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# Highly Permeable Polymer Membranes Containing Directed Channels for Water Purification

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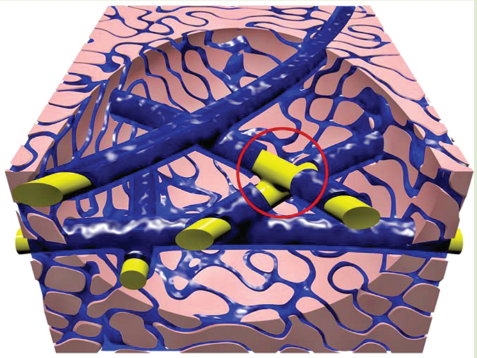
**ABSTRACT:** This viewpoint describes the concept of using nanocomposite barrier layers containing directed water channels to increase membrane permeability for water purification. In one practical approach, the channels, formed at the interface between the interconnected nanofibrous scaffold and the polymer matrix, were used to guide the transport of water molecules in a directed manner and to also exclude contaminant molecules. This concept was demonstrated by embedding overlapped oxidized multiwalled carbon nanotubes into the poly(vinyl alcohol) (PVA) barrier layer for ultrafiltration (UF). We anticipate that the same approach can be extended by substituting oxidized carbon nanotubes with ultrafine cellulose nanofibers (diameter about 5 nm), which are derived from wood pulp and are environmentally friendly as well as more cost-effective, into highly cross-linked polymer barrier layers. The resulting thin-film nanofibrous composite (TFNC) membranes should exhibit a permeation flux significantly higher than those of conventional thin-film composite (TFC) membranes for nanofiltration while maintaining the same rejection capability.



The use of membrane filtration to purify water from diverse sources, such as seawater, produced water, industrial wastewater, and other polluted water, is a cost-effective way to address the emerging problem of a clean water shortage, which has become a major challenge for humanity today.[1] Progress in membrane science and technology during the last few decades has been slow, and some major technical barriers to improve the energy efficiency of filtration, especially when dealing with the removal of small molecules, such as salt ions in seawater (desalination), remain unresolved.

In conventional nanofiltration (NF) and desalination (e.g., reverse osmosis (RO) or forward osmosis (FO)) membranes, the separation principle for removing small contaminant molecules (e.g., sizes less than 1 nm) from water is mainly based on the mechanism of size exclusion or solution diffusion of water molecules in the barrier layer.[2,3] When dealing with the solution-diffusion pathway, the free volume concept is often used to explain the water passage in the amorphous matrix.[4] However, the free volume in the barrier layer of the conventional membrane, as confined by highly cross-linked and restrained polymer chains, is inevitably organized in a tortuous manner. Thus, the permeable water paths are essentially random or nondirected.

Recently, the materials community has been pursuing the concept of incorporating "directed water channels" in the barrier layer to improve the membrane permeability.[5] This concept is based on the mechanism of size exclusion, inspired by the Nobel discovery of hourglass-shaped channels (with a pore size of 0.28 nm) of Aquaporin proteins in the cell membrane.[6,7] These protein channels can selectively pass water molecules and exclude other molecules, thus regulating the flow of water. Recent studies showed that the water permeability in membranes containing such protein channels can be 5−1000 times greater than those of conventional membranes.[5,8,9] Other nanoporous materials, including carbon nanotubes,[10] zeolites,[11] and graphene oxide nanosheets,[12] that possess molecular channels in the nanometer range, have also been introduced into or used directly as the barrier layer. For example, the hollow cores of aligned carbon nanotubes (including single-, double-, and multiwall carbon nanotubes) with an inner diameter of less than 1 nm have been used as water channels, where water molecules could pass through the core with 2−3 orders of magnitude higher flux than those of commercial membranes.[10] Having Na-A type zeolites with entrance pores of 0.4 nm incorporated into the polyamide barrier layer made by interfacial polymerization, the resulting RO membrane showed an 80% increase in permeability when compared with membranes without zeolites.[11] Recently, the barrier layer made of geometrically optimized graphene oxide nanosheets containing intercalated water layers has also been found to exhibit almost unimpeded "water" penetration capability, while rejecting most other small molecules such as helium.[12]

Self-assembly or phase transformation of molecules, such as liquid crystals[13] or block copolymers,[14] are alternative approaches to incorporate directed water channels in the barrier layer. For example, membranes made by post cross-linking of lyotropic liquid crystal molecules in a special QI cubic phase (with a *Pn*3*m* structure) were found to contain continuous water channels having diameters of about 0.75 nm. Such membranes exhibited a rejection ratio higher than

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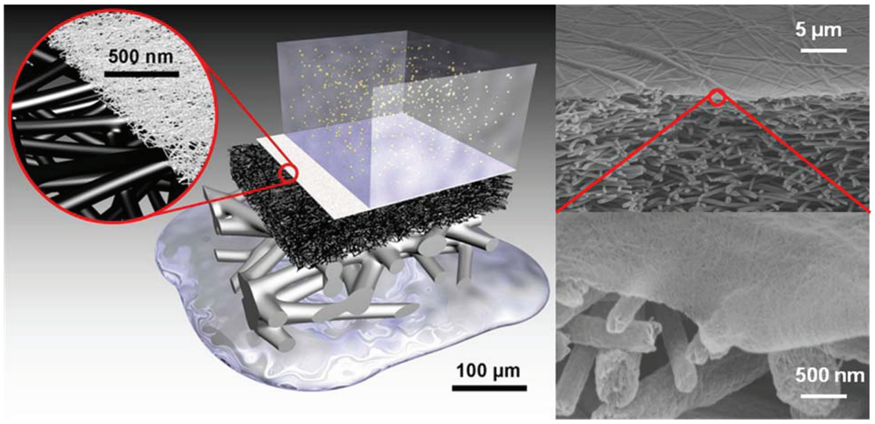

**Figure 1.** (Left) Schematic hierarchical structure of thin-film nanofiber composite membrane containing three layers of randomly deposited fibers with different diameters. (Right) Cross-sectional SEM views of the barrier layer and nanofibrous scaffold in a typical TFNC membrane.[18]

99.5% against sodium chloride and at a comparable flux as the commercial membranes.[13] A recent small-angle neutron scattering (SANS) study of membranes made of sulfonated penta-block copolymers (Kraton, Inc.) also indicated the presence of continuous ionic water channels in the barrier layer, which led to improved permeability.[14]

All of the above-mentioned methods, however, face different challenges for practical applications, in terms of processability, durability, and cost-performance effectiveness. For example, the Aquaporin protein channels have to be imbedded in a polymer matrix to obtain sufficient mechanical stability, while this composite format, representing a substantial reduction on the surface number density of Aquaporin protein channels, greatly decreases the permeability. Aligned carbon nanotubes need to be connected and sealed by a water impermeable binder, where such a fabrication process drastically increases the membrane cost. For zeolite-based membranes, the water transport rate in hydrophilic zeolite inner pores seems to be significantly lower than that in hydrophobic channels of carbon nanotubes or Aquaporin proteins, rendering a low permeability gain. In particular, the graphene oxide-based membrane seems to be only applicable to permeate water molecules in the gaseous phase instead of the liquid phase. The conditions for forming and securing directed water channels from the formation of a liquid crystal phase followed by polymerization are tricky and difficult to scale-up. Finally, the water channels formed in tri/penta-block copolymers are tortuous and not easily tunable, while the permeability advantage over other commercial membranes is not apparent.

In our laboratory, we have been pursuing a different pathway to incorporate directed water channels in the barrier layer. Our approach takes advantage of the natural formation of the interface between an interconnected nanofibrous scaffold and a barrier polymer matrix, where the interface can be used to guide water transport and to exclude predesigned contaminant molecules. Our first publication in support of this approach involved the fabrication of high-flux ultrafiltration thin-film nanofibrous composite (TFNC) membranes, based on a nanocomposite barrier layer containing oxidized carbon nanotubes embedded in cross-linked poly(vinyl alcohol) (PVA), for oil and water separation.[15] In that work, we hypothesized that the increase in water passage is due to the existence of both internal nanochannels (i.e., the inner cores of nanotubes) and external nanochannels (i.e., the interfacial gaps between oxidized carbon nanotubes and the PVA polymer matrix). We now believe that the latter plays the dominant role because (1) the internal nanochannels are not interconnected but the external nanochannels are, since the concentration of nanotubes in the polymer matrix was much higher than the overlap concentration, and (2) the operating pressure (as low as 30 psi) might be too low to induce water molecules entering into the hydrophobic core of carbon nanotubes.[16]

Based on the above findings, we now propose to expand our viewpoint on the directed water channels, which are controlled by the gap between the relatively smooth surface of the oxidized carbon nanotubes and the surface of the barrier polymer matrix.[17] The gap distance determines the effective sieve size. While it is quite easy to fabricate a relatively large gap size for UF membranes, it becomes more challenging with decreasing gap size. To resolve the scale up transformation, we substitute the modified carbon nanotubes with environmentally friendly and more cost-effective ultrafine cellulose nanofibers in the barrier layer to increase the membrane permeability for nanofiltration and beyond. Before we describe the expanded approach, we first briefly review our recent results of using naturally occurring cellulose nanofibers for water purification.[18−21] It has been well-demonstrated that ultrafine polysaccharide (e.g., cellulose and chitin) nanofibers or nanowhiskers can be derived from plant or crustacean materials using a combination of chemical and mechanical treatments.[22] These nanofibers can be considered as nascent crystals or aggregates of nascent crystals in the biomass, where the diameter of these nanofibers ranges from 5 to 20 nm and the length ranges from a few hundred nanometers to micrometers. Variations of these dimensions depend on the sources and processing methods chosen. For example, the surface of cellulose nanofibers derived from wood pulp is naturally covered with hydroxyl groups, which are partially converted into carboxylate and aldehyde groups by the TEMPO oxidation method.[23] In this case, carboxylate groups provide negative charges in water, and aldehyde groups can be thermally cross-linked with hydroxyl groups or chemically bonded with other functional groups.[18] Since a small fiber diameter leads to very high surface-to-volume ratio (>600 $m^2/g$), the ultrafine cellulose nanofibers can be used as a superadsorbent with a high adsorption efficiency to remove charged molecules (e.g., positively charged metal ions,[20] or negatively charged viruses if the carboxylate groups are complexed with positively charged molecules, such as polyethyleneimine (PEI)[24]). Another unique characteristic of these nanofibers is the high crystallinity

(>70%), which significantly increases their chemical stability and bacteria resistance. As a result, ultrafine cellulose nanofibers can be used directly as the barrier layer, where a layer of 100 nm thickness would result in a mean pore size of about 20 nm, suitable for ultrafiltration (UF).[18] Figure 1 illustrates the hierarchical structure of TFNC membranes containing three layers of randomly deposited fibers with different diameters: the top barrier layer based on ultrafine cellulose nanofibers (diameter about 5 nm), the midlayer electrospun nanofibrous scaffold (fiber diameter about 150 nm), and the bottom nonwoven fibrous support (fiber diameter about 20 $\mu$m). As the porosities of each layer are all higher than 65%, the resulting flux in this membrane is 3−10 times higher than those of commercial UF membranes, but with a comparable rejection ratio.[18]

The hierarchical structure in the TFNC membrane (Figure 1) is suitable only for high flux UF applications because the mean pore size (about 20 nm) in the barrier layer is confined by the diameter of ultrafine cellulose nanofibers (about 5 nm) involved.[21] The top layer structure, however, can be used as a scaffold for further fabrication of NF, RO, or FO membranes. To be specific, the pores of the top cellulose nanofiber layer can be filled by a dense polymer matrix to decrease the effective pore size of the barrier layer using the following two approaches based on recent findings. In one illustration, a water-soluble/cross-linkable monomer (e.g., polyethylene glycol diacrylate) mixed with ultrafine cellulose nanofibers could be polymerized as a barrier layer. In the second illustration, interfacial polymerization could be carried out in the top cellulose nanofiber layer of a TFNC UF membrane (as shown in Figure 1) to produce a nanocomposite barrier layer containing the interconnected cellulose nanofibrous scaffold and the highly cross-linked polyamide matrix. There should be a number of different approaches for the introduction of functionalized ultrathin cellulose nanofibers as directed water channels. The key point is that we believe that the surface of ultrathin nanofibers can be used as a practical and cost-effective way to substantially increase the permeability of filtration membranes. Although the improved permeability can be attributed to the formation of water channels in the interface between cellulose nanofibers and the polyamide matrix, the nature of the interface in the above two cases may be different. Further studies are in progress.

A schematic diagram of directed and nondirected water channels in the nanocomposite barrier layer containing the nanofibrous scaffold and the polymer matrix is shown in Figure 2. The directed water channels are formed through the formation of interface between the cross-linked nanofibers and the polymer matrix, while the gap thickness may be regulated by physical interactions or chemical bonding between the two. This thickness can directly affect the selectivity of molecules to be removed. In addition, the nature of the nanofiber surface, that is, neutral versus charged, positively charged versus negatively charged, or hydrophilic versus hydrophobic, should also play a crucial role in fine-tuning the selectivity or the capability to reject the charged molecules, such as metal ions. It is clear that the effects of these parameters on the permeability or the rejection ratio in corresponding membranes are largely unknown, which have become an active and worthy research topic, worthy of further investigations.

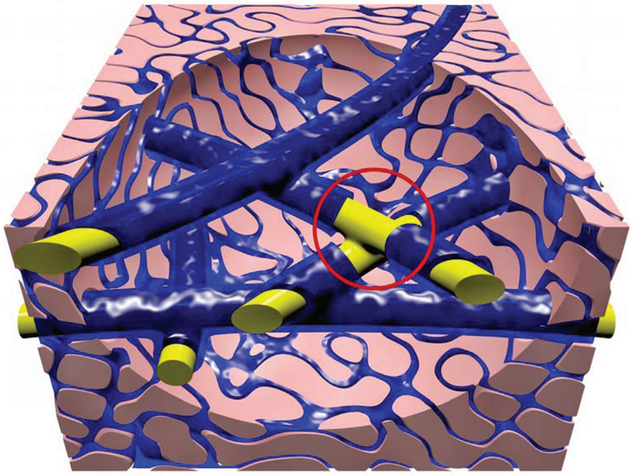

**Figure 2.** Schematic representation of the nature of water channels in the nanocomposite barrier layer. A skeleton of overlapped cellulose nanofibers (yellow) guides a continuously connected system of directed water channels (blue) formed by the connected hollow cylindrical gaps between the nanofibers and the polymer matrix (pink). The cut-out in the red circle sketches the cross-linked nature of the nanofiber interconnects. The nanofiber skeleton is anchored at occasional direct contacts with the polymer matrix (not shown). Nondirected molecular cavities in the polymer matrix also contribute to the overall water flow through the barrier layer.

Although one can expect that water molecules travel a significantly shorter distance through the interconnected interface than through the tortuous path via molecular cavities in the polymer matrix, the water transport rates along the two paths will be very different. Based on recent experimental and computational results of water transport in the cores of carbon nanotubes[10] and protein channels,[8,9] we argue that the hydrophobic nanofiber surface should lead to greater permeability improvement than the hydrophilic nanofiber surface. This hypothesis is being investigated in our laboratory.

In summary, we have demonstrated a practical approach to incorporate directed water channels in the barrier layer that can significantly improve the membrane permeability for nanofiltration and desalination. The formation of water channels is through the natural occurrence of interface between the embedded nanofibrous scaffold and the polymer matrix, instead of the inner cores of nanoporous materials. There are several advantages of adopting directed water channels in the barrier layer through this approach over the conventional barrier layer with nondirected water channels. (1) Directed water channels can be created at the interface between two domains of any bicontinuous phase (e.g., organic and inorganic, crystalline and amorphous, hydrophobic and hydrophilic) in the barrier layer, not confined only by the nanocomposite containing the nanofibrous scaffold and the polymer matrix. (2) The passage distance through directed water channels can be significantly shorter than that through nondirected water channels. (3) The width of the directed water channels is adjustable, depending on the interactions (physical or/and chemical) between the two bicontinuous phases. (4) The selectivity of these directed water channels can be fine-tuned by surface functionalization of one phase (e.g., hydrophilic, hydrophobic, charged, or chelate groups). (5) The density of directed water channels can be controlled by the surface-to-volume ratio of the embedded phase (e.g., interconnected nanofibrous scaffolds with small fiber diameters can provide a particularly high surface-to-volume ratio to increase the throughput for water purification). Finally, we note that, although we have used the unique hierarchical fibrous structure as a support in our NF examples, the same concept is applicable to the use of conventional UF support.

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### Notes

The authors declare no competing financial interest.

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