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Historical perspective

Selective separation of oil and water with mesh membranes by capillarity

Yuanlie Yu ^a, Hua Chen ^b, Yun Liu ^c, Vincent S.J. Craig ^{d,*}, Zhiping Lai ^{a,*}^a Advanced Membrane and Porous Materials Center, Division of Physical Science and Engineering, King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia^b Centre for Advanced Microscopy, Australian National University, Canberra, ACT 0200, Australia^c Research School of Chemistry, Australian National University, Canberra, ACT 0200, Australia^d Department of Applied Mathematics, Research School of Physics and Engineering, Australian National University, Canberra, ACT 0200, Australia

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ABSTRACT

The separation of oil and water from wastewater generated in the oil-production industries, as well as in frequent oil spillage events, is important in mitigating severe environmental and ecological damage. Additionally, a wide range of industrial processes require oils or fats to be removed from aqueous systems. The immiscibility of oil and water allows for the wettability of solid surfaces to be engineered to achieve the separation of oil and water through capillarity. Mesh membranes with extreme, selective wettability can efficiently remove oil or water from oil/water mixtures through a simple filtration process using gravity. A wide range of different types of mesh membranes have been successfully rendered with extreme wettability and applied to oil/water separation in the laboratory. These mesh materials have typically shown good durability, stability as well as reusability, which makes them promising candidates for an ever widening range of practical applications.

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1. Introduction

1.1. Need for oil/water separation

The separation of oil and water from oil/water mixtures is an ancient challenge that is becoming more important [1–3]. Discharged oil can

cause severe environmental and ecological damage directly and because the oil is flammable and can decompose to form other harmful chemicals, further polluting the natural environment and threatening aqueous habitats and affecting human health [2]. Furthermore, chemicals used in clean-up operations can cause environmental harm. Apart from these environmental and ecological issues, a wide range of industrial processes require the separation of oils or fats from aqueous solutions and the scarcity of water in many arid regions adds to the demand for efficient oil/water separation technologies [4]. Another important consideration in choosing the technology used to effect

* Corresponding authors.

E-mail addresses: vince.craig@anu.edu.au (V.S.J. Craig), zhiping.lai@kaust.edu.sa (Z. Lai).

separation is the possible reuse of the recovered oil. Although traditional methods such as skimmers, centrifuges, coalesces, settling tanks, depth filters, magnetic separations, flotation technologies, and ignition of oil can remove oil from oily wastewater, these techniques are mainly useful for oil water mixtures and unstable emulsified oils, as their working mechanisms are sensitive to the oil droplet size and/or the density difference between water and oil [5–7]. Moreover, because they require long processing times or gas or chemical input, these conventional separation systems usually are expensive and require a large amount of space and energy [5,6]. More stringent environmental controls and the pressure of economic development have led to a strong desire to produce more efficient, cost-effective processes for oil and water separation [8].

Utilizing engineered wetting of solid surfaces to design an oil/water separation process based on capillary processes has been recognized as an effective approach [9–11]. For practical applications it is necessary to preferentially maintain one phase at the surface in addition to preventing fouling of the surfaces, therefore materials with extreme surface wettability of two types are employed. These are solids with surfaces that are superhydrophobic and superoleophilic or surfaces with the inverse wettability that are superoleophobic and superhydrophilic. Such surfaces when exposed to mixtures of oil and water preferentially attract one of the phases in order to reduce the overall interfacial energy of the system.

1.2. Weak assembly

From a molecular viewpoint the interfacial energy arises due to the loss of cohesion energy when a molecule is moved from the bulk to the interface. For liquid oil, we can approximate the cohesive energy of a molecule to the translational kinetic energy. Assuming half the cohesive interactions are lost for a molecule at the interface, the molecular energy shortfall at the interface is $\sim 3 K_B T/4$ for an air interface. As such, wetting is an example of weak assembly, where the lowering in interaction energy for an oil molecule moving from the liquid–liquid interface to the liquid–solid interface is $\sim K_B T$, whereas the lowering in interaction energy for a water molecule moving to a hydrophilic surface is $> K_B T$, due to both dispersion and polar interactions and is therefore an example of strong assembly. It is the difference in these energies that is used to effect oil/water separation using mesh membranes. The self-structuring of fluids at the interface can be devised to affect macroscopic separation of the fluids, provided the external forces are insufficient to overcome the capillary force on one phase, but not the other. For separating oil–water mixtures under gravity, a membrane that is superhydrophilic and superoleophobic (when submerged) will allow water to pass but provide a capillary barrier to the passage of oil, provided the hydrostatic head is insufficient to overcome the effect of the Laplace pressure that arises from the weak assembly of the oil molecules. A membrane of the other type (superhydrophobic and superoleophilic) will allow oil to pass and prevent the passage of water.

1.3. Theory of superhydrophobicity and superhydrophilicity

The wettability of a surface is usually quantified by the contact angle of a droplet of liquid on the surface. The droplet can either be in air or in another immiscible fluid. For smooth, homogenous, ideal surfaces the contact angle of a droplet on a surface immersed in another liquid is described by the balance of the interfacial energies in Young's equation;

$$\gamma_{s,l} = \gamma_{s,d} + \gamma_{d,l} \cos \theta_{smooth} \quad (1)$$

where s , is the solid and d is a liquid droplet immersed in a liquid l .

Surfaces are often described as hydrophilic or hydrophobic based on their contact angle with water in air on a smooth surface. There is no widely accepted definition, but a common one is that a hydrophobic surface has a contact angle of $> 90^\circ$ and consequently a hydrophilic

surface has a contact angle $< 90^\circ$. When the surfaces are rough more extreme wetting can be observed. Superhydrophilic surfaces arise when an innately hydrophilic surface is produced in a roughened form (such as from sintered particles) such that the contact angle is reduced to zero. The effect of roughness on the contact angle for a homogenous surface is described by the Wenzel equation, [12]

$$r = \frac{\cos \theta_{rough}}{\cos \theta_{smooth}} \quad (2)$$

where r , is the roughness parameter ($r > 1$), which is the ratio of the projected surface area of the rough surface to a perfectly flat surface. The contact angle of surfaces with oil is less often reported, as oils have low surface tension and therefore wet most flat surfaces. That is, surfaces are typically oleophilic. Therefore a superhydrophilic surface will typically also be a superoleophilic surface. However, when a superhydrophilic surface is first immersed in water it can be both superhydrophilic and (under water) superoleophobic as the water may fill the texture of the surface. This is discussed further below.

Superhydrophobic surfaces can be produced from rough surfaces that are inherently hydrophobic. For a homogenous surface the Wenzel equation (Eq. (2)) also applies, but as $\theta_{smooth} > 90^\circ$, $\theta_{rough} > \theta_{smooth}$. Additionally, gas can be trapped between the solid and the liquid phases forming a heterogeneous composite interface, in which case the contact angle is given by a modified version of the Cassie equation, [13]

$$\cos \theta_{Cassie} = f_1 [\cos \theta_{smooth} + 1] - 1 \quad (3)$$

where f_1 is the fractional area of the surface (or three phase line) in contact with the liquid. For surfaces in which $\theta_{smooth} > 90^\circ$, high effective contact angles result and as f_1 becomes smaller the contact angle approaches 180° . Superhydrophobic surfaces are usually also superoleophilic. Note that as oils do not give surfaces in which $\theta_{smooth} > 90^\circ$ this approach will not work for producing superoleophobic surfaces. However, this can be achieved using surfaces engineered to have a re-entrant structure [14,15].

In membrane separation processes it is important to recognize that air is not present at the interface, that is, both of the fluid phases are liquids, and the desired properties are obtained when the wetting liquid penetrates the surface roughness, as air does in the Cassie state described above. This causes the non-wetting liquid to present with a very high (super) contact angle, as described by Eq. (4) where f_{NW} is the fractional area of the surface (or three phase line) in contact with the non-wetting liquid and $\theta_{NW,smooth}$ is the contact angle of the non-wetting fluid in the presence of the wetting fluid on a solid substrate.

$$\cos \theta_{NW,Cassie} = f_{NW} [\cos \theta_{NW,smooth} + 1] - 1 \quad (4)$$

This heterogeneous wetting state is favored by very rough surfaces. The condition under which this occurs is given by [16];

$$\cos \theta_{W,smooth} > \frac{1 - f_W}{r - f_W} \quad (5)$$

where f_W is the fractional area of the solid surface in contact with the wetting fluid. Thus a critical angle is defined such that when $\theta_{W,smooth} < \theta_C$, the wetting film will impregnate the textured or rough surface such that the non-wetting fluid has a very large contact angle. This is the preferred circumstance for mesh membranes, whether the wetting phase is the aqueous or oil phase as it results in a very high contact angle for the non-wetting phase. For an in-depth discussion of wetting the interested reader is referred to the excellent monograph [16].

Membranes for oil/water separation are readily produced by treating a weave or a mesh to produce rough surfaces with the desired wetting properties. These mesh membranes can effectively separate immiscible oil/water mixtures and oil-in-water or water-in-oil emulsions,

solely driven by gravity, with high permeation rates and separation efficiency. Most importantly, such mesh membranes exhibit good durability, stability and reusability. This, when combined with low cost and scalability, make them promising candidates for practical oil/water separations. In this manuscript, different mesh membranes with superhydrophobicity and superoleophilicity or superhydrophilicity and superoleophobicity induced by either surface modification or micro- and nanostructuring will be reviewed.

1.4. Capillary basis for separation

Mesh membranes use capillarity as the basis for selective permeability of oil and water. To achieve separation it is critical that one phase is allowed to pass readily through the membrane and the other phase is arrested. The wetting phase is readily able to traverse the membrane whereas, if the pores in a mesh membrane are sufficiently small compared to the droplet size, capillary pressure resists the passage of the non-wetting phase, see Fig. 1. When the Laplace pressure of the non-wetting phase is sufficient to counteract external pressure (which is the hydrostatic pressure for gravity filtration) the non-wetting phase will not pass through the mesh. The Laplace pressure is larger when the curvature of the interface is greater. In an ideal two-dimensional mesh made up of overlapping cylinders of radius R with an inter-cylinder separation space of $2D$, this would be achieved when the applied pressure is less than the Laplace pressure of the non-wetting phase. As an approximation we assume that the minimal radius of curvature is where the pore is tightest for all contact angles. The pressure above which the non-wetting phase will pass through the membrane, called the breakthrough pressure, is then given by P_B ,

$$P_B \sim < \frac{-\gamma_{12} \cos \theta_{NW,i}}{D} \quad (6)$$

where γ_{12} is the interfacial tension between the wetting phase and the non-wetting phase, $\theta_{NW,i}$ is the contact angle of the non-wetting phase on the solid surface when both are immersed in the wetting phase.

In some cases, such as electrospun materials deposited onto a mesh, meshes will consist of layers of fibers forming a three-dimensional structure. It is essential that the layers in a three-dimensional mesh material for oil/water separation are spaced such that the re-entrant architecture of the mesh is maintained. This is an essential feature for any superoleophobic surface [17]. Even so the sagging of the interface can lead to breakthrough of the non-wetting phase. For a three dimensional mesh made up of overlapping cylinders of radius R with an inter-cylinder separation distance of $2D$, the change in curvature of the non-wetting phase needs to be considered as it may cause the non-wetting phase to make contact with the next layer of the mesh, which will promote breakthrough. The breakthrough pressure that must not be

exceeded is given below [18] (for a derivation see the appendix of Tuteja et al. [19]).

$$P_B < \frac{2R\gamma_{12}}{D^2} \frac{1 - \cos \theta_{NW,i}}{1 + 2R \sin \theta_{NW,i}/D} \quad (7)$$

This above expression provides clear criteria for the design of mesh membranes for oil–water separations. To increase the hydrostatic pressures required to cause breakthrough of the non-wetting phase, a large contact angle of the non-wetting phase and high interfacial tension between the liquid phases are required. In practice, the hydrostatic pressure does not increase the filtration rate as it is determined by the number of unblocked pores and the sedimentation rate of the wetting phase [18], so systems can be designed to produce low hydrostatic pressures without penalizing the flux.

Cross flow filtration cells have been developed for microfiltration applications employing membranes, primarily as a means of limiting the development of thick filter cakes or blocking of pores that reduce the flux of filtrate through the membrane. Industrially, cross-flow filtration is employed as a continuous operation [20], which has the added advantage of limiting the increase in concentration of the rejected phase in the solution being filtered. Cross flow cells are also ideally suited to mesh membrane applications but for different reasons. In the case of mesh membranes for the separation of two fluids, the development of a filter cake is generally not an important consideration. However cross flow filtration cells mounted horizontally meet both the need to limit the hydrostatic head to prevent breakthrough and minimize the concentration of the non-wetting phase in the solution being filtered, in order to maximize the filtration rate of mesh membranes [21]. Pore blocking is a consideration for oil–water separation using mesh membranes but this is primarily a function of the concentration of droplets of the non-wetting phase as the extreme wettability of the membranes inhibits conventional fouling when only liquids are present. Singh et al. have discussed a range of models for describing the flux through a membrane used to separate oily emulsions using cross-flow [22]. Important operational parameters are the cross flow rate, the trans-membrane pressure and the Reynolds number [21]. For mesh membrane applications the combined trans-membrane pressure and the hydrostatic pressure have to be less than the breakthrough pressure.

Provided the necessary extreme and stable wetting properties can be engineered on a membrane of appropriate geometry, the material used for the membrane is not important for the separation process. Rather, other considerations such as cost, anti-fouling properties, chemical stability, ease of fabrication, temperature stability, pore size and the ability to prepare the membrane on a large scale will govern the choice of membrane material. When considering the method of fabrication it should be recognized that for a given architecture of fibers of radius R , and fiber separation distance of $2D$, in any practical application a single

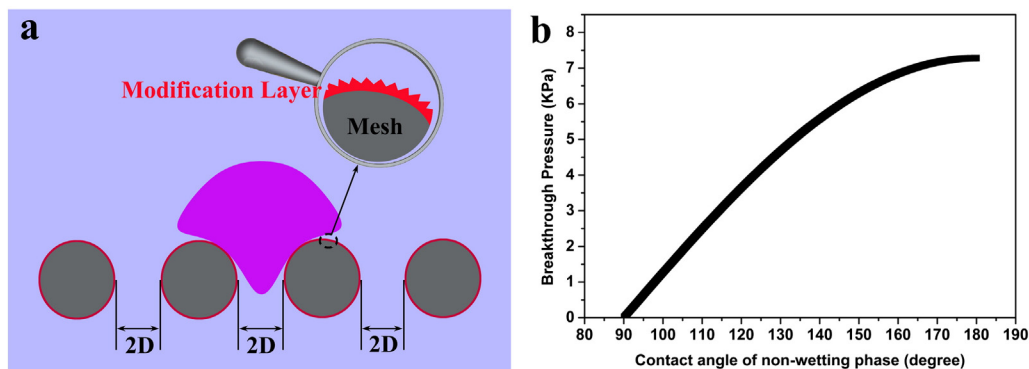


Fig. 1. (a) Schematic of a 2D superhydrophilic and superoleophobic mesh (gray) showing the rejection of an oil droplet (pink) due to capillary forces through the pores of radius D . (b) Breakthrough pressure for a 2D mesh with pore radius of $5 \mu\text{m}$ as a function of the contact angle of the non-wetting oil on the mesh immersed in water calculated using Eq. (6). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

layer mesh (two-dimensional architecture) such as a stainless steel mesh should outperform a fiber mat (three dimensional architecture) as sagging of the interface can lead to breakthrough in the latter case.

2. Materials for coating mesh membranes for oil–water separation

2.1. Polymers

The wettability of solid surfaces is dominated by the morphology and chemical composition of the surfaces [23]. Currently, the most effective way to create a surface with extreme wettability is by coating hierarchical structures with micro- and nano-roughness with chemicals that lead to a low surface-energy [24]. Fluorinated and silanated polymers are thus attractive for fabricating separation membranes. To date, a series of polymer based mesh membranes with extreme wettability have been produced using, PTFE [25], polyacrylamide (PAM) [26], poly(sodium methacrylate) (PNaMA) [27], polydimethylsiloxane (PDMS) [28], poly(sulfobetaine methacrylate) (PSBMA)/polydopamine (PDA) [29] and fluorodecyl polyhedral oligomeric silsesquioxane + x -poly(ethylene glycol) diacrylate (POSS + x -PEGDA) [18]. Fluorodecyl POSS + x -PEGDA coated mesh membranes fabricated by dip coating and drying under nitrogen showed stable superhydrophilicity and superoleophobicity in air and water [18]. As illustrated in Fig. 2, after coating with a layer of fluorodecyl POSS the x -PEGDA surface is completely covered with crystalline domains of fluorodecyl POSS, indicating substantial surface segregation of the fluorodecyl POSS molecules, which are expected to migrate over the surface upon exposure to a wetting phase and thereby produce an extremely low energy surface [17]. Because of the extreme surface wettability, this membrane can separate a range of different oil and water mixtures in a single-unit operation with high separation efficiency, over 99.9%, by using the difference in capillary forces acting on the two phases [18].

PAM hydrogel based mesh membranes prepared via a light-initiated polymerization process exhibited stable superhydrophilicity and underwater superoleophobicity with a contact angle (CA) of $153 \pm 1.8^\circ$ and low oil adhesion of less than $5 \mu\text{N}$ [26]. Here, apart from the superoleophobicity in air, the underwater superoleophobicity is achieved by imbibition of the water phase into the micro- or nano-hierarchical structure of the polymer membrane coating. When the oil

droplets make contact with the polymer based coatings, water remains trapped in the rough micro and nanostructures, forming an oil/water/solid composite interface that greatly decreases the contact area between the oil droplet and the solid surface [30,31]. Thus the oil-adhesion of the surface is extremely low, mimicking the approach that the pitcher plant uses to trap insects that has been adopted for producing antifouling surfaces [32]. This membrane shows a separation efficiency over 99% and good resistance to oil fouling [26].

2.2. Boron nitride nanotubes

Boron nitride nanotubes (BNNTs) possess remarkable mechanical properties, high thermal conductivity, outstanding electrical insulation, excellent chemical stability, as well as superb resistance to oxidation [33]. Additionally, BNNT films are poorly wet by water due to adsorbed hydrocarbon contamination and nanometer scale roughness [34,35]. This water repellency can be further enhanced by partial perpendicular alignment of the BNNTs to the substrate, resulting in superhydrophobicity with a water contact angle (CA) over 150° and reduced CA hysteresis [36]. These properties make BNNTs attractive candidates for use as superhydrophobic surfaces in harsh chemical and thermal conditions. As shown in Fig. 3, Chen's group fabricated a BNNT coated membrane using a vapor–liquid–solid growth followed by high temperature annealing process [37]. This simple, scalable and inexpensive process produced highly dense and pure BNNTs with diameters in the range of 100 to 400 nm that were partially aligned perpendicularly to the stainless steel mesh substrate, producing a superhydrophobic ($CA > 150^\circ$) and superoleophilic ($CA < 1^\circ$) surface, almost without hysteresis, as shown in Fig. 4 [37]. Due to this special surface wettability, BNNT based mesh membranes can be practically used as a highly efficient filtration membrane for the separation of oil and water. Importantly, the BNNTs are strongly adhered to the stainless steel mesh substrates [35], offering the necessary stability and durability for practical applications.

2.3. Metal oxides and hydroxides

Metal oxides and hydroxides are normally hydrophilic, but if the surface is rough or textured and coated with a low energy material it becomes superhydrophobic [9,38–45]. Recently, a series of metal oxide

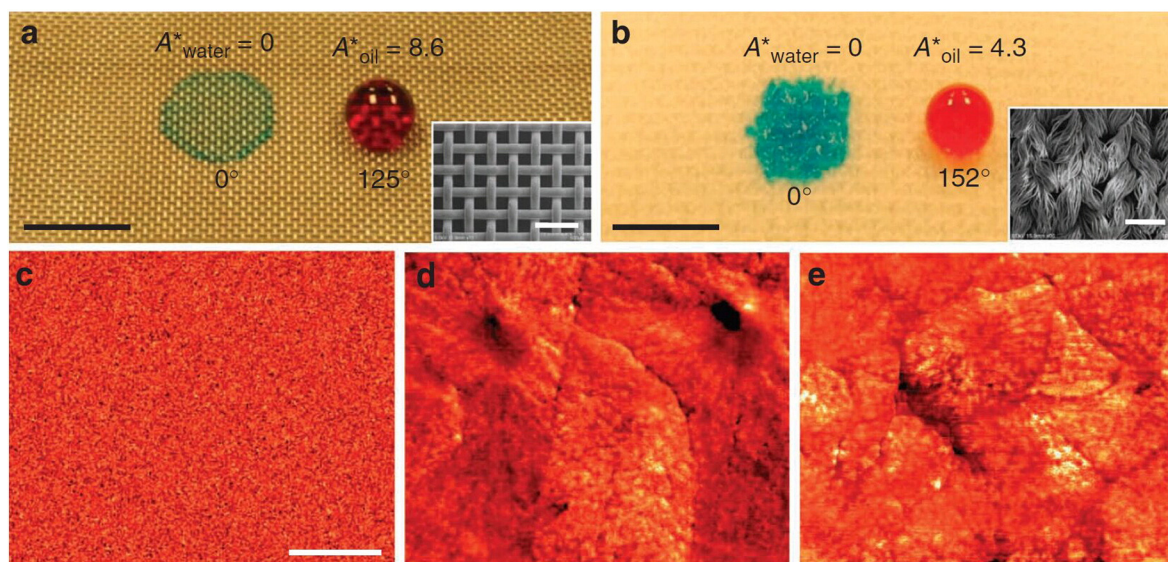


Fig. 2. (a, b) Droplets of water (left, dyed blue) and rapeseed oil (right, dyed red) on coated stainless steel mesh 100 (a) and coated polyester fabric (b). Both surfaces have been dip-coated with a 20 wt.% fluorodecyl POSS + x -PEGDA blend. Scale bars: 5 mm. Insets, morphologies of the respective dip-coated mesh and fabric surfaces. Scale bars: 500 μm . (c–e) AFM phase images of surfaces coated with x -PEGDA (c), a 10 wt.% fluorodecyl POSS + x -PEGDA blend (d) and a 20 wt.% fluorodecyl POSS + x -PEGDA blend (e). The phase angle ranges are 0° – 115° (c), 0° – 25° (d) and 0° – 21° (e). Scale bar: 2 μm . (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

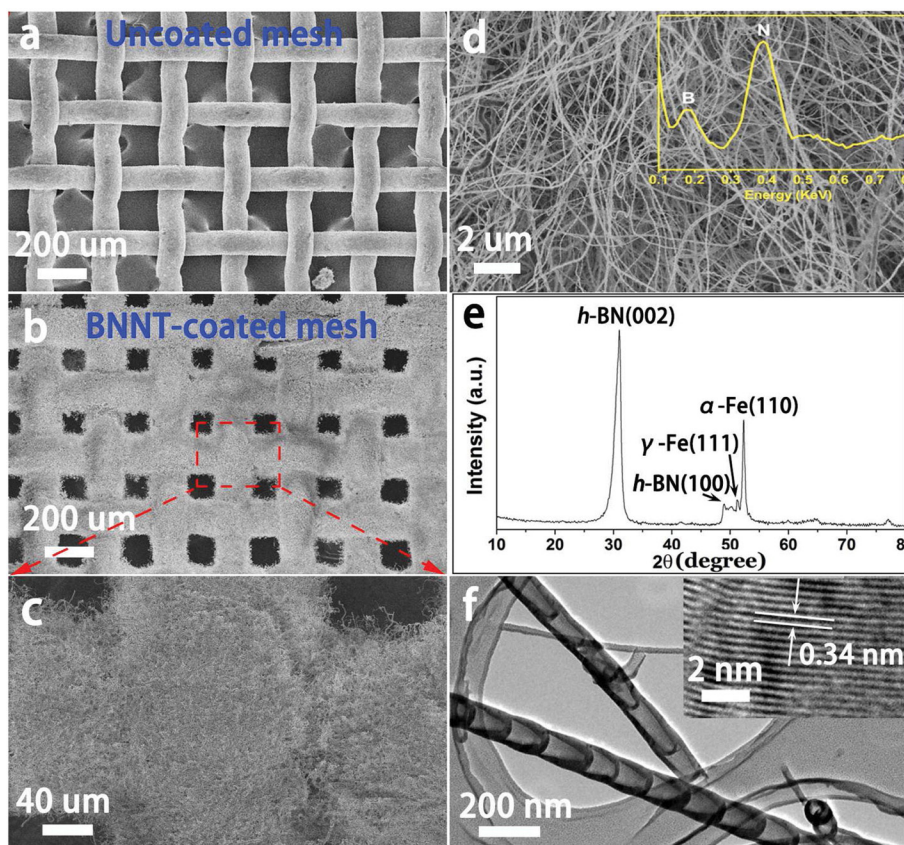


Fig. 3. FESEM images of the (a) uncoated and (b) boron nitride nanotube (BNNT) coated stainless steel meshes, (c) the BNNTs on the mesh surface, (d) the corresponding BNNTs removed from the surface. (e) XRD pattern and (f) TEM image of the BNNTs. The insets in (d) and (f) are the EDS spectrum and high-resolution TEM image of the BNNTs, respectively.

and hydroxide materials such as Cu_2O [40], TiO_2 [39,45], ZnO [38,44], NiOOH [41] and $\text{Cu}(\text{OH})_2$ [9,42,43], have been successfully fabricated onto mesh membranes. An example is the superhydrophilic and

underwater superoleophobic $\text{Cu}(\text{OH})_2$ coated mesh membrane prepared by Jin's group via surface oxidation of a copper mesh in alkaline aqueous solution [9]. After 30 min of oxidation, $\text{Cu}(\text{OH})_2$ nanowires

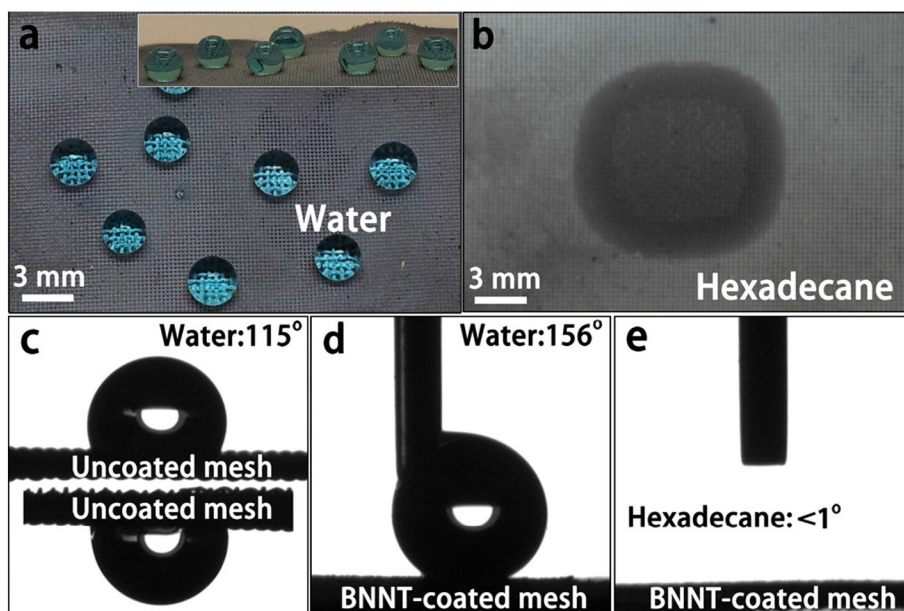


Fig. 4. (a) Photograph of water droplets (dyed with methylene blue) on the surface of a Boron Nitride Nanotube coated mesh (inset: a side view of a water droplet); (b) photograph of an oil droplet completely spread on the coated mesh surface; (c) shapes of water droplets ($6\ \mu\text{L}$) on and adhering to an uncoated mesh (CA of 115°); (d) shapes of water droplets ($6\ \mu\text{L}$) on a coated mesh (CA of 156°); (e) photograph of the hexadecane droplet on the coated mesh surface with a CA of nearly zero. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

with lengths in the range of 10–15 μm and diameters in the range of 200–500 nm were formed, which grow perpendicular to the mesh walls and intertwine with each other, as shown in Fig. 5 [9]. These surfaces exhibit an underwater superoleophobicity for oils (CA > 150°) and an ultralow adhesion force (below 1 μN) [9]. This surface wettability and ultralow oil adhesion can be attributed to the micro/nanohierarchical rough structure arising from the long and densely arrayed $\text{Cu}(\text{OH})_2$ nanowires on the copper mesh and the hydrophilic nature of $\text{Cu}(\text{OH})_2$, such that when immersed in water, water is trapped in the hierarchical structure to form an oil/water/solid interface in the presence of oil [9]. This membrane can effectively separate immiscible oil/water mixtures even some oil-in-water emulsions with extremely high separation efficiency (residual oil in the filtrate after only one pass was lower than 30 ppm) and flux over $1 \times 10^5 \text{ L m}^{-2} \text{ h}^{-1}$. Most importantly, the membrane exhibited excellent anti-oil fouling properties and superior stability, even in strong alkaline conditions (pH ≥ 14) under long term use [9].

Lin's group developed a novel double layer TiO_2 -based mesh membrane and realized the separation of oil from water and the degradation of soluble pollutants in one device [39]. Both layers of TiO_2 coated meshes were prepared by a simple hydrothermal method. The upper layer consisted of only TiO_2 coated mesh, but the lower layer of TiO_2 was modified with octadecylphosphonic acid to impart it with superhydrophobicity and superoleophilicity [39]. The membrane exhibited not only good selectivity but also excellent photocatalytic abilities. Such a membrane can be successfully used for the separation of insoluble oil from water due to its extreme wettability, as well as the degradation of soluble pollutants in water under UV light because of the photocatalytic abilities of TiO_2 [39].

2.4. Graphene oxide

The inherent hydrophilic nature of oxygen-containing functional groups, such as carboxyl and hydroxyl groups, on the basal plane and at the edges of graphene oxide (GO) makes it an ideal candidate for the fabrication of various underwater superoleophobic mesh

membranes that can be used for oil and water separation [46,47]. Hydrophilic GO can be readily coated on a stainless steel mesh through a simple dip-coating process or a drop-coating followed by O_2 plasma treatment (as shown in Fig. 6) [46]. The mesh membranes coated with GO effectively trap water and exhibit underwater superoleophobicity. Due to this extreme wettability, various oils can be simply and efficiently separated from water under gravity with a high efficiency and flux [46]. Importantly, the water trapped in the rough nanostructures provides a strong repulsive force for oils, not only resulting in greater oil contact angles, but also lowering the oil-adhesion force [46]. Therefore, such low adhesion can effectively prevent GO coated meshes from fouling during the oil–water separation processes.

2.5. Diamond-like carbon

Due to the excellent physical and chemical properties, such as good mechanical stability, extreme hardness, high corrosion resistance, and biocompatibility, as well as the tunability of the surface wettability and adhesion, diamond-like carbon (DLC) can also be used as a superhydrophobic coating on a mesh membrane surface for oil and water separation [48,49]. Cortese's group developed a novel superhydrophobic and superoleophilic DLC coated cotton textile by one-step growth of a DLC film using plasma-enhanced chemical vapor deposition (Fig. 7) [49]. The morphology and wettability of the DLC coating can be adjusted by varying the plasma pre-treatment time of the cotton. The highest water CA of about 170° was obtained after 60 min pre-treatment, as shown in Fig. 7 [49]. The reusable DLC coated cotton textiles were effective at separating oil and water mixtures under gravity with high separation efficiency and demonstrated selective oil absorption capacity [49].

2.6. Metals

The surface wettability of pure metals can be altered by surface modification and increasing the roughness [50]. Pure Ag and Cu nanoparticle based mesh membranes have been fabricated for oil and

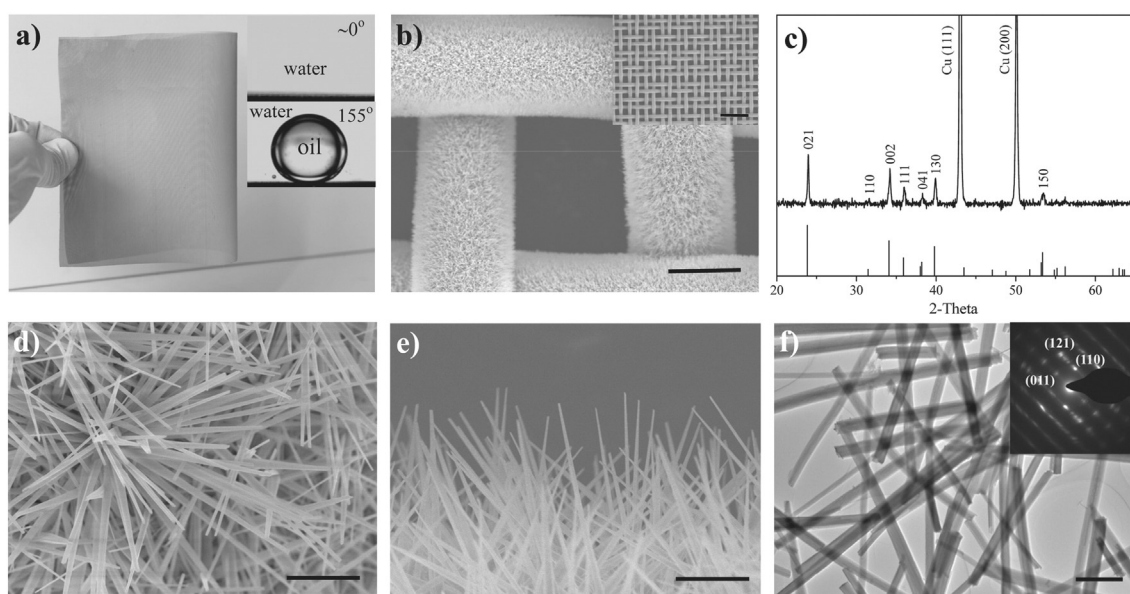


Fig. 5. Characterization of nanowire-haired membrane on a copper mesh after a reaction time of 30 min. (a) Photograph of a large-scale nanowire haired membrane. The insets are photographs of a water droplet on the membrane showing nearly zero contact angle (upper) and an underwater oil droplet (3 μL , 1,2-dichloroethane) on the membrane showing contact angle of 155° (lower). (b) SEM image of nanowire-haired membrane (scale bar: 50 μm). The inset is a low-magnification SEM image with scale bar of 200 μm . (c) XRD spectrum of the nanowire haired membrane. Below is the corresponding diffraction peaks of the $\text{Cu}(\text{OH})_2$ standard card. (d) and (e) Top-view and cross-section SEM images of the nanowire-haired membrane showing the nanowires growing out from the membrane (scale bar: 5 μm). (f) TEM image of nanowires. For TEM characterization, a nanowire haired membrane was treated by ultrasonification to peel off nanowires from the membrane (scale bar: 1 μm).

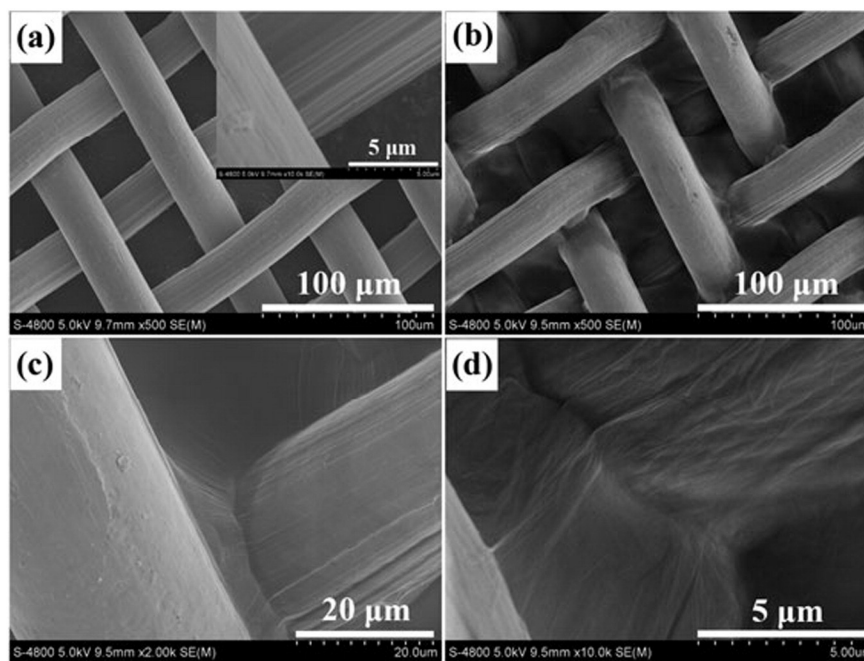


Fig. 6. SEM images of an uncoated stainless steel mesh (a) and graphene oxide coated meshes (b–d) with an average pore diameter of about 38 μm. The inset in (a) shows the magnified view of the smooth surface of an uncoated mesh.

water separation [50–52]. Ag coated meshes were prepared by a simple immersion of copper meshes into an aqueous solution of AgNO_3 at room temperature (Fig. 8) [50]. The obtained Ag-coated mesh surface exhibited extreme wetting with a contact angle of $164 \pm 1.4^\circ$ and a sliding angle of $4 \pm 0.8^\circ$ for water, and a contact angle of 0° for kerosene [50]. Here, carbon contaminants from ambient air are spontaneously adsorbed onto the silver surface resulting in superhydrophobicity and superoleophilicity [50]. This Ag nanoparticle based mesh membrane separated oil from water with efficiencies in excess of 92% in repeated cycles [50]. Furthermore, the membrane possessed excellent resistance to corrosion and was stable at temperatures ranging from -20 to 250°C . Superhydrophobic and superoleophilic Cu nanoparticle based mesh membranes can be prepared by electrodeposition with a subsequent modification process [51,52]. These Cu nanoparticle based

membranes effectively and rapidly separate oil and water. Moreover, these mesh membranes exhibit strong stability as the Cu nanoparticles can bear external pressure, high temperature, and long-term immersion in nonpolar solvents [51].

2.7. Zeolites

Zeolite films have uniform pore size, good thermal and mechanical stability and excellent chemical resistance to acids and salt solutions [53]. Recently, zeolite coated meshes with underwater superoleophobicity have been successfully fabricated by hydrothermal synthesis, as shown in Fig. 9 [53,54]. Various oils can be separated from water with these zeolite based mesh membranes under

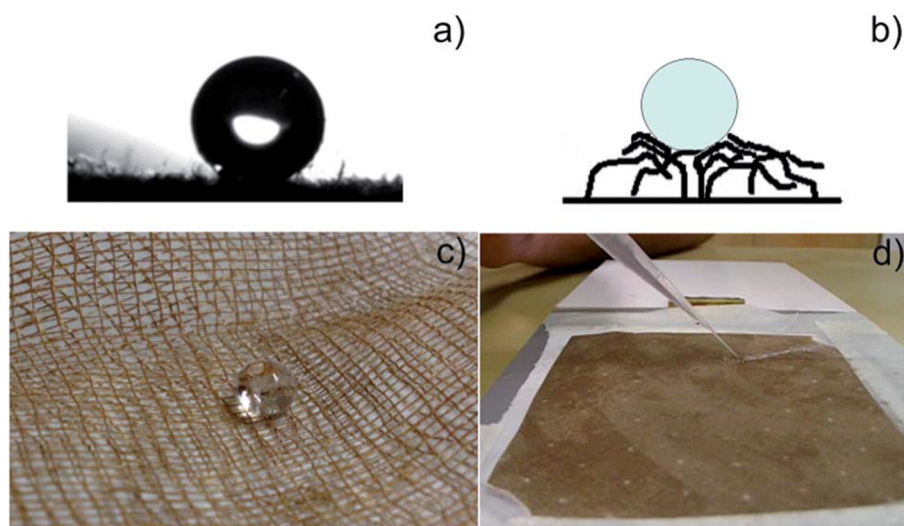


Fig. 7. Wetting behavior of water on Diamond Like Carbon (DLC)-coated cotton. (a) An optical image of static water droplets (3 mL) at a CA of 170° on the respective DLC-coated textiles modified by a 60 min plasma pre-treatment. (b) Schematic of the elastic deformation of the protruding cotton fibers due to bundles formed at the water–air interface. (c) Plasma-treated and DLC-coated gauze showing superhydrophobic properties on a mesh with very large pore size. (d) Optical image demonstrating that a jet of water is deflected by the DLC coated cotton fabrics demonstrating robust superhydrophobic properties.

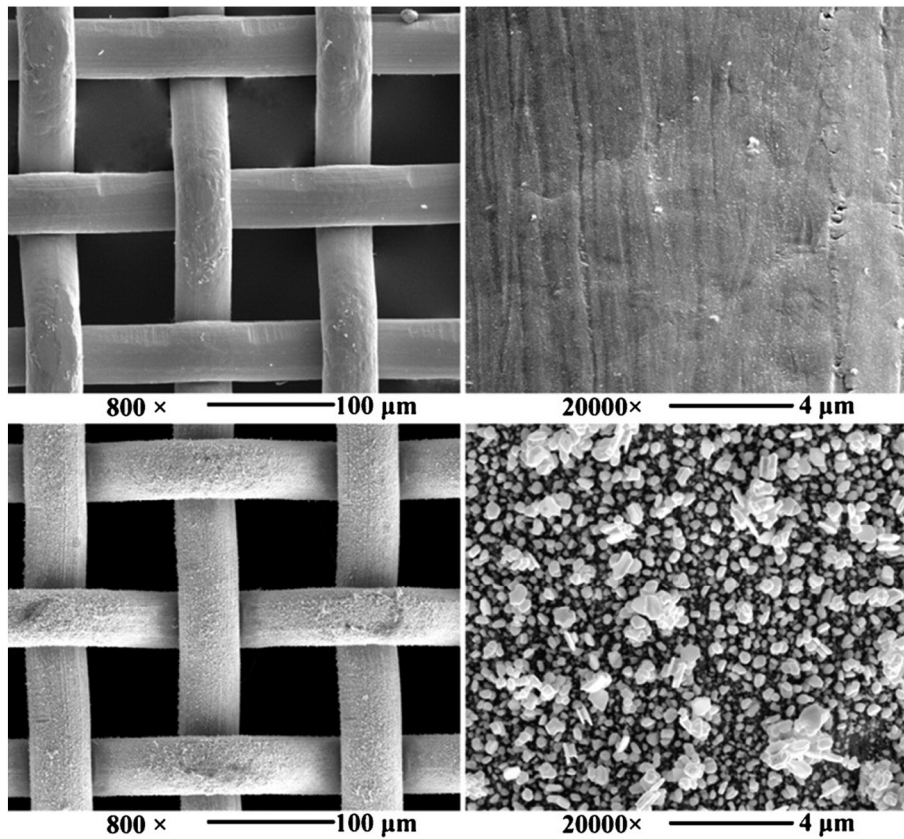


Fig. 8. FE-SEM images of meshes at different magnification: Top) The as-received copper mesh surface. Bottom) The mesh membrane coated with Ag.

gravity with a high flux of $9 \times 10^4 \text{ Lm}^{-2} \text{ h}^{-1}$ and high efficiency (less than 6 ppm oil) [53]. In addition, the separation flux is tunable by changing the pore size which depends on the

crystallization time of the zeolite crystals [53]. More importantly, zeolite based mesh membranes are recyclable by calcination owing to the high thermal stability of zeolite crystals. Further,

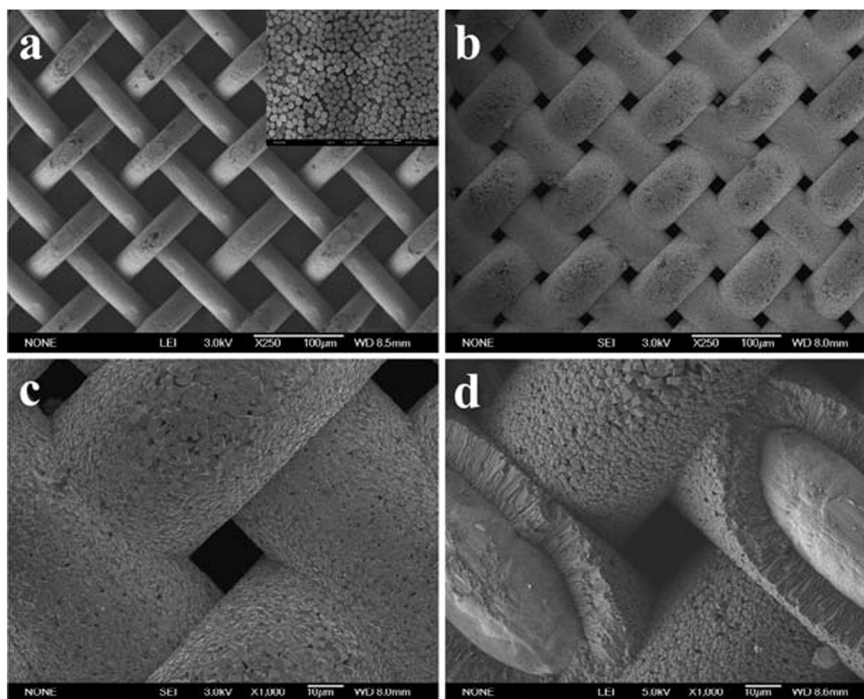


Fig. 9. SEM images of the underlying mesh and zeolite coated mesh membrane. (a) Large scale view of the bare stainless steel mesh with an average pore diameter of about 42 μm , the inset is a magnified image of the mesh after the seeding process. (b) A large scale image of the ZCMF-12 coated mesh membrane. (c) Magnified view of a single pore, and its (d) cross-sectional view.

they are chemically stable in different corrosive conditions [53]. These properties make zeolite based mesh membranes very attractive in harsh environments.

3. Choice of membrane material

The excellent separation performance of mesh membranes achieved in the laboratory is now being applied to a large scale in practical applications. An example is Ferrocep® membranes that utilize a stainless steel mesh coated with titania particles which are used for the removal of oil, grease and fat in a range of applications. We expect that mesh membranes will be applied to many other applications provided membrane production can be scaled up at a suitable cost and that membrane dimensions are reduced to handle the emulsions with small droplet sizes that are more difficult to separate [20]. Additionally, consideration must be given to the effectiveness of mesh membranes in the presence of contaminants and foulants, (such as asphaltene and waxes that are present in crude oil), in many applications. Insufficient laboratory studies focusing on testing and producing mesh membranes resistant to contaminants have been performed to determine the significance of this challenge, though work has shown that polymer coated, metal oxide and graphene oxide mesh membranes exhibit very low adhesion for oil droplets, suggesting this may not be a significant obstacle to practical application. Mesh membranes are unable to reject droplets that are smaller than the pore diameter of the coated meshed. In general mesh membranes employed in laboratory studies have large pore diameters of 100 μm or more. In practical applications droplets of 50 μm or greater are generally very unstable and coalesce, whereas droplets smaller than 10 μm are highly stable and therefore pose a greater separation challenge [20,22]. Thus many practical applications will require mesh membranes with smaller pore diameters in order to effectively separate small droplets. Laboratory studies have paid little attention to the challenge of separating small droplets.

The choice of material for any particular separation process will be governed by a large number of factors including chemical stability, temperature requirements and mechanical strength. We expect that graphene Oxide, BNNT and Diamond like Carbon coated membranes will be difficult to produce on a large scale. Polymer coated membranes generally meet most requirements but are not suitable for high temperature environments. Whilst metals and metal oxides can withstand high temperatures they are not suited to some chemical environments. Zeolites are robust and can withstand high temperatures and harsh conditions but the process of coating meshes with zeolites may prove to be challenging on an industrial scale.

4. Conclusions

A wide-range of materials have been employed for the production of mesh membranes for the separation of oil and water. The basic requirement is that the system must exhibit extreme wettability, whereby a membrane with superhydrophobicity and superoleophilicity or underwater superhydrophilicity and superoleophobicity is fabricated by creating a layer of hierarchical structures on the nano- and micro-scale, on mesh materials. This is followed by modification with low surface-energy chemicals to produce a membrane with superhydrophobicity and superoleophilicity or the introduction of water into the hydrophilic hierarchical structure to produce a membrane that exhibits underwater superhydrophilicity and superoleophobicity. These membranes can effectively separate immiscible oil/water mixtures solely driven by gravity, with high separation speed and efficiency. More importantly, such mesh membranes exhibit good durability, stability and reusability. Different membrane materials offer a choice of secondary properties such as mechanical strength, heat resistance, chemical stability and electrical resistance. The choice of membrane material will ultimately be determined by considerations of the chemical environment in which the membrane will operate, the cost of

production, the scalability of the preparation process and particular specialized requirements.

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