

# Electrospinning Technique as a Powerful Tool for the Design of Superhydrophobic Surfaces

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## Abstract

The development of surface engineering techniques to tune-up the composition, structure, and function of materials surfaces is a permanent challenge for the scientific community. In this chapter, the electrospinning process is proposed as a versatile technique for the development of highly hydrophobic or even superhydrophobic surfaces. Electrospinning makes possible the fabrication of nanostructured ultra-thin fibers, denoted as electrospun nanofibers (ENFs), from a wide range of polymeric materials that can be deposited on any type of surface with arbitrary geometry. In addition, by tuning the deposition parameters (mostly applied voltage, flow rate, and distance between collector/needle) in combination with the chemical structure of the polymeric precursor (functional groups with hydrophobic behavior) and its resultant viscosity, it is possible to obtain nanofibers with highly porous surface. As a result, functionalized surfaces with water-repellent behavior can be implemented in a wide variety of industrial applications such as in corrosion resistance, high efficient water-oil separation, surgical meshes in biomedical applications, or even in energy systems for long-term efficiency of dye-sensitized solar cells, among others.

**Keywords:** electrospinning, superhydrophobicity, wettability properties, polymeric precursors, industrial applications

## 1. Introduction

The measurement of the contact angle (CA) value is one of the most important parameters used for the determination and quantification of the wettability of solid surfaces. This CA is used to describe the behavior of a liquid droplet on a solid surface in air and is measured as the angle between the tangent at three phase points and the solid surface [1]. Accordingly, a surface is considered hydrophilic when the resultant solid surface shows a water contact angle (WCA) less than  $90^\circ$ , whereas a solid surface is considered hydrophobic when the WCA is higher than  $90^\circ$ . Nowadays, due to the development of the nanotechnology, bioinspired surfaces with special wettability properties are continuously emerging in the scientific research areas. Some representative examples are the design of novel surfaces with superhydrophilic (WCA  $< 10^\circ$ ) [2] or superhydrophobic (WCA  $> 150^\circ$ ) [3] behavior measured by water as well as surfaces with superoleophilic (CA  $< 10^\circ$ ) [4] or even superoleophobic (CA  $> 150^\circ$ ) [5] behavior measured by using oil droplets.

By convention, a superhydrophobic surface exhibits an extraordinary water contact angle value that is greater than  $150^\circ$  with a low sliding angle (typically less than  $10^\circ$ ).

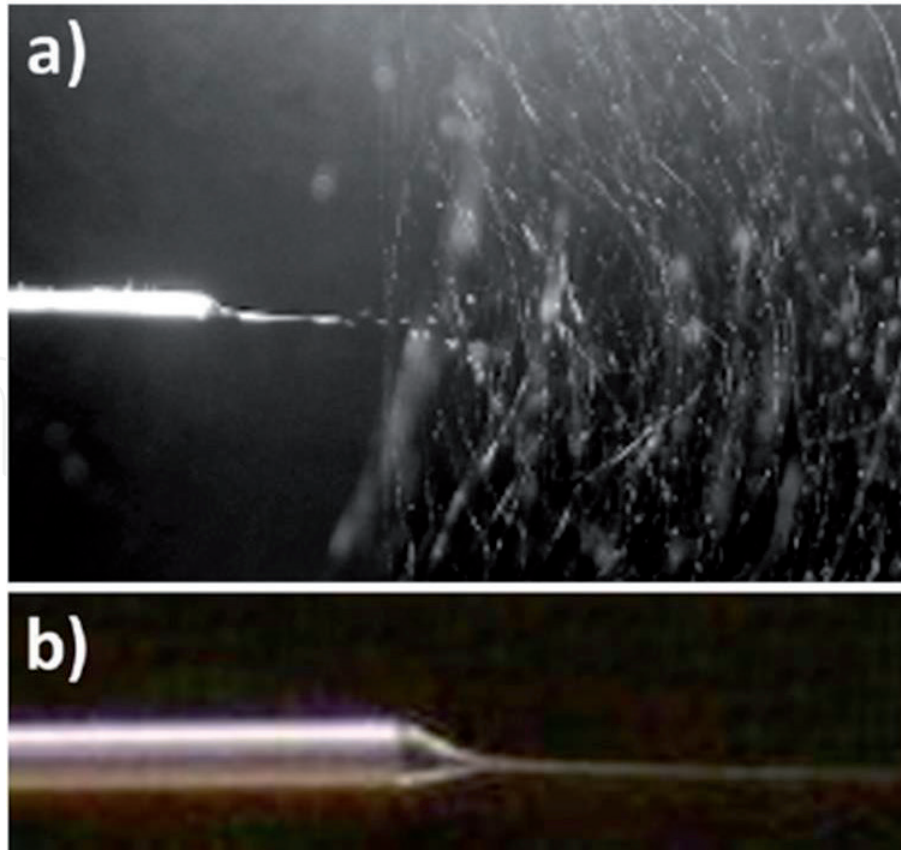
The effect of the surface microstructure on the resultant water repellency can be explained by two distinct models depending on the degree of surface roughness such as the Wenzel model [6] and the Cassie-Baxter model [7]. According to the Wenzel model, the liquid is in contact with the entire exposed surface of the solid because the large interfacial energy at the water-solid interface induces the penetration of water into the surface cavities. However, in the Cassie-Baxter model, the liquid does not penetrate the hollows or cavities of the corrugated surface and the water droplets mostly contact air pockets that are formed between water and a rough solid surface. Consequently, in the Cassie-Baxter model, the superhydrophobic shows a lower sliding angle in comparison with the Wenzel state [8]. Till, the Cassie-Baxter state is preferred because of very small hysteresis and excellent rolling behavior even at till angles of a few degrees. In addition, it is known that some plants (i.e., lotus leaf), animal fur, or insect wings found in the nature can show this superhydrophobic behavior. According to this, in order to simulate this biological surface, the design of synthetic superhydrophobic surfaces is a continuous challenge in the scientific community [9].

The research is focused on the design of surfaces with a low surface energy combined with a hierarchical surface roughness on at least two different length scales (i.e., micrometric and nanometric morphology) [10]. Accordingly, multiple deposition techniques have been implemented for this specific purpose such as layer-by-layer assembly [11], sol-gel process [12], electrochemical deposition [13], chemical vapor deposition [14], lithography [15], physical vapor deposition [16], and chemical etching [17], among others. However, an interesting deposition technique is the electrospinning process because it is possible to induce the dual effect of low surface energy and the desired roughness with multiscale surface morphology, respectively [18]. In the electrospinning process, an electrostatic force is used to obtain electrically charged polymeric jet, which overcomes the surface tension of the polymeric solution. As a result, elongated fibers are accelerated from capillary tip and are then deposited onto collector with the corresponding evaporation of the solvent, thereby making possible the fabrication of fibers with a good control over their corresponding morphological, optical, and wetting properties [19]. In this sense, the fabrication of ultrathin or nanofibers can be obtained as a strict control of the several parameters such as applied voltage, flow rate, and viscosity of the polymeric precursor or distance to collector, among others [20, 21]. The surface modification to control the wettability of electrospun mats is possible due to the presence of fibers with micrometric and sub-micrometric diameter, thereby providing hierarchical surface with superhydrophobic behavior because of the small size of the resultant electrospun mats [22]. Finally, the number of scientific works based on the combination of electrospun fibers and superhydrophobic surfaces published in indexed journals has gradually increased. Potential applications can be found in areas as diverse as removal of oil from water, separation membranes, corrosion protection in metallic surfaces, or even in biomedical applications.

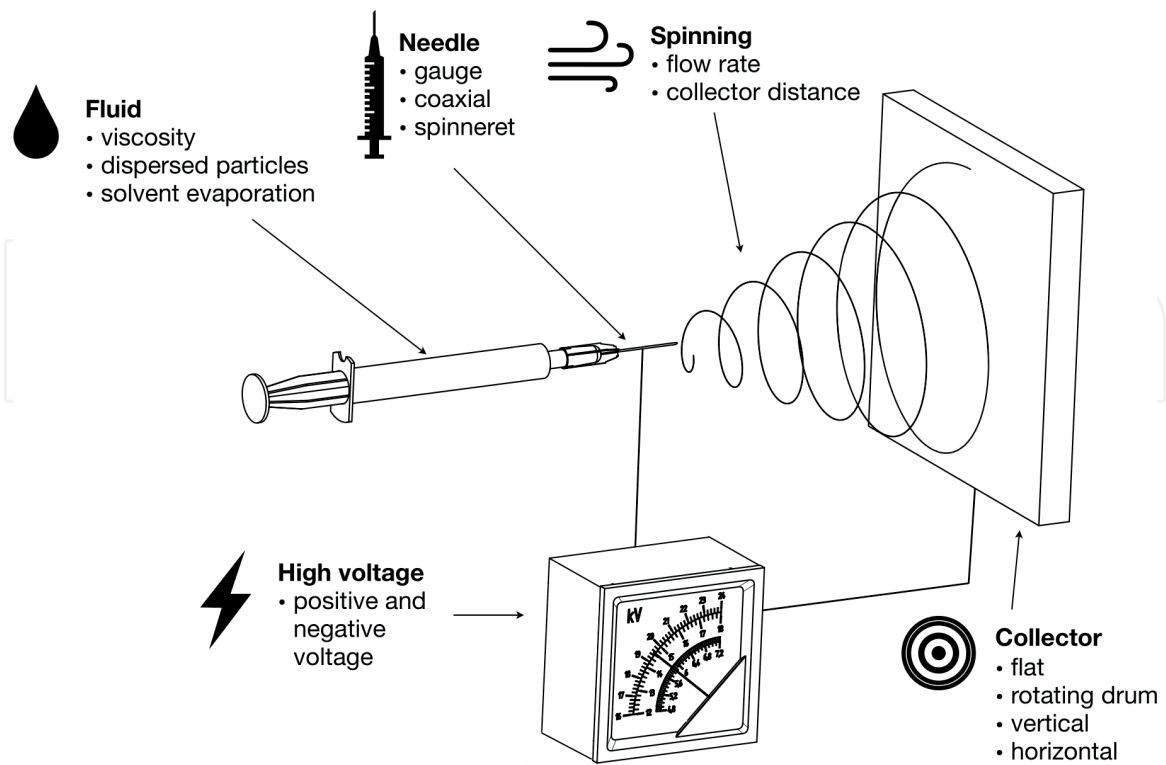
To sum up, this chapter is divided into the following subsections such as operational parameters in the electrospinning process, design of superhydrophobic surfaces composed of electrospun mats, and a summary table of the main applications derived from this work with their corresponding conclusions.

## 2. Operational parameters in electrospinning process

Electrospinning is a very versatile technique that can be implemented in a wide variety of polymeric precursors from biodegradable [23–24], copolymer [25–26], natural [27], or even synthetic nature [28–29]. The fundamentals of this



**Figure 1.**  
 (a) The aspect of the fibers being electrospun from the needle that contains the polymeric precursor solution (poly acrylic acid, PAA). (b) Detail of the “Taylor cone” formed at the tip of the needle as a function of the operational parameters. Reprinted with permission of Rivero et al. [32].



**Figure 2.**  
 Schematic representation of a electrospinning setup for the fabrication of electrospun fibers as a function of variable parameters such as nature of the fluid, nature of the solvent, type of needle, high voltage applied, flow rate, collector distance, and type of collector, respectively. Reprinted with permission of Rivero et al. [38].

deposition technique are based on the use of electrostatic forces with the aim to obtain polymeric electrospun fibers with the desired morphology (submicron or nanometric scale) as a function of the experimental parameters [30, 31]. The basic features of this deposition process are shown in **Figure 1** where a characteristic “Taylor cone” is formed during the projection of the fibers [32]. Under the action of the electric field, the droplets formed in the tip of needle are gradually elongated forming a characteristic conic shape. In addition, when the polymeric precursor has traveled through the air, the solvent is gradually evaporated during the flight of the fibers, and as a result, the fibers are finally deposited onto the corresponding collector [33, 34].

**Figure 2** shows the three main key factors that have to be controlled to obtain the electrospun fibers with the desired morphology. The first factor is related to the nature of the polymeric precursor, which is associated with its molecular weight, viscosity, molar concentration, surface tension, electrical conductivity, and solvent nature [35]. The second factor is inherent to the operation of the electrospinning setup such as applied high voltage, the flow rate, and tip-to-collector distance [36]. And the third factor is derived by the external environmental conditions such as the relative humidity and temperature [37].

### **3. Design of superhydrophobic surfaces obtained by electrospun fibers**

By convention, a superhydrophobic surface exhibits an extraordinarily water contact angle value that is greater than  $150^\circ$  with a low sliding angle (typically less than  $10^\circ$ ). According to this, many plants (i.e., lotus leaf), animal fur, or insect wings found in the nature show this superhydrophobic behavior. In this sense, in order to simulate this biological surface, the design of synthetic superhydrophobic surfaces is a permanent challenge for the scientific community. The research is focused on the design of surfaces with a low surface energy combined with a hierarchical surface roughness on at least two different length scales (i.e., micrometric and nanometric morphology) [10]. And this dual effect can be perfectly controlled by the electrospinning technique because it is possible to generate continuous ultrathin fibers with micrometric and sub-micrometric diameter, thereby providing the hierarchical surface with superhydrophobic behavior because of the small size of the resultant electrospun fibers.

An interesting approach is shown in [39] because the intrinsic properties of polyvinylidene fluoride (PVDF) can be enhanced by fabricating electrospun nanocomposite PVDF fibrous mats of predetermined morphology. In this work, the effect of five different factors such as polymeric concentration, nanoparticles loading, volumetric ratio of the solvents, flow rate, and spinning distance have been analyzed on the morphology and wettability by using a screening Design of Experiments (DoE) statistical methodology. The results clearly indicate that among all the factors examined, the PVDF concentration has been found to show the most significant effect on both the morphology and wettability.

Other representative example is presented by Rawal [40] where it is theoretically demonstrated by a simple analytical mode that it is possible to obtain superhydrophobic behavior of an electrospun nonwoven mat by controlling important design parameters such as porosity and fiber orientation distribution. According to this, simply by enhancing the porosity of an electrospun fibers can show a superhydrophobic behavior. This effect of the resultant porosity is evaluated in [41] where the first example of successful production of self-standing fibrous membrane of polymers with intrinsic microporosity (PIM-2) by electrospinning technique is shown, showing a great interest as a potential membrane material

for adsorption and separation applications. The fibers are composed of a mixture of 5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-spirobisindane (TTSBI) and decafluorobiphenyl (DFBP). The resultant coatings have shown bead-free and uniform fibers with an average diameter of  $5.5 \pm 1.5 \mu\text{m}$ , showing a superhydrophobic with a water contact angle value of  $155 \pm 6^\circ$ . According to this, numerous articles can be found based on the fabrication of superhydrophobic electrospun coatings for oil-water separation. Wang et al. [42] described an electrospinning process to obtain superhydrophobic thermoplastic polyurethane nanofiber mat after decorating with modified nanosilicas. The water contact angle increases with the nanosilica concentration which it is ascribed to the increase in roughness of the TPU films as well as the low surface energy of the nanosilicas, being of great interest for separating mixtures of oil and water due to both superhydrophobicity and superoleophilicity. A similar work can be found in [43] with ultrathin electrospun fibrous PVDF membranes with both superhydrophobic and superoleophilic properties. The PVDF membranes are governed by the surface morphology and diameter of the PVDF fibers, which can be controlled by the PVDF concentration in the electrospinning solution. As the diameter of the PVDF fiber is increased, the surface roughness of the PVDF membrane is also increased. The ultrathin electrospun fibrous PVDF membranes carried out the highest water contact angle of  $153^\circ$  and an oil contact angle of  $0^\circ$ , being an interesting approach in high-efficiency liquid separation membranes for separating emulsified water-in-oil solutions. Other different types of polymeric precursor such as polymethyl methacrylate (PMMA) can be also used for the fabrication of superhydrophobic-superoleophilic fibrous membranes by electrospinning [44], thereby showing a high water contact angle up to  $153.9^\circ$  and nearly  $0^\circ$  oil contact angle. This super wettability property is associated with the hierarchical macro- and nanostructure on the surface of PMMA surface fibers, which is adjusted by weight ratio of the employed solvents. Other interesting work is presented in [45] for the preparation of a potential adsorbent with superhydrophobic ( $>150^\circ$  in water) and superoleophilic ( $0^\circ$  in oil) wetting properties for selective removal of crude oil from water. In this work, expanded polystyrene (EPS) was electrospun to produce beaded fibers in which zeolite was introduced to the polymeric matrix with the aim to impart rough to non-beaded fiber. Due to the use of EPS, a novel work is presented in [46] whereby the first time recycled expanded polystyrene foam with various proportions of titanium dioxide nanoparticles ( $\text{TiO}_2$  NPs) and aluminum microparticles ( $\text{Al } \mu\text{Ps}$ ) have been successfully spun into superhydrophobic nanocomposite fibers using the electrospinning technique, showing a contact angle value of  $152^\circ$ .

Other interesting approach can be found in [47] where a novel method is proposed to fabricate hollow and surface porous PS fibrous membranes for the removal of oil from water. In this work, the spinning solutions were prepared by using camphene and tetraethoxysilane (TEOS) as pore-forming agents, and as a result, hollow PS fibers with 100–400 nm pores on the surface have been obtained by electrospinning and freeze-drying, being this type of membrane a great alternative and promising tool for oil of spill cleanups. In other work [48], the enhanced mechanical properties of superhydrophobic microfibrillar polystyrene mats via polyamide 6 nanofibers (PA6) are evaluated. It has been corroborated that fibrous mats formed with the number ratios of jets 2/2 (PS/PA6) have shown a water contact angle of  $150^\circ$  with three times increased tensile strength compared with only pure fibrous PS mat, respectively. Other important study is presented in [49] where electrospun nanofibrillar mats (ENMs) have been fabricated from blends of a host hydrophilic polymer, polysulfone (PSF), and small quantities of fluorinated polyurethane additive (FPA), respectively. The ENMs have been tested in desalination by membrane distillation, thereby showing competitive permeate fluxes with stable low permeate electrical conductivities.

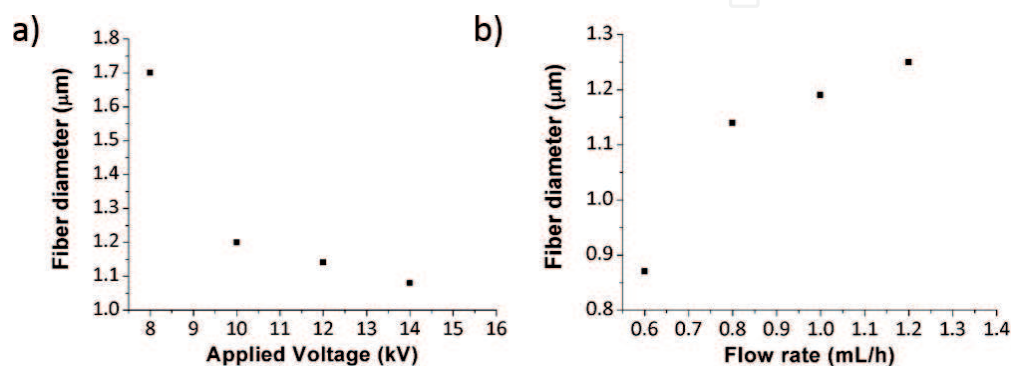
Other aspect to be remarked is that the electrospinning technique can be also implemented by using copolymers. A clear example can be found in [50] where segmented polyimide-siloxane copolymers have been prepared using 4,4'-oxydianiline (ODA) and 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) as hard segments and aminopropyl terminated polydimethyl-siloxane (APPS) and BTDA as soft segments. The water contact angle values of the electrospun mats have increased with increasing the siloxane content, and scanning electron microscopy (SEM) images reveal the bead formation known as pop-corn model, this finding being used specifically for self-cleaning materials.

Hang et al. [51] demonstrated the high versatility of the electrospinning because the coaxial electrospinning is presented by using Teflon AF as sheath material and polycaprolactone (PCL) as core material. The resultant electrospun fibers exhibit both superhydrophobic and oleophobic behaviors, and these coaxial fibers also preserve the core material properties as demonstrated with mechanical tensile tests. The use of coaxial electrospinning is also used in [52] where the design and fabrication of a composite electrospun membrane composed of polylactide:poly(vinyl pyrrolidone)/polylactide:poly(ethylene glycol) (PLA:PVP/PLA:PEG) core shell fibers loaded with bioactive agents, as functionally integrated wound dressing for efficient burn treatments. In addition, the electrospinning can be easily combined with other deposition techniques as it can be appreciated in [53]. In this work, superhydrophobic fabrics are produced by electrospinning and chemical vapor deposition. According to this, first electrospun PCL fibers are deposited and second, a thin layer of hydrophobic polymerized perfluoroalkylethyl methacrylate (PPFEMA) is deposited on the electrospun fibers, thereby yielding a superhydrophobicity behavior with a contact angle value of  $175^\circ$  and a sliding angle less than  $2.5^\circ$ . A similar approach based on the use of two different deposition techniques is shown in [54] where the preparation of hierarchically structured PCL superhydrophobic membranes are obtained via combination of electrospinning and electro-spraying techniques. Dizge et al. [55] fabricated an electrospun cellulose nanofiber membrane and then, two different deposition techniques such as sol-gel and CVD are implemented onto this electrospun membrane, thereby showing both superhydrophobicity and oleophobicity (also known as omniophobic), as demonstrated by its wetting resistance to water, ethanol, surfactant, and mineral oil. An application of this omniophobic membrane is in direct contact membrane distillation (DCMD) to separate water from saline feed solutions containing low surface tension substances. Deka et al. [56] presented the high flux and non-wettability of electrospun nanofiber membranes fabricated by electro-spraying of aerogel/polydimethylsiloxane (PDMS)/polyvinylidene fluoride (PVDF) over electrospinning polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP) membrane. The use of aerogel and PDMS is preferred as materials with low surface energy could be a safer alternative to perfluorinated compounds for environmental applications. In addition, the experimental results demonstrate non-wetting membrane distillation performance over continuous 7 days operation of saline water (3.5% of NaCl) and high anti-wetting with harsh saline water 0.5 mM sodium dodecyl sulfate (SDS) and synthetic algal organic matter.

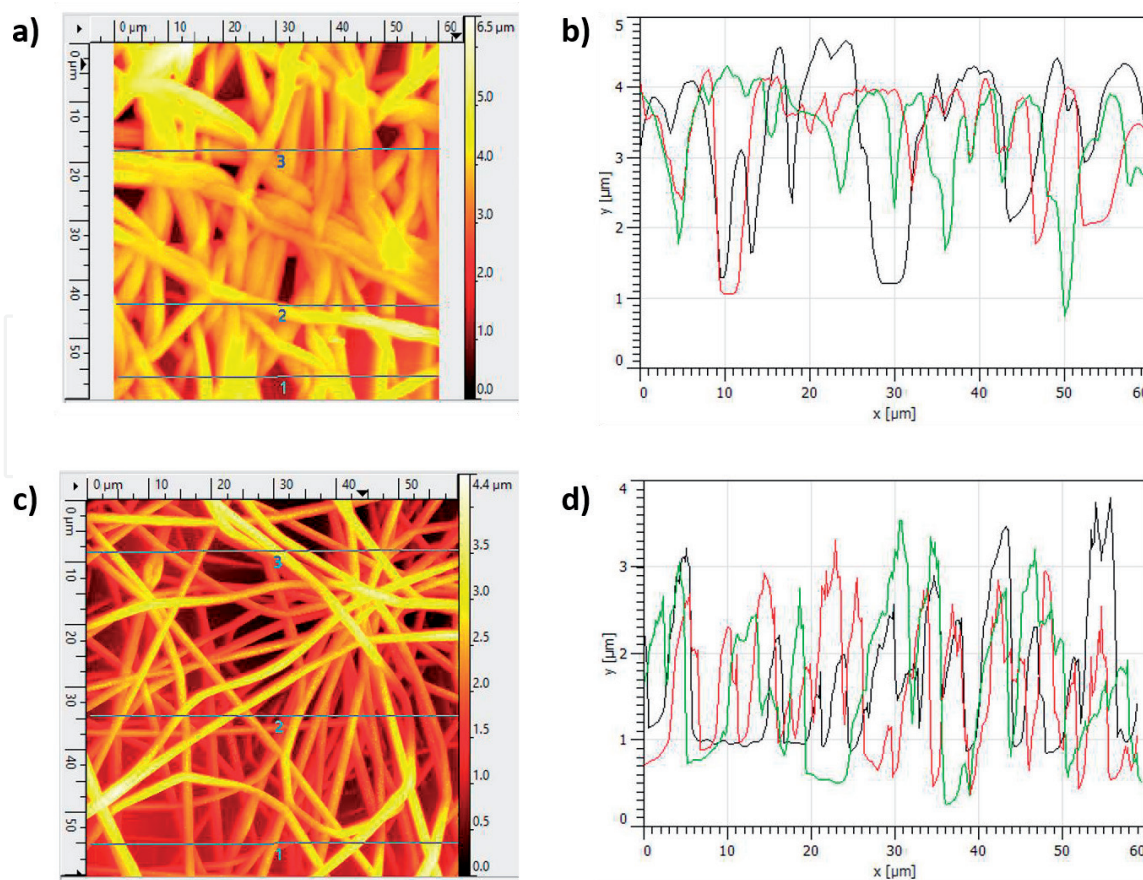
Other clear example of the implementation of these superhydrophobic electrospun fibers is for the development of anticorrosion surfaces where polymeric precursors with an intrinsic hydrophobic behavior are used such as polystyrene (PS), poly(vinyl chloride) (PVC), and polyvinylidene fluoride (PVDF), among others. Cui et al. [57] reported a simple and controllable electrospinning technology to fabricate polymeric nanofibers composed of polyvinylidene fluoride (PVDF)/stearic acid (SA) that are successfully deposited onto metallic substrates (aluminum sheets). The resultant electrospun nanofibers show a clearly superhydrophobic

behavior with water contact angle value of  $155 \pm 2^\circ$ , thereby exhibiting excellent long-time corrosion resistance. In other works, metal oxide nanoparticles such as zinc oxide (ZnO) or alumina ( $\text{Al}_2\text{O}_3$ ) are used, which are perfectly embedded in the electrospun fibers and act as efficient corrosion inhibitors. In addition, the presence of this type of nanoparticles between the interstices of the electrospun fibers can increase the surface roughness as well as the air entrapment, and as a result, an increase in the water repellent behavior is obtained. According to this, Radwan et al. [58] reported the addition of ZnO nanoparticles to the polymeric precursor of PVDF with the aim to improve the corrosion resistance, maintaining the same superhydrophobic behavior ( $155 \pm 2^\circ$ ). In addition, by using the same corrosion inhibitor (ZnO), Iribarren et al. [59] presented multifunctional protective PVC-ZnO nanocomposite coatings deposited on aluminum alloys by electrospinning. In the first step, an exhaustive study about the evolution of the resultant fiber diameter as a function of the applied voltage and the flow rate is evaluated. **Figure 3** shows that the fiber diameter of PVC electrospun fibers is reduced when the applied voltage is increased from 8 up to 14 kV (see **Figure 3a**), whereas the resultant fiber diameter is increased when the flow rate is gradually increased (see **Figure 3b**) from 0.6 up to 1.2 mL/h. Once it has been evaluated, the operational parameters in the corresponding fiber diameter, the electrospun PVC-ZnO nanofibers were deposited by using a voltage of 14 kV and a flow rate of 0.6 mL/h because it has been demonstrated that an increase in the water repellency behavior is observed when the diameter among bead-free fibers is reduced. And this effect has been corroborated because the resultant surface wettability of the electrospun coating presents similar water contact angle values in the range of  $145\text{--}155^\circ\text{C}$ .

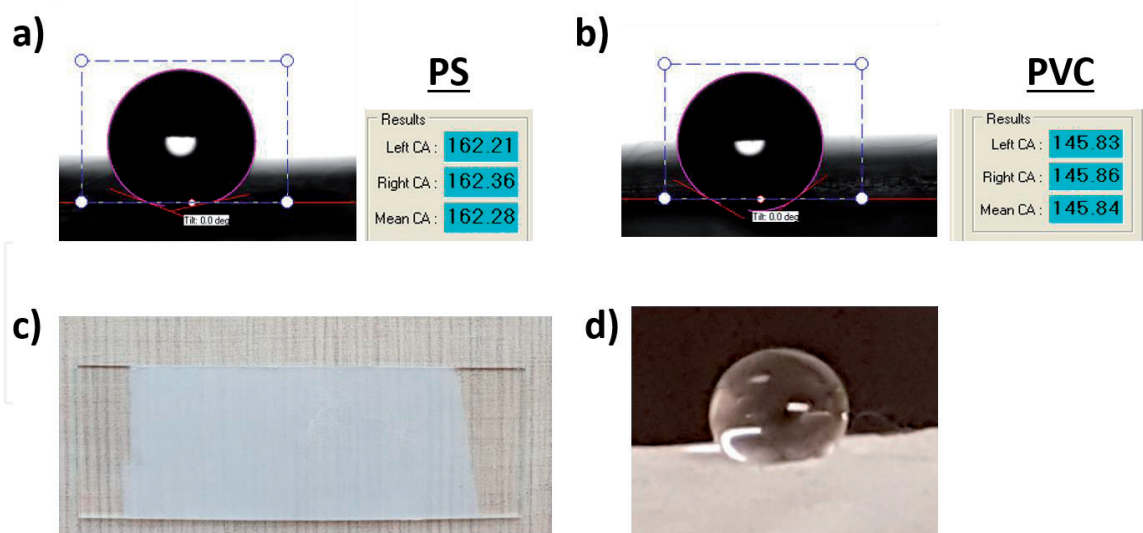
Rivero et al. [60] presented a comparative study of multifunctional coatings based on electrospun fibers with incorporated ZnO nanoparticles by using two different polymeric precursors such as PVC and PS, respectively. In order to characterize the morphology of the resultant electrospun fibers, atomic force microscopy (AFM) was performed, as it can be appreciated in **Figure 4**, showing an important difference in the fiber diameter. In this sense, 2D AFM images with their corresponding profiles (three evaluation lines) clearly reveal that a bigger size in diameter fiber is obtained for PS samples (**Figure 4a** and **b**) in comparison with PVC samples (**Figure 4c** and **d**). In addition, the arithmetic average roughness  $R_a$  of the PS coating was found to be 505.7 nm, which is higher than that in PVC coating with a value of 427.5 nm. This result is in concordance with the high value of WCA because an increase in the hydrophobicity is clearly obtained by the increment in the resultant surface roughness, and due to this, the WCA values for PS samples are higher than PVC samples (see **Figure 5**).



**Figure 3.** (a) Evolution of the resultant fiber diameter as a function of the applied voltage with a specific fixed flow rate of 0.8 mL/h. (b) Evolution of the fiber diameter as a function of the flow rate with a specific fixed applied voltage of 12 kV. Reprinted with permission of Iribarren et al. [59].



**Figure 4.** 2D-AFM images for a dimension of  $60 \times 60 \mu\text{m}^2$  of the PS electrospun fibers (a, b) and PVC electrospun fibers (c, d) with their corresponding profiles. Reprinted with permission of Rivero et al. [60].



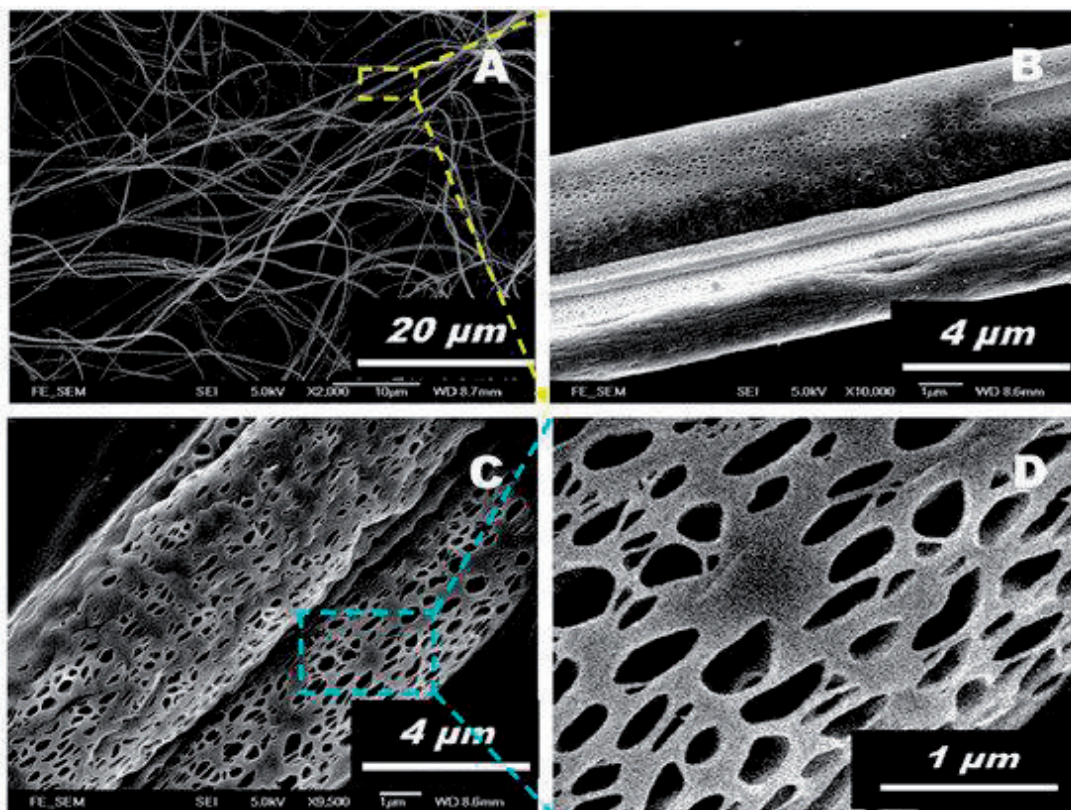
**Figure 5.** Optical image of the water contact angle (WCA) value for PS (a) and PVC (b) samples; (c) aspect of the electrospun fibers with a characteristic white coloration deposited onto a standard microscope glass slide; (d) picture of the water drop onto the electrospun fibers. Reprinted with permission of Rivero et al. [60].

These two previous polymeric precursors of PS and PVC have been also studied in [61] where the superhydrophobic behavior as a function of the fiber diameter, the presence of  $\text{TiO}_2$  nanoparticles, and the effect of heat treatment in the nanocomposite fibers are evaluated. The main purpose is for energy systems, as it can be used in the design of dye-sensitized solar cells (DSSCs) for anti-icing and self-cleaning



materials with the aim to show long-term efficiency of the cells. The results show that TiO<sub>2</sub> nanocomposite fibers have higher contact angle values, which is attributed to the nanoscale gaps/bumps/voids formed on the fiber in the presence of TiO<sub>2</sub> nanoparticles, thereby reaching superhydrophobicity on the nanocomposite electrospun fiber films. Azimirad et al. [62] presented a dual layer of dip-coated TiO<sub>2</sub> film (top layer) and electrospun polystyrene (bottom layer) deposited onto stainless steel with the aim to show both superhydrophobicity and corrosion resistance, thereby showing great important and potential applications, especially in marine industries. Other interesting approach is presented in [63]. In this case, the optimum conditions to produce electrospun polystyrene (PS) and aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) nanocomposite coating with the highest roughness and superhydrophobic properties are 25 kV of applied voltage and 1.5 mL/h of flow rate at 35°C. The experimental results indicate a water contact angle value of 155 ± 1.9 and contact angle hysteresis of 2 ± 4.2°.

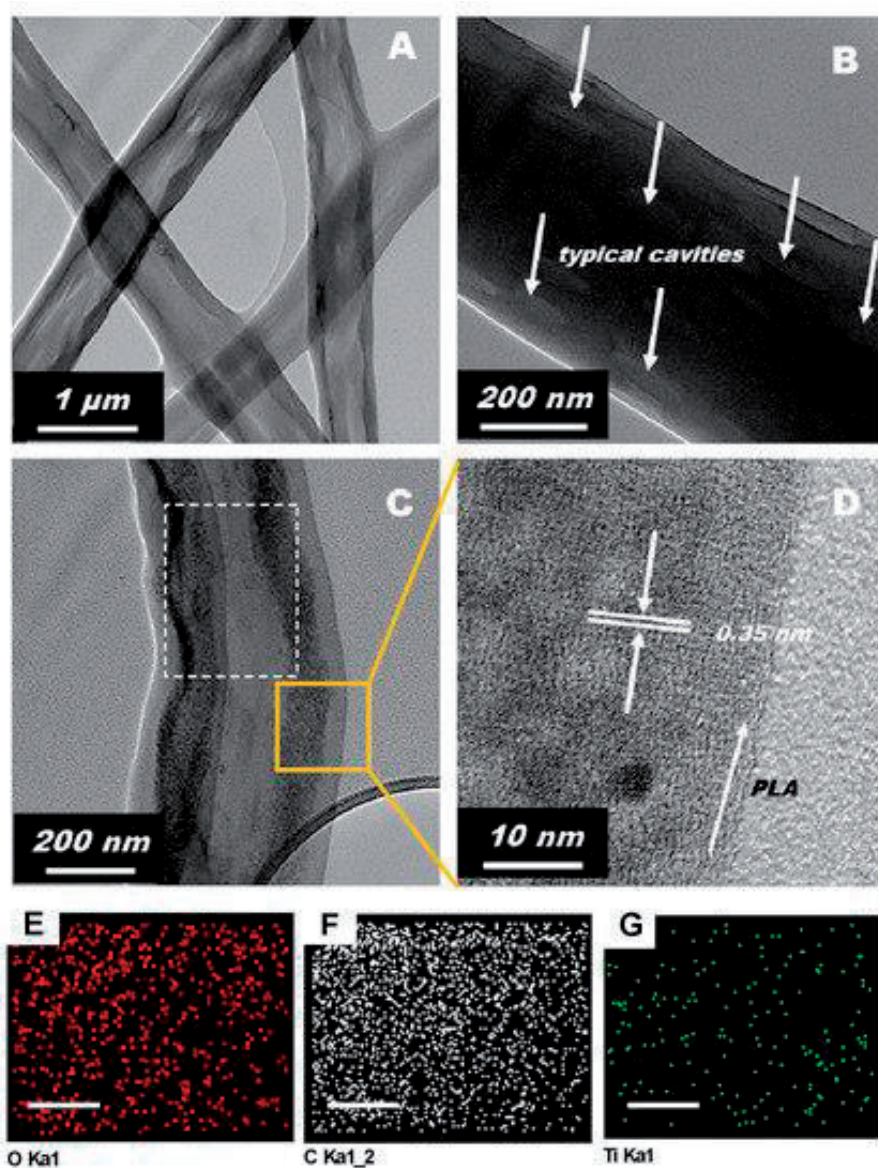
Finally, other interesting application field for the electrospun fibers is the design of biomaterials with application as surgical meshes, sutures, or in artificial tissue [64]. In this work, a superhydrophobic poly(L-lactic acid) (PLLA) surface is obtained by dispersing synthetic talc (ts) into PLLA fibers. This synthetic talc, characterized by the presence of long aliphatic chains in the structure, is soluble in the electrospinning solvent mixture, whose viscosity is significantly modified by small amount of talc. The evaporation during the electrospinning process promotes the synthetic talc dispersion into the polymer matrix (PLLA), thereby obtaining a nanometric size scale distribution of the talc. In addition, among the parameters studied, the relative humidity (RH) was found significantly to affect the fiber morphology. By keeping all the electrospinning parameters constant



**Figure 6.** (A–D) FESEM images of the prepared ES PLA/TiO<sub>2</sub> fibers at different magnification scales. Note that the images (B) and (D) are magnified from the locations indicated in images (A). Reprinted with permission of Wang et al. [65].

and increasing the relative humidity (Rh), the morphology completely changes. This increment increases the homogeneity of the PLLA/ts fibers and turns out to be opposite with respect to PLLA fibers. Moreover, the influence of the electrical field by decreasing the voltage shows that the homogeneity tends to decrease. The dispersion of the synthetic talc on the nanofiber produces an evident effect in the wettability, as the PLLA/ts electrospun mat is highly hydrophobic by exhibiting an increment in the WCA value from 92 up to 140°. Other aspect to remark is that the presence of talc has promoted the development of a small amount of crystallinity during the electrospinning process, thereby making possible the development of  $\alpha$ -crystallographic form during the annealing.

Other interesting work based on the use of biodegradable polymer is presented in [65] where polylactide/TiO<sub>2</sub> composite fiber (PLA/TiO<sub>2</sub>) scaffolds with both superhydrophobic and superadhesive porous surfaces have been obtained for water



**Figure 7.**

TEM images of the prepared typical ES PLA/TiO<sub>2</sub> fibers. (A) Low-magnification TEM image of ES PLA/TiO<sub>2</sub> fibers. (B) Magnified TEM image of an ES PLA/TiO<sub>2</sub> fiber captured for the observation of typical cavities. (C) Magnified TEM image of an ES PLA/TiO<sub>2</sub> fiber captured for the observation of TiO<sub>2</sub> nanoparticles. (D) High-resolution TEM image zoomed in from the marked area in (C) for the identification of the lattice fringe of TiO<sub>2</sub> nanocrystallites. (E–G) The O, C, and Ti element mapping images of the location are indicated in image (C) with a dashed rectangle. The scale bars in all the mapping images (E–G) are 100 nm. Reprinted with permission of Wang et al. [65].

immobilization, antibacterial performance, and deodorization. The size of the pores of the as-fabricated PLA/TiO<sub>2</sub> electrospun fibers observed on the surface has shown to have a length of  $200 \pm 100$  nm and a width of  $150 \pm 50$  nm demonstrated by using field-emission scanning electron microscopy (FESEM) (see **Figure 6**) and transmission electron microscopy (TEM) (see **Figure 7**), respectively. As it can be appreciated in both figures, the formation of regular pores elongated along the fiber axis was observed on the fiber surface and it is associated with the rapid phase separation during the electrospinning process as induced by the voltage solvent evaporation and the fast solidification. In addition, according to the TEM image of **Figure 7**, the distribution of the TiO<sub>2</sub> nanoparticles over the electrospun surface fiber has been analyzed by using energy dispersive X-Ray (EDX) elemental mapping technique (**Figure 7E–G**). According to this, a uniform Ti element distribution has been observed, indicating that TiO<sub>2</sub> NPs have been homogeneously dispersed in the PLA electrospun fibers. In addition, a powerful adhesive force can be associated with the van der Waals forces and the accumulated negative pressure forces of the as-spun PLA/TiO<sub>2</sub> fibers. Other important aspect to remark is that the resultant PLA/TiO<sub>2</sub> composite fiber presents a high antibacterial efficiency against three different types of bacteria (*Escherichia coli*, *Staphylococcus aureus*, and *Candida albicans*) as well as high deodorization efficiency because the reduction of two typical pollutants such as ammonia and formaldehyde have been reduced after exposition to visible light radiation. To sum up, this multifunctional biodegradable fiber scaffold can bring promising benefits to the real world in specific biomedical or even bioengineering applications.

#### 4. Summary table of potential industrial applications

To sum up, in order to have a better understanding of the different superhydrophobic coatings analyzed in this work, a summary of the different electrospun fibrous coatings with their corresponding employed solvents as well as their potential industrial applications can be appreciated in **Table 1**.

#### 5. Conclusions

In this work, electrospinning is presented as a novel engineering technique for the design of superhydrophobic surfaces. In order to obtain this special wettability, it is necessary to control two crucial factors such as a low surface energy and a hierarchical surface roughness on at least two different length scales (i.e., micrometric and nanometric morphology). The electrospinning is a good candidate because it is possible to control both parameters as a function of the operational parameters such as applied voltage, polymeric precursor concentration, flow rate, and tip-to-collector distance. A good control over these parameters makes possible the fabrication of electrospun fibers with a desired morphology (mostly size, porosity, and fiber diameter).

Finally, a summary of different potential industrial applications is presented due to the design of corrosion-resistant surfaces, high-efficient water-oil separation membranes, long-term efficiency of dye sensitized solar cells, or even in biomedical applications for the development of antibacterial surfaces with a high efficiency against bacteria or pollutants. To sum up, it has been demonstrated that this deposition technique can be used as a promising alternative in the real world in several disciplines of the science and technology.

Electrospun fiber coating	Solvent	Research field	Ref.
TTSBI + DFBP	Tetrachloroethane (TCE)	Adsorption applications	[41]
TPU decorated with modified nanosilicas	N,N-dimethylformamide (DMF) and tetrahydrofuran (THF)	Water-oil separation	[42]
PVDF	N,N-dimethylformamide (DMF) and acetone	Water-oil separation	[43]
PMMA	N,N-dimethylacetamide (DMAc) and acetone	Water-oil separation	[44]
EPS and EPS/zeolite	Tetrahydrofuran (THF)	Water-oil separation	[45]
PS/TEOS/camphene	N,N-dimethylformamide (DMF)	Water-oil separation	[47]
PSF	N,N-dimethylacetamide (DMAc) and acetone	Desalination by membrane distillation	[49]
PAA	N,N-dimethylacetamide (DMAc) and tetrahydrofuran (THF)	Self-cleaning	[50]
Teflon AF (sheath)/PCL (core)	2,2,2-trifluoroethanol (TFE)	Microfluidics	[51]
PLA:PVP/PLA:PEG	Dichloromethane	Burn wound healing and skin regeneration	[52]
PCL	Chloroform and methanol	Fabrics	[53]
PCL	N,N-dimethylformamide (DMF) and chloroform	Water-oil separation	[54]
Cellulose acetate	N,N-dimethylacetamide (DMAc) and acetone	Water-saline solution separation	[55]
PVDF-HFP	N,N-dimethylformamide (DMF) and acetone	Desalination by membrane distillation	[56]
PVDF/SA	N,N-dimethylformamide (DMF)	Corrosion protection	[57]
PVDF-ZnO	N,N-dimethylacetamide (DMAc) and toluene	Corrosion protection	[58]
PVC-ZnO	N,N-dimethylformamide (DMF) and tetrahydrofuran (THF)	Corrosion protection	[59]
PVC-ZnO PS-ZnO	N,N-dimethylformamide (DMF) and tetrahydrofuran (THF)	Corrosion protection	[60]
PS-TiO <sub>2</sub> PVC-TiO <sub>2</sub>	N,N-dimethylformamide (DMF) and N,N-dimethylacetamide (DMAc)	Energy systems (DSSC devices)	[61]
PS-TiO <sub>2</sub>	N,N-dimethylformamide (DMF)	Corrosion protection	[62]
PS-Al <sub>2</sub> O <sub>3</sub>	N,N-dimethylacetamide (DMAc) and tetrahydrofuran (THF)	Corrosion protection	[63]
PLLA	Toluene and chloroform	Biomedical applications	[64]
PLA/TiO <sub>2</sub>	Chloroform and acetone	Water immobilization, antibacterial performance, and deodorization	[65]

**Table 1.**

*Summary of the different sensitive electrospun coatings, the metallic substrates used, and the resultant corrosion tests for the development of new and innovative protective coatings with good anticorrosion properties.*

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