Superhydrophobic Membranes with Ordered Arrays of Nanospiked Microchannels for Water Desalination

Zeyu Ma, Yan Hong, Liyuan Ma, and Ming Su*

Nanoscience Technology Center, Department of Mechanical, Materials, and Aerospace Engineering, University of Central Florida, Orlando, Florida 32826

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Membrane distillation can desalinate seawater using low-grade heat energy or solar heat, but it has limited mass fluxes and membrane fouling issues. Glass membranes with integrated arrays of nanospiked microchannels and a narrow pore size distribution are made through a process that involves glass fiber drawing, dissolving template material from microchannels and differential chemical etching. After surface modification, superhydrophobic glass membranes with water contact angles of over 160° are produced because of the formations of ordered arrays of spiked nanostructures. The superhydrophobic membrane has shown better antifouling ability and higher flux than those of existing polymer membranes, especially at high salt concentrations, owning to its large pore diameter, straight pore shape, narrow pore size distribution, high chemical and thermal stabilities, and water-repelling ability.

We have fabricated superhydrophobic glass membranes that have ordered arrays of nanospiked microchannels using a process that combines fiber drawing, template removal, differential etching, and surface modification. These superhydrophobic membranes are designed to enhance hydrophobicity, maximize allowable pore sizes, and minimize pore wetting in order to enhance the mass flux of vapor molecules. The superhydrophobic membranes have structural features appropriate for water desalination using membrane distillation: (1) these membranes have large water contact angles, which allow large pore sizes and high mass fluxes; (2) the diffusion lengths and resistances of vapor molecules are reduced in straight microchannels; (3) the narrow pore size distribution reduces pore wetting by liquid water; and (4) the superhydrophobic membranes retard fouling during operation.

The global shortage of clean water calls for energy-efficient methods of water desalination.1 Without taking much energy to boil water, membrane distillation can treat brackish water at relatively low temperature using low-grade thermal or solar heat.2 In membrane distillation, the feedwater is heated to generate vapor, which permeates hydrophobic micropores and condenses on the cold side of a polymer or ceramic membrane.3-5 However, the implementation of this technique is limited by low mass flux across the membrane and the membrane fouling issue. Although flux enhancement can be achieved by applying mechanical excitation, vacuum on the cold side of the membrane, or turbulence promoters inside fluid cells,6-8 these approaches require high-grade electrical energy, extra facility, or high pumping power and thus should be used as an additive means to enhance mass flux. From a membrane perspective, both the mass flux and membrane fouling issues are strongly related to the microstructures and materials of membranes.

Depending on the ratio of pore diameter to the mean free path of vapor, the mass flux through pores in membrane distillation is governed by Knudsen or molecular diffusion.9 In both cases, the flux is proportional to pore diameter, porosity, and the vapor pressure difference between the feedwater and the permeate water and is inversely proportional to the thickness and tortuosity factor of the membrane. The diffusion resistance in straight pores (with a tortuosity factor of 1) is small because of shorter collision times between vapor molecules and pore walls. However, most synthetic polymer or ceramic membranes have large tortuosity factors, which lead to large diffusion resistances to water vapor molecules. Although larger pore diameter leads to higher vapor flux, the allowable pore sizes of existing membranes fall in the range of 50 to 200 nm as restricted by membrane hydrophobicity. At normal hydrophobicity (contact angle of ~110°), liquid water will overcome the surface tension and enter large micropores, which is responsible for the efficiency reduction and low salt rejection.10 In addition, having a narrow pore size distribution can be helpful in avoiding pore wetting by choosing an operating pressure that is appropriate for the majority of pores. Polymer membranes with monodisperse pore diameters have been made by casting polymer solutions under humid conditions,11-13 but there is no report on their surface property and desalination performance. This lack of information is due to two reasons: (1) the allowable pore sizes are relatively small as a result of the normal hydrophobicity of the membrane and (2) the membranes are too thin to survive the hot, corrosive desalination conditions. Heat conduction through the membrane tends to decrease the evaporation driving force (i.e., temperature and vapor pressure differences across the membrane), thus membranes with low thermal conductivities will be more efficient in generating water vapor.14

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However, a trade-off exists between heat conduction and vapor diffusion: increasing membrane thickness or porosity can decrease heat conduction and lead to a long diffusion path and a large diffusion resistance of vapor molecules.\(^{(15)}\) However, membrane fouling, including the irreversible attachment of organic fouling, scaling, and colloidal biofouling, would lead to pore wetting or blocking, high pumping pressure, short service time, and extra energy needs.\(^{(16)}\) Current efforts to mitigate membrane fouling include changing surface charges, hydrophilicity, roughnesses, adding polymer barriers or chemicals, and so forth,\(^{(16,17)}\) but such practices will also decrease the mass flux by reducing the vapor pressure of water (in the case of polymer barriers) or shorten the lifetime of the membrane (in the case of chemicals such as chlorine). For membrane distillation, an ideal membrane should have straight pores with a maximal pore diameter, a narrow pore size distribution, sufficiently high hydrophobicity, low thermal conductivity, and good fouling-resistant capability.

Superhydrophobic surfaces that have water contact angles greater than 150° have been designed by mimicking the self-cleaning ability of lotus leaves.\(^{(18)}\) On the basis of the combination of surface textures and surface chemistry, water drops will bead up or roll over superhydrophobic surfaces.\(^{(19)}\) Superhydrophobic surfaces have been produced by the layer-by-layer deposition of nanoparticles or polymers or by surface modifications of vertical nanowires or microfabricated structures,\(^{(20–24)}\) where the microstructures can lift a water drop above the surface by an air gap (i.e., Cassie state).\(^{(25)}\) If microporous membranes can be made to be superhydrophobic, then the allowable pore sizes will be much larger than those of normal membranes if the operating pressure were the same, thus allowing higher mass flux. However, available superhydrophobic surfaces are investigated mostly for water repellancy purposes without considering vapor permeability. In limited cases, random nanowire films or ordered metal meshes with superhydrophobicity have been used to separate oil–water mixtures.\(^{(26,27)}\) Even though not being explored for water desalination, the pore sizes and pore size distributions may not be suitable, and heat conduction through nanowires or metal meshes may be too large to meet the need for high-flux water desalination. In addition, although glass nanopore arrays and superhydrophobic glass nanospike arrays are fabricated by fiber drawing,\(^{(28–30)}\) there has been no effort to develop novel superhydrophobic membranes with high vapor permeability and water repellancy by integrating nanospikes and microchannels because the current fiber-drawing technique is limited to making micro/nanostructures with a single repeating geometry, which restricts the achievable function of one system. Therefore, a technological breakthrough is needed in order to achieve multiple functions (vapor permeability and superhydrophobicity) in an integrated manner for water desalination.

We have used a modified glass fiber drawing method to produce glass membranes with ordered pore sizes and nanospikes (Figure 1). Preforms for fiber drawing consist of commercial Pyrex glass tubes of two compositions, which are chosen in such a way that they have similar softening temperatures and coefficients of thermal expansion but dissimilar resistances to a chemical etchant. Salt powders (i.e., sodium chloride) are placed into a glass tube that can be etched slowly by the etchant (hard glass), and this tube is inserted into another glass tube that can be etched rapidly (soft glass) by the same etchant. The soft glass contains more borate oxide and thus reacts faster with hydrofluoric acid (HF) than the hard glass. The melting temperature of salt (801 °C) is close to the softening temperatures of glasses (~820 °C). The preforms are drawn into long microfibers (diameter of 400 μm), which are cut into short pieces of equal length. Next, the short pieces are packed to form a parallel bundle that has an ordered hexagonal arrangement in the cross-sectional direction. The bundle is drawn again to form a long microfiber and is cut into short pieces, where the diameter and spacing of hard glass and the salt core are reduced from millimeters to micrometers. The centimeter-long pieces from the second draw are subsequently assembled to form another bundle, which is annealed to form a glass rod and cut into thin plates. After the plates are polished using cloths of different grits, the thin plates are immersed in water to dissolve the salt and etched in HF to make nanospiked microchannels.

Figure 2A shows a scanning electron microscopy (SEM) image of nanospiked microchannels made by etching a polished glass plate in a 1% v/v HF solution for 30 min. The porosity derived from the surface area ratio of microchannels in the SEM image is about 26%. The pore diameter has a narrow distribution that is centered at 3.4 μm with 90% of the pore diameters falling in the range of 3 to 4 μm (Figure 2B). Figure 2C shows a high-resolution image taken at a 30° tilt angle, where the height, the bottom width.
and the top width of a typical nanospike are measured to be 2.84 μm, 1.2 μm, and 170 nm, respectively, from which the cone angle of the nanospike at the cross section is determined to be 20.4°. The size reduction in the fiber drawing process has been studied by measuring the diameter and spacing of microchannels and the diameters of surrounding glass in the tapered piece left after each drawing cycle. The tapered pieces are sliced to thin plates of identical thickness. Each slide is then polished and etched slightly to develop nanospiked microchannels. As the diameters of surrounding glass decrease from 520 to 7 μm, the diameter (square) and spacing (triangle) of the microchannel decrease linearly to 3.4 and 2 μm (Figure 2D), respectively. The two lines in this Figure have different slopes, from which the ratio of the coefficients of thermal expansion of glass to salt is derived to be 0.42. Taking the ratio into account, we can derive the diameter and spacing of microchannels after each draw using

\[ d_n = \frac{d_1^{n-1}}{2(r + t)^{n-1}(R + T)} \]

\[ l_n = \frac{l_1^{n-1}}{2(r + t)^{n-1}(R + T)} \]

where \( d_n \) and \( l_n \) are the diameter and spacing after \( n \) draws, respectively, \( d_1 \) is the outer diameter of the microfiber, \( R \) and \( T \) are the inner radius and thickness of the glass tube used in the first draw, respectively, \( r \) and \( t \) are the inner radius and thickness of the glass tube used to bundle microfibers together, respectively, and \( \beta \) is the ratio of coefficients of the thermal expansion of glass materials and salt at the fiber drawing temperature (assuming two glass materials have similar coefficients of thermal expansion). This method has good control over the diameter and spacing of microchannels: the diameter and spacing obtained from the equation are 3.1 and 1.8 μm, and the actual diameter and spacing measured from the images are 3.4 and 2.0 μm, respectively. Furthermore, the sharpness (i.e., cone angle) of the nanospike can be controlled by changing the etching conditions. We have fabricated cone-shaped nanospikes by using the same method, where the preform is formed by inserting a rod of hard glass into a tube of soft glass. The preform is drawn into long microfibers, which are cut into short, even pieces, and bundled together for the next draw cycle. After the second draw,
contact angle change is consistent with the previous observations: the water contact angle depends on the sharpness (cone angle) of the nanospikes, provided that the diameter, spacing, and area density of the nanospikes are the same.\textsuperscript{29} To evaluate the performances of superhydrophobic membranes in water desalination, an air gap membrane distillation system is established where one side of a membrane is in contact with the hot feedwater and the other side is exposed to air at ambient conditions (i.e., 22 °C and 1 atm). The mass fluxes and the conductivities of permeate water are measured continuously by an electronic balance and a conductivity meter, respectively. An electrical heating tape is used to heat the feedwater that contains a certain amount of salt in deionized water. The temperature at the interface of the membrane and feedwater is monitored by an electric thermometer that is inserted close to the membrane from the feedwater side. The operating pressures are maintained at 1700 Pa, and the feedwater is kept stationary. Figure 3C is the temperature-dependent mass changes of the permeate water through a superhydrophobic glass membrane that has a pore diameter of 3.4 μm, an interpore spacing of 2 μm, a porosity of 26%, a thickness of 500 μm, and a water contact angle of 165°. The stepwise mass change is induced by the intermittent outflow of condensed water. The mass fluxes at 55, 65, 75, 85, and 95 °C for 5% salt concentration are determined to be 1.8, 3.3, 5.12, 8.4, and 11.1 kg/m² per hour from the slopes of lines and the membrane areas after compensating evaporation loses (squares in Figure 3C inset). As the feedwater temperature increases, the flux increases because it has a high vapor pressure. Figure 3D indicates the thickness- and salt-concentration-dependent mass fluxes at a temperature of 95 °C, where the diamonds, triangles, and circles represent the mass fluxes of membranes with thicknesses of 1200, 800, and 500 μm, respectively. Briefly, a thinner membrane has a higher flux because of the small diffusion resistance for vapor; the flux decreases as the salt concentration increases as a result of the low vapor pressure of the feedwater. Furthermore, we have measured the mass fluxes of a commercial microporous polypropylene membrane obtained from Chemplex (catalog no. 325), which has an average pore diameter of 220 nm, a porosity of 55%, a thickness of 25 μm, and a contact angle of 115°. Although the squares in Figure 3D show that the polymer membrane has similar mass flux values to the 500-μm-thick superhydrophobic membrane at a temperature of 95 °C for the feedwater containing 2.5% salt, the mass fluxes of the polymer membrane decrease to 8.24, 7.28, and 5.03 kg/m² per hour at salt concentrations of 5, 10, and 20%, respectively. In contrast, the mass flux of the 500-μm-thick superhydrophobic membrane is nearly constant (changing from 11.3 to 9.63 kg/m² per hour) when the salt concentration is increased from 2.5 to 20%. In the temperature range between 55 and 95°C, the polymer membrane has a lower flux than the 500 μm superhydrophobic glass membrane for 5% salt solution as indicated in the Figure 3C inset. If glass membranes could be made thinner by fine polishing or reactive etching prior to chemical etching or more porous by using starting glass tubes of various geometries, then the mass fluxes could be even higher.

We have studied the effect of the water contact angle on the mass flux and salt rejection of glass membranes, both of which are related to the liquid entry pressure of water (LEPW) (i.e., the minimal pressure at which liquid water and salt will overcome surface tension and enter hydrophobic pores). LEPW depends on the diameter and spacing of spiked nanostructures, the water contact angle, the surface tension, and the temperature of feedwater. For simplicity, we have derived the relationship between the LEPW and the structure of cone-shaped nanospikes. The LEPW of an ordered array of cone-shaped nanospikes could be derived from the geometries and area densities of nanospikes. Assuming that a circular water—solid—vapor contact line was formed around each nanospike, the LEPW of the nanospike array can be derived by maximizing the surface tension pressure (\(P\)) using the following equation\textsuperscript{29}

\[
\text{LEPW} = P_{\text{max}} = 2\rho \frac{\pi}{4} \sin \phi \sin (\theta - 90^\circ - \phi)
\]

where \(\rho\) is the area density of a nanospike with units of number/μm², \(\alpha\) is the fraction of wetted area on each nanospike relative to the total projected area, \(\sigma\) is the surface tension of the feedwater, \(\theta\) is the contact angle of a flat glass after surface modification (112.4°), and \(\phi\) is the half-cone angle of a nanospike. \(\alpha\) can be changed from nearly 0% (Cassie state) to 100% (Wentzel state) as water is gradually pushed into the array of nanospikes. Figure 4A shows the simulated relationships between the LEPWs, the half-cone angles of a nanospike, and the fraction of wetted areas. The LEPW increases until the half-cone angle reaches 7.5°, which can also be derived from \(\phi = (\theta - 90^\circ)/3\) as the first-order solution to the LEPW equation. We have measured the LEPWs of several glass membranes that have identical pore geometries (i.e., diameter and spacing) but different cone angles and water contact angles. The LEPWs are measured by applying increasing hydraulic pressure to each membrane and monitoring the appearance of water drop on the other side of the membrane. Figure 4B indicates the LEPW of each membrane as a function of the water contact angle, where the membrane with a larger water contact angle supports a higher pressure. For the membrane with a water contact angle of 165°, the effective area density of the spiked nanostructures is derived as 0.044/μm² from the equation using an LEPW of 4760 Pa, \(\phi\) of 10.2°, \(\alpha\) of 100%, and \(\sigma\) of 0.072 N/m. Because this effective area density is larger than the number density of ring-shaped, nanospiked microchannels counted from the corresponding SEM image (0.031/μm²), we conclude that one
spiked nanostructure is equivalent to 1.42 normal cone-shaped nanospikes for the enhancement of membrane hydrophobicity.

Furthermore, we have measured the mass flux and salt rejection ability of membranes with water contact angles of 122, 135, 146, and 165°, where the salt rejection is evaluated by measuring the resistivity of permeate water. Figure 4C shows an opposite trend between the mass flux and salt rejection of these glass membranes (pore diameter of 3.4 μm, interpore spacing of 2 μm, and thickness of 500 μm) at a temperature of 95°C and an operating pressure of 1700 Pa. A membrane with a small contact angle has a large mass flux, but the permeate water contains more salt as a result of pore wetting. Although the mass flux of a flat glass membrane is greater than 80 kg/m² per hour, this membrane will leak at the same operating pressure and temperature because of its small water contact angle (122°). In addition, although the LEPWs of two membranes (water contact angles of 135 and 146° measured at 22°C) are higher than the operating pressure, the surface tension of water and the water contact angle decrease at high temperature, which causes low allowable pressure and poor salt rejection. For the superhydrophobic glass membrane (water contact angle of 165°), the passage of salt through the micropores is completely blocked, and the mass flux is about 10 kg/m² per hour.

The superhydrophobic glass membranes have shown much better fouling-resistance abilities than polymer membranes in an accelerated fouling evaluation process. We have observed the morphologies of the superhydrophobic glass membrane with a contact angle of 165° and the commercial polypropylene membrane with a contact angle of 115° after 15 h of desalination at 95°C in a 10% salt solution contained in a steel tube. A piece of copper that can react electrochemically with the steel tube is placed inside the tube to stimulate the accelerated fouling condition. Figure 4D shows that, after desalination, the polymer membrane is covered with a thick layer of yellow stains, presumably the copper deposits generated by the corrosion reaction. In contrast, the superhydrophobic glass membrane has shown only a few stains at the same magnification (Figure 4E). Furthermore, compared with superhydrophobic glass membranes, the polymer membrane has low robustness and low chemical and thermal stabilities, which is confirmed by the easy formation of microcracks and low salt rejection after operating at high temperature for a long time (>30 h).

In our membrane distillation process, the mean free path of a water vapor molecule is shorter than the pore diameter (~3 μm), thus the mass flux is controlled by molecular diffusion as

\[
J = \frac{1}{8} \frac{r^2 \varepsilon \Delta p}{\chi \eta RT} = \frac{1}{8} \frac{r^2 \varepsilon}{\chi \eta} K
\]

where \( r \) is the pore radius, \( \varepsilon \) is the tortuosity factor of pores, \( \delta \) and \( \eta \) are the thickness and porosity of the membrane, \( M \) is the molecular weight, \( p \) is the vapor pressure in the pores, \( K \) is the vapor pressure difference across the membrane, and \( \eta \) is the viscosity of the vapor. Assuming the same \( K \) at operating conditions, the flux across our glass membrane (with a pore radius of 1.7 μm, thickness of 500 μm, tortuosity factor of 1, and porosity of 26%) can be much higher than that across a polymer membrane (average pore radius of 110 nm, thickness of 25 μm, tortuosity factor of 2, and porosity of 55%). In our experiment, the mass flux of a superhydrophobic glass membrane is 2 times that of a hydrophobic polymer membrane at a salt concentration of 20% (Figure 3D). If the glass membrane could be made thinner or more porous, then the mass flux would be enhanced more. From a heat conduction perspective, an air gap is formed between the feedwater and the nanospiked superhydrophobic membrane. The equivalent thermal conductivity \( k_{eq} \) of the membrane can be determined by the volume fraction of air or vapor and membrane material using the following equation

\[
k_{eq} = k_{air} \frac{V_{air}}{V} + k_{spike} \frac{V_{spike}}{V}
\]

where \( k_{air} \) and \( k_{spike} \) are the thermal conductivities of air and the membrane material, \( V_{air} \) and \( V_{spike} \) are the volumes of the air gap and spiked nanostructure, respectively, and \( V \) is the total volume of the air gap and spiked structure. In air gap membrane distillation, one side of the membrane is in contact with water, and the other side is in contact with air. We have calculated the thermal conductivity of a superhydrophobic glass or polymer membrane with a pore diameter \( b \) of 4 μm, a nanospike height \( m \) of 10 μm, an interpore spacing \( a \) of 5.35 μm, and a cone angle \( \theta \) of 30° (Figure 1), where the thermal conductivities of glass, polymer, and air are taken to be 1.1, 0.16, and 0.025 W·m⁻¹·K⁻¹, respectively. In Table 1, the thermal conductivities of flat glass and a polymer membrane with the same features and thickness are also listed for comparison, where the pore size \( b \) is 4 μm and the spacing \( a \) is 5.35 μm. Because the thermal conductivity of air is lower than those of glass and polymer, replacing part of the membrane materials with either air or vapor could reduce the heat conduction through membrane, which will enhance vapor generation at certain operating temperature. As the membrane becomes thinner, the fraction of thermal conductivity reduction due to this material replacement is increased. Furthermore, making nanospike-based superhydrophobic polymer membranes could reduce heat conduction more than those of superhydrophobic glass ones with the same structure because of the relative low thermal conductivities of polymers, but polymer membranes have low thermal and chemical stabilities and thus short lifetimes in hot corrosive feedwater. At last, for either a glass or polymer membrane, incorporating superhydrophobic spiked nanostructures can mitigate fouling issues by reducing water–membrane contact areas. Thus, optimizing membrane structures and materials to enhance superhydrophobicity and mass flux further will be important for future research.

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Letter

Table 1. Calculated Thermal Conductivities of Nanospiked Membranes, (W·m⁻¹·K⁻¹)

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