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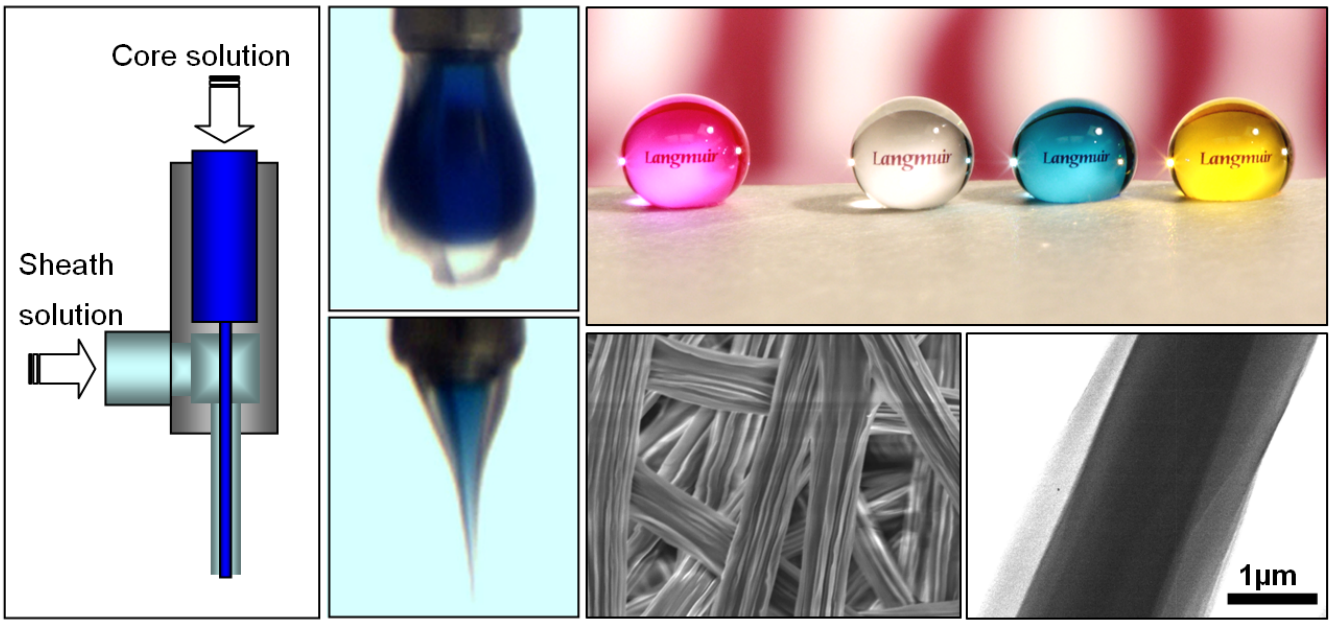

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Superhydrophobic and Oleophobic Fibers by Coaxial Electrospinning

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Control of surface wetting properties to produce strongly hydrophobic or hydrophilic effects is at the heart of many macro- and microfluidic applications. In this work, we have investigated coaxial electrospinning to produce core−sheath-structured nano/microfibers that combine different properties from individual core and sheath materials. Teflon AF is an amorphous fluoropolymer that is widely utilized as a hydrophobic material. Hydrophobic fluoropolymers are normally not electrospinnable because their low dielectric constant prevents sufficient charging for a solution to be electrospun. The first Teflon electrospun fibers are reported using coaxial electrospinning with Teflon AF sheath and poly(ε-caprolactone) (PCL) core materials. Using these core/sheath fibers, superhydrophobic and oleophobic membranes have been successfully produced. These coaxial fibers also preserve the core material properties as demonstrated with mechanical tensile tests. The fact that a normally nonelectrospinnable material such as Teflon AF has been successfully electrospun when combined with an electrospinnable core material indicates the potential of coaxial electrospinning to provide a new degree of freedom in terms of material combinations for many applications.

Introduction

Superhydrophobic materials and surfaces that produce water contact angles in excess of 150° are being intensively studied in order to provide superior water repellency and self-cleaning behavior. This unique property is very useful in many industries, such as microfluidics, textiles, construction, automobiles, and so forth. The fundamental mechanisms of the wetting and dewetting of surfaces have been excellently reviewed in several papers, including those of Zisman[1] and de Gennes.[2] Many examples of superhydrophobicity are found in nature, especially in plants and insects. For example, lotus leaves are superhydrophobic because of their rough-surface microstructure.[3] Self-cleaning occurs as water droplets remove surface particles as they roll off the leaves. Superhydrophobicity also provides good buoyancy for floating on water. Another example from nature is the lady's mantle leaf that obtains its superhydrophobicity from a furlike coverage of bundled hairs.[4] Interestingly, individual hairs are hydrophilic. However, the elastic deformation of the bundled hair ends away from the substrate results in a superhydrophobic surface. The bundling of the hairs is an example of the importance of curvature in hydrophobicity. This curvature effect is also very important in determining[5] the oil-repellent ("oleophobic") properties of the surface. Water strider feet[6] and bird feathers[7] are other famous examples of superhydrophobicity present in nature. By observing these features, one realizes that superhydrophobicity results from a combination of low surface energy and high surface roughness.

Research is intensively being conducted to understand, produce, and control superhydrophobicity. Several approaches have been reported for combining materials of low surface energy with high surface roughness. One approach is to roughen a normally smooth surface of a hydrophobic material. Plasma etching is widely used for this purpose.[8] Mechanical stretching[9] and microphase separation of fluorinated block copolymers[10] have also been used. A second approach is to treat a rough surface with a hydrophobic material. Etching, lithography,[11−13] and nanowires/nanotubes by chemical vapor deposition (CVD)[14] have been used to produce a rough surface, followed by a hydrophobic coating to produce a low surface energy. Whereas these approaches are two-step processes, single-step approaches, such as sol−gel phase separation[15] and plasma polymerization,[16] can also produce a rough surface with low surface energy.

Electrospinning. Electrospinning is a versatile technique for producing micro/nanofibers from many kinds of polymers.[17,18] In a laboratory environment, electrospinning requires a high-power supply, a conducting substrate, and a syringe pump. The electrospinning process is initiated by a high electric field between the syringe (containing viscous polymer solution) and the conducting substrate. Because of the high electrical potential, a charged liquid jet is ejected from the tip of a distorted droplet, the so-called

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Taylor cone.[19] The liquid jet experiences whipping and bending instabilities within a sufficient distance to evaporate its solvent thoroughly and, consequently, becomes a solid nonwoven micro/nanofiber membrane on the substrate. Oriented polymer nanofibers can also be produced by modifying the ground electrode geometry[20] and/or rotating[21,22] it and by using a microfluidic chip[23] to deliver the solution to the ejection tip.

Electrospinning has been used to make membranes with rough surfaces, followed by the deposition of hydrophobic material, and to produce superhydrophobic membranes in a single-step process. In the former case, rough membranes are electrospun first and then coated with hydrophobic material by deposition techniques such as CVD[24] and the layer-by-layer technique.[25] In the latter case, the electrospun fiber itself can provide superhydrophobicity by electrospinning a blend of polymer and hydrophobic material[5,26] and/or by introducing secondary structures[27−29] such as pores and beads. Nanoparticles have also been introduced to increase roughness and to produce superhydrophobicity.[30]

Coaxial Electrospinning. Coaxial electrospinning expands the versatility of electrospinning by enabling the formation of core−sheath-structured micro/nanofibers. As shown in Figure 1a, a coaxial nozzle consists of a central tube surrounded by a concentric annular tube. Two polymer solutions for the core and sheath materials are separately fed into the coaxial nozzle from which they are ejected simultaneously. A compound pendant droplet is seen to emerge from the coaxial nozzle in Figure 1b. Upon application of a sufficient voltage, a compound Taylor cone is formed (Figure 1c) and a liquid jet is ejected that consists of the core material enveloped by the sheath material. The compound liquid jet undergoes the same process as in conventional electrospinning: being pulled by the electric field and whipped and stretched by the bending instability, followed by evaporation of the solvent leading to the formation of solid-state fibers. Using the coaxial electrospinning method, different characteristics from each polymer can be combined into one fiber. Sun et al.[31] first demonstrated coaxial electrospinning using different polymers for the core and sheath. Li and Xia[32] produced TiO_2 hollow nanofibers with controllable dimensions by coaxial electrospinning. Coaxial electrospinning for tissue engineering application has also been reported.[33,34] The use of multiple spinnerets fed by a microfluidic manifold has been reported[35] to greatly increase the rate at which nanofibers can be produced by electrospinning.

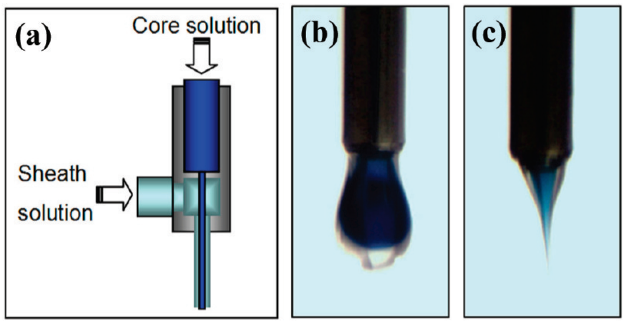

Figure 1. Coaxial electrospinning operation: (a) diagram of the coaxial nozzle; (b) core−sheath droplet without bias; and (c) Taylor cone and coaxial jet formation at 12.5 kV.

In this article, the first demonstration of superhydrophobic membranes produced by coaxial electrospinning is reported. Coaxially electrospun superhydrophobic fiber membranes exhibit a water droplet CA $>155°$. These membranes also exhibit an extremely low minimum tilt angle for droplet roll-off (rolling angle) of ∼5°. Figure 2a,b clearly shows the difference between a gelatin-only fiber membrane and a membrane consisting of coaxially electrospun gelatin fibers coated with Teflon AF (2,2-bis-trifluoromethyl-4,5-difluoro-1,3-dioxole with tetrafluoroethylene). In water, the gelatin-only fiber membrane is immediately hydrated whereas the coaxially electrospun gelatin/Teflon AF fiber membrane is floating with no water absorption. Figure 2c,d shows droplets of water (5 μL) and dodecane oil with red dye (∼100 nL−2 μL) on Teflon AF-coated polymer (poly (ε-caprolactone), i.e., PCL) fibers produced by coaxial electrospinning. As can be seen, the coaxially electrospun fiber membrane exhibits both superhydrophobicity and oleophobicity. Figure 2e,f shows examples of the core−sheath structure of coaxially electrospun fibers using fluorescence microscopy and transmission electron microscopy (TEM).

Compared to alternative methods of fiber formation, coaxial electrospinning has many advantages: (a) a simple one-step process for the conformal coating of polymer fiber with hydrophobic material; (b) high cost-effectiveness; and (c) a large variety of available materials for both core and sheath. Coaxial electrospun fibers do not require treatment by vacuum, high temperature, plasma, or sophisticated chemistry. A polymer blend with hydrophobic material can also provide superhydrophobicity with single-nozzle electrospinning. However, the properties of core polymer such as mechanical strength and conductivity will not be preserved after blending with hydrophobic material. Using coaxial electrospinning, one can preserve the core polymer properties independently of the properties of hydrophobic material for the sheath.

Teflon AF fluoropolymer is a very useful and commercially successful hydrophobic fluoropolymer because of its low surface energy (∼16 mN/m), chemical resistance, mechanical robustness, thermal stability, optical transparency, and highly insulating properties with the lowest relative dielectric constant (∼1.90) of any plastic.[36] Electrospinning of Teflon AF has not been successful because its low dielectric constant makes it hard to be sufficiently charged to eject a continuous liquid jet with the necessary whipping characteristics. Burkarter et al.[37] have succeeded in electrospraying an aqueous PTFE fluoropolymer dispersion and showing superhydrophobicity after heat

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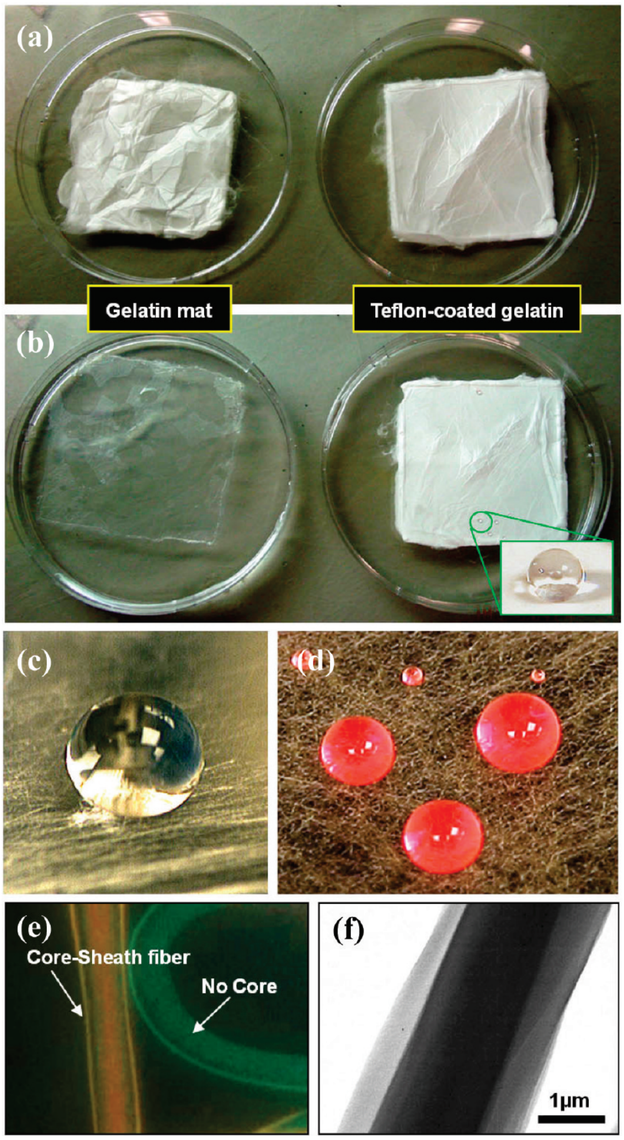

Figure 2. Collage of photographs of gelatin and Teflon-coated gelatin membranes: (a) prehydration, (b) posthydration, (c) superhydrophobic, and (d) oleophobic. Structure of core/sheath fibers: (e) PCL/gelatin fibers fluorescence image and (f) PCL/Teflon fiber TEM cross-section.

treatment. Electrosprayed microsized particles were produced, but no fiber formation was reported.

Most reports of coaxial electrospinning have used two electrospinnable polymer solutions for the core and sheath.[33,34,38−40] Interestingly, coaxial electrospinning with a core solution that is normally nonelectrospinnable was demonstrated by Li and Xia.[32] Inspired by this idea, we have demonstrated coaxial electrospinning with a normally nonelectrospinnable sheath solution of Teflon AF 2400 and have produced hydrophobic micro/nanofibers that have Teflon AF as a sheath layer. Teflon AF solution is immiscible with most solvents, thus minimizing core−sheath material intermixing. This enables the fiber core to preserve its normal properties without degradation. Successful coaxial electrospinning requires a good understanding of the complex interaction between many material and process properties, including the viscosity, vapor pressure ratio, flow rate ratio, dielectric constant, and surface tension.

Methods

Experimental Setup. The coaxial electrospinning setup has been previously described.[34] Stainless coaxial nozzles, a copper grid mesh with an aluminum-foil-wrapped metal plate for the conducting substrate, and a digital thermometer are placed in a transparent glovebox. Two Labview-controlled syringe pumps, a high-voltage supply, and the digital imaging system are located adjacent to the glovebox to avoid electric field interference during electrospinning. Coaxial nozzles purchased from Nisco (Zurich, Switzerland) have core inner and outer diameters of 0.3 and 0.6 mm, respectively, and a sheath inner diameter of 0.8 mm.

Materials. For the core solution, we have used PCL (M_n = 80 kDa) purchased from Sigma-Aldrich (St. Louis, MO) and the solvent 2,2,2-trifluoroethanol (TFE, 99.8% purity) purchased from Acros Organics (Geel, Belgium). Amorphous fluoropolymer Teflon AF 2400 1 wt % in FC-75 solvent (400-S1-100-1, purchased from DuPont, Wilmington, DE) is used for the sheath solution.

Electrospinning. Both solutions are fed by NE-1000 syringe pumps at 1.5 mL/h for the PCL 10 wt % core solution and 1.0 mL/h for the Teflon AF2400 1 wt % sheath solution. For lower PCL concentrations, lower flow rates for solution were used. The total dispensed volumes of the core and sheath solutions were 150 and 100 μL, respectively. The distance between coaxial nozzles and the bottom metal plate was 25 cm, and the applied voltage over the gap was 12.5 kV. The ambient temperature and humidity were ~70−75 °F and ~20−45%, respectively. For conventional electrospinning of the PCL 10 wt % solution, most parameters are the same as for coaxial electrospinning except that only PCL solution was fed by syringe pump with a flow rate of 1.45 mL/h.

Mechanical Tensile Test. For mechanical tensile tests, electrospun fiber membranes were cut into dog-bone-shaped samples. The gauge dimensions of the sample are 3 mm width by 13 mm length. The fiber diameter and fiber membrane thickness are within ~1 to 2 μm and ~250 to 300 μm ranges, respectively. More than six samples were prepared for each case. The thickness was measured using a digital caliper, and the mechanical properties were measured using a TestResource 100R series tensile tester with a 112 lbf load cell and an extension speed of 1.5 mm/s.

Theoretical Basis

The effect of roughness on hydrophobicity has been established by Wenzel[41] and by Cassie and Baxter.[42] Their models are described by the following equations

$$\cos \theta_W = r \cos \theta_Y \quad (1)$$

$$\cos \theta_{CB} = -1 + \phi_s(1 + \cos \theta_Y) \quad (2)$$

where θ_W and θ_{CB} are the apparent contact angles on a rough surface, the equilibrium (Young's) contact angle (CA) on a smooth surface θ_Y, the roughness factor r, and the wet solid fraction ϕ_s.

In the Wenzel state, the textured surface has a higher effective surface area than does a smooth surface. The water droplet completely penetrates the surface texture and wets a smaller apparent area, resulting in a higher CA compared to that on a smooth surface. However, as predicted by eq 1, this CA

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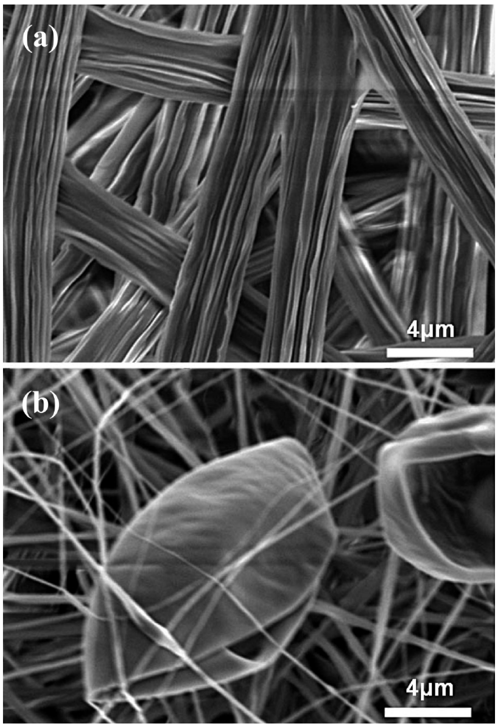

Figure 3. Morphology of PCL/Teflon fibers obtained with different PCL concentrations: (a) PCL 10 wt % with 1.5 mL/h and Teflon 1 wt % with 1.0 mL/h; (b) PCL 7 wt % with 1.4 mL/h and Teflon 1 wt % with 1.4 mL/h. Electric field for all samples: 500 V/cm.

enhancement occurs only for hydrophobic materials that have a $\theta_Y > 90°$ on a smooth surface. For $\theta_Y < 90°$, surface roughness makes the material more hydrophilic. Although the Wenzel state can result in enhanced CA, it is not preferred for many applications because it has very high (wetting/dewetting) hysteresis and pinning behavior on the substrate.

In the Cassie–Baxter state, the droplet does not make continuous contact with the solid surface. Instead, the water droplet sits on the composite surface of trapped air and solid. This composite surface has a higher CA because of the air/liquid interface and can result in superhydrophobicity. The Cassie–Baxter state is preferred because of very small hysteresis and excellent rolling behavior even at tilt angles of a few degrees.

Results

Morphology. As the ejected liquid jet from the core solution penetrates the sheath droplet, sheath solution is extracted along with the core liquid jet as a result of shear stress between two solutions. The ejecting volume of sheath solution is closely related to its viscosity because the shear stress is proportional to the viscosity. Using a Teflon AF 0.5 wt % sheath solution, its flow rate needs to be limited to ≤0.7 mL/h to prevent dripping problems. However, when a more viscous Teflon AF 1 wt % solution is used, its flow rate can be increased to 6 mL/h or higher with no dripping. Therefore, a 1 wt % solution of Teflon was utilized for the results presented here.

Morphologies of coaxially electrospun PCL/Teflon AF fibers are shown in Figure 3. The concentration of the PCL core solution had a marked effect on the fiber diameter and morphology. Using a 10 wt % PCL solution results in fiber diameters of ~1 - 2 μm and a secondary structure of striation, as seen in Figure 3a. At lower PCL concentrations, beads are observed (Figure 3b) and the fiber diameter abruptly decreases since a large fraction of material

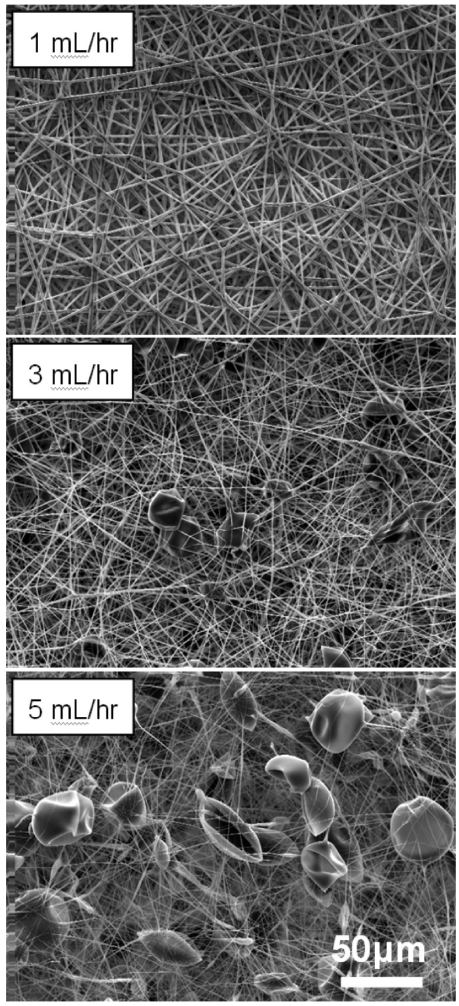

Figure 4. Effect of Teflon sheath solution flow rate on fiber morphologies. PCL 10 wt % solution is used for core and Teflon AF 1 wt % solution is used for sheath. The flow rate for the core solution is fixed at 1.5 mL/h, and the flow rate for the sheath solution is labeled in each panel. All SEM photographs are taken at 500× magnification. An excess flow rate of the sheath solution results in a higher bead density and thinner fiber diameter.

volume is used in bead formation. Greatly increasing the Teflon AF flow rate also leads to increasing bead formation as continuous and uniform fiber formation is hindered by the nonelectrospinnable Teflon AF sheath solution. (Figure 4)

It is well known that thinner fiber diameters and higher bead densities improve the superhydrophobicity.[24] However, in practical applications, beaded fibers are not desirable because of their poor mechanical properties. However, the striation structure enhances the superhydrophobicity, but it does not degrade the fiber mechanical properties.

Whereas the results presented here utilize PCL, we have also demonstrated superhydrophobicity using poly(methyl methacrylate) (PMMA) for the core material. Potentially, many synthetic and biopolymers can be used for the core material.

Composition. The chemical composition of coaxial PCL/Teflon fibers has been analyzed using energy-dispersive X-ray spectroscopy (EDX). As shown in Figure 5a, the PCL-only fiber does not have a fluorine peak, but the coaxial fiber shows the fluorine peak clearly. The EDX peak intensity of fluorine in the coaxial fiber is seen to increase monotonically with the flow rate of the Teflon AF solution used in fiber formation (Figure 5b.)

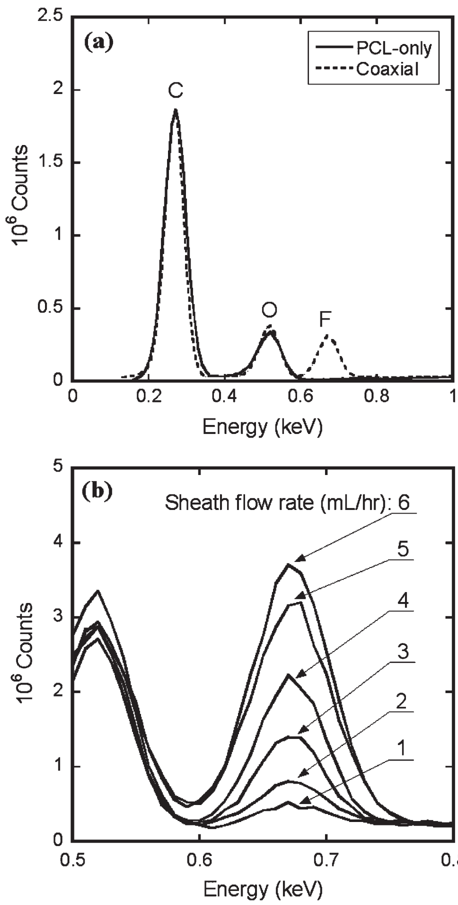

Figure 5. Composition of PCL/Teflon fibers by EDX spectroscopy: (a) comparison between the PCL-only fiber and coaxial PCL/Teflon fiber and (b) fluorine peak intensity change with different Teflon dispensing rates.

Contact Angle. The contact angle is the most widely utilized measure of hydrophobicity. CA examples on different substrates are shown in Figure 6. The left-hand panels in Figure 6a are typical of liquid−solid interactions on the relatively smooth surface of thin films. The water droplet on spin-coated PCL and a Teflon AF film exhibits contact angles of 69° (hydrophilic) and 120° (hydrophobic), respectively. On coaxially electrospun fiber membranes, the water droplet is either in the Cassie−Baxter state or the metastable Cassie−Baxter state, and the CA is increased as a result of surface roughness and entrapped air within the fibers. As shown in the center panels of Figure 6a, the PCL fiber membrane results in a CA of 125°, and the coaxial PCL/Teflon fiber membrane produces a CA of 158° (superhydrophobic). Interestingly, the coaxially electrospun fiber membrane shows oleophobicity whereas the PCL-only fiber membrane is oleophilic. As shown in the right-hand panels of Figure 6a, when a 2 μL droplet of dodecane (~23 mN/m) is placed on the electrospun PCL-only fiber membrane, the dodecane spreads thoroughly and its contact angle is almost 0°. However, on the coaxially electrospun PCL fiber coated with Teflon AF the dodecane droplet has a CA of ~130°, preventing oil spreading.

The contact angles of various liquids with different surface energies were measured on Teflon AF films and coaxial PCL/Teflon AF fiber membranes. As can be seen from Figure 6b, the coaxial fiber membrane is strongly oleophobic for all of the oils evaluated except for octane. Indeed, the CA on the coaxial membrane is larger than the water CA on a Teflon AF film. For oils with surface tension higher than ~50 mN/m, the coaxial is superoleophobic with CA > 150°.

In Figure 6c, the contact angles of the liquids on the coaxial fiber membrane and on a Teflon surface are compared. Also plotted in Figure 6c are the Wenzel and Cassie−Baxter equations. Using a simple geometrical model of the membrane surface with fibers present at an average distance and with an average diameter, one can calculate the approximate surface roughness and the amount of surface wetting. To calculate the critical angle, we have used the measured porosity (~80%) and average fiber diameter (~2 μm) to obtain the surface roughness factor (1.8) and the fraction of the wetted surface (22%). The crossover between the Cassie−Baxter state and the Wenzel state is calculated to occur at a contact angle of θ_C = 120°. From Figure 6c, it can be seen that water is in the stable Cassie−Baxter state. However, most of the alkanes are in the metastable Cassie−Baxter state; in other words, they follow the C−B equation rather than the Wenzel equation for contact angles of less than θ_C on smooth surfaces. As the surface tension of the alkanes decreases, they begin to depart from the metastable C−B state. Finally, octane (with a surface tension of 22 mN/m) is in the Wenzel state with a contact angle of ~0°. These results indicate that the direction for further improvement of oleophobic properties of electrospun fibers is toward increasing the effective fiber membrane surface roughness with higher secondary (and tertiary) fiber surface structure. Higher roughness will decrease θ_C, bringing additional alkanes into the stable C−B regime.[43]

Rolling Angle. In practical applications, dynamic behavior such as water droplet rolling and bouncing after impact are more important than static characteristics such as the contact angle. Coaxially electrospun fiber membranes have excellent water rolling behavior. To measure the rolling angle, 10 μL droplets of water are first placed on Teflon AF films, coaxial fiber membranes, and PCL-only fiber membranes. Then the stage is tilted until the droplet rolls off. As can be seen from Supporting Information Figure S1, the rolling angle is ~5° on the coaxial fiber membranes, whereas on the Teflon AF film the angle is ~25°. On the PCL-only fiber membranes, the water droplet is pinned to the surface, even though it has a high contact angle of ~125°.

In many cases, it is advantageous if water droplets can roll off in a specific direction. A groove pattern aligned parallel to the rolling direction is known[44] to improve the rolling behavior of liquids. Interestingly, this is an advantage for using electrospinning fiber production because aligned fibers can be conveniently produced. During the electrospinning process, the polymer liquid jet is electrically charged and is affected by an electric field distribution that can be easily designed using patterned electrodes on the bottom substrate.[20]

Droplet Impact on Surfaces. Another important dynamic behavior is the bouncing behavior of water droplets after surface impact. In many practical applications, the water-repellent properties of the superhydrophobic surface have to be maintained when water drops reach the surface with relatively high energy. Depending on the surface structure and properties of the hydrophobic material, energetic water droplets can penetrate the surface, squeezing into below-surface air pockets and becoming pinned. Resistance to total impalement (Wenzel state) is critical to maintaining the water-shedding property under energetic impact. Figure 7 clearly shows the difference in water-bouncing

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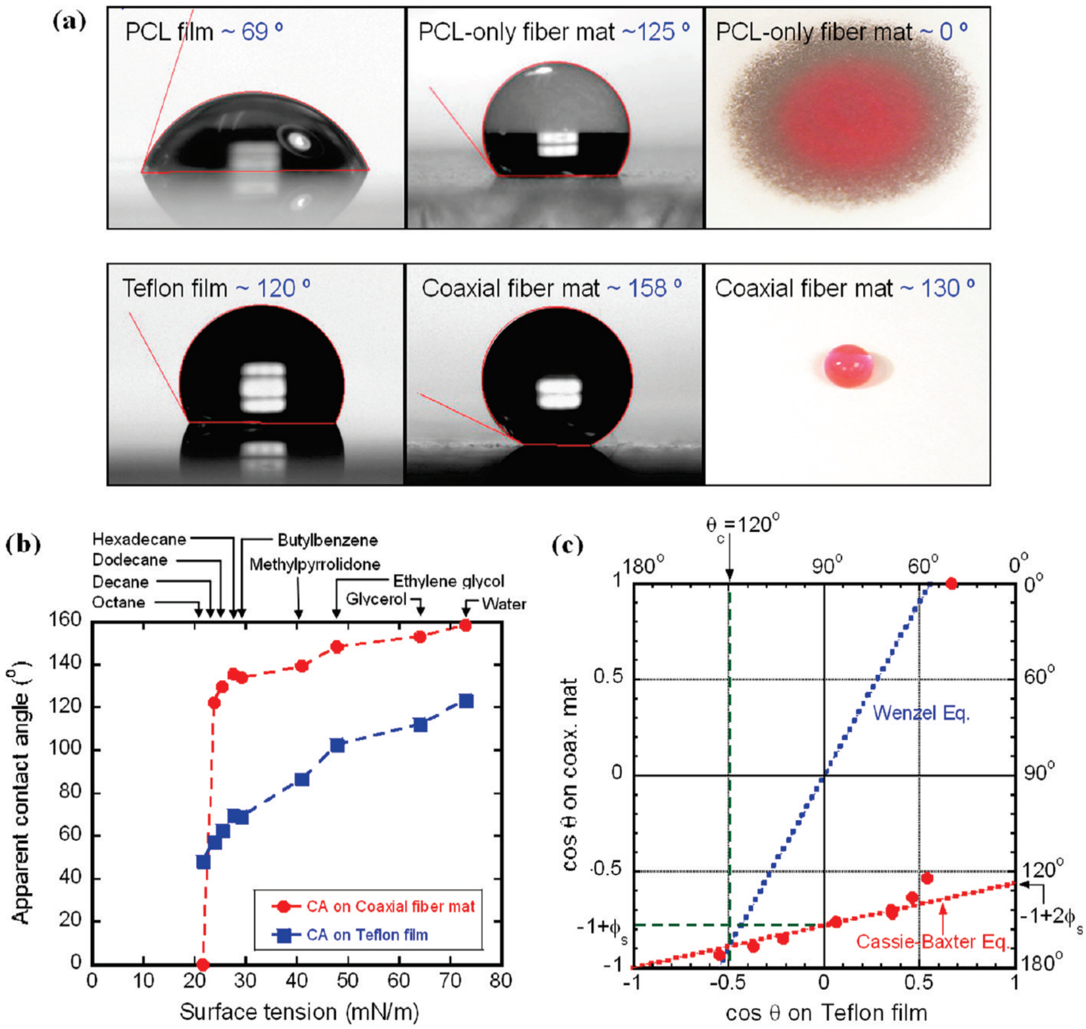

Figure 6. Contact angle measurements: (a) water droplet (2 μL) on a PCL film, Teflon film, PCL-only fiber membrane and coaxial PCL/Teflon fiber membrane; dodecane droplet (2 μL) on fiber membranes of PCL-only and coaxial PCL/Teflon; (b) contact angles of various solvents including water and oils on Teflon films and on PCL/Teflon coaxial fiber membranes; and (c) comparison between theoretical and experimental results.

behavior between a PCL-only fiber membrane (Supporting Information Movie S1) and a coaxial PCL/Teflon AF fiber membrane (Supporting Information Movie S2). The surface roughness of multiple scales has been shown[45,46] to be very important in preventing total impalement and concomitant droplet pinning. The coaxial fiber membranes show excellent water-bouncing behavior at the falling speed of 1.44 m/s with 10 μL volume. Even when a water stream of 500 μL was directed at the surface for 0.5 s with energy much higher than that of a free-falling small droplet, the water jet bounced off the surface, with just a few small droplets becoming attached with a contact angle of > 150° (Supporting Information Movie S3.) It is clear that the coaxial fiber membrane surface structure, which combines macro-roughness (spacing between fibers) with microroughness (striation of individual fibers), is very effective at preserving the water-shedding properties of energetic water streams.

Mechanical Properties. Because we have used two immiscible Teflon AF and PCL solutions for coaxial electrospinning, there is no diffusion between core and sheath layers. Therefore, their properties should be preserved with no degradation. To confirm this aspect, mechanical properties of PCL-only fiber and coaxial PCL/Teflon AF fiber membranes were measured as shown in Figure 8a. As previously reported,[34] using two partially miscible solutions for coaxial electrospinning can still produce very good core−sheath-structured fibers because the interdiffusion time constant between the two solutions is much longer than the travel time of the liquid jet from the needle to substrate. However, even a relatively low level of diffusion between the core and sheath can result in the degradation of mechanical properties, especially for failure strain, because breaks in the gelatin sheath layer act as cracks for the core polymer.

Teflon AF has good stiffness and ultimate tensile strength (UTS) but poor elongation,[36] whereas PCL has good elongation and UTS but low stiffness. As shown in Figure 8b, because of the Teflon AF sheath layer, the stiffness (stress/strain ratio) of the coaxial fiber is twice that of the PCL-only fiber membranes. As expected, the stiffness of the coaxial fiber membranes (~13 MPa) is much lower than that of solid Teflon AF films (~1.5 GPa). One must bear in mind that the coaxial fiber uses a very small amount of Teflon in the form of a coating that is only a few tens of nanometers thick. This represents only ~1% of the material in a solid Teflon film. Therefore, the equivalent stiffness of the Teflon material in the fiber is ~1.3 GPa, which is close to that of Teflon AF films. As shown in Figure 8a, the coaxial PCL/Teflon AF fiber

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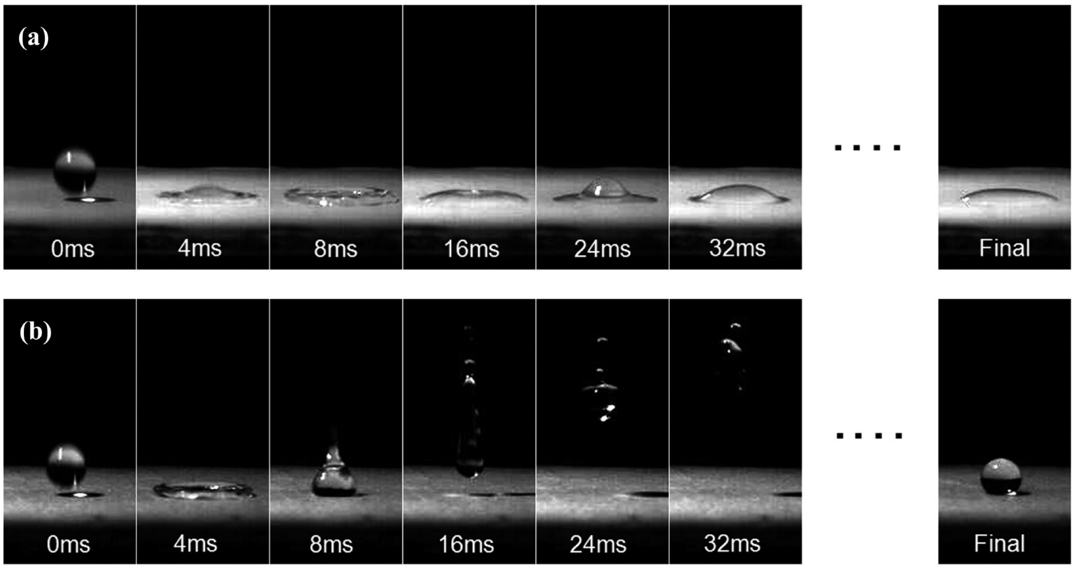

Figure 7. Time sequence of water droplet impact on (a) PCL-only fiber membranes and (b) coaxial fiber membranes.

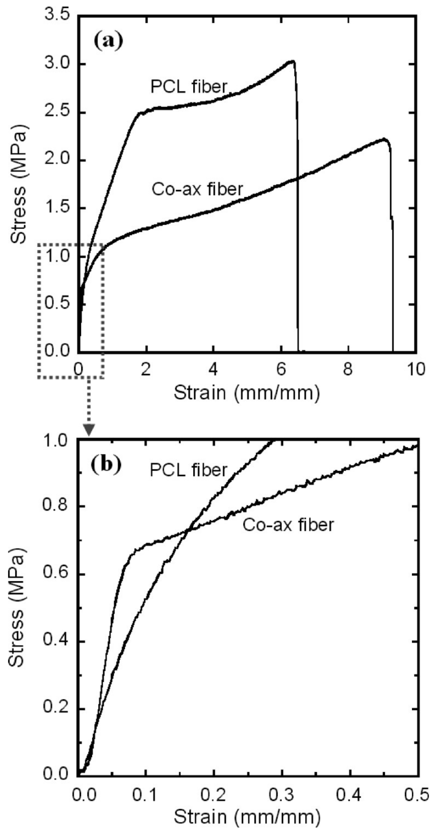

Figure 8. Stress−strain characteristics of PCL-only fiber membranes and coaxial PCL/Teflon fiber membranes.

membranes have a higher strain failure value of ~9.6 mm/mm compared to that of the PCL-only fiber membranes of ~6.3 mm/mm. Interestingly, the coaxial fiber membranes exhibit a lower UTS of ~2.3 MPa compared to that of PCL-only fiber membranes of ~3.1 MPa. One can adjust the UTS value of the coaxial fiber for the weight fraction of PCL and the porosity of electrospun membranes. The adjusted UTS of ~2.7 MPa is still lower than that of PCL-only fiber membranes. These differences are caused by the physical interdiffusion between individual electrospun fibers due to residual solvent still present after electrospinning, especially for PCL-only fibers. The coaxial fiber membranes can also experience interdiffusion between Teflon AF sheath layers. However, during the mechanical tensile test, the interdiffused sheath layers will break at low strain values as a result of the poor

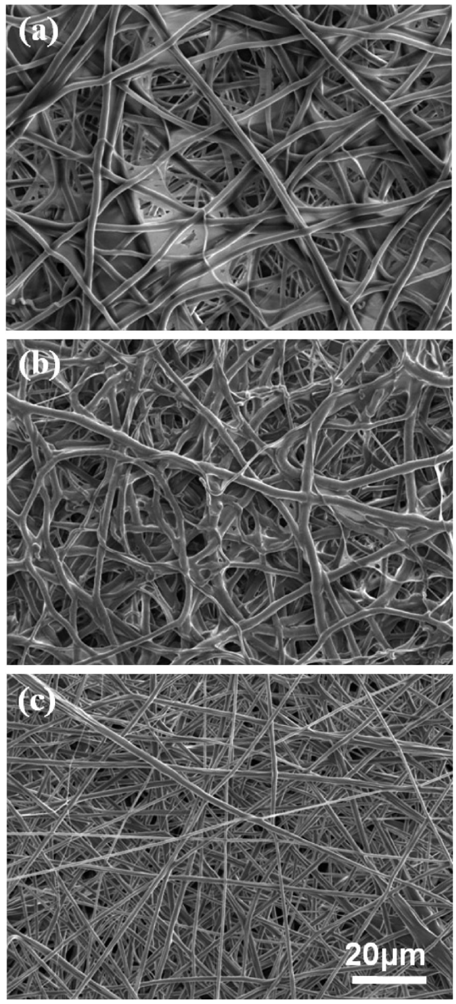

Figure 9. Comparison of PCL-Teflon membranes by electrospinning and sol−gel processes: (a) a Teflon AF spin-coated PCL membrane, (b) a Teflon AF dip-coated PCL membrane, and (c) a coaxially electrospun PCL/Teflon AF membrane.

Table 1. Summary of Hydrophobic Properties and Mechanical Properties of Teflon Film and Electrospun Fibers

	water contact angle (deg)	contact angle hysteresis (deg)	rolling angle (deg)	dispensed Teflon solution (μL)[a]	Teflon mass fraction (%)	mechanical properties UTS (MPa)	max Strain (mm/mm)	stiffness (MPa)
Teflon Film	120	~5	~25	500	100			
PCL-only Fiber	125	~79	> 90	0	0	3.1	6.3	6.3
Coax-eSpin with Teflon 1 wt %	158	~3.8	~7	24	8.8	2.3	9.6	13.0
Coax-eSpin with Teflon 0.5 wt %	153	~23	~20	6	3.3	2.23	8.5	8.9
Figure 10 (conventional to coaxial eSpin)	155			35	0.57			

[a] Dispensed Teflon 1 wt % solution on a 2.5 cm × 2.5 cm area.

elongation property of Teflon AF and thus do not affect the UTS and failure strain values that occur at much higher strain values. Consequently, the mechanical properties of the PCL core have been preserved with no degradation.

Compared to sol−gel processes, such as spin-coating and dip-coating of PCL fiber membranes with Teflon AF solution, coaxial electrospun PCL/Teflon AF fiber membranes consume less Teflon AF and provide better porosity and roughness. A comparison of these techniques in illustrated in Figure 9. The spin-coated membrane used a two-cycle process consisting of a spread cycle of 500 rpm for 10 s followed by a spin cycle at 4000 rpm for 40 s. The dip-coated membrane was withdrawn from solution at a rate of 1.4 mm/s.

We have also demonstrated the direct fabrication of multilayer membranes in a single process as shown in Figure 10. Simply by controlling the flow rates for the core and sheath solutions, it is possible to switch between single and coaxial electrospinning. Whereas 2.14 mL of a PCL 10 wt % core solution was used, only 140 μL of a Teflon AF 1 wt % sheath solution was used for a large membrane with dimensions of 5 cm × 5 cm × 600 μm. The weight fraction of Teflon AF is only ~0.57 wt % in the membrane.

Discussion and Conclusions

Superhydrophobic and oleophobic core/sheath PCL/Teflon AF fibers have been fabricated using a simple, versatile single-step coaxial electrospinning technique. The main characteristics are summarized in Table 1.

The electrospinnable core polymer that provides surface roughness is conformally coated with nonelectrospinnable Teflon AF fluoropolymer that provides low surface energy. The combination of these two properties produces superhydrophobicity. Compared to other fabrication techniques for superhydrophobic materials, coaxial electrospinning is a simple process (1) requiring only relatively simple equipment; (2) capable of fiber alignment for improved rolling behavior; (3) able to form superhydrophobic membranes without any permanent supporting substrate; and (4) using less hydrophobic material.

Moreover, one can switch from conventional electrospinning to coaxial electrospinning during the fiber-formation process so that very thick superhydrophobic membranes can be produced with a small amount of Teflon AF fluoropolymer. In our preliminary demonstration of the multilayer concept in Figure 10, the fiber membrane was not formed on a fabric substrate. Therefore, we did not measure the mechanical stability of the overall structure. However, mechanical adhesion to the fabric is an important consideration and will be characterized in the future.

An ideal coaxial fiber material will provide superhydrophobicity with a very small amount of fluoropolymer. The challenge will be to ensure that the core fibers are conformally coated and durable with the least amount of hydrophobic material.

Once a perfectly conformal fluoropolymer sheath is obtained, the coaxial fibers also have the potential to be used for chemically resistive textile/membrane applications, such as filtration membranes and protective clothing, because of their excellent chemical resistance.

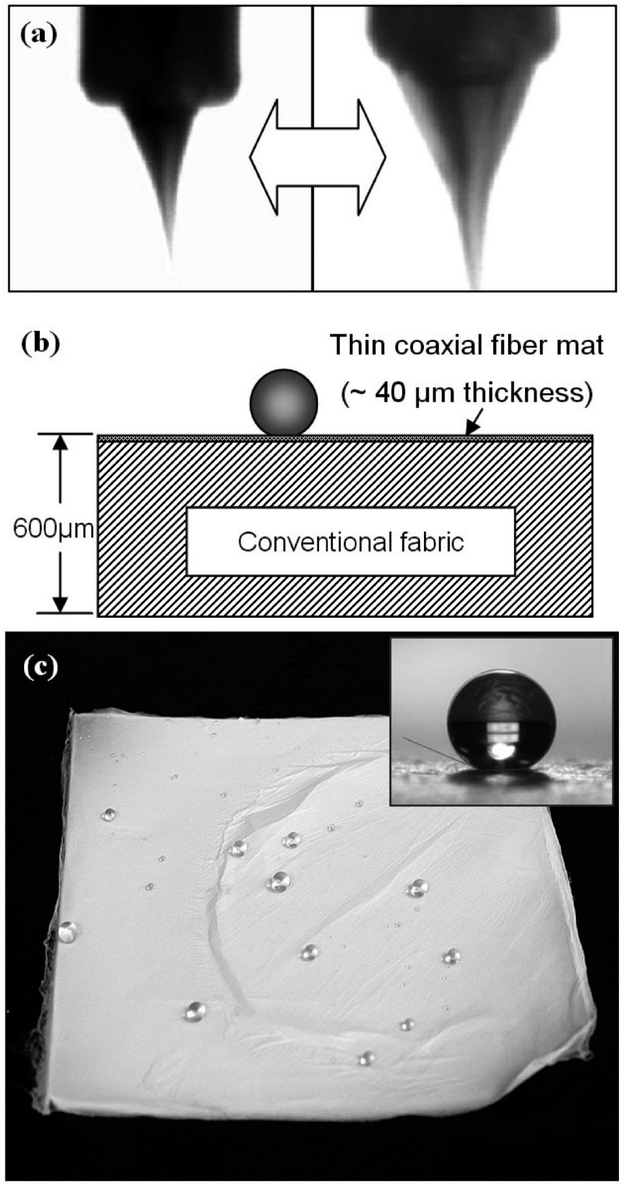

Figure 10. Fabrication of thick superhydrophobic membrane using conventional PCL electrospinning followed by coaxial PCL/Teflon AF electrospinning: (a) continuous and reversible Taylor cone formation between single and coaxial electrospinning; (b) diagram of a very thin coaxial fiber membrane on a thick electrospun fiber membrane; and (c) photograph of a two-layer membrane (inset: high-magnification photograph of a water droplet on a surface).

As part of the experiments described in this article, different core polymers such as PCL, PMMA, and gelatin have been used with Teflon AF for the sheath material. Many other normally nonelectrospinnable functional materials can also be electrospun using the coaxial electrospinning technique with the help of an electrospinnable core material. Coaxial electrospinning has the potential to provide a new paradigm for obtaining material combinations that are very attractive in many fields.

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Supporting Information Available: (Figure S1) Droplet rolling angle measurement: 10 μL of a DI water droplet with colored dye (top − Teflon film; center − coaxial fiber membranes; bottom − PCL-only fiber membranes). The water droplet on coaxial fiber membranes rolled off at 5°, and on a Teflon film, at 25°; on a PCL-only fiber membrane, the droplet does not roll off even at 90°. (Movie S1) High-speed movie clips for water-bouncing experiments: 10 μL water droplet falling on electrospun PCL-only fiber membranes (1 kfps). (Movie S2) High-speed movie clips for water-bouncing experiments: 10 μL water droplet falling on coaxially electrospun PCL/Teflon fiber membranes (2 kfps). (Movie S3) High-speed movie clips for water-bouncing experiments: 500 μL water stream directed on coaxially electrospun PCL/Teflon fiber membranes (2 kfps). This material is available free of charge via the Internet at http://pubs.acs.org.