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Electrospun Fibers for Oil-Water Separation

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The increasing worldwide oil pollution intensifies the needs for new techniques of separation of oil from oily water. Separation by the use of electrospun fibers with selective oil/water absorption is a relatively new but highly promising technique. Owing to their highly specific surface areas, interconnected nanoscale pore structures and the potential to incorporate active chemistry on a nanoscale surface, electrospun fibers have become a promising versatile platform for the separation of oil/water mixtures and emulsions. In this review, after a short introduction to the imperative for oil/water separation and electrospinning technique, we will focus on superhydrophobic/superoleophilic electrospun fibers for oil/water separation, including the preparation of electrospun fibers with superhydrophobic/superoleophilic surfaces, superhydrophobic/superoleophilic fibrous membrane for oil absorption and oil filtration. Further, superoleophobic/superhydrophilic electrospun fibers and their application for oil-water separation will be discussed as well. Finally, conclusions about this review will be presented while addressing remaining problems and future challenges.

1. Introduction

There is an increasing worldwide concern about the separation of oil-water mixtures to combat environmental issues similar to the recent catastrophic spill in the Gulf of Mexico[1]. Oil-water separation is becoming more crucial due for multiple reasons. First of all, oil spill accidents often occur during its exploitation, transportation, transfer, utilization and storage[2]. Frequent oil spill accidents are of great concern, as they result in energy loss and waste of resources while posing long-term threats to the ecological environment on which our society depends[3-7]. Oily waste water is a major problem in many industries such as crude oil production[8], petroleum refineries[9], lubricant[10], metallurgical[11], food[12] and textile processing[13], making it one of the most common pollutant all over the world. In addition, for maritime oil transportation, even a trace amount of water in fuel oil may threaten the safety of transportation[14].

Conventional oil-water separation methods such as adsorption[15],

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gravity separation[16], biological treatment[17], sedimentation in a centrifugal field[18] and electro-coagulation[19] have been widely used for oil-water separation. At present oil-water separation is mainly conducted by physical, chemical and biological methods. However, these methods do not provide a completely satisfactory solution. On one hand, chemical and biological methods may often cause secondary pollution to the surroundings. For instance, oil/water mixture is usually collected by mechanical skimmers from spill oil, which is still difficult to be treated. On the other hand, physical adsorption materials such as linoleum, activated carbon, sponge, cloth, metal wire mesh and other porous materials for oil-water separation present the disadvantages of low absorption rate, small absorption capacity and restricted recyclability due to water absorption exerting a lot of restrictions to recyclability. In order to solve this problem, researchers have adopted chemical vapor deposition, press, and phase separation method to change the surface structure and composition, thus giving the contrary wettability of water and oil in the resulted porous materials. However, limitations including a complicated preparation process, low efficiency, and the generation of secondary pollutants restrict their practical applications. With increasing environmental awareness and tighter regulations, it is imperative to put forward novel strategies to separate oils from industrial wastewaters, polluted oceanic waters, and oil-spill mixtures[20].

Membrane technique has been proved to be one of the best methods for the separation of oil from oil-water mixtures, which have been widely adopted in the food processing, pharmaceutical, desalination and fuel cell industries. In comparison to skimming and chemical treatment[10, 21, 22], membrane separation technology offers

higher oil removal efficiency, stable effluent quality and lower energy cost making it one of the most effective ways to separate oil-water mixtures for a wide range of industrial effluents[23, 24].

Electrospinning[25-35] is a versatile technique that can create nonwoven mats containing continuous fibers with diameters ranging from micrometers to a few nanometers. Although the concept of electrospinning can be traced back to 1745[36], it did not gain substantial attention until the activities of the Reneker group in the 1990s[36]. Thereafter, numerous electrospinning fibers with complex structures have been reported, including hollow[37], core-shell[38] and honeycomb structures[39] as well as structures ranging from single fibers[40] to orders arrangements of fibers[41]. After decades of development, electrospun fibers have found various potential applications: e.g. filtration[42], protective textiles[43], drug delivery[44], tissue engineering[45], electronic and photonic devices[46], sensor technology[47] and catalysis[48].

In regard to oil-water separation, recent research efforts have used electrospinning to fabricate nanofibrous absorbent and filtration membranes[49], which have gained increasing attention in oil-water separation applications since the late 1990 s[49-58]. Electrospun nanofibers have high specific surface areas[57], highly interconnected pore structures, nano scale pore sizes, the potential to incorporate active chemistry on a nanoscale[59] and low initial solidifies. These properties result in high permeability in oil-water separation, which can not only improve the separation efficiency but also reduce the energy consumption of the process. In addition, favored by its controllable fiber diameter ranging from micrometers to a few nanometers, electrospun fibrous membranes are effective in separation of emulsified oil-water mixtures.

While many good review papers on the development of electrospinning technique in, e.g. biomedicine have been published[29, 60-71], the application of electrospun fibres in oil/water separation has not been summarized to the best of our knowledge. Considering the fast development of this area, the development of electrospun fibers for oil/water separation is reviewed in this contribution aiming to highlight this exciting technique and provide a new insight in water disposal. We will, in section 2, start with highlighting recently development in the fabrication of electrospun fibrous membrane with superhydrophobic/superoleophilic surface, which is the key property for the separation of oil and water. Then, the application of superhydrophobic/superoleophilic membrane for oil absorption and oil/water mixture filtration will be discussed. In section 3, the application of superhydrophilic/superoleophobic electrospun fibers for oil-water separation will be discussed. A summary of the review and an outlook of this technique will be provided in section 4.

2. Superhydrophobic/superoleophilic electrospun fibers for oil-water separation

Most electrospun fibers used for oil-water separation have superhydrophobic/superoleophilic surface. Due to the hydrophobic properties of the surface, the separation membranes/sponges are unlikely to be contaminated by bacteria. In addition, superhydrophobic/superoleophilic electrospun fibrous materials can filter or absorb oil from floating and disperse oil-water mixture selectively and efficiently. In this section, the fabrication and application of superhydrophobic/superoleophilic electrospun fibers for oil-water separation will be discussed.

2.1 Fabrication of electrospun fibers with superhydrophobic surface

Hydrophobicity describes the physical property of a molecule/surface that repels water[72]. Materials with surface water contact angle (WCA) higher than 90° is considered to be hydrophobic. A hydrophobic surface can easily be developed using building blocks with low surface energy or by surface modification. Superhydrophobic surfaces (WCA higher than 150°), however, require not only low surface energy but also hierarchical structures
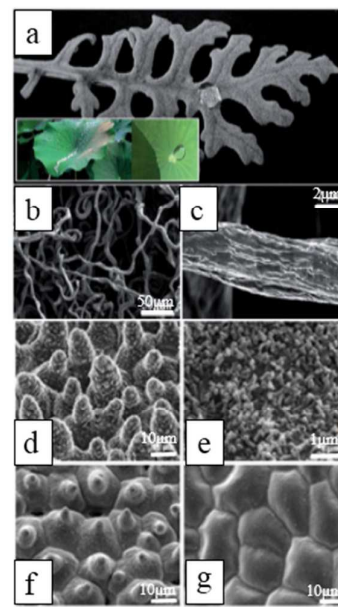
Fig. 1 Hierarchical structures of lotus leaf and silver ragwort leaf. (a) Lotus leaves and silver ragwort leaf, which exhibit extraordinary water repellency on their upper side. (b) Silver ragwort leaf SEM images at low magnifications. (c) Silver ragwort leaf SEM images at high magnifications.[73] (d) Scanning electron microscopy (SEM) image of the upper leaf side prepared by 'glycerol substitution' shows the hierarchical surface structure consisting of papillae, wax clusters and wax tubules. (e) Wax tubules on the upper leaf side. (f) Upper leaf side after critical-point (CP) drying. The wax tubules are dissolved, thus the stomata are more visible, Tilt angle 15°. (g) Leaf underside shows convex cells without stomata.[52] Reproduced with permission from ref. 73. © iopscience 2006. And ref. 52. © Beilstein Journal of Nanotechnology 2011.

on the surface, as inspired by nature[74]. Lotus leaf, silver ragwort leave and water strider legs exhibit remarkable superhydrophobic properties, attributed to multiple nano and micrometer structures on the surfaces (see Fig. 1-2)[52, 53, 73, 75-80]. To fabricate superhydrophobic electrospun fibers, both low surface energy, moist and hierarchical structures are momentary on the surface. Accordingly, this can be achieved by either direct electrospinning of hydrophobic polymers/fibers or by surface modification of electrospun fibers. In this section, the electrospinning of superhydrophobic fibrous materials will be briefly discussed. Previous reviews provide a detailed discussion and progress review of superhydrophobic electrospun fibers[81, 82]. Hence, only a short review on recent progress on the electrospinning of superhydrophobic fibers will be discussed in this section.

2.1.1 Direct electrospinning hydrophobic materials

Various hydrophobic polymeric materials have been used for direct electrospinning of (super) hydrophobic fibers[83-86], such as polystyrene (PS)[27, 73, 76, 87], fluorinated silane functionalized polymers[88, 89], Polydimethylsiloxane (PDMS)[90, 91] and fluorinated polymers[50, 92, 93]. For instance, Chen et al.[94] have prepared superhydrophobic polyvinylidene fluoride (PVDF) membranes via electrospinning PVDF and its functionalized counterpart as well as fluorinated silane coupling agents. Associated contact angle experiments show that superhydrophobic membranes with a WCA

of 156° and 152° can be achieved by electrospinning PVDF and silyl functionalized poly (vinylidene fluoride) (SFPVDF) coupled with fluorinated silane, respectively (Fig. 3a-b). Jiang et al.[83] prepared electro hydrodynamic films of different morphologies from PS/DMF solutions of different concentrations. Randomly oriented nanofibrous films fabricated from a 25 wt% solution of PS in DMF exhibits a WCA of 139° (Fig. 3c). In contrast, a diluted PS/DMF solution of 5 wt% composed of particles with a diameter range of 2-7 nm allowed the formation of micro/nanostructures with a hollow conical shape covered by nanopapilla of 50-70 nm (Fig. 3d). These structures presented a showing superhydrophobic properties (WCA = 162.1°). Agarwal et al.[95] have also shown that with the presence of micro-sized particles and nanofibers (diameter < 200 nm), increased superhydrophobicity (WCA = 150°) could be achieved
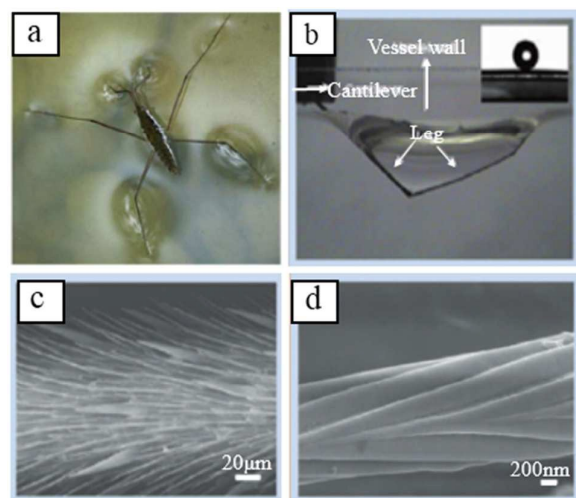

Fig. 2 (a) Photo of an insect water strider.[53] (b) Typical side view of a maximal-depth dimple just before the leg pierces the water surface. Inset, water droplet on a leg. this makes a contact angle of 167.6°. c, d, Scanning electron microscope images of a leg showing numerous oriented spindly microsetae. (b) and the fine nanoscale grooved structures on a seta.[77] Reproduced with permission from ref. 53 © IEEE 2007. And ref. 77. © nature 2004.
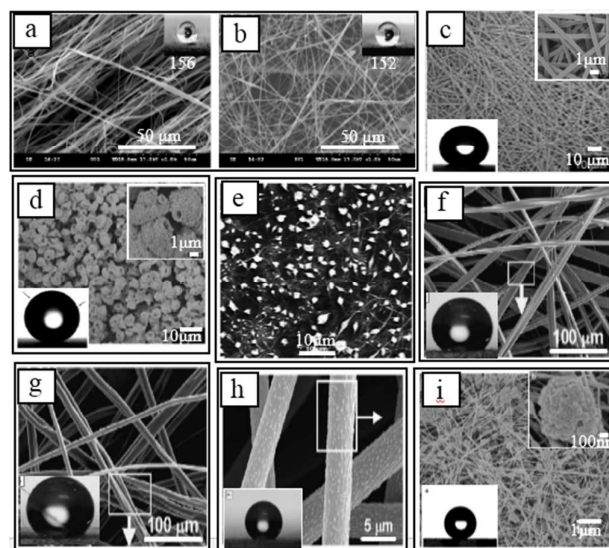

Fig. 3 (a) SEM images of membranes prepared from PVDF/PFOTES. (b) SFPVDF/PFOTES using electrospinning method.[94] (c) SEM image of film prepared from a 25 wt% PS/DMF solution and magnified part of (b) and water droplets on (b) film. (d) SEM image of film fabricated from a 5 wt% PS/DMF solution and magnified image of porous microparticles and water droplet on film.[83] (e) SEM micrographs PFS–styrene copolymer 5% solution in THF:DMF (1:1 v/v).[95] (f) FESEM images of electrospun PS fibers from 30 wt% PS solutions in THF and the images of the water droplet on the surface of the electrospun PS membranes from 30 wt% PS solution in THF. (g) FESEM images of electrospun PS fibers from 30 wt% PS solutions in CHCl3 and the images of the water droplet on the surface of the electrospun PS membranes from 30 wt% PS solution in CHCl3. (h) FESEM images of electrospun PS fibers from 35 wt% solutions in DMF and water droplet on electrospun PS fibers from 35 wt% solutions in DMF.[96] (i) SEM image of an electrospun PANI/PS composite film prepared from a 3.72 wt% PS: ABSA/DMF solution and the shape of a water droplet on a PANI/PS composite film with CA of 166.5°.[97] Reproduced with permission from ref. 94, 96. © Elsevier 2009, 2008. And ref. 83, 95, 97. © Wiley 2004, 2006, 2006.

(Fig. 3e). Solvent type and mixture composition can significantly influence fiber morphology and subsequently the hydrophobicity of a surface. Kang et al.[96] have demonstrated electrospun PS in several solvents, including THF, chloroform and DMF. It was found that when PS/THF solution was electrospun, the obtained fibers had porous surface morphology with a contact angle of 138.1 ± 0.7° (Fig. 3f). An electrospun PS/CHCl₃ solution exhibited large-scale grooves on individual fibers and membranes had an increased WCA (138.8 ± 0.5°) (Fig. 3g). In contrast, electrospun PS:DMF fibers under comparable conditions were protuberant on individual fibers and the water contact angle was remarkably increased to 154.2° ± 0.7° (Fig. 3h). Miyauchi et al.[73] have also investigated the influence of the composition of THF/DMF solvent mixtures on the electrospinning of PS and pointed out that the ratio of the two solvents was a key parameter for determination of surface structure.

Apart from solvent, external additives, such as nanoparticles[98], ionic liquid[99] and polyaniline (PANI)[97] can also influence the morphology and the surface roughness of resultant fibers. Zhu et al.[97] fabricated a stable superhydrophobic surface with WCA of 167° and SA of less than 5° (Fig. 3i) utilizing conducting PANI blended with PS. They found that the content of PS has a great effect on the morphology of the PANI/PS composite films. Furthermore, electrospun superhydrophobic conductive and magnetic Fe_3O_4-filled carbon nanofibers exhibit a water contact angle of 156.5°[100] (Fig. 4a). The combination of superhydrophobic surfaces with the conductive and magnetic properties of carbon nanofibers could prevent the intrusion of water into nanostructures in a natural environment.
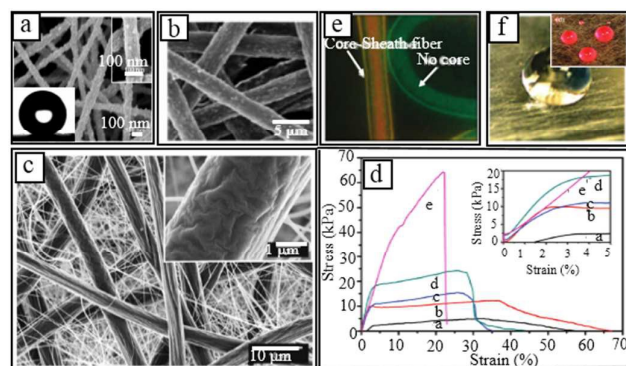

Fig. 4 (a) SEM image of Fe_3O_4-filled CNFs with 40 wt% $FeAc_2$.[100] (b) FE-SEM image of fibrous PS mats formed from DMF loaded with 14.3 (wt%) contents of silica.[85] (c) FE-SEM images of fibrous mats formed with various number ratios of jets of PS/PA₆ 2/2. (d) Stress-strain behavior of fibrous mats formed with various number ratios of jets of PS/PA₆.[101] (e) PCL/gelatin core/sheath fibers fluorescence image and PCL/Teflon fiber TEM cross-section. (f) PCL/gelatin core/sheath fibers superhydrophobic and oleophobic.[102] Reproduced with permission from ref. 100. © Wiley 2006. And ref. 102. © American Chemical Society 2009. Reproduced from ref. 85, 101.

Besides organic materials, considerable efforts have been made to fabricate superhydrophobic surfaces based on inorganic fibers or micro/nano particles including ZnO[86], TiO_2[103], and Fe_3O_4-filled carbon nanofibers[89]. Nano-sized SiO_2 has been most frequently applies for fiber improvement due to its non-toxic and non-polluting characteristics, high temperature applicability, and corrosion resistance fibers[22, 82, 104]. Ding et al.[85] fabricated superhydrophobic hierarchical fibrous films via electrospinning of a PS solution with 14.3 wt% incorporated silica nanoparticles that exhibited superhydrophobicity (WCA = 157.2°) (Fig. 4b).

A common disadvantage of electrospinning superhydrophobic porous microsphere/nanofibers membranes is inadequate mechanical integrity[105]. Multi-jet electrospinning[101, 106-108] has potential to fabricate fibrous membranes with good mechanical properties. With a four-jet electrospinning setup, Li et al.[101] blended PS and polyamide 6 (PA6) fibers to fabricate a large-scale superhydrophobic electrospun mat with enhanced mechanical properties. The optimized fibrous mats were obtained with 2 PS and 2 PA6 jets exhibiting a WCA of 154° (Fig. 4c) and two times larger tensile strength than the pure fibrous PS mats (Fig. 4d). Besides multineedles electrospinning, coaxial electrospinning has also been employed to improve the mechanical properties of superhydrophobicity fibers by forming core-shell structures[102, 109]. Han et al.[102] investigated coaxial electrospinning to obtain core-sheath structured nano- or microfibers that combine the properties of core and sheath materials. They electrospun Teflon fibers with Teflon AF sheath and poly (ε-caprolactone) (PCL) core materials via coaxial electrospinning to obtain a series of superhydrophobic and oleophobic core/sheath fibers membranes with excellent mechanical tensile strength (Fig. 4e-f). Similarly, coaxial electrospinning also allowed Muthiah et al.[109] to produce core-sheath superhydrophobic AF-PVDF nanofiber mats with water contact angles greater than 150°. Compared to other techniques for superhydrophobic fiber production, coaxial electrospinning is able to form fibers without permanent supporting substrate and using less hydrophobic material. However, it is still challenge to ensure core fibers are conformally coated and durable with minimal hydrophobic material.

Layer-by-layer (LBL) self-assembly technique[110-112] has recently been reported as a method of fabricating hierarchical structured electrospun fibrous membranes[55, 113-117]. The introduction of LBL self-assembly enhances the mechanical strength of the membrane while also promoting the trap of air between the water droplet and fiber surface, leading to improved hydrophobicity. Ogawa et al.[89] reported the fabrication of superhydrophobic fibrous membrane composed of fluoroalkylsilane (FAS)-modified LBL structured with multilayer films coating (Fig. 5a). In addition, the hydrophobicity of the prepared surfaces with a different number of deposition bilayers was investigated. It found that the fibers coated with ten bilayers of LBL films showed the highest WCA (162°) and lowest water-roll angle (2°) (Fig. 5b). Ma et al.[21] have LBL self-assembled
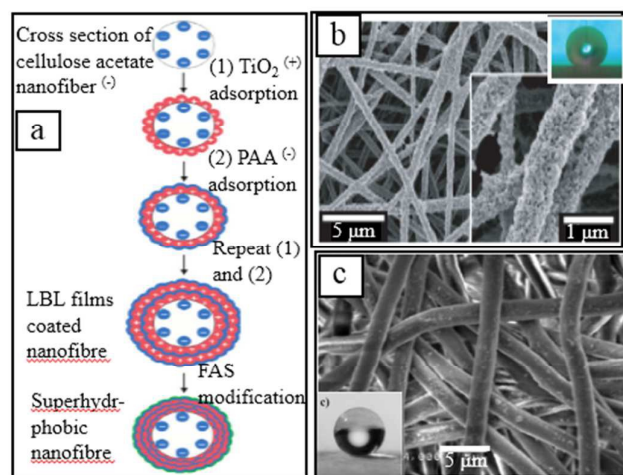
Fig. 5 (a) Schematic diagram illustrating the preparation of super-hydrophobic surfaces via LBL coating and FAS surface modification. (b) SEM images of FAS-modified LBL film-coated cellulose acetate fibrous membranes deposited with 10 bilayers of TiO_2/PAA.[89] (c) SEM images of treated electrospun nylon fibers.[21] Reproduced with permission from ref 89. © iopscience 2007. And ref 21. © Wiley 2007 .

positively charged poly (allylamine hydrochloride) (PAH) and negatively charged silica nanoparticle coated electrospun nylon mats. Subsequently, depositing a semifluorinated silane onto the surfaces lead to superhydrophobic membranes with a WCA of 168° (Fig. 5c). The high hydrophobicity of the decorated fibrous mats was ascribed to the second level of roughness that composed of nanometer-scale pores or particles.

2.1.2 Surface modification to construct superhydrophobic electrospun fibers

Unlike direct electrospinning of superhydrophobic fibers, the surface modification of rough electrospun fibers may also lead to superhydrophobic fibers[118]. Such a two-step process comprising the inherent roughness of electrospun fibrous materials and versatile surface modification techniques may result in electrospun fibrous materials with both good mechanical properties and tunable surface wettability[118, 119]. Here we discuss surface coating, hydrothermal, plasma treatment and chemical vapor deposition (CVD) as methods of surface modification to introduce low surface energy for the electrospun fibers.

Low-surface-energy fluoride-bearing agents such as fluorine-based 1H,1H,2H,2H-Perfluorodecyltrichlorosilane (FDTS)[22], perfluoroalkyl ethyl methacrylate (PFEMA)[120], fluoroalkylsilane (FAS)[89] and 1H,1H,2H,2H-perfluorooctyltrichlorosilane (PFOTS)[121] or silicone-based silanes[122] are used for electrospun fibers coating to prepare a superhydrophobic surface. Ma et al.[120] have reported the fabrication of superhydrophobic nonwoven fabrics by a two-stage process of electrospinning PCL with surface roughness followed by

coating with a thin layer of PPFEMA. Stable superhydrophobicity with a WCA of 175° and a threshold sliding angle less than 2.5° was obtained (Fig. 6a). Recently, an alternative multi-step process has allowed Pisuchpen et al.[122] to fabricate a superhydrophobic fibrous surface with WCA of 168° and hysteresis of 0°. This procedure used multiple cycles of $SiCl_4$/H_2O to treat PVA fiber mats, then silanization with PFOTS. Adding silica to the PVA matrix can increase the rigidity and thus fibers can be protected from collapse, air trapping within the fibrous structure and greater water repellency of the surface (Fig. 6b).

Hydrothermal is an effective technique for substance crystallization from aqueous solutions under high-temperature and high vapor pressures[123]. Through electrospinning, calcination as well
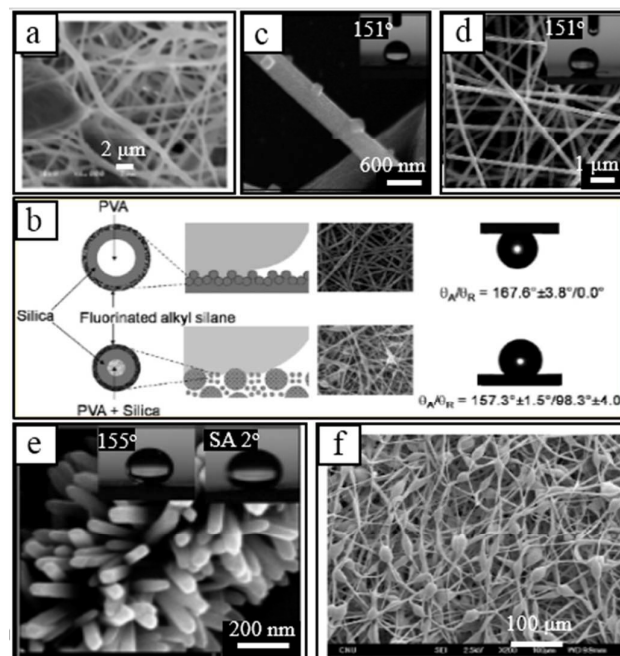
Fig. 6 (a) Typical SEM images of the PCL electrospun mats after iCVD coating, Insets are corresponding before iCVD coating and contact angles.[120] (b) Schematic illustration of the proposed wetting behaviour of the PVA-silanol fiber mat and PVA/silica-silanol fiber mat after silanization with PFOTS.[122] (c) SEM images of fibers prepared using a precursor solution aged for a t_{aging} of 50 h after calcination. Insets are contact angles on the membranes. (d) SEM images of fibers prepared using a precursor solution aged for a t_{aging} of 24 h and $t_{electrospinning}$ of 120 min. Insets are contact angles on the membranes. (e) SEM images of titania nanomembranes after hydrothermal treatment for 120 min. Insets are corresponding contact angles and sliding angle (t_{aging}) = 24 h and membrane pore size = 0.786 μm).[103] (f) Surface sprayed during 2 h and the water droplet shape (inset) showing the superhydrophobic surface.[124] Reproduced with permission from ref 120, 122, 103. © American Chemical Society 2005, 2001, 2009. And ref 124. © Elsevier 2008.

as surface modifying with 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane (POTS) hydrothermal treatment allowed Tang et al.[103] to fabricate stable superhydrophobic hierarchical titania membranes. As shown in Fig. 6c-e, when t_{aging} increased from 24 h to 50 h, the corresponding contact angle rose from 143° to 151°. With 60 min of hydrothermal treatment, nanoparticles with diameter of 20-30 nm formed on the fiber surface, which grew in the vertical direction into rod-like crystals after 120 min of hydrothermal treatment. This corresponded to an increased WCA of 155°.

Plasma treatment involves exposure of the material to the gas plasma to change surface properties, and has been used for the surface modification of electrospun fibers[107]. Yoon et al.[124] fabricated poly (3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) fibers with various bead-on-string structures by electrospinning. The WCA increased from 141° to 158° after CF_4 plasma treatment for 150 s. On this basis, they fabricated superhydrophobicity nano/micro-fibrous cellulose triacetate (CTA) mats, which exhibited a WCA as high as 153° after plasma treatment for 60 s (Fig. 6f). Besides CF_4, other non-fluorinated gases such as Ar or O_2 have been reported for plasma treatment. Furthermore, results are influenced by other factors including specials of plasma, treatment time, working atmosphere, the real contact area, surface roughness and surface chemistry .

CVD enables fabrication of chemically well-defined thin polymeric films with micro- and nano-scale features[125-127]. The combination of CVD with electrospinning is a versatile method for producing superhydrophobic fabrics[128, 129]. Ma et al.[120] produced superhydrophobic fabrics by combining electrospinning and initiated chemical vapor deposition (iCVD) to apply a thin layer of conformal coating of fluorinated polymer on electrospun mats. The hierarchical surface roughness inherent in PCL electrospun mats and the extremely low surface free energy of iCVD coated layer yielded a stable superhydrophobic surface with WCA of 175° and a threshold sliding angle less than 2.5° (Fig. 7a). Sarkar et al.[130] reported a straightforward polymer-derived ceramics technology for the fabrication of superhydrophobic polymer-derived ceramic fibers mats by electrospinning solid per-ceramic polyalumina silazane and chemical vapor deposition of perfluoro-silane onto rough fibers followed by pyrolysis (Fig. 7b). The resulting ceramic fibrous mats showed both superhydrophobic surface properties as well as chemical and thermal stability.

2.2 Superhydrophobic/superoleophilic electrospun fibrous materials for oil absorption

The use of sorbent electrospun fiber membranes is an attractive method for oil spill cleanup[51]. The applicability as an absorbent is mainly attributed to the surface superhydrophobicity and superoleophilicity of the fibrous materials[131]. Electrospun fibers are advantageous for simplicity, efficiency and low cost for their inherent adaptability and applicability, which gives them promise for effective oil-water separation[67].
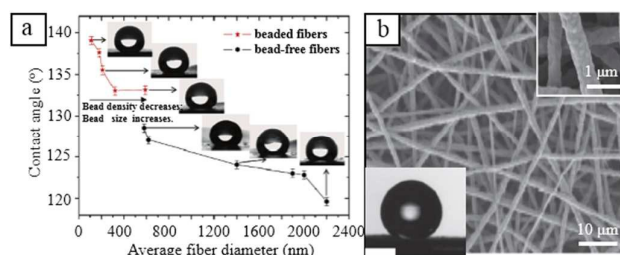
Fig.7 (a) Contact angle for the as-spun PCL mats.[120] (b) Scanning electron microscopy images of polysilazane-derived ceramic fibers electrospun from a 1:1 chloroform/N,N-dimethylformamide mixture.[130] Reproduced with permission from ref 120. © American Chemical Society 2005. And ref 130. © Wiley 2008.

In recent years, many organic synthetic fibers, such as nonwoven polypropylene (PP) fibers, have been used as sorbents for oil-water
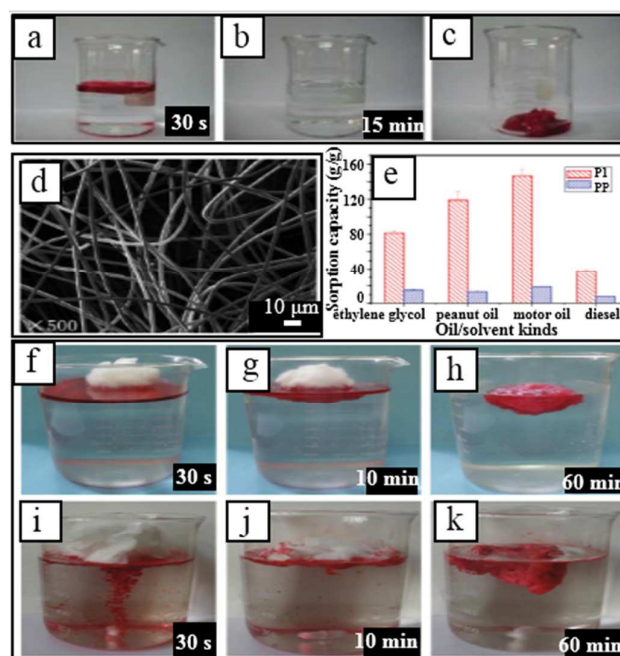
Fig. 8 (a) The PS fibrous film is placed on the motor oil initially. It floated on the oil surface with high buoyancy. (b) After 15 min, the sorbent adsorbed all given motor oil. The oil–water mixture becomes clear and transparent, only leaving water in the container. (c) The PS oil sorbent sample after oil adsorption.[56] (d) SEM images of P1 sorbent. (e) Maximum sorption capacities of P1 and PP for various oils or solvents. (f) - (k) Cleanup of motor oil film (dyed with Oil Red) on water by the obtained P1 sorbent.[132] Reproduced with permission from ref 56, 132. © American Chemical Society 2012, 2011.

separation for their hydrophobic and oleophilic properties, excellent oil-water selectivity, low density and large-scale fabrication. However, conventional PP suffers from a low oil capacity of 15-30 g/g due to extremely low porosity and large fiber diameter[67]. Recently, a low-cost, high-oil-adsorption PS fibers film was extensively investigated for selective oil absorption. Results showed that a thinner porous nanofibrous PS film presents excellent oil/water selectivity; the oil adsorption capacity for motor oil was approximately 131.63 g/g (Fig. 8a-c)[56]. As a comparison to a commercial PP, polyvinyl chloride (PVC)/PS nanofibrous sorbents have shown high porosity (> 99.7%), low density (2-3 mg/cm^3), excellent oil/water selectivity and 5-9 times increased sorption capacities (146 g motor oil/g PVC/PS sorbent) (Fig. 8d-e). This provides new insight into fabrication of highly efficient and low-cost oil sorbents for oil-water separation (Fig. 8f-k)[132]. Sorption selectivity between oils and water has been studied; Lin et al.[133] further investigated different morphologies of PS fibers on the influence of oil sorption capacities. The results showed that the porous fibers with small diameters and smooth surfaces obtained the highest oil sorption capacities while rough fiber surfaces with numerous short grooves saw lower values.

Some research has assessed the formation of micro- and nanostructures direct electrospinning of PS fibers. Recently, Lin et al.[134] subtly regulated the micro and nanostructures of electrospun PS fibers by varying the molecular weights of polymers with different sources, solvent compositions, solution concentration (Fig. 9a-b). They found the motor oil and sunflower seed oil absorption capacity of porous PS fibrous were 84.41 and 79.62 g g^{-1} respectively, nearly three times larger than comparable values for commercial PP non-woven fabric (Fig. 9c). Besides the surface morphology, the fiber porosity and inter-fiber voids can also be controlled via varying the electrospinning parameters by multi-nozzles spinning.

The use of two different polymeric fibers is also an effective way to improve mechanical properties. In one example, polyurethane (PU) fibers were added to the fibrous mats to regulate inter-fiber voids and enhance the mechanical properties via multi-nozzle electrospinning. The presence of a small number of PU fibers in these composite fibrous mats resulted in higher oil absorption capacities (Motor oil = 30.81 g g^{-1}, Sunflower seed oil = 24.36 g g^{-1}) with good reusability (Fig. 9d-e)[57]. An approach to tackle the poor reusability of electrospun fibers for oil sorption is the construction of a core-shell structure. A core-shell structure of fibers developed by co-axial electrospinning gives the opportunity for unique material properties. Lin et al. developed PS-PU composite fibers with a high specific surface area via co-axial electrospinning for use as oil sorbent. Oil sorption capacities of these fibrous mats were significantly influenced by the inter-fiber voids among the fibers instead of the fiber porosity. High oil sorption capacities of 64.40 and 47.48 g g^{-1}, with regards to motor oil and sunflower seed oil respectively, can be obtained, which are approximately 2-3 times that of conventional polypropylene (PP) fibers. After five sorption cy-
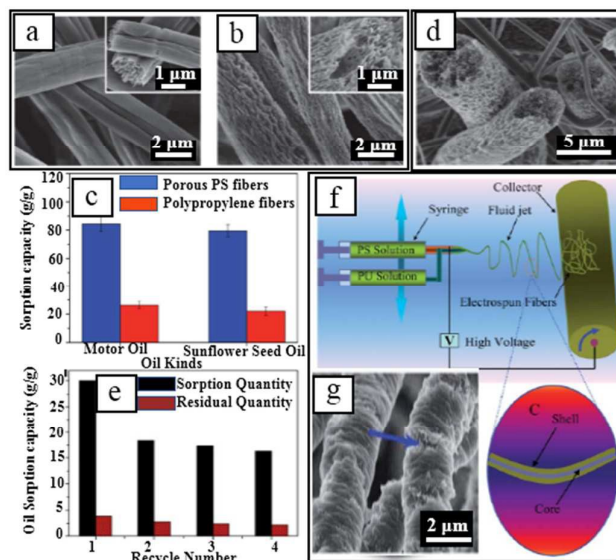

Fig. 9 (a) FE-SEM images of electrospun PS fibers formed with molecular weights of Mw = 350000 g mol^{-1}. (b) FE-SEM images of electrospun PS fibers formed with molecular weights of 208000 g mol^{-1}. (c) Maximum absorption capacities of the porous PS fibrous mats and commercial PP nonwoven fibers for motor oil and sunflower seed oil.[134] (d) FE-SEM images of fibrous mats formed at a RH of 45% with a 4/1 PS/PU nozzle ratio from different PS solutions 30 wt% PS. (e) Reusability of the fibrous mat shown in (d).[57] (f) Schematic representation showing the core–shell electrospinning setup used in this study. (B) Photograph of the co-axial spinneret. (g) FE-SEM image of fibers shown in c after stretching and an illustration of the electrospun core–shell fiber.[75] Reproduced from ref. 134, 57, 75 .

cles, the fibrous mats were able to maintain a high oil sorption capacity (Fig. 9f-j)[75] .

Beyond PS homopolymer, copolymerization of styrene with other monomers (e.g. butyl acrylate) is another method of electrospun PS fibrous membrane property improvement, evident through decreased glass transition temperature and enhanced low-temperature flexibility. Ning et al.[135] synthesized several polymers via suspension polymerization of styrene and butylacrylate, and electrospun these materials into fibrous membranes. The membranes had good hydrophobicity and lipophilicity (WCA = 155°), thus suggesting a good capability for separating oil from water. They further showed a maximum oil removal efficiency of 97.3%, and maintenance of an oil removal efficiency of 74.2% when the fibrous membrane was used for the seventh time. Interestingly, the fibrous membranes could make an O/W emulsion appear clear via oil absorption from water.

Recovery is another critical problem in oil-water separation. To aid in recovery of the sorbent material, the provision of magnetic properties in the composite mat could be beneficial. Among available nanoparticles, magnetic iron oxide (Fe$_3$O$_4$/γFe$_3$O$_4$) has

proven to possess a low degree of cytotoxicity, even at high concentrations[136]. Proper dispersion in composite polymeric materials and magnetic properties would lay a profound foundation for use in oil-sorption sorbents. Jiang et al. [137] fabricated a magnetic nanocomposite mat composed of PS/PVDF nanofibers with selective incorporation of iron oxide (Fe_3O_4) nanoparticles (NPs) to provide magnetic properties via a facile two-nozzle electrospinning process for oil-in-water separation. The mats were highly-porous with improved mechanical properties when compared to a pristine PS mat. Additionally, the addition of Fe_3O_4 nanoparticles in a composite mat provided a magnetic property that helps in easy sorbent recovery. Adequate sorption capacity (35-45 g/g), fiber porosity, interconnected pore structure, good mechanical property, and hydrophobic surface all suggest that the resultant electrospun magnetic $PVDF/Fe_3O_4@PS$ nanofibers could be useful in environmental remediation of oil spills in water and recovery of sorbent material.

2.3 Superhydrophobic/ superoleophilic electrospun fibers for oil filtration

Electrospun nanofibrous membranes used for oil-water separation by filtration are highly efficient. Using nanofibrous membranes in coalescence filtration is an effective way to separate secondary emulsions that contain water droplets with diameters less than 50 μm. Fiber size and wettability are the key factors that control the performance of coalescer filter media. C. Shin et al.[138] investigated the coalescence separation of water droplets in a water-in-oil mixture using glass fiber media and glass fiber supplemented with electrospun nanofiber media for the purpose of experimentally assessing the relationship between bed pressure drop and separation efficiency. Micro glass fibers are most frequently used for water in oil emulsion separation in petrochemical industries. Composite filters of glass fibers mixed with polymer nanofibers showed improved separation efficiency over only glass fiber media; the overall separation efficiency increased with a decrease of fiber size and lower flow rates performed better than higher flow rates. One year later, recycled expanded polystyrene nanofibers were used by Shin et al. to replace the micro glass fibers[139]. The addition of expanded polystyrene nanofibers to conventional micron sized fibrous filter media increases the separation efficiency of the filter media by 20%. SEM image (Fig. 10) reveals the mixed glass and electrospun expanded polystyrene nanofiber[140]. The same group further compared the influence of fiber diameter on the coalescence separation of water-in-oil mixture using glass fiber media supplemented with electrospun polyamide nanofibers[141]. This study showed that addition of polyamide nanofibers (1% mass) to conventional micron-sized glass fiber filter media improved the separation efficiency from 71 to 84%. However, the addition of comparable amounts of polyamide microfibers did not significantly increase the filter efficiency. In further work, Lee et al.[142] prepared solid surfaces with well-controlled superhydrophobic and superoleophilic properties for water–oil separation by single-step
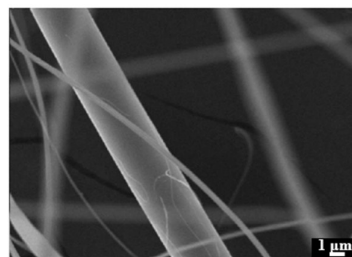

Fig. 10 (a) SEM picture of electrospun EPS nanofiber and commercial glass fiber.[140] Reproduced with permission from ref 140. © Elsevier 2005.

deposition of PS nanofibers onto a stainless steel mesh via electrospinning. The cost-effective and simple combination of low free energy PS nanofibers with the three-dimensional network structures of the membrane enhanced the nonwetting of water while maintaining the intrinsic wetting of oil, supported by contact angles of diesel (0°) and water (155° ± 3°) on the prepared PS nanofiber membrane. More importantly, these membranes easily separated liquids with low surface tension, such as gasoline, diesel, and mineral oil, from water. The PS nanofiber membranes efficiently separated oil from water in a single step of only a few minutes' duration and also exhibited excellent superhydrophobicity even after many cycles of the oil–water separation process. This confirmed their applicability for removal of many types of organic solvents or oils from water at large production scales.

Hollow fiber (HF) module is one of the most common membrane configurations, desired for its large surface area per unit volume, low separation module volume and low cost of operation. Using hollow fibers for oil-water separation gives a very high packaging area per unit volume. It also increases the pressure drop inside and between the nanofibrous membranes. Therefore, R. Halaui et al.[143] have developed HF-PCL and poly(vinylidene fluoride co-hexafluoropropylene) (PVDF-HFP) ultrafiltration (UF) membranes using asymmetric microtubes produced by co-electrospinning. The micro-scale HF-UF membranes can exhibit relatively high rejection values and considerable flux of 30-60 L/m^2 h. This presents great potential for the use of micro-scale HF membranes in oil-water separation.

Recently, much attention has been paid to the fabrication of high filtration efficiency nanofibers membranes because of their high surface area to volume ratios and the recyclability[79, 80, 144-146]. For example, Yang et al.[113] developed polydopamine-coated PS nanofibrous membranes by immersing PS mats in dopamine alkalinities buffer solution for 24 h. The Michael reaction of the polydopamine coating with undecanethiol (UT) or 11-mercaptoundecanoic acid achieved oil-water separation (Fig. 11a). The long alkyl chains of UT anchored on the membrane surface increased the contact angle of water distinctly, allowing oil to pass

smoothly through the membrane while water was blocked completely (Fig. 11b-c).

Recently, Tang et al.[55] fabricated superhydrophobic and superoleophilic nanofibrous membranes by a facile combination of electrospun poly(m-phenylene) (PMIA) nanofibers and an *in situ* polymerized fluorinated polybenzoxazine (F-PBZ) functional layer that incorporated silica nanoparticles (SiO_2 NPs) (Fig. 11d). By employing F-PBZ/SiO_2NPs, hydrophilic PMIA nanofibrous membranes possessed a WCA of 161° and exhibited superoleophilicity (oil contact angle (OCA) = 0°). Furthermore, the as-prepared membranes exhibited high thermal stability (350 °C) and good repellency to hot water (80 °C). The composite has an excellent mechanical strength of 40.8 MPa while employing a gravity driven process for fast and efficient separation of oil-water mixtures, suggesting their applicability to this use (Fig. 11e). Shang et al.[147] fabricated superhydrophobic and superoleophilic nanofibrous membranes exhibiting robust oil–water separation performance by a facile combination of electrospun cellulose acetate (CA) nanofibers and an *in situ* polymerized fluorinated polybenzoxazine (F-PBZ) functional layer that incorporated SiO_2NPs. By employing the modification of F-PBZ/SiO_2NPs, hydrophilic CA na-

Fig. 11 (a) Schematic illustration of the preparation of porous functional membranes using a Pdop-coated PS nanofibrous membrane as a platform. (b) Optical images of the water contact angle with as-synthesized. (c) Optical images of the water contact angle with Pdop-coated.[113] (d) Illustration showing the synthesis procedure of F-PBZ/SiO_2NP modified PMIA nanofibrous membranes and the relevant formation mechanism. (e) The facile oil–water separation using FPMIA-1/SNP-2 membranes, the water and oil were dyed by methyl blue and oil red, respectively.[55] Reproduced from ref. 113, 55.

nofibrous membranes were endowed with superhydrophobicity (WCA = 161°) and superoleophilicity (OCA = 3°). Furthermore, the as- prepared membranes exhibited fast and efficient separation of oil–water mixtures and excellent stability over a wide range of pH conditions, which makes them a good candidate in oil-water separation (Fig. 12a-c). Many superwetting materials have been fabricated by the combination of superhydrophobic properties and surface modification[148, 149]. These electrospun fibers are not applicable for the separation of oil-water microemulsions (droplet size < 20 μm)[150, 151]. Huang et al.[58] presented a novel methodology to fabricate superhydrophobic and superoleophilic nanofibrous membranes for the gravity driven separation of oil-water microemulsions. *In-situ* F-PBZ on the surface of silica nanofibers presented high flux (892 L m^{-2} h^{-1}), good thermal stability, and durability, suggesting the practically of these composite membranes for emulsified oil-water separation. Although it has been known that superhydrophobic coatings could be prepared from PBZ[152], this was the first applications of flexible PBZ modified nanofibrous membranes for oil-water separation. Although leading to robust filtration, the complex fabrication procedures and potential toxicity of fluorochemicals have focused researchers' attention on non-toxic additions to fabricate modified nanofibrous membrane for oil-water separation. Significantly, immobilization of various nanoparticles onto complex 2D or 3D macroscopic surfaces could provide a simple strategy to construct hierarchical roughness on target surfaces. In this regard, an environmentally friendly electroless plating technique is often considered to construct a hierarchically rough structure. Li et al.[153] fabricated superhydrophobic and superoleophilic electrospun nanofibrous membranes exhibiting excellent oil-water separation performance by combining the amination of electrospun polyacrylonitrile (APAN) nanofibers and immobilization of a Ag nanocluster with an electroless plating technique, followed by n-hexadecylmercaptan (RSH) surface modification. The resultant APAN nanofibrous membranes were endowed with a superhydrophobicity (WCA = 171.1 ± 2.3°) and superoleophilicity (OCA = 0°), self-cleaning, low water-adhesion property, remarkable separation efficiency in both hyper-saline environment and a range of pH conditions, as well as excellent recyclability. These properties make this a promising candidate for treatment of industrial oil-contaminated and water marine spilt oil spills, providing a new prospect to achieve functional nanofibrous membranes for oil-water separation.

Recently, polysulfone (PSF) electrospun nanofiber membranes modified using SiO_2 NPs and Graphene Oxide (GO) NPs were used by M. Obaid et al.. for petroleum fractions/water separation[154]. The membranes were successful in separation, and SiO_2 NPs addition strongly enhanced the flux. Furthermore, SiO_2 NPs addition improved Young's modulus, while GO presented a negative influence on mechanical properties. PSF-SiO_2 NPs electrospun nanofiber membranes possessed a high flux for gasoline (100 m^3/m^2), kerosene (115 m^3/m^2) and hexane (187 m^3/m^2) separation. On the other hand, incorporation of GO had relatively small impro-

vement in the PSF electrospun membrane separation performance, presenting the benefits of PSF membranes modified with SiO_2 NPs.

TiO_2 is an attractive semiconductor nanoparticle addition to superhydrophobic surfaces for its UV-shielding capacity, high stability and safety. Huang et al.[155] prepared TiO_2@fabric composite by a facile strategy for preparing marigold flower-like hierarchical TiO_2 particles through a simple one-pot hydrothermal reaction on a cotton fabric surface. Then, the superhydrophilic TiO_2@fabrics was modified with FAS to generate a superhydrophobic/oleophilic material. Optimal TiO_2 surfaces were constructed with a potassium titanium oxalate concentration of 0.75-1.0 mM; with 20-30 h of construction duration a dual-scale hierarchical structure exhibited high superhydrophobic activity (WCA = 160°) and a sliding capillary action suggesting its promise for removing oil pollutants from water for oil-water separation[133]. In addition, the robust superhydrophobic F17/TiO_2@fabrics show e-

xcellent anti-wetting, mechanical and environmental stability, anti-UV transmittance, self-cleaning against water and dust, ease of recycle and selective separation of oil from oil–water mixtures. Previously, squeezing or distillation mainly used aerogels as oil absorbents and focused excessively on the oil absorption capacity, while ignoring the time and cost consuming oil recovery procedures. Therefore, recent work has assessed the construction of a porous, selectively wettable, and mechanically robust aerogels capable of efficient, cost-effective separation of oil-water emulsions. Si et al.[114] first made efforts to use electrospun nanofibers for the preparation of emulsion separation aerogels. They created fibrous, isotropically bonded lastic reconstructed (FIBER) aerogels with a hierarchical cellular structure and superelasticity by combining electrospun nanofibers and the freeze-shaping technique. Then the intrinsically lamellar deposited electrospun nanofibers were assembled into elastic bulk aerogels with tunable porous structures and wettability on a large scale. Their resulting FIBER aerogels exhibit the integrated properties of ultralow density (<30 mg cm^{-3}), rapid recovery from 80% compression strain, superhydrophobic-superoleophilic wettability, and high pore tortuosity. More interestingly, the FIBER aerogels can effectively separate surfactant-stabilized water-in-oil emulsions in a gravity driven process, with high flux (maximum of 8140 (220 L m^{-2} h^{-1}), high separation efficiency, superior antifouling properties, ease of recycle, and good usability, which match well with the requirements for treating the real emulsions on a wide scale (Fig. 12d-e).

In 2015, Gregory C. Choong et al.[156] demonstrated microfiltration of emulsions of oil (dodecane) in water using electrospun membranes of poly (trimethylhexamethyleneterephthalamide) (PA6(3)T) and compared several fouling models with resistance in both series and parallel.

Fig. 12 (a) Schematic for the strategy using the in situ polymerization approach to the synthesis of F-PBZ/SiO_2 NPs modified CA nanofibrous membranes. (b) FE-SEM images and the corresponding optical profiles of water droplets of FCA-1/SNP-2. (c) The facile oil–water separation using FCA-1/SNP-2 membranes, the water and oil were dyed by methyl blue and oil red, respectively.[147] (d) Droplets of dyed water and oil on the top of a FIBER aerogel. (e) Separation apparatus with the facile gravity-driven separation of water-in-oil emulsions using the FIBER aerogels and the microscopic images of emulsions before and after separation.[114] Reproduced from ref. 147. Reproduced with permission from ref 114. © American Chemical Society 2015.

Creating micro/nanostructures on a hydrophobic surface and surface modification to construct superhydrophobic electrospun fibers are promising way to fabricate superhydrophobic electrospun fibers for oil-water separation. However, one of the disadvantages of superhydrophobic electrospun fibers is that it is not fit for gravity-driven oil-water separation as most of the oil has a lower density than water. This causes the formation of a barrier layer in gravity driven oil-water separation. Furthermore, materials with oleophilics are extremely vulnerable to pollution in the process of use, which make greatly limits application. Therefore, superoleophobic electrospun fibers have drawn increasing attention for oil-water separation.

3. Superoleophobic/Superhydrophilic electrospun fibers

3.1 Electrospun fibers with superoleophobic surface

Typical superoleophobic surfaces possess OCA larger than 150° and extraordinarily low water contact angle hysteresis (WCAH)
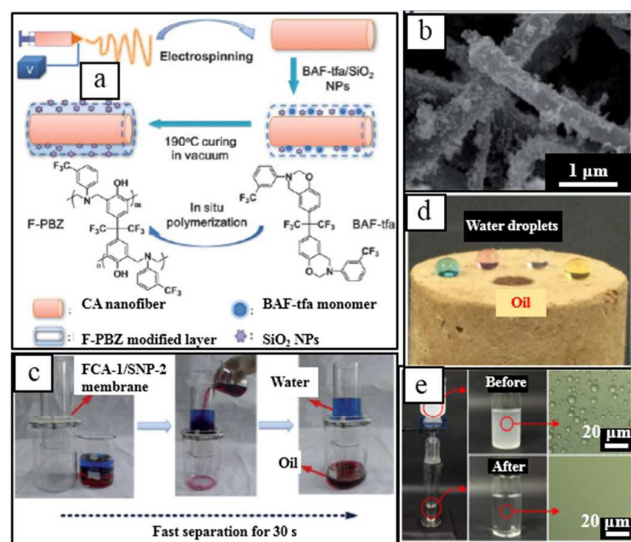
typically less than 10°. The construction of surface superoleophobicity is different from that of surface superhydrophobicity because the surface tension of oil or other organic liquids is lower than that of water. Superoleophobic electrospun fibers are advantageous due to their excellent performance, high reusability and high resistance to oil. Since conventional membranes are suffering from the low flux resultant of limited permeability and surface fouling are critical problem, scientists have placed attention on electrospun fibers with superoleophobic surfaces. For instance, Tuteja et al.[157] have synthesized a series of hydrophobic polyhedral oligomeric silsesquioxane (POSS) functionalized by perfluoroalkyl groups, such as 1H,1H,2H,2H-heptadecafluorodecyl (referred to as fluorodecyl POSS) and 1H,1H,2H,2H-tridecafluorooctyl (fluorooctyl POSS) (Figure. 13a). The high surface concentration and surface mobility of -CF_2 and -CF_3 groups, together with the relatively high ratio of -CF_3 groups with respect to -CF_2 groups, results in a strongly hydrophobic material with low surface energy. Blends of a moderately hydrophilic polymer and fluorodecyl POSS showed that θ_{adv} and θ_{rec} for water on spin-coated films of PMMA and fluorodecyl POSS vary with the mass fraction of fluorodecyl POSS (Figure. 13b). Further, fibers prepared by electrospinning a 5% (w/w) mix of FD-POSS-PMMA exhibited superhydrophobicity and extreme oleophobicity with a FD-POSS mass fraction higher than 0.1, beads on a string, multiple scales of roughness and high porosity. However, all of the corresponding spin-coated surfaces are oleophilic (Figure. 13c-e). The conclusion can be made that local surface curvature is extremely important for the development of surface oleophobicity. The cooperation of electrospinning processes and surface coating enables fiber deposition on fragile and natural substrates in order to confer oleophobicity. Tuteja and his workers[158] further proposed four design parameters that predict contact angles for a liquid droplet, as well as the robustness of the composite interface on a textured surface. Accounting for the various thermophysical and geometric properties that parameterize the system, they developed families of surfaces that are superamphiphobic with the help of systematic variation of chemical and topological surface features. Thus, beads-only, beads-on-strings and fiber-only structures are formed with the concentration increase from 2%, 5% to 10% (w/w). It is expected these three surfaces have similar surface energies as a result of equal fluorodecyl POSS concentration. However, the advancing and receding contact angles of hexadecane are completely different. Recently, Kaur et al.[159] blended a series of PVDF polymers with hydrophilic surface modifying macromolecules before electrospinning to minimise membrane fouling. The macromolecules were prepared from a urethane prepolymer with poly (ethylene glycol) (PEG) and poly (propylene glycol) of various average molecular weights. Electrospinning was compared to the phase inversion to verify that the contact angle varied significantly from 0° to 54° after blending with a PEG-based surface modifying macromolecule. In addition, the water flux of blended EM was higher than the non-blended electrospun PVDF membrane.
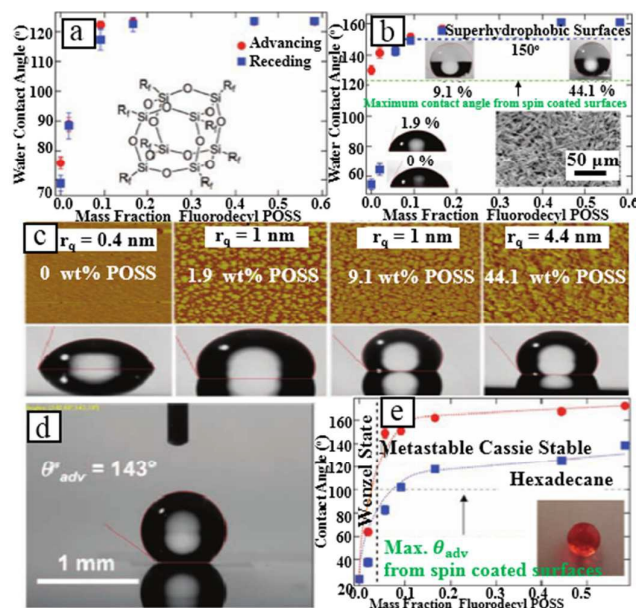

Fig. 13 (a) q_{adv} and q_{rec} for water as a function of the mass fraction of fluorodecyl POSS. The inset shows the general molecular structure of fluoroPOSS molecules. The alkyl chains (R_f) have the general molecular formula –$CH_2CH_2(CF_2)_nCF_3$, where n = 0, 3, 5, or 7. (b) q_{adv}* (red dots) and q_{rec}* (blue squares) for water on the electrospun surfaces. The inset shows a SEM micrograph for an electrospun surface containing 9.1 weight % POSS. The maximum contact angle for water on the spin-coated surfaces is also shown. (c) The phase angle scale on the AFM images is 0° to 10° for the 0, 9.1, and 44.1 weight % POSS images and 0° to 90° for the 1.9 weight % POSS image. The RMS roughness (r_q) for each film is also given. By comparison, r_q for a Si wafer is ~ 0.2 nm. (d)A droplet of water on top of unsilanized SiO_2 micro-hoodoos (2D = 10 mm). (e) q*$_{adv}$ (red dots) for hexadecane on the electrospun surfaces. The maximum contact angles on corresponding spin-coated surfaces (q_{adv}) are also shown. The inset of shows a drop of hexadecane (dyed with Oil Red O) on a 44 weight % fluorodecyl POSS electrospun surface.[157] Reproduced with permission from ref 157. © Science 2007.

3.2 Oil-water separation by superoleophobic electrospun fibers

Superoleophobic electrospun fibers also demonstrate promise for oil-water separation. Much attention has been placed on multilayered electrospun composite fibers for oil-water separation via water filtration, for higher water flux and filtration efficiency. Moreover, the properties of chitosan for hydrophilic, water-resistant, and water-permeable coatings can play a significant role in filtration. For example, Yoon et al.[160] demonstrated a novel high flux ultra-/nanofiltration system based on a polyacrylonitrile (PAN) electrospun nano-fibrous scaffold, with a thin to player of natural chitosan. They fabricated a three-tier composite membrane, coarse

nanofiber PAN/fine nanofiber PAN/chitosan, observing flux rates more than an order of magnitude higher than commercial nanofiltration filter after 24 h operation while maintaining good filtration efficiency. Three-layer composite structure of thin film nanocomposite (TFNC) membranes has also been constructed for water desalination[161]. Such electrospinning membranes have shown higher permeated fluxes and less fouling than conventional membranes during nanofiltration of water[54] (Fig. 14a-b). Recently, a novel three tier arrangement of composite membranes was developed[116]. Wang et al..[116] fabricated a high flux filtration medium with a three-tier composite structure that consisted of a nonporous hydrophilic polyether-*b*-polyamide hydrophilic nanocomposite coating top layer, an electrospun PVA nanofibrous substrate mid-layer, and a conventional nonwoven microfibrous support for oil-water separation. A water soluble polymer such as PVA was electrospun on the non-woven microfibrous support and then chemically cross linked with glutraldehyde. The resultant membranes exhibited excellent water resistance and mechanical properties. The top layer of PVA membrane coated with hydrophilic multiwalled carbon nanotube (MWNT) was tested for selective water-oil emulsion filtration exhibited a high flux rate (up to 330 L/m^2 h) and an excellent total organic solute rejection rate (99.8%). Figure. 14c presents tensile strength of membranes with and with-

Fig. 14 (a) Typical SEM cross-sectional image of PVA nanofibrous composite membrane. (b) Relations of permeate flux and solute rejection of the nanofibrous composite membranes with the degree of crosslinking in the PVA hydrogel coating for separation of oil/water emulsion.[54] (c) Tensile stress and strain curves of electrospun nanofibrous substrates.[116] (d) Schematic illustration of the fabrication process for thin film nanofibrous composite membranes based on PAN electrospun nanofibrous substrate and cross-linked PVA barrier layer.[162] Reproduced with permission from ref 54, 162. © Elsevier 2006, 2010. And ref 116. © American Chemical Society 2005.

out crosslinked electrospun PVA, which suggests improved properties in comparison to other nanofibers produced from polyvinylidenefluoride and PAN. An interfacially polymerized polyamide barrier layer composed of various ratios of piperazine and bipiperidine had been evaluated for the modification of PAN electrospun nanofiber scaffolds or PAN ultrafiltration membranes [163]. The authors found that the piperazine concentration played a major role in the interfacial polymerization to optimize the flux and rejection performance. Recently, a double-layer mat was fabricated by electrospinning PVA/surface oxidized MWNT layer on electrospun PAN nanofibrous substrate for high flux thin nanofibrous composite membranes to separate an oil/water emulsions[164]. The incorporation of MWNTs into the PVA barrier layer was found to improve the water flux significantly. The mechanically robust, double-layer membrane possessed a high water flux (270.1 L/m^{2}h) with a high rejection rate (99.5%) in oil/water emulsion separation even under low pressures.

To understand the effects of electrospun nanofibrous structures on the filtration performance, a series of nanofibrous membranes with different fiber diameters, diameter distributions and membrane thicknesses were prepared and investigated by Wang et al.[49, 59]. The results indicate that a thicker membrane with a smaller average fiber diameter greatly favors the formation of a smaller pore size and narrower pore size distribution. Based on successful control of the total composite structure, electrospun PAN/non-woven polyethylene terephthalate (PET) was obtained, which presents two to three times higher flux than conventional microfiltration membranes. Such optimized electrospun membrane holds high potential for drinking water purification and oil-water separation. Yoon et al.. described a membrane system containing PAN electrospun nanofibers as the mid-layer scaffold and cross-linked PVA as the top layer coating. The critical parameters, such as the thickness of the coating layer and the mid-layer, were optimized to achieve a higher flux than that of the conventional membranes with high rejection ratio (>99%) for separation of oil-water mixture (1500 ppm in water) over a long time period under practical pressure range[50]. In addition, electrospun PAN membrane with chitosan surface coating was also fabricated for high flux ultrafiltration membranes[160]. Their studies demonstrated that electrospun UF/NF membranes top layer coated with hydrophilic water permeable chitosan provide high flux. The same group also investigated the oil-water separation characteristics of nanofibrous membranes consisting of UV-cured PVA hydrogel barrier layer over electrospun nanofibrous PVA mid-layer and PET nonwoven substrate (Fig. 14d)[162].

To increase the flux rates of conventional UF membranes, Mehrdad Khamforoush et al. manufactured a new type of thin film composite (TFC) membranes comprised of a nonwoven PET support, an electrospun PAN nanofibrous mid-layer and a PSF composite co-ating top layer for the separation of water/oil emulsion. To evaluate the reliability of the TFC membrane, a conventional UF membrane was also fabricated as reference to. A
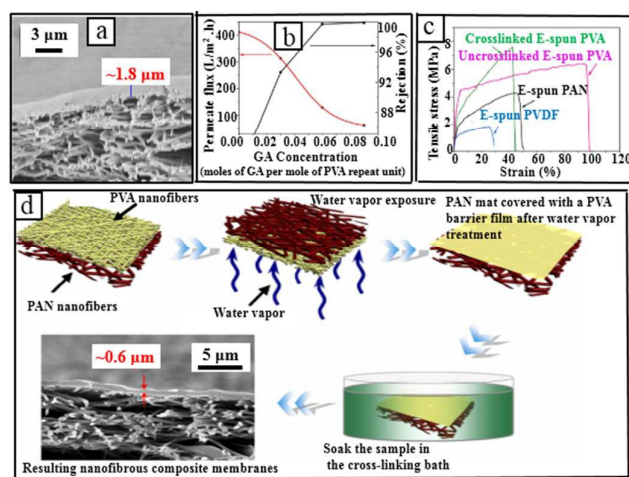
considerable increase in pure water flux (20-160%) and a downward trend in rejection were noticeable. The results also indicated that with the application of TFC membrane, the efficiency of rejection improved by 2% on average.

Cellulose ionic liquids solution deposited on PAN nanofibrous scaffolds has presented a high permeation flux in the filtration of an emulsified oil-water separation (above 99.5%) after prolonged operation[52, 55]. Similarity, ultrafine polysaccharide nanofibers with 5-10 nm diameters were also employed as barrier layers to form thin-film nanofibrous composite membranes for oil-water separation with a 10-fold increase in permeation flux and a 99.5% rejection ratio[165]. Recently, progress in superoleophobic electrospun fibers have been made by constructing superoleophobic surfaces by surface modification[58]. For instance, Aikifa Raza et al.[166-170] created superhydrophilic and prewetted oleophobic nanofibrous membranes with a novel and scalable strategy by the facile combination of in situ cross-linked polyethylene glycol diacrylate nanofibers supported on polyacrylonitrile/polyethylene glycol nanofibrous (x-PEGDA@PG NF) membranes to overcome the challenge of creating a practical and energy-efficient method for effective oil–water mixtures, especially those stabilized by surfactants. Furthermore, these membranes have good mechanical strength (14 MPa), mean pore sizes between 1.5 and 2.6 μm, a high flux rate (10975 L m^{-2}h^{-1}) and high separation efficiency (the residual oil content in filtrate is 26 ppm). More importantly, the membranes exhibit high separation capacity (10 L) oil removal from a mixture without a decline in flux) and excellent antifouling properties for long term use, thus making them important candidates for oil-water separation. Yang et al.[171] fabricated superhydrophilic and underwater superoleophobic silica nanofiber using an in situ synthesis strategy. Film characteristics included flexibility, hierarchical structure, thermally stability, robust mechanical strength, good antifouling properties, and ease of recycling, which facilies separation of oil-in-water microemulsions with effective surfactant-stabilization. In addition, with 2.0 (wt%) SiO$_2$NPs additive, the underwater OCA increased significantly to 161° (Fig. 15a). Most importantly, the membranes exhibit high flux (2237 L m^{-2}h^{-1}), robust mechanical strength, high thermal stability, and easy cycling for long-term use. All of these characteristics make it a promising way to effectively separate oil-in-water microemulsions.

Besides SiO$_2$ NPs, TiO$_2$ NPs were used to combine carbonaceous materials such as carbon nanofibers to fabricate TiO$_2$ nanosheet-anchored carbon nanofibrous membranes for oil-water separation. Recent reported that using a solvothermal method in preparation membranes of a novel carbon nanofibers with TiO$_2$ nanosheet-anchored, which possess superhydrophilic and underwater superoleophobic properties as a benefit of hierarchical TiO$_2$ micro/nanostructure that develop on the surface[172]. SEM images show a carbon nanofibrous membrane after TiO$_2$ coating; a double diameter of nanofiber is achieved and roughness of the surface is wrapped by TiO$_2$ (Fig. 15b-d). Experimental results present oil-

water separation efficiency greater than 99%, as well as the highest breakthrough pressure up to 3.63 m ever reported. Membrane stability is exhibited in ultrasonic, thermal and extreme pH conditions. To the best of our knowledge, this was the first presentation of TiO$_2$ growth onto a free-standing carbonaceous membrane for purpose of oil-water separation.

Organic materials, such as fluorinated materials, were also combined with electrospinning for the fabrication of modified superoleophobic surface in the application of oil-water separation materials. Ahmed et al.[173] used impregnation of cellulose ionic liquid solution into a nanofibrous polymer membrane to solution, thus a composite cellulose/electrospun PVDF-HFP
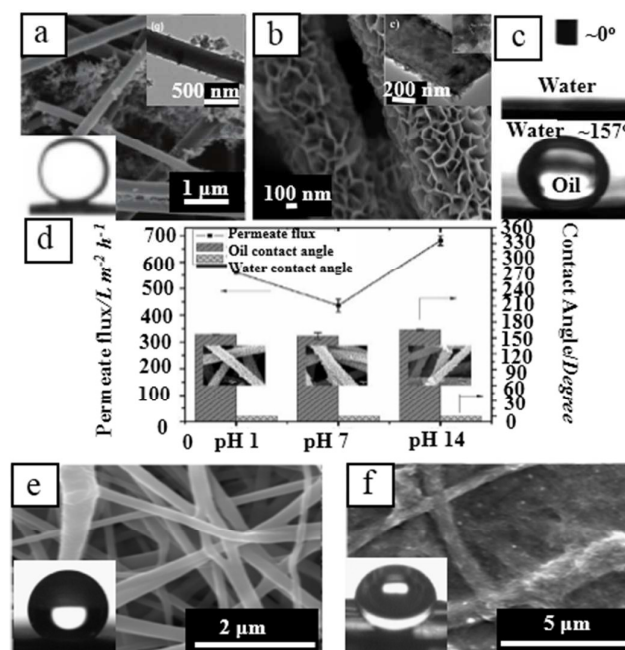
Fig. 15 (a) FE-SEM images of SNF membranes with concentration of SiO$_2$ NPs of 2 (wt%).[171] (b) FESEM image of electrospun carbon nanofibers after TiO$_2$ nanosheets coating. inset TEM image showing TiO$_2$ nanosheets are coated onto the surface of carbon nanofibers. (c) Photograph of a water droplet on the membrane in air (top) and oil droplet depositing on the membrane in water (Down). (d) The pH stability of the membranes in terms of permeate flux, water contact angle in air and oil contact angle in water. The inset shows the morphology of the membrane at each pHs.[172] (e) SEM image of electrospun PVDF–HFP surface, inset electrospun PVDF–HFP cross-section. (f) SEM image of cellulose/electrospun PVDF–HFP composite surface and inset cellulose/electrospun PVDF–HFP composite cross-section.[173] Reproduced from ref. 171. Reproduced with permission from ref 172. © International Journal of Environmental Science and Development 2015. And ref 173. © Elsevier 2014.

membrane displaying superhydrophilicity and underwater develop a novel cellulose/electrospun PVDF-HFP composite membrane. Modifying with cellulose regenerated from ionic liquid superoleophobicity (WCA = 0°, OCA = 169°) was obtained. Moreover, small pores, narrow pore size distribution, excellent thermal stability and high separation efficiency make the performance of membrane comparable to that of commercial ultra-filtration oil-water separation membranes (Fig. 15e-f).

Poor stability in oil media and the presence of hydrophobicity of PSF electrospun membranes have hindered its wide application in oil/water separation. M. Obaid et al.[174] produced superhydrophilic PSF electrospun membranes that exhibit high stability in oils by electrospinning PSF solution containing NaOH nanoparticles followed by the activation of the final electrospun nanofiber mats by deposition of polyamide thin layer on the surface using m-phenylenediamine and 1,3,5-benzenetricarbonyl chloride. The nanofibrous morphology and good thermal stability of the PSF membranes are not affected by the addition of NaOH, and they present super-hydrophilicity (WCA = 3°), excellent stability in oil media and distinct performance in oil-water separation processes. Further, novel effective and reusable membranes with better hydrophilicity, fouling and reusability properties for oil–water separation were developed on the basis of PSF electrospun nanofiber mat modification. This method used incorporation of solid NaOH nanoparticles inside the PSF nanofibers, and formation of a thin layer from polyamide on the surface of the electrospun mat[174]. The incorporation of NaOH and the formed polyamide decreased the WCA from 130° to 13°. The modified PSF electrospun nanofiber membranes were found capable of separate oil–water mixture with very high removal efficiency of oil for at least three successive cycles at a relatively high water flux while exhibiting reusability features.

Biodegradable and biocompatible polylactide (PLA) has attracted attention for the water permeability of its electrospun membranes and related hydrophilicity-based separation of oil/water emulsion. Zhang et al.[175] produced membranes with complete water permeability by electrospun blend of PLA and another biodegradable and biocompatible poly (3-hydroxybutyrate-co-4-hydroxybutyrate) (P34HB). Compare with PLA membrane, the membranes consisting of blend fibers exhibit superior water permeability and highly efficient removal of water from oil/water emulsions under gravity.

4. Conclusions

The disposal of oil/water mixtures has become an imperative task for industry, especially for the mixtures with the presence of surfactant. Moreover, the deep-sea oil leakages generate large scale emulsions, which are a waste of energy and a great cause of harm to ocean and human life. A robust treatment for those contaminated water or oil can not only cleanup the water, but also

retrieve oil resource. Electrospun nanofibers have drawn considerable attention in absorption/filtration of oil/water mixtures for their high surface to volume ratio. Electrospinning can produce highly porous nanofibrous structures from a variety of polymers, both organic and inorganic indifferent configurations and assemblies. Moreover, the toolbox for post-modification of electrospun nanofiber membranes can optimize important features of the resulted materials by the means of chemical or physical treatment, which allowed the tailor of specific applications. For example, in an attempt to achieve higher permeation fluxes and separation efficiencies, thermal treatment has been used to control pore size and thickness.

In this feature article, we have discussed the development of various special electrospun fibrous materials for oil-water separation. These include the creation of micro/nanostructures on hydrophobic surface, surface modification to construct superhydrophobic electrospun fibers. The development of superhydrophobic/superoleophilic electrospun materials for oil/water absorption and filtration were then discussed in detail. In addition to superhydrophobic/superoleophilic membranes, fibrous materials with superoleophobic surface have also found applications in oil/water separation via filtration, as discussed in section 3. Electrospun fibrous materials present advantages comparing with conventional oil-water separation materials due to a highly porous and interconnected pore structure, submicron pore sizes and a large surface area to volume ratio. Amazingly, the separation of an oil-in-water, water-in-oil and surfactant-stabilized emulsions were achieved very recently using electrospun nanofibrous membranes with maximum oil-water separation efficiency larger than 99.999%[176].

Although electrospun materials show great potential in oil-water separation, there is a long way to go before they can be used in large scale industrial application. There are some reasons which can account for this. First of all, there is a need for fabrication of electrospun materials with resistance to acid and alkali corrosion which has long term stability. This is a challenge, as the fine structure on the surface of electrospun fibers to construct roughness is fragile and easily damaged by external influences. This exposes great restriction on future applications. Secondly, even though electrospinning can produce nanofibrous membrane consisting of nanofibers with diameters ranging from micron to nanometer scale, the poor mechanical properties is still a major drawback for industrial applications. Moreover, the surface roughness of membranes and the degree of pollution are considered to be contradictory. Therefore, to the development of materials in separation of oil-water emulsions with droplet sizes from micrometer to nanometer scale with high separation efficiency and throughput is still a challenge. Last but not least, most of papers mentioned above have been devoted to of the separation of low viscous oil-water emulsions. However, the separation of high-viscous oil/water mixtures is more complex, which sometimes more close to the real applications. Although

challenging, we are convinced that the oil/water separation has been deeply influenced by electrospinning technique; an industrial application of electrospun materials on oil/water separation can be expected in the near future.

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Notes and references

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