



Bio-inspired superhydrophobic and superoleophilic nanofibrous membranes for non-aqueous solvent and oil separation from water



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ABSTRACT

The separation of apolar, or non-aqueous, solvents from polar ones is an important challenge in water and wastewater treatment applications. Superhydrophobic and superoleophilic membranes present unique opportunities for such separations. Inspired by the lotus leaf effect, superhydrophobic membranes were prepared having hierarchical surface roughness made of carbon black nanoparticles. A hydrophobic nanofibrous support was produced through electrospinning using polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP). Hydrophobic carbon black nanoparticles were then coated onto the support via an electrospraying technique under varying conditions to generate surfaces having unique micro- and nano-scale roughness features. Membranes made using a polymer concentration of 8% w/w and nanoparticle to polymer ratio of 1 showed the smallest bead size ($4.9 \pm 2.0 \mu\text{m}^2$) and highest bead area density (74.3%), with corresponding average and root mean square roughness values of $3.69 \pm 0.07 \mu\text{m}$ and $4.63 \pm 0.05 \mu\text{m}$, respectively. When tested for surface wettability, the prepared membrane showed water contact angle, sliding angle and contact angle hysteresis values of 160.8° , 7.0° and 5.3° , respectively; however, liquids with surface tensions $\leq 36.6 \text{ mN/m}$ had zero contact angle on the membrane surface (superoleophilicity). The optimized membrane showed significantly higher gravity-driven flux (1275–2163 LMH) than the nanofibrous support membrane (933–1424 LMH) for the tested non-aqueous solvents.

1. Introduction

In the past decade the development and study of superhydrophobic surfaces has grown substantially. Previous efforts have sought to use these surfaces in diverse applications, such as in the formation of self-cleaning, anti-icing, and anti-fouling surfaces as well as for making membranes for oil/water separation [1–6]. Superhydrophobic surfaces, commonly defined as surfaces with a water contact angle (CA) $\geq 150^\circ$ and sliding angle (SA) $\leq 10^\circ$, received increased attention after the report of the “lotus effect” mechanism by Barthlott and Neinhuis [7]. This effect is attributed to the combination of two characteristics: a low surface energy waxy layer and hierarchical surface roughness with micro- and nano-scale structures [8]. Accordingly, artificial superhydrophobic surfaces are usually manufactured in two stages: (1) fabrication of hierarchical micro/nano-structures to improve roughness and (2) modification of surface chemistry to reduce surface free energy [9,10]. In general, the effects of surface roughness on wettability differ according to the liquid surface tension and solid surface free energy. Based on the Wenzel model, if the liquid spreads on the surface with CA $< 90^\circ$, like low surface tension organic liquids on a solid surface

with high surface energy, roughening the surface increases the affinity of the solid surface toward the liquid. This increase in affinity is observed as a decrease in the CA. On the other hand, if the liquid CA is $> 90^\circ$, like water on a low surface energy (hydrophobic) surface, surface roughness reduces surface wettability (low affinity). In this case, roughness can result in air being trapped between the liquid and solid phases, and lead to a heterogeneous surface with low solid-liquid adhesion and high CA as illustrated by the Cassie-Baxter model [11].

Apart from water, the wettability of organic liquids, such as oil, to membrane surfaces is of interest. The difference between the surface tension of water (72.8 mN m^{-1}) and oil ($< 35 \text{ mN m}^{-1}$) is the reason why most superhydrophobic surfaces are at the same time oleophilic or superoleophilic (oil CA $< 5^\circ$). As previously mentioned, the low surface energy of the solid is a key factor to achieving superhydrophobicity; however, as these surfaces are normally characterized by surface energy values $> 35 \text{ mN m}^{-1}$, they tend to be oleophilic. Superhydrophobic/superoleophilic membranes are great candidates for oil/water separation either by adsorption, filtration, or a combination thereof. Using superhydrophobic/superoleophilic membrane separation presents a variety of advantages for oil/water separation compared to

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Nomenclature

3D	three dimensional
Al ₂ O ₃	aluminum oxide
CA	contact angle
DMF	N,N-dimethylformamide
FESEM	field emission scanning electron microscopy
LSM	laser scanning microscopy
PVDF-HFP	poly(vinylidene fluoride-co-hexafluoropropylene)
SA	sliding contact angle
SDS	sodium dodecyl sulfate
SiO ₂	silicon dioxide
TiO ₂	titanium dioxide

Symbols

A	membrane area
D_e	density of ethanol
D_p	density of dry membrane
d_p	maximum pore size
f_{lv}	liquid-air interface
f_{sl}	fractional contact area between the droplet and solid

J	filtration flux
M_0	mass of oil before separation
M_m	mass of oil after separation
M_s	mass of oil adsorbed in the membrane
R	separation efficiency
r	Wenzel roughness factor
S_a	average roughness
S_q	root mean square roughness
V	the volume of the permeated solvent
W_w	wet weight
W_d	dry weight
ε	porosity
ΔP	water entry pressure
γ	surface tension
θ	contact angle
θ_{H_2O}	water contact angle
θ_Y	Young's contact angle
θ_W	Wenzel contact angle
θ_{CB}	Cassie-Baxter contact angle
Δt	permeation time

more conventional techniques like gravity separation, skimming, coagulation, magnetic separation, flotation, and membrane filtration [12]. For example, conventional techniques are limited by the droplet size of the non-aqueous liquid, surface fouling resulting in reduced water fluxes, and the need for chemical addition resulting in the production of low purity residual streams [13,14].

Various methods such as layer-by-layer assembly, low temperature hydrothermal, dip coating and phase inversion have been used to produce superhydrophobic surfaces [15–18]. Despite all of the previous studies, the commercial production of superhydrophobic/superoleophilic membranes has been hindered by complex production steps and poor mechanical stability and flexibility in practical environments [19]. Following the two step process of introducing surface roughness and reducing surface energy, all these methods consisted of a multi-step fabrication process using various chemicals. For instance, Meng et. al. used the dip coating technique to produce superhydrophobic membranes containing TiO₂ nanoparticles [18]. A precursor sol, a mixture of Anhydrous ethanol, perchloric acid (HClO₄), acetylacetone (AcAc), titanium (IV) isopropoxide (TTIP) and Milli-Q water, was mixed with a solution of a templating agent in anhydrous ethanol to prepare a sol-gel. Afterwards, membranes were dip coated in the sol-gel for 8 s. Then, membranes dried at 120 °C for 16 h and rinsed and placed in a water bath at 90 °C for 24 h. Finally, membranes were rinsed again and UV irradiated in water for 24 h. The whole process was repeated 4 times for each sample to achieve surface roughness. The secondary step of reducing surface energy was applied to enhance surface hydrophobicity. For this reason, a solution of toluene and 1H,1H,2H,2H-perfluorododecyltrichlorosilane (FTCS) was filtered through modified membranes at 0 °C under low vacuum. The filtered membrane was kept at 120 °C for 2 h, then, backwashed with ethanol for 5 min at 100 kPa.

One alternative synthesis technique that overcomes many of the aforementioned challenges to making superhydrophobic membranes is electrospinning. Electrospinning is a simple and versatile technique to fabricate nonwoven, highly porous fibrous mats with inter-connected pore structures [20,21]. Over the past decade, the progress in electrospinning technology, such as moving collectors and multi-needle systems, has offered new possibilities for mass production of nanofibers [22]. Furthermore, the emergence of needle-less electrospinning techniques has opened a new commercial outlook for nanofiber production [23]. Considering the promising outlook of nanofibrous membranes, investigating their potential applications is highly relevant.

Furthermore, while this technique has shown great promise in making macroporous membrane structures their performance in non-aqueous phase separations has not been extensively documented.

Recently, electrospaying of polymer and nanoparticles mixtures has been emerged as a promising method for introducing hierarchical surface roughness, consisting of micro- and nano-scale roughness features. When a solution is under a relatively high electrostatic force, the spinning jet destabilizes and solution moves toward the collector as fine droplets, which is electrospaying [24,25]. During the droplets flight time, solvent evaporates and beaded structures form after their deposition onto the collector. While the polymeric beads provide micro-scale roughness features, nanoparticles can protrude from the surface of individual beads and add roughness features in nanometer scale [24]. To achieve superhydrophobicity, however, requires that the surface chemistry of the nanoparticles be made to be hydrophobic, if it is already not so. A summary of some of the different groups that have been used to functionalize nanoparticles for making superhydrophobic membranes is given in Table 1. Silane and fluorinated groups are the main functional groups used in previous studies to date. The toxicity of fluorinated-based chemicals poses environmental consequences that may hinder their practical application [26,27]. Additionally, post-surface modification can reduce the stability of the membrane surface coating leading to a gradual loss of superhydrophobicity [27]. Hydrophilic nanomaterials have been generally used during membrane synthesis to facilitate their adhesion to the membrane support structure.

Table 1

Summary of functional group types used to reduce the surface energy of different nanomaterials for fabricating superhydrophobic membranes.

Nanoparticle	Functional group	Water contact angle (°)	Refs.
TiO ₂	(Heptadecafluoro-1,1,2,2-tetrahydrodecyl) triethoxysilane	162.7	[9]
	(Tridecafluoro-1,1,2,2-tetrahydrooctyl) triethoxysilane	163.2	[9]
	(3,3,3-Trifluoropropyl) trimethoxysilane	165.3	[9]
SiO ₂	Hexamethyldisilazane	160	[28]
SiO ₂	Octamethylcyclotetrasiloxane	157	[29]
TiO ₂	1H,1H,2H,2H perfluorooctyltriethoxysilane	153.4	[30]
SiO ₂	1H,1H,2H,2H-perfluorodecyltriethoxysilane	NA	[31]
Al ₂ O ₃	γ -Methacryloxypropyltrimethoxysilane	144	[32]

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