered on the surface of nanofibrous membrane of HPU with long fluorinated chain. Adapted with permission from ref [173].

Controversially, Wu et al.[176] reported that electrospun membranes of PU elastomers containing PFPE segments showed unusual low fluorine content on the surface, while a bulk aggregation of fluorinated moieties was observed. This phenomenon was attributed to the electrospinning process, as a fluorine enrichment of the surface was obtained for solution cast films. The authors pointed out that the selected solvent (i.e., DMF/THF) was not suitable for the fluorinated segments and these groups were wrapped within the hydrogenated segments; the very fast evaporation process occurring during electrospinning did not allow the PFPE moieties to unwrap and migrate toward the surface.[176]

3.6 Electrospinning of fluorinated polyimides

Fluorinated polyimides (FPIs) are extensively studied for optoelectronics and microelectronics fields, owing to their excellent transparency, proper dielectric properties, low optical losses (in near IR, visible and UV regions), thermal resistance, and hydrophobicity.[177]

Conventionally, the electrospinning of polyimides (PIs) is performed through solution electrospinning of polyamic acid (PAmA) as the polymer precursor, followed by imidization upon thermal treatment to convert the electrospun PAmA membrane into a PI membrane. FPI electrospun membranes can be obtained either by this two-step method or direct solution electrospinning, thanks to the improved solubility of FPIs compared with the pristine PIs.

Following the first strategy, Li et al.[178] synthesized different PAmA, including a fluorinated one (Figure 15a), then used for electrospinning and imidization at high temperature (Figure 15b). The porous membranes structure and their fluorination reduced the polymer dielectric constant.

Other works report the solution electrospinning of FPIs.[179] For example, fibrous membranes of fluorine-containing triptycene-based PI were prepared and proposed for application in oil/water separation.[180] The fluorinated chemicals improved the hydrophobic feature (Figure 15c-e): the membranes showed high WCA (121 °) and high separation efficiency (≈99% over ten successive runs).[180] Moreover, FPIs membranes also led to superhydrophobic surfaces (WCA=158 °).[181] Surprisingly, such membranes exhibited the petal effect (water adhesion of 98.3 μN) owing to the FPI composition and superior surface roughness of the fibrous structure.

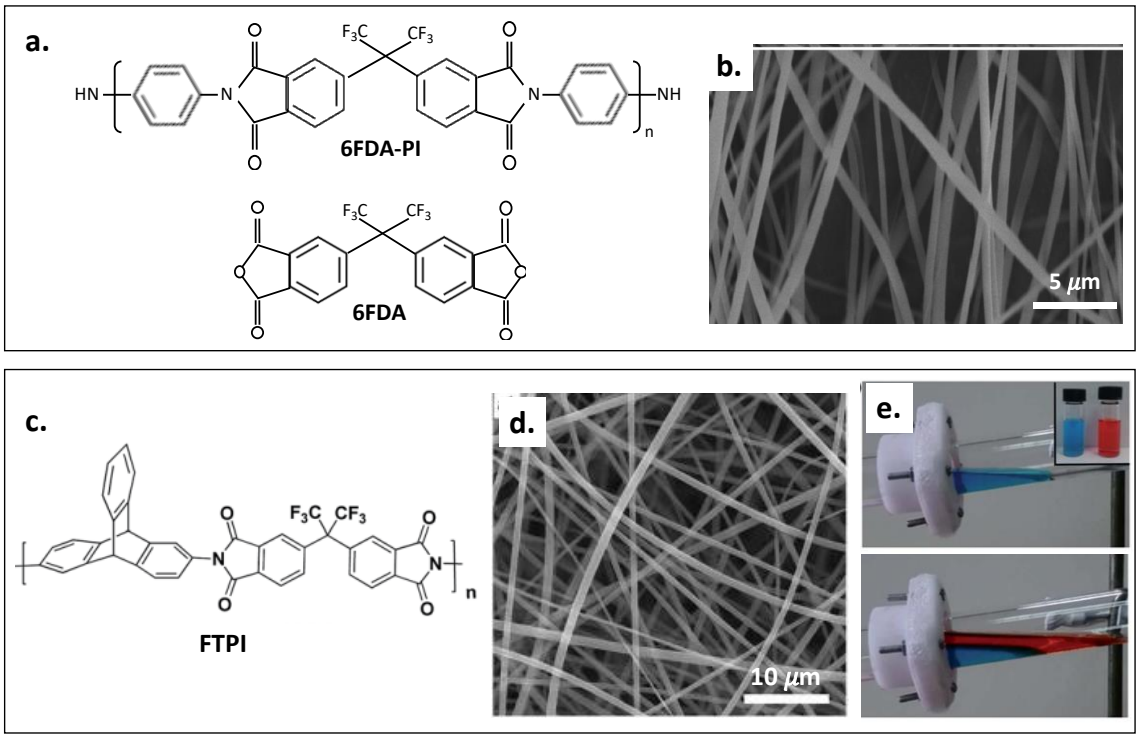

Figure 15. Examples of electrospinning of fluorinated polyimides (FPIs). a. Chemical structure of 2,2'-bis(3,4-dicarboxyphenyl) hexafluropropane dianhydride (6FDA) and 6FDA-PI (6FDA polyimide); b. SEM images of electrospun fibers of 6FDA-PI. Adapted with permission from ref [178]. c. Chemical structure of fluorine-containing triptycene-based polyimide (FTPI); d. FESEM. images of electrospun membrane of FTPI; e. water/oil separation process. Adapted with permission from ref [180].

3.7 Electrospinning of aromatic fluorinated polymers

Novel and synthetic fluoropolymers are mainly developed for obtaining superhydrophobic characteristics. For instance, Agarwal et al.[182] synthesized different copolymers of polystyrene (PS) and aromatic fluorinated poly(2,3,4,5,6-pentafluorostyrene). After solution electrospinning, the resulting membranes were superhydrophobic with a low water-roll angle (i.e., the surface angle at which a water droplet rolls away) down to 0 °. Similarly, three different fluoroalkyl end-capped PSs were synthesized and utilized for electrospinning (Figure 16a and b).[183] In particular, C_8F_{17} end-groups were introduced into PS as surface modifying moieties at low concentration (<10 wt.%), to prevent their aggregation. The spontaneous surface segregation of the fluoroalkyl groups during electrospinning decreased the surface energy

and consequently increased the hydrophobicity of PS membranes (WCA=153 °) even at a very low concentration (4 wt.%) of two- or three-functional fluoroalkyl moieties, whereas a flat film with the same composition exhibited a much lower WCA (≈100 °). Furthermore, annealing the fibrous membrane above the T_g can enhance the surface segregation but changes the fibrous morphology reducing the surface roughness. Therefore, selecting the proper temperature to promote the fluorine enrichment without destructive effects on fibrous structure is vital.[183] In another study,[184] the electrospinning of biphenyl perfluorocyclobutyl aryl ether (BP-PFCB) of two number-average molar masses was studied (Figure 16c-e). By changing the electrospinning parameters (e.g., solution parameters, flow rate, voltage and working distance), WCA of the electrospun membranes reached 152 °.

In addition, Satilmis et al.[185] synthesized fluorine-rich polymers of intrinsic microporosity (PIMs) (PIM-2 is represented in Figure 16f) used for the fabrication of self-standing electrospun membranes for separation and adsorption application. For the electrospinning process, the synthetic fluorinated PIM-2 was dissolved in tetrachloroethane at high concentration (43 %) to obtain bead-free fibers (Figure 16g-i) with superhydrophobic behavior (WCA=155 ± 6 °, compared with 93 ± 3 ° for its solvent cast dense membrane). The internal available surface area of PIM-2 fibrous membrane was slightly lower than that of the powder form (580 m^2/g vs. 600 m^2/g, respectively) due to the presence of the high boiling temperature solvent in the pores. However, it exhibited high adsorption ability for solvents (DMSO and 1,4 dioxane) and oils.

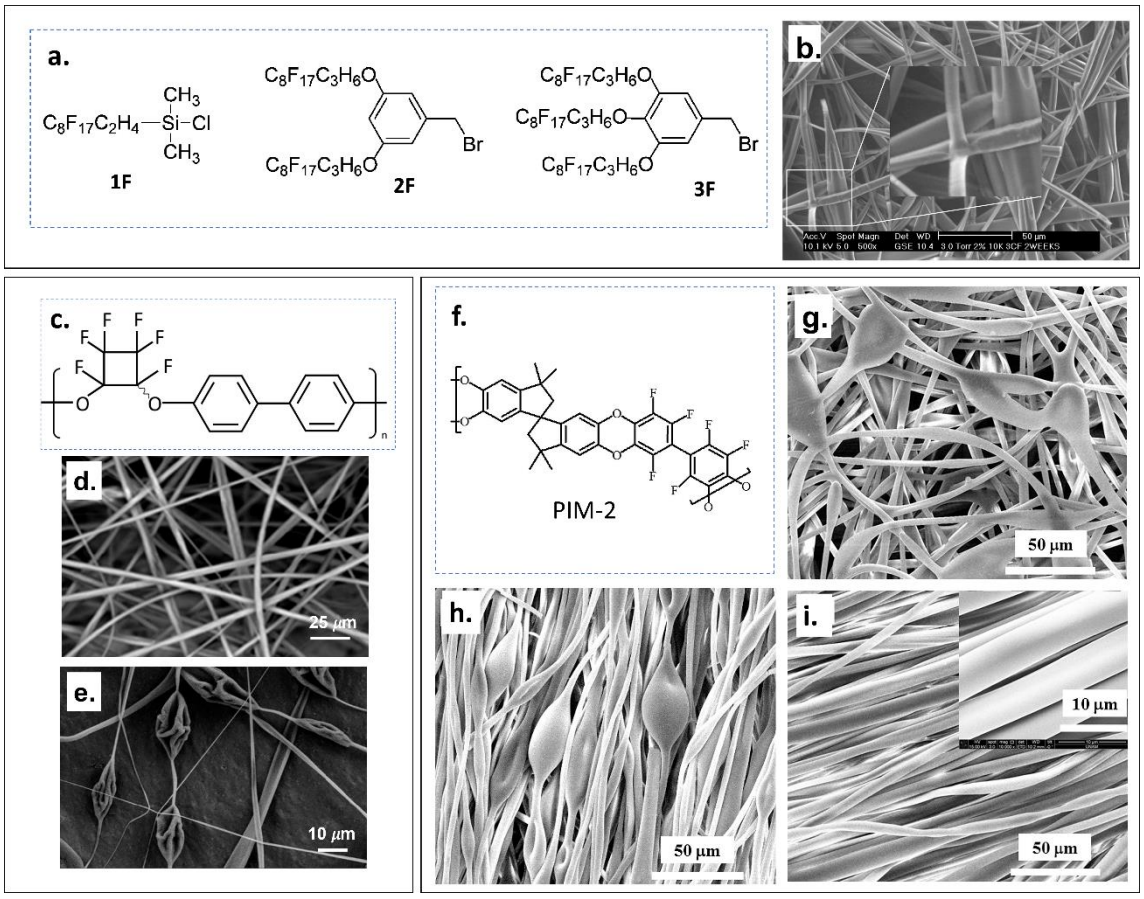

Figure 16. Electrospinning of aromatic fluorinated polymers. a. Chemical structure of three C_8F_{17} fluoroalkyl products; b. FESEM image of electrospun mat of fluoroalkyl end-capped polystyrene. Adapted with permission from ref [183]. c. Chemical structure of biphenyl perfluorocyclobutyl aryl ether polymer (BP-PFCB); SEM images of electrospun membranes with d. fibrous morphology and e. beaded fibers. Adapted with permission from ref [184]. f. Chemical structures of fluorine-rich polymer of intrinsic microporosity PIM-2; SEM images of PIM-2 electrospun membrane prepared by using a rotating drum and different polymer concentration: g. 38 % (w/v) and 100 rpm, h. 38 % (w/v) and 1000 rpm, and i. 43 % (w/v) and 1000 rpm. Adapted with permission from ref [185].

4. Surface modification of electrospun membranes

Remarkable properties of fluoropolymers are their surface characteristics, namely a low surface tension which in turn ensures water and oil repellency and antiadhesion behavior. However, fluoropolymers suffer from difficult processability and high cost, therefore the exploitation of their surface properties is affordable more easily by using them as additives (i.e., modifiers). In fact, it is possible to benefit from the properties of fluoropolymers even when their content is very low. Surface modification of electrospun

fibers and nonwoven mats with fluorinated compounds can then be achieved by different strategies, e.g., the application of a coating and the exploitation of the spontaneous surface segregation the fluorine-rich segments. For instance, Khayet et al.[186] improved the hydrophobicity of polysulfone fibers by using a small quantity (6 wt.%) of a FPU additive. The spontaneous surface segregation of the additive during electrospinning allowed to reach a WCA > 150 °. Fluorinated additives were also used in PMMA electrospinning. An example deals with the electrospinning of PMMA with the addition of hyperbranched perfluorinated and alkylated polyethyleneimine additive (PFA).[187] The PFA presence in the electrospinning solution inhibited the bead formation during the electrospinning process for low PMMA concentration: PFA lowers the surface tension and consequently leads to smoother fiber formation. Additionally, hyperbranched polymers have the tendency to migrate to the surface, and the fluorinated moiety can further enhance their surface migration, which was proved by XPS analysis: the F/C elemental ratio on the surface of electrospun fibers increases with the PFA content, till it reaches a plateau due to the surface fluorine saturation.

Interestingly, thanks to the migration of fluorine towards the free surface, a core-shell electrospun structure can also be obtained by a single spinneret set-up, when a fluoropolymer is one of the constituents. In fact, during the electrospinning process, the fluoropolymer tends to travel to the surface of the jet of polymer, and consequently a gradient of fluorine is formed along the fiber thickness: the surface of the fiber is rich in fluoropolymer, while the core is non-fluorinated or contains only a small fluoropolymer amount. For instance, core-shell polyacrylonitrile (PAN)/PVDF [188] and PVP/PVDF [189] nanofibers were fabricated by single spinneret electrospinning. Guex et al.[82] exploited this technique to prepare fibers with a fluorine-enriched surface by electrospinning a PU/P(VDF-*co*-HFP) blend, in order to obtain a reduced protein

absorption, particularly for both albumin and fibrinogen, which are the main causes of thrombus formation.

In an interesting work, the capability of fluorinated moieties to segregate to the free surface was used to produce photo-sensitive electrospun membranes by introducing in a PAN solution a photo-initiator containing a fluorinated aliphatic chain.[190] The surface of the PAN fibers was enriched with the fluorinated photo-initiator during electrospinning. The photo-sensitive membrane was subsequently impregnated with tripropylene glycol diacrylate (TPGDA) monomer and subjected to UV light, which triggered the TPGDA polymerization on the fibers surface. As a result, core-shell PAN/TPGDA nanofibers were obtained, showing a crosslinked shell with tunable thickness (Figure 17a).

As an example of coating electrospun mats with fluoropolymers, a thin layer of polymerized perfluoroalkyl ethyl methacrylate was deposited by initiated CVD on a PCL electrospun substrate, and a WCA as high as 175° was obtained.[191]

The surface of electrospun materials can also be modified by fluorine gases [193, 194] and plasma treatments with fluorinated compounds. Thorvaldsson et al.[195] modified the surface of cellulose electrospun fibers by fluorine plasma. It was demonstrated by electron spectroscopy that a fluorine deposition in form of CH_2-CF_2, C-F and -CF_3 occurred, and the presence of CH_2-CF_2 and C-F implied the formation of covalent bonds of fluorine with the surface, which is promising for long-term applications. The electrospun coated samples were superhydrophobic (WCA > 154 °). In another work, CF_4 plasma was used to treat silk fibroin nanofibrous membranes,[196] then proposed as guided bone regeneration membrane, which are barrier membranes to inhibit the epithelial or other soft tissues to migrate to osseous defect, consequently the bone can be regenerated from osteogenic cells without interfering the other fast-growing cells. CF_4

plasma treatment (microwave) was also used to modify the wettability of poly(L-lactide) (PLLA) electrospun membranes.[197] During the treatment both etching and grafting processes took place, thus affecting the final surface wettability of PLLA fibrous membranes. Lower plasma power mainly led to the etching effect and to a lower grafting of CF_4, subsequently hydrophilicity increased. Whereas, for higher plasma power, a high surface fluorine content was detected through XPS measurement and consequently the hydrophobicity was improved.

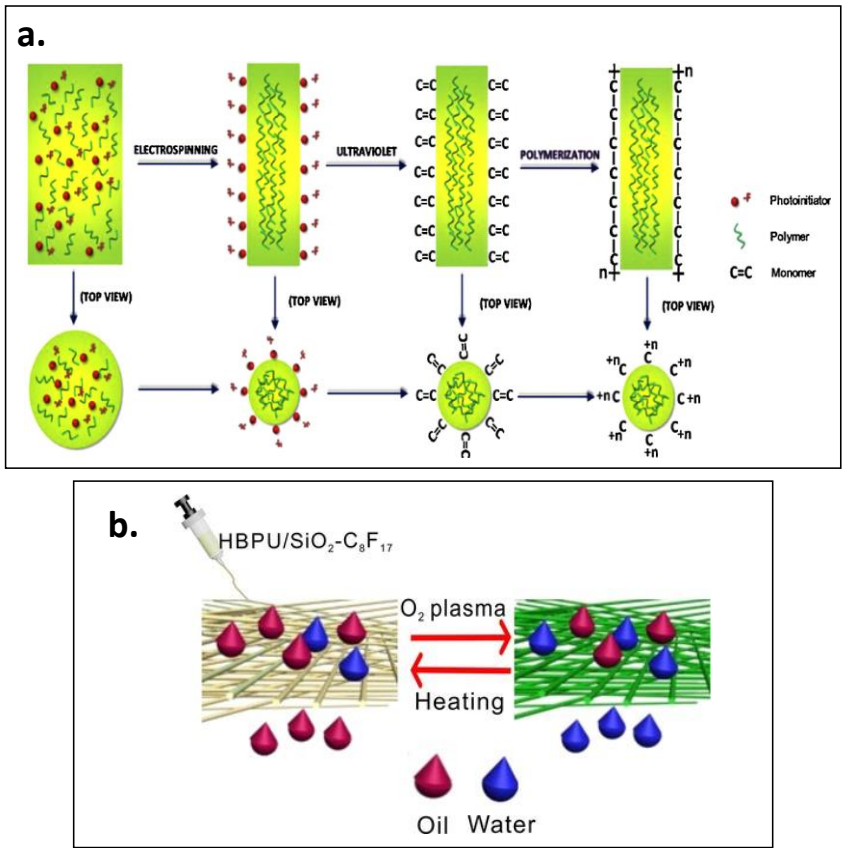

Figure 17. Schematic illustration of surface modification of non-fluorinated electrospun membranes. a. Photo-sensitive core-shell PAN/tripropylene glycol diacrylate nanofibers having fluorinated photo-initiator on the shell, subjected to UV-induced graft polymerization on the surface. Adapted with permission from ref [190]. b. HBPU (hyperbranched polyurethane)/F-SiO_2 (fluorinated silica) composite electrospun membranes with tunable wettability. Adapted with permission from ref [192].

In another study,[192] the plasma treatment was employed to increase the wettability of electrospun membranes. In fact, superhydrophobic membranes of hyperbranched PU with fluorine-modified SiO_2 nanoparticles were fabricated. The plasma treatment can change

the surface chemical composition of the membranes, leading to a superhydrophilic behavior. By heating the membrane at 30 °C for 6 h, the surface can switch back to superhydrophobic. The durability of the fabricated membranes was controlled over 7 cycles and the superhydrophobicity lasted up to a WCA of 148 °. Such membranes with tunable wettability showed high efficiency in separation for oil in water or water in oil emulsions (Figure 17b).

Also fluorinated fibrous membranes can be subjected to different treatments to modify and further improve their properties. For instance, Yadav et al.[198] prepared superhydrophobic PVDF electrospun membranes by inducing a hierarchical surface roughness thanks to silica nanoparticles and then performing a two-step post-modification.

5. Applications of fluorinated electrospun materials

Fluoropolymers have been electrospun to form original materials involved in various advanced applications, presented in this section.

5.1 Filtration

5.1.1 Water treatment

Membrane distillation (MD) technique is based on a thermal separation process:[199, 200] the porous membrane is placed between a hot flux and a cold permeate, allowing only the vapor molecules to pass through it (Figure 18a).[201] In MD technique, a microporous hydrophobic membrane is used for the separation of non-volatile solutes from liquid streams. The optimal vapor transport through the membrane is the main objective of the membrane design, although the hydrophobicity is vital for such

structures. The main MD membrane features are thickness, porosity, pore size and pore size distribution, tortuosity, hydrophobicity, thermal conductivity, and liquid entry pressure (LEP). The LEP, which is defined as the pressure that water should overcome in order to penetrate into the membrane, should be as high as possible to prevent the membrane from wetting. Two approaches for improving LEP aim at increasing the hydrophobicity of the membrane and decreasing the pore size (with uniformly distributed pores).[200] Moreover, the membrane fouling is a matter of concern: this phenomenon is defined as the accumulation of unwanted foulants on the membrane surface or inside its pores, thus hindering the permeate flux and/or degrading the membrane functionality, for instance by lowering its hydrophobicity.[200]

Electrospinning has attached significant importance as a method to improve the MD efficiency, i.e., enhancing the permeate flux and tackling the fouling problem. By electrospinning technique, the production of thin membranes embracing excellent properties such as high porosity and pore interconnectivity as well as high specific surface area and high strength-to-weight ratio is feasible. Furthermore, properties such as thickness, fiber diameter, porosity and membrane functionality can be tailored by changing and optimizing the electrospinning parameters. Aside from the material intrinsic wettability properties, electrospun fibrous membranes exhibit a higher hydrophobic characteristic, in comparison with conventional flat membranes, due to their rougher surface. It should be pointed out that, although the progress in preparation of superhydrophobic membranes for MD application through electrospinning is promising, the concerns regarding durability and robustness, mechanical stability, and simplicity of preparation still need to be addressed.[87, 202]

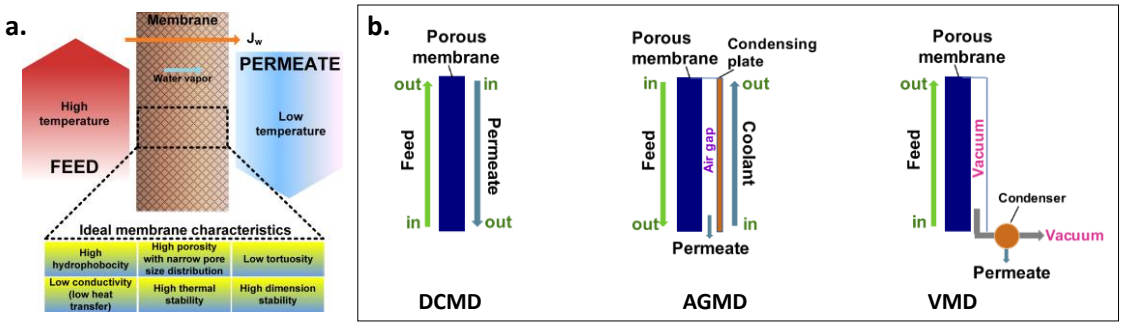

Figure 18. a. Membrane distillation principle. b. Schematic representation of direct contact membrane distillation (DCMD), air gap membrane distillation (AGMD), and vacuum membrane distillation (VMD) configuration. Adapted with permission from ref [200].

Thanks to its aforementioned properties such as high thermal stability, high chemical resistance, and quite low surface energy, PVDF is a popular choice for MD membranes. Up to now, it is the most studied material prepared by the electrospinning for MD applications. However, pure PVDF in the form of fibrous mat does not provide sufficient hydrophobicity and mechanical strength for long term operation required for MD. Consequently, further modifications such as the incorporation of nanofillers are necessary.[97] PVDF-based electrospun membranes have been proposed for direct contact membrane distillation (DCMD), air gap membrane distillation (AGMD), in which the conduction heat loss from the membrane is reduced by introducing an air gap between the membrane and the condensing plate, and vacuum membrane distillation (VMD), in which the vapor permeate is kept under vacuum and the membrane is placed between the hot feed and a vacuum chamber (Figure 18b).[203]

Hereafter, some studies on electrospun nanofibrous membranes made of PVDF or VDF copolymers for DCMD are reported. For instance, the pore wetting issue of PVDF electrospun nanofibers was assessed by adding different Cloisite clay amounts.[204] The membrane with 12 wt.% of clay exhibited no flux decrease (meaning no pore wetting) throughout the DCMD measurement. Similarly, the salt rejection did not drop during the 8 hr-test for the membranes with the highest clay amount.[204] Also silver nanoparticles,

which were deposited onto PVDF fibrous membranes, enhanced the DCMD performance of the fluorinated material.[205]

In addition, multilayer composite structures have also been developed for DCMD applications. PVDF electrospun membranes modified by hydrophobic surface additive macromolecules and PVP were fabricated and combined with a cast membrane: the composite structure displayed enhanced DCMD performance for 48 h.[206] In another work,[207] two dual-layer composites for water treatment application were designed. The former was a support layer of porous PVDF electrospun membrane with a thin layer of PVDF/ SiO_2 nanocomposite nanofibers deposited on top. It is worth noting that SiO_2 was modified by α,ω-bis(triethoxysilane)-terminated perfluoropolyether ($(EtO)_3Si$-PFPE-$Si(OEt)_3$) to be hydrophobic. The latter was a commercially available nonwoven support layer on which the PVDF/SiO_2 nanofibers were deposited. 40 hr-DCMD-test indicated a stable flux for both membranes. The modified SiO_2 fillers enhanced the anti-wetting properties and increased the membrane hydrophobicity.

P(VDF-*co*-HFP) electrospun membranes have also been proposed for application in DCMD. Lalia et al.[65] tuned the electrospinning parameters to optimize the nanofibrous structure. After electrospinning, a hot-pressing post-processing was performed in order to enhance the pore size and the pore distribution, as well as the membrane thickness. The efficiency of the membranes in DCMD applications was confirmed by monitoring the LEP. The same authors used nanocrystalline cellulose as filler for P(VDF-*co*-HFP) electrospun and hot-pressed nanofibrous membranes. The final product exhibited enhanced mechanical properties alongside high flux rate and salt rejection.[208] Such a P(VDF-*co*-HFP) copolymer was also employed for the fabrication of multilayer structured membranes. For example, a dual layer membrane was composed of a thick layer (60 μm) of P(VDF-*co*-HFP) electrospun fibers as substrate and a thin outer layer

(20 μm) of PVDF/CNT.[87] The presence of CNT increased further the surface roughness leading to higher WCA in comparison with the pristine P(VDF-*co*-HFP) electrospun membrane. Moreover, better flux performance and salt rejection than those of a commercially available PVDF membrane were observed.

Regarding AGMD applications, PVDF electrospun membranes containing superhydrophobic modified Al_2O_3 nanoparticles were developed [203] and proposed for heavy metal removal (particularly Lead) from wastewater. The membranes had a higher WCA (150 °) compared to that of pristine PVDF fibrous membrane and to commercially available PVDF membrane, and displayed a comparable LEP, as well as a higher heavy metal rejection for 6 hr-experiment (>99%). In another work, a dual layer hydrophobic/hydrophilic fibrous membrane for application in AGMD was investigated:[209] the top layer (or active layer, in the feed side) was made of P(VDF-*co*-HFP) electrospun fibers while the back side (permeate side) was composed of hydrophilic nanofibers of either PAN, Nylon-6 or PVA. After electrospinning, the dual membranes were subjected to heat-press post-treatment in order to improve their mechanical and physical properties. The P(VDF-*co*-HFP)/Nylon-6 membrane demonstrated the best AGMD performances.

It is well-known that PTFE is more hydrophobic than PVDF,[1, 24] but due to its challenging solubility and processability for electrospinning, this perfluoropolymer has been less studied than PVDF in the form of electrospun membrane for MD applications. However, in recent years, electrospun PTFE systems have attracted a growing interest, as they can be obtained by emulsion electrospinning and sintering, or by co-axial electrospinning. The challenges in MD design are to reach high hydrophobicity, high porosity, sufficient strength, as well as durable wetting repellency. Electrospun PTFE membranes can thus be an excellent option and, as an example, they can be produced by

hollow fibers through emulsion electrospinning (PTFE/PEO) and sintering.[142] The effect of the sintering temperature on both the mechanical properties and the fibrous morphology was investigated. Such membranes showed enhanced permeate flux (3.2–11.6 times higher) in comparison with commercially available PTFE hollow fiber membranes.

Moreover, membranes made of both PVDF and PTFE were studied for VMD applications. PVDF/PTFE nanofibrous membranes were deposited onto a PTFE microporous substrate through blend solution electrospinning.[210] The fabricated membrane (with PVDF/PTFE ratio of 15/12) exhibited superhydrophobicity, stable distillation performances for 15 h, and high salt rejection (>99.99%).

5.1.2 Oil/water separation

The principle of a membrane for oil/water separation is very simple: the membrane acts as a semipermeable film that allows water (or oil) to wet the surface and flow through, while it catches the other liquid. Electrospinning of both PVDF and PTFE has been proposed for the fabrication of fluorinated membranes for oil/water separation. Such membranes are generally superhydrophobic and superoleophilic, allowing oil droplets of an oil/water emulsion to be removed by passing through the membrane.[211]

PVDF electrospun membranes with different fiber diameters (and thus surface roughness) were demonstrated to be superhydrophobic and superoleophilic by Zhou et al.,[212] and were tested with a surfactant-free water and oil emulsion. Without any external driving force, the emulsion was efficiently separated. In another work,[213] PVDF electrospun membranes modified with superhydrophobic silica nanoparticles resulted in excellent water/oil separation efficiency (99 %) under multiple cycle performance (Figure 19). Instead, Mehranbod et al.[214] proposed a PVDF-based electrospun membrane with

superhydrophilicity (WCA=0 °) and under water superoleophobicity (oil contact angle ~154 °). The highly hydrophobic PVDF electrospun membranes were modified with a chitosan-graphene oxide nanostructured coating in presence of glutaraldehyde. The modified membranes showed high water/oil separation efficiency (>99%), high anti-fouling properties and reusability.

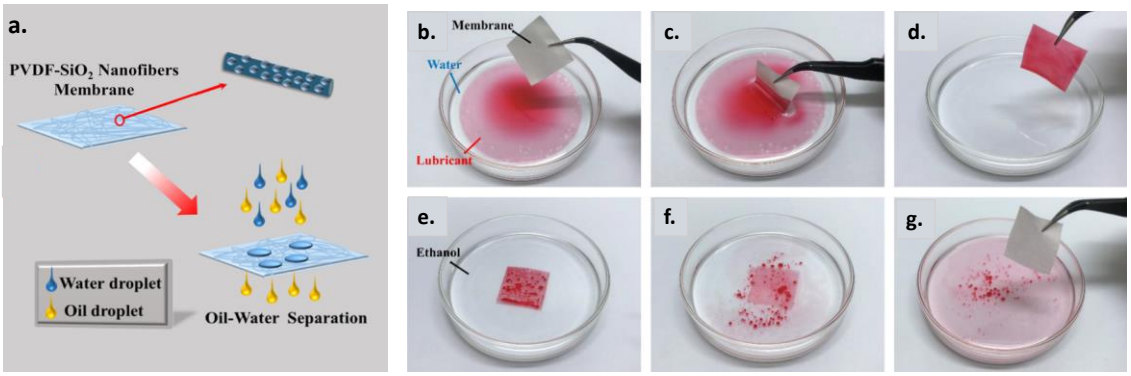

Figure 19. a. Schematic representation of PVDF-SiO_2 nanofibers membrane for application in water/oil separation; b–d. absorption of lubricating oil (in red, dyed with Sudan IV) in water, and e–g. recovery of PVDF-SiO_2 nanofibers membrane in ethanol. Adapted with permission from ref [213].

An example of a superhydrophobic and superoleophilic electrospun PTFE membrane for oil/water separation was instead reported by Qing et al.,[141] who fabricated the PTFE fibers by emulsion PVA/PTFE electrospinning, followed by a sintering treatment. In another work, PTFE/ZnO composite electrospun membranes, prepared through emulsion electrospinning and sintering, were examined for oil/water separation application. By tuning the ZnO quantity, superhydrophobicity could be obtained (WCA up to 160.1 °), and the fluorinated membranes exhibited excellent separation efficiency.[215]

A pH sensitive PVDF-*graft*-PAA electrospun membrane for water/oil separation was also developed,[216] based on the fact that the protonation/deprotonation of PAA in response to pH can alter the wettability properties of the membrane. This switchable wettability was assessed in gravity driven separation and its efficiency was evidenced. Additionally, the results revealed the reversibility of the transition for this smart membrane.

5.1.3 Air filtration

Fluorinated electrospun nanofibrous membranes have been actively explored as advanced filters for removing pollutants, such as particulate matters (PMs) in a liquid or solid form, toxic ions, and organic molecules, from air. In fact, the high porosity, good interconnectivity, micrometer-sized interstitial space, and large surface-to-volume ratio make electrospun mats superior membranes for air filtration. Electrospun membranes made from PTFE or PVDF led to several studies. For instance, a thin layer of PTFE electrospun fibers, obtained from emulsion electrospinning and sintering, on a PTFE microfiber substrate showed improved hydrophobicity and filtration efficiency for PM2.5 and PM7.5 (i.e., particles with aerodynamic equivalent diameters less than 2.5 and 7.5 μm, respectively), compared to the uncoated PTFE substrate.[217] Moreover, Mazhar et al.[147] proposed PTFE-ZnO composite electrospun membranes for VOC adsorption and for PM filtration. In particular, the membranes had an enhanced VOC adsorption ability (up to 20 % higher) compared to that of pure PTFE.

Regarding electrospun PVDF, fibrous PVDF/Ag/Al_2O_3 composites were used for special filters,[91] demonstrating high antibacterial properties (>99.0%) thanks to silver nanoparticles, and purification characteristics. In fact, detoxification studies revealed that by increasing Al_2O_3 particles content, the paraoxon concentration (i.e., the investigated chemical pollutant) decreased. In addition, these membranes showed good permeability with proper pore size and high particulate filtration efficiency.

An interesting work describes the application of a PDMS/PVDF electrospun fibers coating on a macroporous Al_2O_3 support, and the use of this structure for CO_2 absorption.[218] The composite membrane exhibited good mechanical properties, and

was subjected to a functionalization with fluoroalkylsilane (FAS) in order to further enhance its hydrophobicity. In practice, CO_2 passes through a hydrophobic membrane from one side and is absorbed by an aqueous amine solution flow on the other side of the membrane. To maintain the CO_2 flux as high as possible, the membrane should be water repellent, otherwise the CO_2 absorption would be reduced in wetted membrane. The results demonstrated that the fabricated membrane exhibits high CO_2 absorption capacity (1.5 mmol/m^2 s) with high durability and reusability and can be promising for large-scale CO_2 absorption applications (Figure 20).

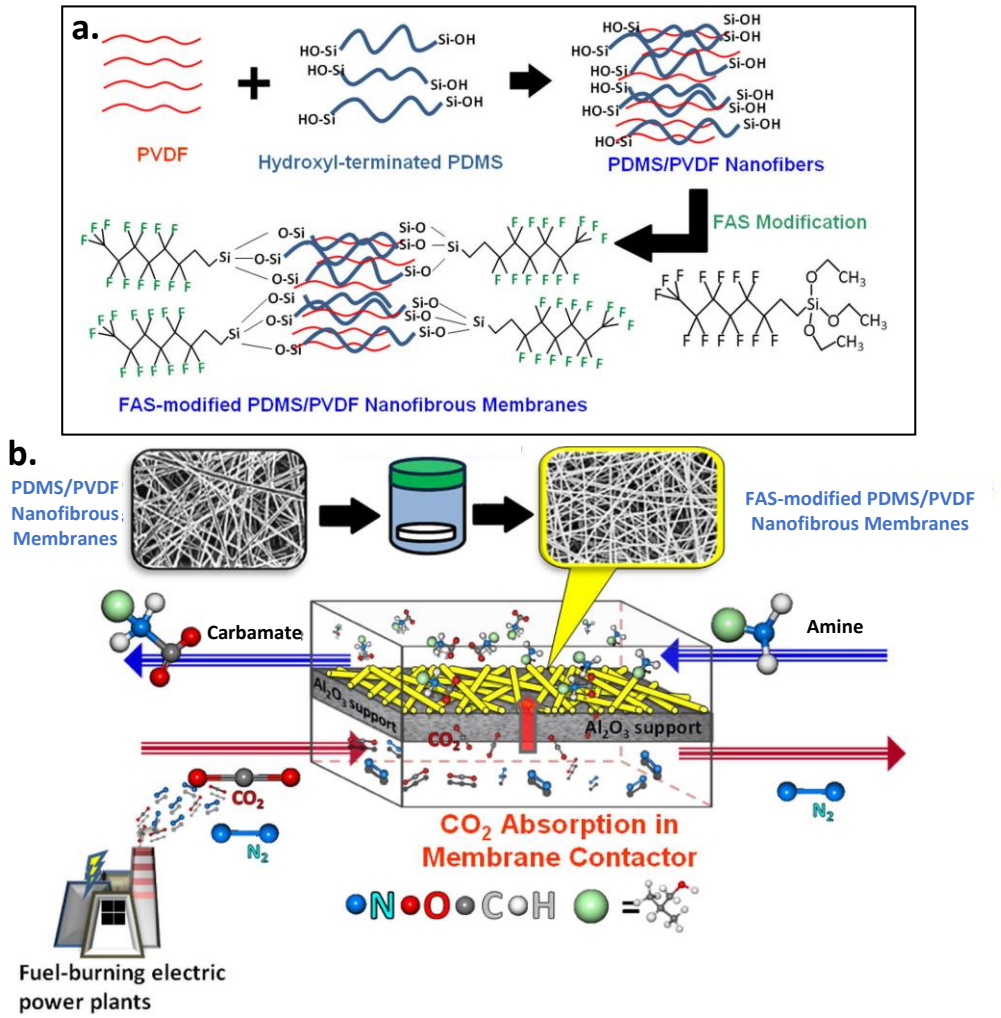

Figure 20. a. Schematic representation of FAS-modified PDMS/PVDF nanofibrous membranes preparation, b. CO_2 gas absorption in the hydrophobic membrane contactor. Adapted with permission from ref [218].

In this particular era, due to COVID-19 pandemic, face masks are essential part in our daily lives. Correspondingly, Shen et al.[219] investigated the use of PVDF-based electrospun membranes for application in personal protective equipment (PPE) as air filters for airborne transmission of SARS-CoV-2. In fact, a much smaller pore size of electrospun membranes compared to surgical masks makes these ultrafine fibrous structures appealing for PPE. In this work, PVDF electrospun fibers were deposited on a layer of polypropylene (PP) fabric and, in order to induce virus removal by electrostatic forces, a negatively or positively charged polyelectrolyte (i.e., poly(vinylphosphonic acid) and poly(ethyelenimine), respectively) was coated on the PVDF electrospun layer. The customized aerosolization setup presented in the work showed capturing of 99% of Coronavirus aerosols, thus the filters performed better than many commercial face masks.[219]

5.2 Superhydrophobic coatings

A surface is identified as superhydrophobic if it exhibits high WCA (>150 °) and low contact angle hysteresis (<10 °) as well as low sliding angle (<5 °). Superhydrophobic surfaces have versatile applications in the coating field, such as water-resistant, anti-fogging, anti-corrosion, self-cleaning, and anti-biofouling coatings.[220] Hereafter, some examples of applications of electrospun fluoropolymers (mostly PVDF) as superhydrophobic coatings are presented. Fluorinated electrospun membranes can be used as coatings exploiting their low surface energy, which is peculiar of fluoropolymers and/or can be achieved by using fluoropolymers as surface modifiers as described above. Moreover, electrospinning is a suitable technique for producing fluorinated superhydrophobic surfaces exhibiting the petal effect, thus characterized by a high water adhesion behavior, for instance by using hyperbranched FPU [173] and FPI.[181]

In general, the hydrophobicity of electrospun mats can be improved with the addition of nanofillers. For instance, it was demonstrated that, by increasing the nanoparticle content in epoxy siloxane modified SiO_2/PVDF electrospun fibers, the hydrophobicity was significantly improved.[90] In particular, the SiO_2/PVDF system in 5/1 ratio exhibited the highest WCA of 161 °.

PVDF is a commonly used polymer for anti-corrosive coatings, because of its excellent anti-oxidation and anti-corrosion properties,[34] thermal and chemical stability, and mechanical strength. Having a WCA of ca. 85 °, further modification for decreasing the surface energy of PVDF is crucial for anti-corrosive coating applications. In fact, for long-term durability, superhydrophobic anti-corrosive coatings should embrace both micro and nanostructured roughness as well as low surface energy compounds.[32, 221] Cui et al.[221] proposed electrospun PVDF/stearic acid (SA) mats as anti-corrosive coatings for different metal substrates. This PVDF/SA fibrous material was superhydrophobic (WCA=155 ° with a sliding angle of 5 °). This feature was attributed to the lower free surface energy of SA and to the higher roughness of the fibrous surface. In another study,[222] superhydrophobic PVDF/ZnO electrospun composite coatings for Al substrate displayed a higher corrosion resistance compared with bare Al as well as with Al coated by solely electrospun PVDF. Such a higher performance was due to the higher hydrophobicity of electrospun composite coating: as expected, ZnO enhanced the hydrophobicity by decreasing the pore size and increasing the trapped air on the surface. Moreover, the ions penetration was hindered through the coating because of the pores generated by the inorganic filler at the surface.

5.3 Textile and sportwear

Electrospun fluorinated membranes (especially made of PVDF) with high resilience, excellent stability, intrinsic hydrophobicity and low free energy have received huge interest for applications in functional, waterproof and breathable garments.[223, 224]

With the aim of obtaining two critical comfort-related properties in sportwear, namely thermal balance and low friction, Dong et al.[188] designed a two layered composite mat. The inner layer, which is in contact with the body, was composed of thin PAN/PVDF electrospun fibrous structure fabricated by single spinneret electrospinning, whereas the outer layer was a thick cellulose acetate fibrous film. As expected, the PAN/PVDF fibers evidenced a core-shell structure, in which the PVDF tends to go toward the surface, while PAN stays in the core part of the fibers. Accordingly, the core-located PAN and some PAN residue on the fiber surface improves the wettability of PVDF and facilitates the moisture transport from the skin towards the thick hydrophilic cellulose acetate layer. Indeed, this moisture movement is problematic through pure PVDF membrane due to its poor wettability. Besides, the PVDF exhibited a very low friction coefficient favoring the comfortability of the textile.

Electrospun membranes can also be used in developing wearable electronics for harvesting biomechanical energies. Biomechanical motions, such as finger motion, body shaking or walking-related motions, are renewable energy sources that can be turned into electricity through a wearable triboelectric nanogenerators (TENG). Li et al.[225] designed a breathable and wearable TENG made of PVDF nanofibrous membrane for harvesting the body motion energy (Figure 21). Such a multi-layer device consisted of a supporting PMMA layer, an electrospun layer of PDMS-modified-PVDF and an electrospun PAN/PA6 layer, attached to the copper electrode layers on both sides. The designed TENG, with an effective area of 16 cm^2, can produce an output current and a

voltage up to 110 µA and 540 V, respectively, just by tapping a finger. This wearable, self-powered, flexible TENG system is proposed for application in thermometer, electronic watches and LEDs that can accompany a sportwear.

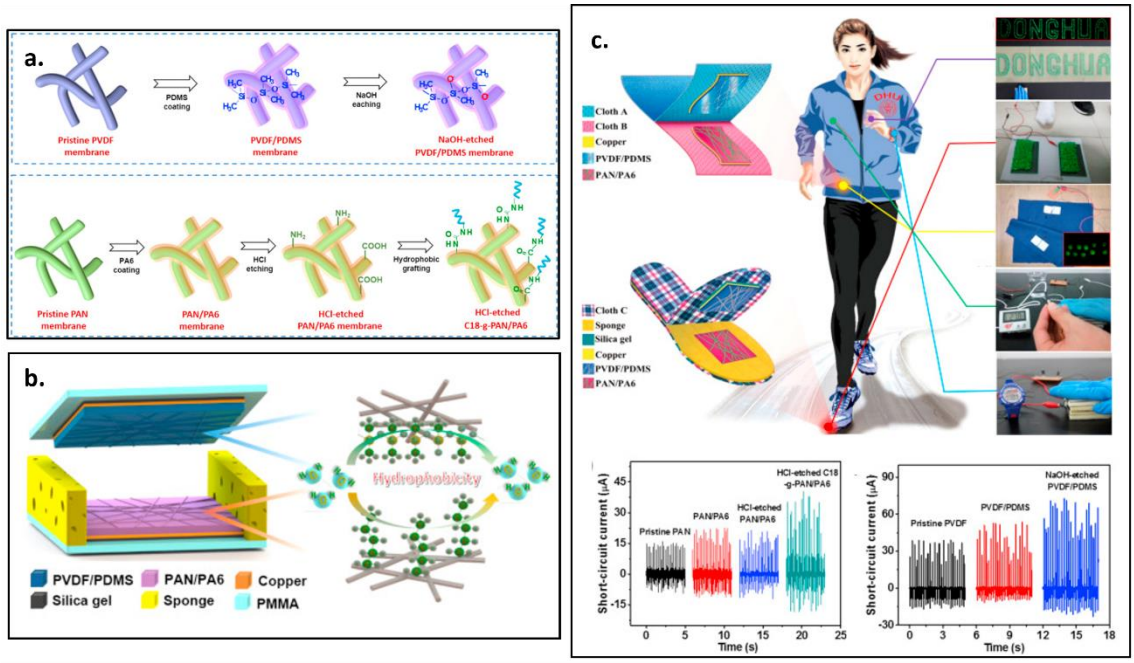

Figure 21. Schematic representation of: a. surface modification of PVDF and PAN electrospun fibrous layers, b. the designed triboelectric nanogenerator (TENG) made of electrospun layers. c. Examples of applications of constructed wearable TENG in sportwear. Adapted with permission from ref [225].

5.4 Energy applications

5.4.1 Li-ion batteries (LIBs)

Conventionally, rechargeable LIBs consist of three functional components: two solid electrodes, namely anode and cathode, and an electrolyte as a liquid medium (Figure 22a).[226] The Li-ions travel between both electrodes through the electrolyte, which is composed of the lithium salts dissolved in a solvent (or multiple solvents). Alternatively, gel polymer electrolytes (i.e., *quasi*-solid state systems formed by a polymer soaked in a liquid electrolyte) have been proposed as more stable and safer alternatives.

5.4.1.1 Liquid electrolytes

The Li-ions in the electrolyte pass through a porous membrane, which is the separator between both electrodes. This membrane isolates the electrodes and prevents from the possible physical contact between them.[227] Required properties for designing a separator are: i) structural properties (including thickness, porosity, pore size distribution, tortuosity, and anti-shrinkage, and structural stability); ii) physico-chemical properties, such as chemical and electrochemical stability, fire resistance, thermal stability, electrolyte wettability and mechanical properties; and iii) functional properties (e.g., ionic conductivity, electrical resistivity, air permeability, puncture stress and auto-shot down ability).[85, 227] Membranes obtained by electrospinning technique can be ideal candidates as separator, due to their properties such as high porosity, interconnected pores along the thickness, large surface area and high permeability. Although many advantages emerged from this technique, electrospun membranes suffer from weak mechanical properties and slow production scale.[85, 227]

PVDF is the most studied fluoropolymer as electrospun membrane, electrospun coating as well as cathode binder for application in LIBs as separator.[85] This polymer is in fact suitable for such application due to its chemical, electrochemical and thermal stability, as well as high affinity for Li-ions. The main drawbacks of PVDF are its high crystallinity, which causes low conductivity, slowdown of Li^+ ion transport, and its low mechanical stability when it is in form of fibrous membrane. Studies showed that the crystallinity and the mechanical properties of PVDF can be controlled by copolymerization of VDF with other comonomer(s) or by preparing composites through the addition of fillers.[85, 227] Generally, fillers can be classified into: i) active fillers, which directly participate in the conduction process and enhance ionic conductivity and Lithium-ions transport number, and ii) passive fillers, which do not directly participate in the conduction process.[228] Passive fillers, incorporated into PVDF and VDF copolymers electrospun matrices, are

inert ceramic oxides, such as SiO_2,[229, 230] Al_2O_3,[231] TiO_2,[232] and $AgTiO_2$,[233] ferroelectric ceramics with high dielectric constant, such as barium titanate ($BaTiO_3$)[234] and montmorillonite,[110] carbonaceous fillers (e.g., graphene, graphene oxide and CNT), and zeolites,[235] such as NaY.

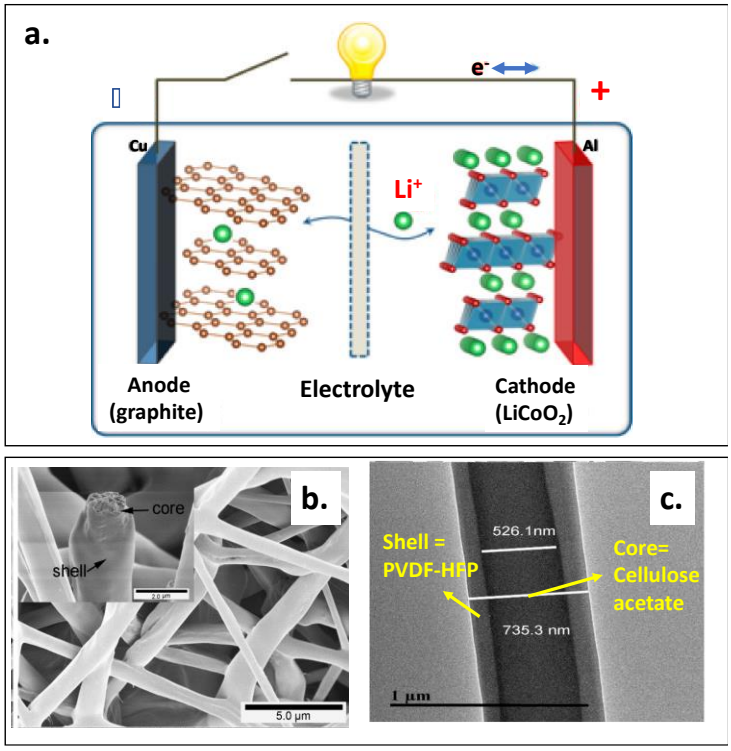

Figure 22. a. Scheme of a Lithium-ion battery. Adapted with permission from ref [226]. b. SEM and c. TEM images of co-axial cellulose acetate/P(VDF-*co*-HFP) core-shell nanofibers separators for LIBs. Adapted with permission from ref [132].

In the study presented by Huang and coworkers,[132] cellulose acetate/P(VDF-*co*-HFP) core/shell fibers were fabricated through co-axial electrospinning. The copolymerization of VDF with HFP enables to decrease the crystallinity of the resulting copolymer, leading to better properties for application as LIB separator. Moreover, $Li_{0.33}La_{0.557}TiO_3$ was added to the P(VDF-*co*-HFP) solution to obtain a filled shell (Figure 22b and c). Excellent thermal stability, improved electro-chemical performance and good electrolyte wettability, as well as decent mechanical properties, were obtained. Moreover, the electrospun membrane had lower interfacial resistance and higher ionic conductivity than Celgard® 2300 commercial separator. In another work,[230] SiO_2 particles were used to

enhance the adhesion properties between the fibers and decrease the PVDF crystallinity for better electrolyte uptake and higher ionic conductivity, which was found higher than that of conventional Celgard® 2400 membrane. Additionally, SiO_2 increased the heat resistance of the separator for tackling the safety issue of LIBs. Wang et al.[236] used Sb_2O_3 nanoparticles to improve the mechanical properties of electrospun membranes of P(VDF-*co*-CTFE). The composite electrospun systems, in addition to enhanced ionic conductivity, lower interfacial resistance and proper electrochemical stability compared to conventional polyethylene separators, also exhibited flame retardancy properties with excellent thermal stability and resistance to shrinkage.

As explained earlier, PVDF-based electrospun mats can be utilized as coatings, modifying substrates employed also for LIBs. For instance, commercial microporous PP Celgard® 2400 membrane was coated with P(VDF-*co*-HFP)/P(VDF-*co*-CTFE) blend electrospun fibers with different composition ratios.[63] For examining the coating adhesion (between the electrode and the separator), peel tests were performed showing a comparable adhesion for coated and uncoated separators. Besides, the thin electrospun coating enhanced the separator electrolyte uptake attributed to the gelation capability of PVDF as well as the higher porosity and capillary effect of electrospun fibers.

5.4.1.2 Gel polymer electrolytes

Liquid electrolytes suffer from relatively short durability and stability mainly due to volatility of organic liquid electrolyte, leakage and internal shortening. Accordingly, gel polymer electrolytes (GPEs), as *quasi*-solid state electrolytes, have received considerable attention as a substitute to overcome durability, stability and safety issues.[237] For this purpose, polymeric solid systems are soaked in a liquid electrolyte, which is absorbed, and these gel state electrolytes with proper ionic conductivity provide durability and mechanical integrity, suppressing the liquid electrolyte evaporation. Due to their

morphology, nanofibrous electrospun membranes are suitable to form GPEs. Fluoropolymers, being characterized by good electrochemical stability and affinity to liquid electrolytes, received significant attention as a matrix for GPEs.[238] Particularly, PVDF-based GPEs are an excellent choice for energy applications. Moreover, blending can be performed with the aim of enhancing the electrolyte uptake, the ionic conductivity and the electrochemical and mechanical properties, as well as lowering the crystallinity and the interfacial resistance. Accordingly, electrospun membranes of PVDF,[238, 239] P(VDF-*co*-HFP)[240] and PVDF blends such as PVDF/PAN,[241] PVDF/PVC,[73] PVDF/TPU,[242] and PVDF/PMMA [243] have been proposed as GPEs. The results presented in some of these works are summarized in Table 6.

For instance, Kim et al.[238] studied microporous electrospun PVDF membranes. Although in general the copolymer P(VDF-*co*-HFP) is preferred for its lower crystallinity, in this work, PVDF with a high crystallinity was chosen for its higher thermal stability. An ionic conductivity as high as 10^{-3} S/cm and a stable charge-discharge capacity were obtained for the fluorinated electrospun membranes. In fact, the ionic conduction is conveyed through the liquid electrolyte trapped within the interconnected porous electrospun fibers, and crystalline PVDF did not interfere with this phenomenon. In addition, by decreasing the average fiber diameter, the conductivity could be further enhanced. In another work,[244] a PVDF-based electrospun membrane filled with polyhedral oligomeric silsesquioxane-chloropropyl (POSS-$(C_3H_6Cl)_8$) and deposited onto a commercially available PP separator was proposed as GPE. The addition of POSS-$(C_3H_6Cl)_8$ enhanced the ionic conductivity, the cyclic performance, the charge-discharge capacity and the electrochemical stability of the membrane with respect to the PP separator. Moreover, the modified GPE displayed some flame-retardant characteristics.

Table 6. Main characteristics from the literature of fluorinated electrospun membranes as gel polymer electrolytes for LIBs.

Polymeric system	**Electrochemical stability by LSV[1] (V)**	**Ionic conductivity (mS/cm)**	**Resistance[2] (Ω)**	**Charge–discharge capacity ($mAhg^{-1}$)**	**Liquid electrolyte uptake (%)**	**Reference**
PVDF	~5	>1	R_b<0.3	~130 (at 25 °C and 60 °C)	320–350	[238]
PVDF	>5 (at 20 °C)	1.6–2.0	R_i~300 (after 28 days)		~350	[239]
PVDF/PMMA-TiO_2	5.1	3.9	R_b=1.15		342	[245]
TPU/PVDF 1/1	5	3.2	R_b=1.4	141.5–168.9	342	[246]
PVDF/PVC 8/2	5.1	2.25 (at 25 °C)	R_b=1.93	130.8–145.1	~290	[247]
PVDF-SiO_2 (7 wt.%)		4.7 (at RT)	R_b=1.1		500	[229]
PVDF- POSS-$(C_3H_6Cl)_8$	5.7	2.03	R_i=470	160.2 (at 0.1 C)	271	[244]
P(VDF-*co*-HFP)		2.7 (at 30 °C)		161.5 (at 0.1 C), 113.5 (at 3 C)	>200	[248]
P(VDF-*co*-CTFE) modified by Sb_2O_3	3.8	2.88	R_b=0.67	167 (at 1 C), 93 (at 32 C)	356 ± 10	[236]

[1]LSV: linear sweep voltammetry

[2]R_b: bulk resistance; R_i: interfacial resistance

Alternatively, ionic liquids (ILs) were incorporated into fluorinated electrospun mats for the preparation of polymer electrolytes.[249] ILs are in fact salts at the liquid state and are advantageous over liquid electrolytes by excluding volatile and flammable solvents and by having a high electrochemical and thermal stability. However, ILs need a host polymer to get immobilized. For instance, they were incorporated into electrospun mats of P(VDF-*co*-HFP).[250] In particular, the fluorinated copolymer was functionalized with sulfonic acid in order to enhance the proton conduction for diffusion of large cations. On the one hand, the sulfonic acid groups contribute to the proton conduction, while on the other hand they stimulate the IL dissociation, improving the electrolyte ionic conduction.

5.4.2 Lithium-metal batteries

Although LIBs were revolutionary in portable devices, new transportation means and grid sector, nowadays the graphite anode-based LIBs are reaching their theoretical limit and cannot meet the increasing demand in this new era. Thus, alternative battery designs with higher energy density are foreseen. In this regard, lithium-metal batteries (LMBs) are very promising: in fact, replacing the graphite anode by lithium metal results in the increase in specific energy and energy density (~35% and ~50%, respectively). However, this generation of batteries still suffers from several challenges, such as dendrite growth (leading to short circuit of the battery, sometimes borrowed by fire), corrosion of metallic Li, short lifetime and low columbic efficiency.[251–253] The dendrite outgrowth is mainly caused by the instability of the solid electrolyte interphase (SEI) on the lithium anode. A stable SEI limiting and preventing the dendrite formation can thus highly enhance the applicability of LMBs. In this regard, fluorinated SEIs are promising candidates, allowing both the modulation of the deposition of Li (homogenously) and the

increase in the safety of the batteries.[254] Hereafter, some examples of fluorinated electrospun systems used in LMBs are presented.

With the aim of addressing the dendrite growth issue, Dong et al.[255] designed an interface layer for LMBs using polysulfone/molybdenum oxide (MoO_3) composite electrospun fibers deposited on the Li anode. The hybrid electrospun interface (containing both organic and inorganic compounds) can provide the proper mechanical and elastic properties, and can also permit the uniform Li^+ ion flux thanks to its porosity. The authors showed that an optimum area density of polysulfone leads to lithium deposition underneath the fibrous layer acting as a solid interface (with dendrite-free morphology) rather than a lithium host (leading to stable increasing of resistance). The results revealed a high initial capacity (155 mAh g^{-1}), a high lifespan (600 cycles) and stable charge capacity (80% after 500 cycles).[255] Focusing on safety issues, Deng et al.[256] prepared a *quasi*-solid state three-dimensional network of PVDF-based GPE with flame-retardant properties through electrospinning and thiol-ene crosslinking. The addition of highly fluorinated carbonate plasticizers further improved the flame-retardant properties. Moreover, the fabricated network exhibited high ionic conductivity (4.41 mS/cm at 30 °C), restraining dendrite growth properties, good cycling performance and high specific capacity. Similarly, in another work,[257] a single-ion polymer electrolyte containing fluorinated polysulfonamide as plasticizer was fabricated by an *in-situ* thiol-ene crosslinking and was grafted on a PVDF electrospun membrane, used as a standing frame. The results demonstrated a significant increase of Li-ion transference number, approaching the unity (~0.9), with high electrochemical stability, high ionic conductivity (5.5 mS/cm at 28 °C) and long-term stability.

5.4.3 Dye sensitized solar cells (DSSCs)

DSSCs are conventionally composed of nano-crystalline titanium dioxide (TiO_2) photo-anode sensitized by a dye that acts as the photosensitizer, a counter electrode and an electrolyte separating the two electrodes. DSSC technology can be considered as an artificial photosynthesis process.[258] In general, electrospun materials have been utilized in photoelectrodes and electrolytes of DSSCs. In particular, fluorinated electrospun membranes have received considerable attention as GPEs for tackling the liquid electrolyte drawbacks such as leakage and volatilization.[259] For example, Bandara et al.[237] fabricated an electrospun P(VDF-*co*-HFP) GPE for application in DSSCs, and compared it with liquid electrolyte and conventional GPE. The electrospun GPE showed an energy conversion efficiency comparable to that of the liquid electrolyte (5.36% vs. 6.01%) and higher than that of conventional GPE (4.70%). Regarding the resistance value for charge transport and the durability (i.e., lifetime duration), the highest one was obtained for the conventional GPE, followed by the electrospun system and finally the liquid electrolyte.

In another work, the same P(VDF-*co*-HFP) was used to fabricate polymeric ILs by grafting of 1-butylimidazolium iodide with different molar ratios.[260] The polymeric ILs were prepared through electrospinning and were used as *quasi*-solid state electrolytes for DSSCs. The authors established a higher power conversion efficiency (~9.26%) and a better long-term stability over 1500 h compared to those of standard liquid electrolytes.

5.4.4 Fuel cell membranes

As stated in Section 3.3 Electrospinning of perfluorosulfonic acid polymers (PFSA), ionomeric Nafion™ membranes (as well as Aquivion™, Fumion™, Flemion™, 3M™Membranes) have been extensively studied for application in proton exchange membrane fuel cells (PEMFCs). Briefly, a PEMFC, as illustrated in Figure 23a,[261] is

composed of a gas diffusion layer, a catalyst layer (platinum for O_2-H_2 fuel cells), bipolar plates and a PEM, and is rechargeable. The H_2 and O_2 as supplied gases undergo oxidation and reduction, respectively, while the PEM separates the anode and the cathode. At the anode, the H_2 at the catalyst layer dissociates into two protons and two electrons, the protons pass through the PEM and the electrons flow in the outer circuit towards the cathode. The O_2 at the cathode side reacts with the protons and the electrons, hence releasing water and heat.[262] Generally, the recent research work on fuel cells is attributed to reduce the production costs by decreasing the catalyst Pt loading in the cathodes, while maintaining the performance of the fuel cells. Incorporation of Nafion™ as a proton conductor into the fuel cell structure can significantly reduce the Pt loading.[263] Additionally, the fluoropolymer can enhance the adhesion between the catalyst layer and the PEM, and reduce the interfacial resistance. For instance, Yoshino et al.[264] modified the catalyst layer of the fuel cell by Nafion™ electrospun fibers from a Nafion™/PEO blend solution and consecutive electrospray on the fibers of the catalyst ink containing Pt/C and Nafion™ (Figure 23b-e). The designed catalyst structure exhibited improved cell performances, meaning improved transport of oxygen and water as product in varying humidity and temperature (<80 °C).

In the study conducted by Park et al.,[265] the nanofiber composite membrane of Nafion™/PVDF was prepared for application in a H_2/Br_2 regenerative fuel cell. PVDF in this composite membrane reinforced the mechanical properties and controlled the Nafion™ fibers swelling. In addition, PVDF displays excellent chemical resistance against bromine degradation.[32, 34] In another study,[266] a simultaneous electrospinning/electrospraying process was used to form fluorinated PEMFCs. The electrospraying solution contained Pt/C catalyst and Nafion™, while the electrospinning solution was composed of Nafion™/PAA/PTFE mixture. The PTFE addition was aimed

at further reducing the Pt loading and also increasing the hydrophobicity of the membrane, favoring the mass transport. The proposed assembly showed improved fuel cell performance (evaluated by the polarization curve), even having only 1 wt.% of PTFE.

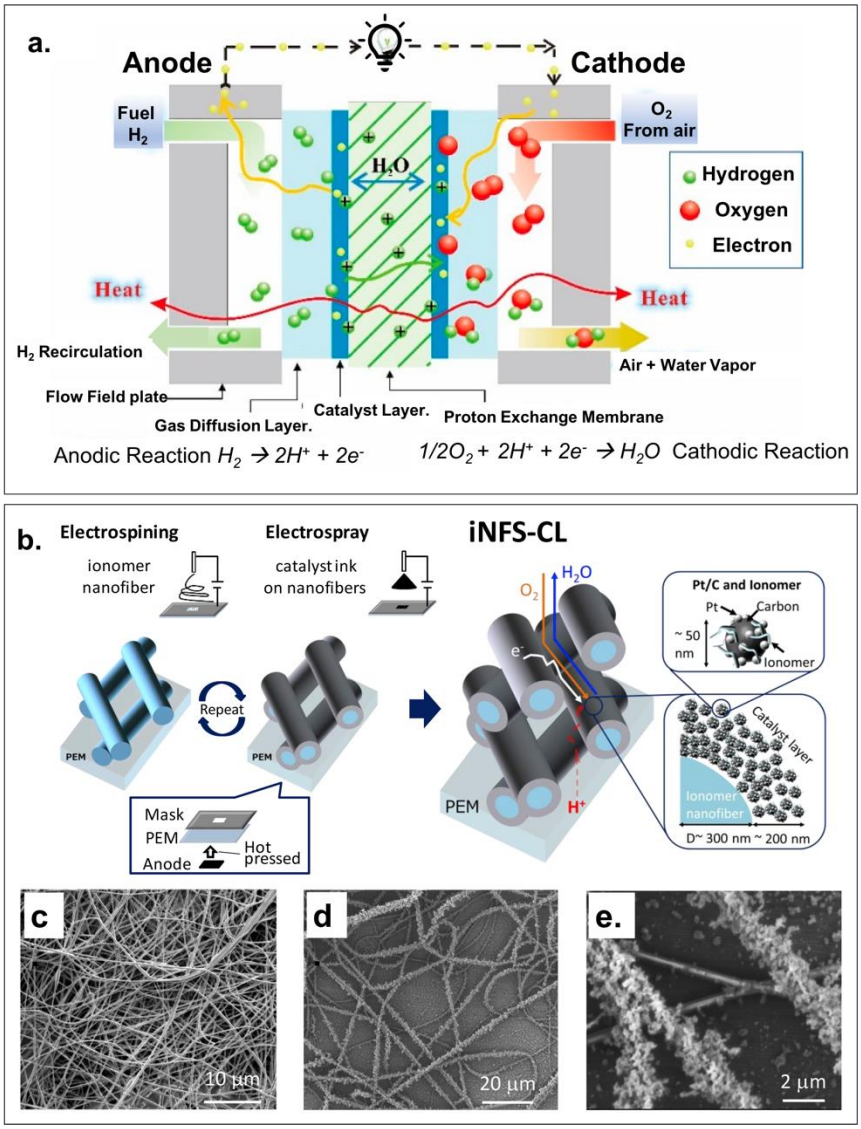

Figure 23. a. Scheme of a proton exchange fuel cell fueled by H_2. Adapted with permission from ref [261]. b. Schematic representation of the fabrication process and the structure of catalyst layers with ionomer nanofiber scaffolding (iNFS-CL); SEM images of: c. electrospun Nafion™ nanofibers, d. iNFS-CL, and e. catalyst particles separately electrosprayed onto aluminum foil. Adapted with permission from ref [264].

5.5 Sensing and electroactive applications

Fluoropolymers, particularly PVDF with its extraordinary characteristics, such as piezo-, pyro-, ferroelectric properties, accompanied by high deformability and chemical

resistance, especially in corrosive and harsh environment, are promising materials in transducers and sensors field.[36] However, PVDF in form of film is very rigid with low air permeability, which limits its application for flexible tactile force sensors. Additionally, PVDF films generally require electrical, mechanical or thermal treatment for improving the *β*-phase content.[66] On the contrary, electrospun PVDF-based systems, in addition to high *β*-phase content, are flexible and highly porous (breathable), tackling the aforementioned challenges. Therefore, PVDF and its copolymers in form of ultrathin fibrous membranes can be used as functional layers for dynamic tactile membranes. Their properties can be further improved by aligned fibers orientation and addition of nanofillers.[267] Generally, tactile sensors based on the sensing mechanisms are classified in several groups such as piezoelectric, piezoresistive, triboelectric, capacitive, and optical sensors.[267]

An example of PVDF-based flexible sensor is a pressure sensor made of P(VDF-*co*-TrFE) electrospun mat, with the fluorinated nanofibers wrapped by reduced GO (rGO) sheath, sandwiched between two PDMS thin films (Figure 24).[268] This sensor was proposed as an e-skin and wearable diagnostic device for real-time health monitoring. In particular, the sensor application in cardiovascular disease diagnosis or speech recognition was evaluated by following and monitoring the blood pressure, engaged muscle traction and movement. The results demonstrated a very fast response time (5 ms), ultrahigh sensitivity (15.6 kPa^{-1}) with low detection limit (1.2 Pa), low operating voltage (1.0 V), high stability and durability (over 100,000 cycles).[268]

The main drawback of PVDF sensors is the thermal interference: PVDF-based blends or copolymers (e.g., P(VDF-*co*-TrFE)) nanofiber materials are considered as ideal functional materials for flexible tactile sensors, thanks to their higher *β*-phase content,

better sensitivity, better stability and lower detection limit compared to those of pure PVDF electrospun materials.

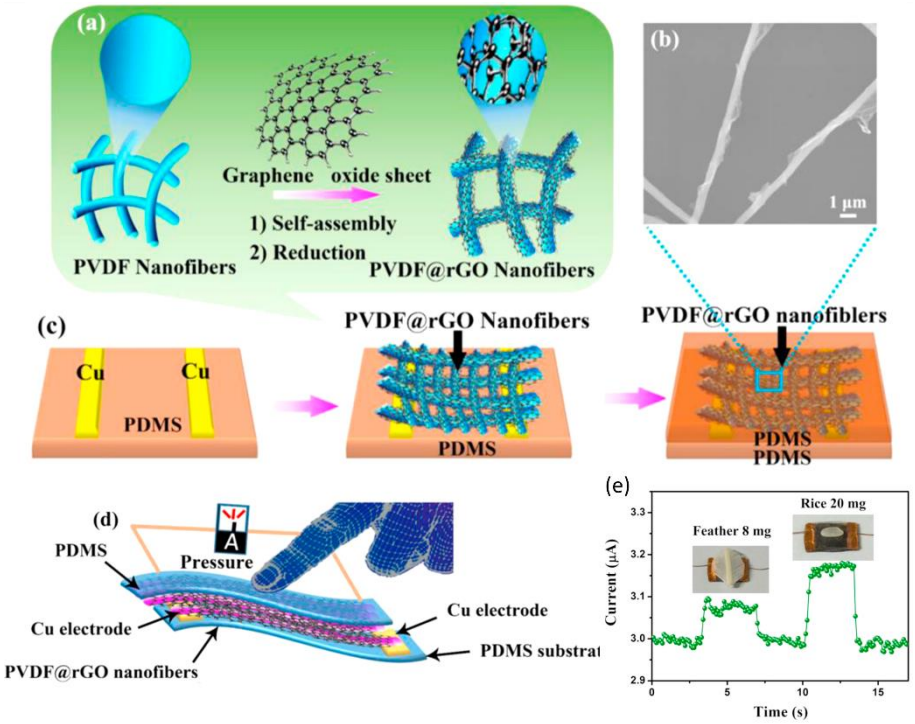

Figure 24. Wearable sensor based on PVDF nanofibers. a. Schematic illustration of the mechanism for the formation of PVDF fibers coated by rGO nanosheets, followed by electrostatic interaction; b. FESEM image of the rGO nanosheets coated PVDF fibers; c. schematic illustration of the fabrication of a flexible pressure sensor; d. schematic of a typical pressure sensor; e. transient response to the loading and removal of a feather (8 mg) and a rice (20 mg), the fronted corresponding to a pressure of only1.2 Pa. Adapted with permission from ref [268].

Energy harvesting from the biomechanical movements and our daily environment is a renewable and a sustainable source of energy that can be applied in powering a nano-, micro- and also mega-scale energy systems.[269] Fluoropolymers, particularly PVDF, are smart materials that can respond to a variety of stimuli (e.g., pressure, sound). Several examples of nanogenerators and actuators based on electrospun fluorinated systems are thus present in the literature.[54, 140, 270] For instance, Garain and coworkers [271] developed a highly sensitive, flexible pressure sensor based on Ce^{+3} doped PVDF/graphene composite nanofibers. Ce^{+3} was employed as CeO_2 is commonly used as an additive for lead-free ceramics to further improve their density and piezoelectric properties.[272] The proposed sensor could detect pressure as low as 2 Pa and could

generate an output voltage of 11 V and a current density of 6 nA/cm^2 by the application of a 6.6 kPa of pressure amplitude, which is comparable to the finger touch pressure.[271] This nanogenerator was suggested as a mechanical energy harvester and effective power source for wearable electronics. As another example, Ren et al.[273] developed a coaxial rotatory freestanding triboelectric nanogenerator (CRF-TENG) with PVDF electrospun membrane for wind energy harvesting (Figure 25). The PVDF membrane acts as triboelectric material based on the triboelectric or contact-induced electrification effect, in which potential differences due to opposite charge transfer are generated when two contacted triboelectric materials are separated. The developed wind energy harvesting unit was used for self-powered water splitting set-up for H_2 production, and an efficiency of 6.97 μL/min H_2 production was reported for a wind speed of 10 m/s.

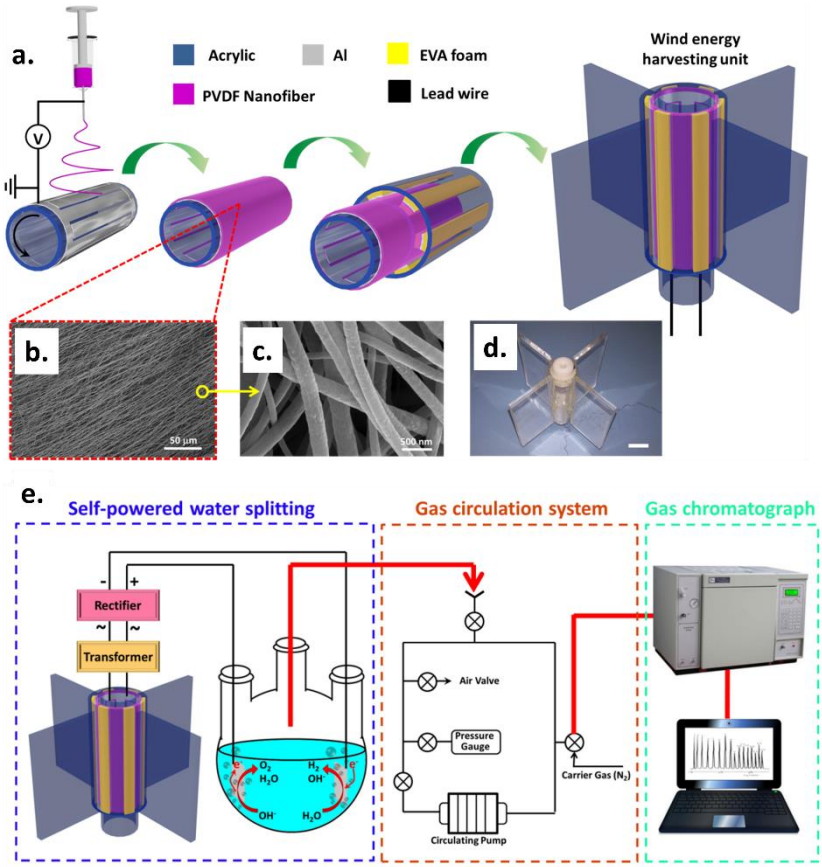

Figure 25. a. Sketch of the fabrication process of wind-energy harvesting set-up; b. and c. SEM images of PVDF nanofibrous membrane; d. photograph of the fabricated coaxial rotatory freestanding triboelectric nanogenerator (CRF-TENG) wind harvester; e. self-powered water splitting by fabricated CRF-TENG wind harvester. Adapted with permission from ref [273].

Electrospun PVDF membranes with high β-content and excellent piezoelectric properties are also promising for acoustic nanogenerators (i.e., the vibration and the friction generated from the sound waves after striking a material is converted into electrical energy by piezoelectric materials). The fibrous and porous membranes, with high available surface area and loose structure, are favorable for sound absorbing applications. Accordingly, electrospun PVDF and PVDF/CNT nanofibrous membranes were developed for such application.[274] Actually, PVDF-based fibrous materials have a higher sound waves absorption capacity in the middle-frequency region (315–1250 Hz) compared to PVDF films, because of a larger surface area, as well as in the 50-250 Hz low frequency region. Particularly, the electrospun PVDF/CNT composite absorbs sound waves in lower frequencies and reached the highest absorption coefficient at 100 Hz. This sound absorption enhancement can be attributed to the addition of CNTs, able to further improve the piezoelectricity of electrospun fibers through interfacial polarization.

5.6 Biomedical applications

In addition to the above-mentioned properties, PVDF and other fluoropolymers exhibit biocompatibility, and thus can be potential candidates for biomedical applications.[9, 275, 276] Moreover, many fluoropolymers, including PVDF and PTFE, are bio-inert (i.e., inert to biomolecules such as proteins or cells), thus suitable for different medical applications.[277] The main drawback of solution spinning of fluoropolymers is the toxicity of the solvents, which can negatively affect the cell viability and proliferation. Moreover, as conventional electrospinning produces only 2D structures, complicated processes (e.g., coupling of electrospinning and bioelectrospraying or cell layering) have to be developed to fabricate 3D scaffolds.[278]

Electrospun PVDF and P(VDF-*co*-TrFE) copolymer have been particularly studied in bone and neural tissue engineering.[57, 279] Piezoelectric scaffolds in bone tissues, by experiencing mechanical stresses, can induce charges and promote the bone regeneration, while in neural tissue can stimulate the neurite outgrowth and regeneration in response to electrical pulses.[9, 280]

In the work of Arinzeh et al.,[281] scaffolds for neural tissue engineering were fabricated from annealed electrospun P(VDF-*co*-TrFE) copolymers. The thermal treatment was performed in order to enhance the *β*-phase content. Both scaffolds with randomly oriented and aligned fibers were investigated, and the P(VDF-*co*-TrFE) scaffolds were demonstrated to be compatible with neuron cells. In particular, compared to PVDF and P(VDF-*co*-TrFE) films, P(VDF-*co*-TrFE) electrospun scaffolds displayed enhanced cell adhesion and neurite outgrowth. The cellular interaction with the substrate during the adhesion can induce some extent of deformation to the scaffold and the subsequent piezoelectric response can trigger the nerve tissue regeneration.

Another application field of fluorinated electrospun mats deals with vascular tissue engineering. Augustine and coworkers [282] investigated nanocomposites electrospun systems made of P(VDF-*co*-TrFE)/ZnO: human endothelial cells led to higher cell viability and proliferation on the composite electrospun scaffolds, compared to control plates and neat P(VDF-*co*-TrFE) scaffolds (without filler addition). Interestingly, the angiogenesis was also improved *in vivo* after implantation in rats.

Moreover, electrospun fluorinated membranes can find application in skin tissue engineering [52] and wound healing (Figure 26). For instance, electrospun scaffolds of PU/PVDF blends of different compositions were examined and the 1/1 ratio demonstrated the optimum balance of mechanical and piezoelectric properties.[81] The piezoelectricity arising from mechanical bending and deformation (i.e., from body movement) could

stimulate the fibroblast activities in both set of *in vitro* and *in vivo* experiments, leading to a pronounced wound healing activity.

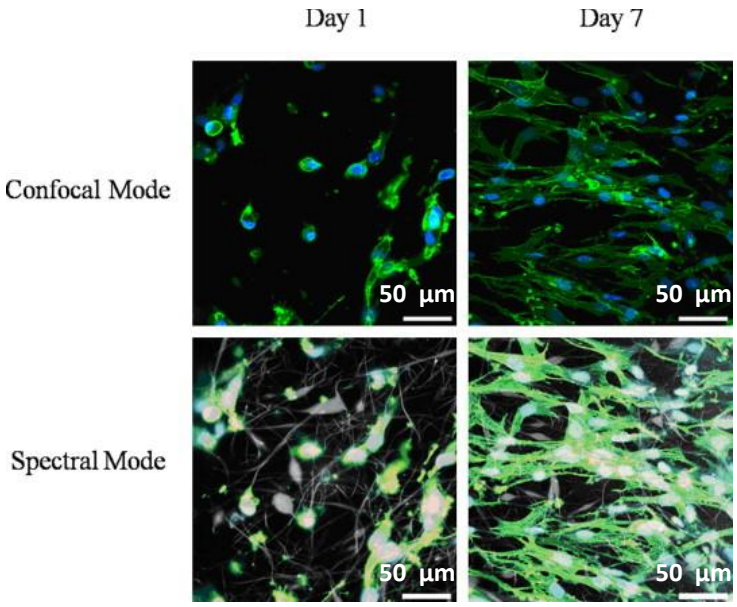

Figure 26. Confocal fluorescence microscopy images of human skin fibroblasts growth on the PVDF-*co*-TrFE electrospun scaffold after 1 and 7 days of cell culture (cytoskeleton, green color; nucleus, blue color). Adapted with permission from ref [52].

Fluorinated electrospun membranes have also been used in drug delivery systems in both passive and active controlled release approaches.[275] Drug-loaded wound dressings made of PVDF-based electrospun membranes have been developed to control the sustained release of therapeutic agents.[283–285] As the surface energy of PVDF can be a barrier for its functionality in aqueous medium, the grafting of PVDF with a hydrophilic polymer has been proposed as viable solution.[286] Fluoropolymers can also serve as a platform for specific drug targeting responding to different stimuli (e.g., mechanical, electrical, magnetic responses to magnetoelectric or piezoelectric effects).[287] Fluorination of electrospun fibers in order to restrict the initial burst of the drug release and enhance the long-term release is also reported in the literature.[194]

5.7 Photocatalyitic applications

Photocatalyst particles (e.g., TiO_2, CdS, Fe_2O_3) can generate electron-hole pairs and consequently charge carriers by absorbing light. Therefore, they are used in different environmental applications, such as for pollutant degradation and water splitting. Photocatalyst powders easily aggregate and degrade, hence limiting their applications. To address this issue, inorganic and polymers carriers are utilized. Among carriers, fluoropolymers, thanks to their thermal and chemical stability as well as their radiation resistance, are suitable as catalyst carriers. Moreover, the nanofibrous structure, by providing high surface area for superior enrichment, can further improve the photo-catalytic efficiency. Fan et al.[115] used the electrospun poly (HFBA-*co*-MAA)/PVDF as a carrier, and $ZnIn_2S_4$ as a photocatalyst is deposited onto carboxylic fluoropolymer fiber by a hydrothermal method. In another work, He et al.[75] proposed electrospun membranes made of poly(MAA-*co*-TFA)/PVDF as carrier for TiO_2 for photocatalytic activity. Both works showed decent photo-catalytic activity of such systems.

6. Environmental issues of fluorinated membranes

Although fluoropolymers are characterized by outstanding properties and regarded as polymers of low concern, they are normally environmentally persistent and can generate toxic byproducts, either from pyrolysis or from end-processes.[288] Albeit they have high molar mass and thus they unlikely can penetrate into cell membranes, their extreme persistence and both the emissions and the aid-processing associated with their production, use, and disposal can be a concern for environmental and human health.[288] Moreover, they generally need toxic solvents to be processed and consequently industrial scaling-up of these products is troublesome. Generally, during the processing of fluoropolymers, at elevated temperature, toxic gases can be generated. For instance, in

the case of PTFE, as the temperature reaches around 450 °C, carbonyl fluoride and hydrogen fluoride can be produced in air, and thus an adequate ventilation is required.[289]

In this section, some works suggesting the substitution of fluoropolymers are briefly described. In particular, fluorine-free superhydrophobic electrospun membranes have been developed. An example is an electrospun membrane of polybenzoxazine (PBA)/PAN, free of fluorine and silicon, exhibiting low surface energy with superhydrophobic behavior (WCA=154 °), high adhesion to water (due to the abundant hydrogen bonding between PBA/PAN and water), and anti-biofouling properties (Figure 27a-c).[290] In the work of Ding et al.,[291] hydrophilic electrospun membranes of cellulose acetate were turned into superhydrophobic surfaces by performing a sol-gel coating of decyltrimethoxysilane and tetraethyl orthosilicate. The WCA on the coated surface was 153° and 156° (for electrospinning solution concentration of 10 wt% and 8 wt.%, respectively), which is much higher than those for cellulose acetate cast films coated with the sol-gel film (103°).

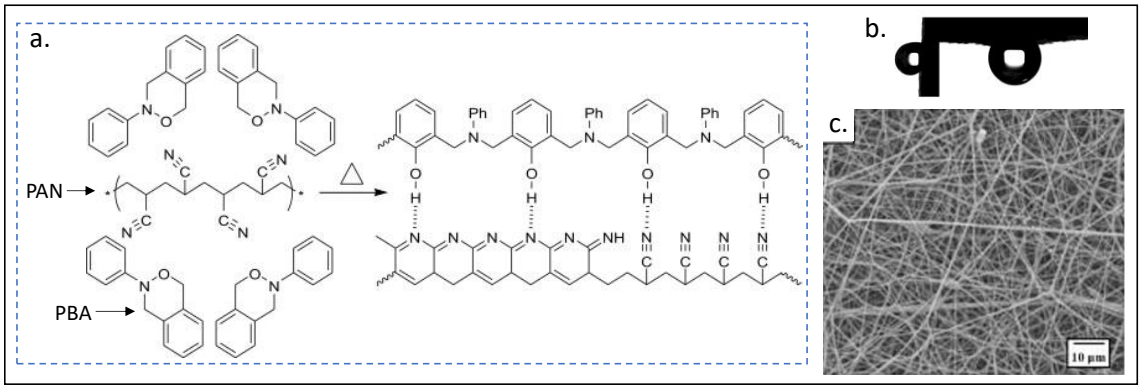

Figure 27. a. Chemical structure of polybenzoxazine/polyacrylonitrile (PBA/PAN) and intermolecular hydrogen bonding between hydroxyl groups of PBA chains and PAN after curing; b. superhydrophobic surface of electrospun membrane of PAN/PBA (50:50) with high water adhesion characteristics; c. SEM image of electrospun membrane of PAN/PBA. Adapted with permission from ref [290].

In another work,[292] PDMS/PS blend electrospun membranes were proposed as superhydrophobic fluorine-free systems for CO_2 absorption. Pure PS electrospun membranes, although superhydrophobic (thanks to the optimization of the solvent system), easily got wetted in aqueous amine solution. Thus, PDMS was added to PS solution for electrospinning in different wt.% in order to enhance the anti-wetting behavior in aqueous amine solution. The fabricated blend membranes showed durability, superhydrophobicity and high CO_2 absorption, comparable with fluoropolymers.[292] In addition to blending, coating technique can be used to decrease the wettability of electrospun membranes. For examples, polyimide electrospun membranes, coated by fluorine-free PBA and modified by silica nanoparticles,[293] led to superhydrophobic and superoleophilic membranes, which were used for oil/water separation. A high separation efficiency (above 99%) as well as excellent chemical and thermal stability with durability after 20 cycles were demonstrated.

7. Conclusions and perspectives

Electrospinning of most fluoropolymers can be achieved either from the melt or from solutions: poly(fluoroolefin)s, fluorinated acrylic polymers, fluorinated polyurethanes, and fluorinated polyimides can be processed to obtain nanofibers and fibrous membranes. By controlling the processing parameters and the polymer composition, it is possible to tune the fiber size, the mat morphology and in turn the material properties. Even employing fluoropolymers that are insoluble or with a high T_m (e.g., PTFE), as well as in the case of fluoropolymers that are not electrospinnable (e.g., Nafion^{TM}), nanostructured fibrous materials can be obtained thanks to the development of innovative electrospinning methods.

As highlighted by many examples reported in this review, electrospun fluoropolymers have demonstrated their suitability for wide-reaching applications, such as filtration,

superhydrophobic coatings, textile and sportwear, energy, sensing, electroactive, biomedical, and photocatalytic applications. The use of fluorinated electrospun structures is particularly interesting thanks to the outstanding properties of fluoropolymers, such as high thermostability and superior chemical resistance. In addition, as fluoropolymers are characterized by a low surface energy, their hydrophobicity is further enhanced by the intrinsic surface roughness of electrospun fibrous materials. When the fluoropolymers present highly interesting electroactive properties (as PVDF and especially VDF-based copolymers), electrospinning can induce and enhance the electroactive β-phase formation during the nanofibers fabrication. Finally, in the case of perfluorosulfonic acid polymers, the high proton conductivity is yet improved in the form of electrospun nanofibrous membranes, due to their large surface area and porosity. Thus, stemming from the combination of the high performance of fluoropolymers and of their nanostructuring through the processing applied, electrospinning of fluorinated polymers has demonstrated a strong potential for the development of innovative products from filtration systems to advanced coatings and energy devices.

Nowadays, most part of the research on nanofibrous fluorinated materials as presented in this review is still confined within the academic and research environment. In fact, several challenges remain to be addressed and overcome before large scale usage of such materials. In the perspective of industrial manufacture and commercial applications, the main issue of electrospinning is the low production rate. To increase the throughput of the fluorinated nanofibers preparation, innovative variations of the conventional electrospinning set-ups, such as multi-needle and needleless electrospinning, may be further developed. Although extensive work has to be carried out in order to realize the industrial scalability, the ongoing development provides great promise for cost-efficient

and sustainable industrial production and massive commercialization of electrospun fluorinated fibers in the near future.

Another fascinating challenge is the fine control of the fluorinated electrospun fibers composition and micro- and nanostructure, as well as their relationship, by the synthesis and development of new fluoropolymers. For instance, tuning the nanofibers chemistry, modulating their crystallinity, enhancing their physico-chemical properties, reducing their dimension, and functionalizing their surface are important research topics. Advanced nanofiber configurations, such as core-shell, hollow, multilayer, and multicomponent nanofibers, with well-controlled orientation and size, have been obtained. Nevertheless, controllable and reliable production of these unique nanofibers is still challenging. Moreover, the development of manufacturing techniques able to produce 3D fibrous structures (typically by combining electrospinning and other processes) is of great interest.

Environmental and safety issues are other concerns in the development of electrospinning of fluoropolymers. In fact, electrospinning processes usually involve volatile, toxic and corrosive organic solvents, while fluorinated compounds are normally environmentally persistent and can generate toxic byproducts when heated at high temperature. It is thus of great significance to develop non-toxic and environmentally friendly processes and materials.

Although many challenges still exist, electrospinning of fluoropolymers has been demonstrated to be capable of producing unique nanofibrous structures that can be widely applied in a number of different applications. Tackling the aforementioned limitations, the combination of the versatile technology of electrospinning and the highly performant fluoropolymers will make significant breakthroughs in moving beyond the current state-

of-the-art, and will lead to new paths towards innovative fibrous materials with commercial viability and significance in our everyday lives.

8. List of symbols and abbreviations

Ac Acetone
APTES Aminopropyl triethoxysilane
CA Cellulose acetate
CNC Cellulose nanocrystal
CNT Carbon nanotube
CTFE Chlorotrifluoroethylene
CVD Chemical vapor deposition
DSSC Dye sensitized solar cells
DMAc Dimethylacetamide
DMF Dimethylformamide
DMSO Dimethyl sulfoxide
FAS Fluoroalkylsilane
FCP (P(MMA-*r*-FDMA)) Fuorinated random copolymer of poly(methyl methacrylate-*random*-perfluorodecyl methacrylate)
FPI Fluorinated polyimide
FPU Fluorinated polyuretane
GO Grafene oxide
GPE Gel polymer electrolyte
HFP Hexafluoropropylene
IL Ionic liquid
ITP Iodine transfer polymerization
LEP Liquid entry pressure
LIB Lithium-ion battery
LMB Lithium-metal battery
LSV Linear sweep voltametry
MD Membrane distillation
MMT Montmorillonite
NFES Near field electrospinning
PAA Polyacrylic acid
PDA Polydiacetylene
PEG Polyethyelen glycol
PEGDMA Polyethylene glycol dimethacrylate
PEM Proton exchange membrane
PEMFC Proton exchange membrane fuel cell
PEO Polyethylene oxide
PFA Perfluorinated and alkylated polyethyleneimine additive
PFPE Perfluoropolyether
PFSA Perfluorosulfonic acid polymers
PIM Polymers of intrinsic microporosity
PP Polypropylene
PPE Personal protective equipment
PS Polystyrene
PTFE Polytetrafluoroethylene
PTFEMA Poly(2,2,2-trifluoroethyl methacrylate)
PU Polyurethane
PVA Polyvinyl alcohol
PVC Polyvinyl chloride
PVDF Polyvinylidene fluoride
PVP Polyvinylpyrrolidone
RAFT Reversible addition fragmentation transfer
R_b Bulk resistance

RDRP Reversible deactivation radical polymerization
RH Relative humidity
R_i Interfacial resistance
SEI Solid electrolyte interphase
TENG Triboelectric nanogenerator
T_g Glass transition temperature
T_m Melting temperature
TNT Trinitrotoluene
TPGDA Tripropylene glycol diacrylate
TrFE Trifluoroethylene
UV Ultraviolet
VDF Vinylidene fluoride
VOC Volatile organic compound
WCA Water contact angle

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