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## **Nanotechnology Applications to Desalination: A Report for the Joint Water Reuse & Desalination Task Force**

T.M. Mayer, P.V. Brady and R.T. Cygan

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## **Executive Summary**

Nanomaterials and nanotechnology methods have been an integral part of international research over the past decade. Because many traditional water treatment technologies (e.g. membrane filtration, biofouling, scale inhibition, etc.) depend on nanoscale processes, it is reasonable to expect one outcome of nanotechnology research to be better, nano-engineered water treatment approaches. The most immediate, and possibly greatest, impact of nanotechnology on desalination methods will likely be the development of membranes engineered at the near-molecular level. Aquaporin proteins that channel water across cell membranes with very low energy inputs point to the potential for dramatically improved performance. Aquaporin-laced polymer membranes and aquaporin-mimicking carbon nanotubes and metal oxide membranes developed in the lab support this. A critical limitation to widespread use of nanoengineered desalination membranes will be their scalability to industrial fabrication processes. Subsequent, long-term improvements in nanoengineered membranes may result in self-healing membranes that ideally are 1) more resistant to biofouling, 2) have biocidal properties, and/or 3) selectively target trace contaminants.

## **Introduction**

The world faces growing demands on supplies of fresh water due to increased population and domestic consumption, agricultural withdrawals, and withdrawals for power production and industrial uses. This increase in demand is coupled with a non-uniform distribution of fresh water and water demand, changing climate and precipitation patterns, and impairment of many surface and ground water resources throughout the world. As a result, water planners are examining a number of options for: 1) water conservation techniques and technologies that may make our existing supplies go further; 2) better management of water resource allocation to reflect changing demographics and the economic value of water resources, and 3) planning alternative sources of fresh water and the technologies to produce additional fresh water supplies from saline or impaired water sources. While the first two points represent the most immediate and responsible approaches to managing our water supplies, it is recognized that supplementing existing supplies from alternative sources, such as wastewater or seawater through membrane filtration, will be an inevitable and pressing necessity in the future.

This is where nanotechnology—the use of materials and processes that operate over a length scale of roughly 1 to 100 molecular diameters—is expected to help. Nanoscience and nanotechnology have been widely touted as the basis of the next industrial revolution. The National Science Foundation estimates that nano-related goods and services could be a \$1 trillion market by 2015. Nanotechnology receives roughly \$10 billion of R&D investment each year and over 4,000 U.S. nanotechnology patents exist. Already, products of nanotechnology are on the consumer market, from biocidal surfaces for refrigerators to stain and water-resistant fabrics, and more products are appearing each year. Advances in nanotechnology and nanomaterial synthesis are expected to result in new water treatment technologies (Savage and Diallo 2005; Shannon, Bohn et al. 2008). An increasingly refined, molecular level understanding of water and contaminant behavior at membrane and filter media interfaces should point to better water treatment technologies (Cygan, Brinker et al. 2008) including new materials for treatment and new ways to manufacture them. Staged nanotechnologies, for example, may enable lower-cost decentralized water treatment in the future (see e.g. Savage and Diallo 2005). Additionally, novel methods for water disinfection (e.g. Stewart, Trudell et al. 2009) and contaminant detection (e.g. Wernette, Liu et al. 2008) rely on specific molecular configurations to be effective.

Traditional water treatment practices including flocculation, filtration, and scale inhibition have fundamental mechanisms that are controlled by nano-scale processes. Many of the polymers, clays, zeolites, and metal oxides that are routinely used in water treatment can be classified as nanoparticles. How can one survey the future of nanotechnology applications when so much of the present is nano in nature? Here, we will focus on the *intentional* design of nano-scale processes and, in particular, their application to desalination. What we specifically examine is the potential for reduction in cost and energy use in desalination processes through the exploitation of new nanomaterials and methods of fabricating such materials with enhanced performance. We examine the emerging field of ‘nanotechnology’ for ideas and understanding of processes that occur at nanometer length scales, and means of manipulating and fabricating structures at these length scales that can lead to significantly improved performance, or new functionality, that can be applied to desalination processes. The potential exists for improved membrane transport and selectivity that can lead to reduced energy consumption, and reduced expenses resulting from the modified membrane area required for a given water production

volume, smaller pumps, and overall plant footprint. Improved control of membrane scaling and fouling can lead to increased membrane life and reduced maintenance costs. Enhanced heat transfer and control of scaling in thermal processes can likewise reduce operation and maintenance costs.

Several of the potential applications of nanotechnology are straightforward, and are currently being implemented. Others are quite speculative and will likely take years of development. In many instances a fundamental understanding of the interaction of water and other substances with surfaces and nanometer-scale structures is lacking, and a full realization of the potential benefits of nanotechnology will require substantial investment in basic research in these areas. The large and sustained investments that have been made in nanotechnology worldwide provide some confidence that nanotechnologies will have an economic impact on water treatment technologies in the future.

The emerging field of nanotechnology comprises a very broad scope. This survey is not intended to be exhaustive, and very likely we have missed many potentially important developments that may have some application in desalination. Our intention is to identify the overlaps of nanotechnology with the major targets for improvements in desalination that have been identified in the recent 'roadmapping' efforts. We will limit ourselves primarily to those technologies that can improve membrane materials primarily through surface modifications.

## **Desalination**

A number of desalination processes have been developed and refined for commercial use over the past few decades, and are now in wide use around the world. However the cost of these processes is still too high for many communities, and even nations, to consider desalination as a major component of water supply and management strategies. In the past decade a number of studies have focused on identifying the major hurdles to more widespread adoption of desalination technologies, and highlighting the research and development activities that will help us to overcome these hurdles (U.S. Bureau of Reclamation and Sandia National Laboratories 2003).



Desalination technologies developed and commercialized over the past few decades include three major approaches:

1. *Thermal distillation.* This process mimics the hydrologic cycle that transports water evaporated from the oceans and deposited on land in the form of precipitation. Energy is supplied to vaporize water, leaving dissolved salts and most other dissolved components of seawater behind, and the water vapor is condensed back to liquid in the form of pure distilled water. Various implementations of the basic distillation process have been developed, and are in widespread use.

2. *Pressure-driven membrane processes.* Identified primarily with reverse osmosis (RO), this class of desalination produces fresh water by forcing salt water through a selective membrane, using externally applied pressure to overcome the natural osmotic pressure gradient which would tend to draw water from the fresh to saline side of a membrane. In this case, the energy consumption is determined by the pressure required to overcome the osmotic pressure, and the water and salt transport characteristics of the membrane that limit its performance.

3. *Electric field-driven membrane processes.* Commonly known as ‘electrodialysis’, this process uses an externally applied electric field to draw positively and negatively charged ions from saline water through ion selective membranes, depleting the source water of salt until deemed ‘fresh’. Energy is consumed in resistive losses in electric current transport in the water and membranes, and in electrochemical reactions at the electrodes.

Many ‘alternative’ desalination processes are variations of these three basic approaches, and it does not appear that any fundamentally new methods of desalination are on the horizon.

The thermodynamic requirements for energy consumption in desalination are well understood (Spiegler and El-Sayed 2001). The goal is to come as close to the theoretical minimum-

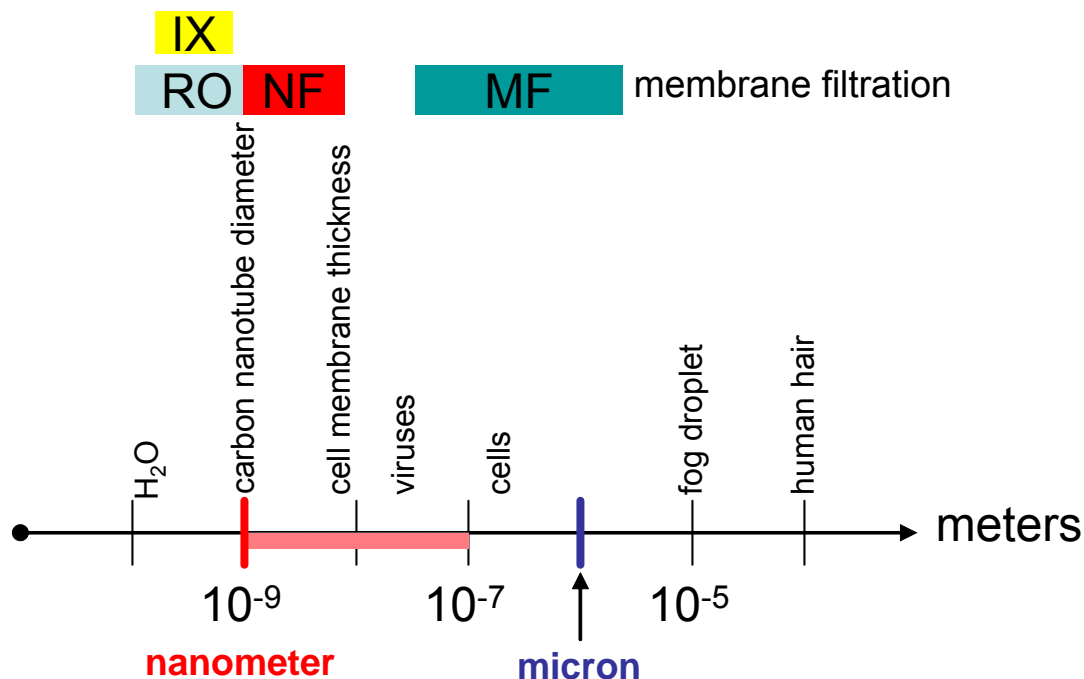
required energy use as possible, consistent with minimizing overall cost of the process. For distillation processes, additional costs are primarily the capital expense of the boilers, heat exchangers, vacuum pumps, water pumps, etc. Maintenance cost associated with scaling of heat transfer surfaces by inorganic precipitates can be significant. Additional costs in membrane systems are associated with the capital expense of membranes, pumps, pressure vessels, etc., and maintenance of the system while in operation. A major contributor to maintenance costs is fouling of membranes by inorganic suspended solids and precipitates, dissolved organic compounds, and biofilms produced by biological activity in the membrane system. To mitigate fouling concerns, extensive pretreatment of source waters is often necessary, which may incorporate additional membrane processes and costs to remove some of these fouling components.

Cost reduction on many fronts is necessary to make desalination processes affordable and accessible. Significant progress has been made in engineering design and operation to minimize material cost and energy use. Energy use has declined for both thermal and membrane systems through more efficient heat exchanger development, higher performance membranes, and energy recovery schemes for pressure driven membrane processes. The most obvious area to consider deploying advances in nanotechnology is in the design of better membranes.

## **Nanotechnology**

At its roots, nanoscience deals with the fundamental principles and properties of matter at the nanometer ( $10^{-9}$  m) scale. Nanotechnology is the application of these structures into useful nano-scale processes or devices. The appellation 'nano' is commonly applied to structures and processes having at least one dimension in the 1-100 nanometer range (see Figure 1). Three to five atoms could potentially be lined up in a nanometer. A cell membrane is 6-10 nm thick. This size range is somewhat unfamiliar to most scientists and engineers who are accustomed to working either at the atomic and molecular scale ( $< 1$  nm), or on the scale of the bulk properties of materials ( $> 100$  nm). This is largely the result of our abilities to probe and fabricate structures of these more assessable dimensions. For centuries, engineers have worked with bulk properties of materials to build much of our current infrastructure, while chemists and

physicists have developed theoretical and experimental techniques for probing the atomic and molecular structure of matter. It is only in the last few decades that we have developed theoretical and experimental tools to observe and study the properties of materials at these intermediate length scales.



**Figure 1.** Comparative length scales of filtration and particle sizes. Shaded area denotes nanotechnology realm. IX = ion exchange; RO = reverse osmosis; NF = nanofiltration; MF = microfiltration.

The dawn of nanoscience is commonly dated to a lecture by Nobel Prize-winning physicist Richard Feynman in 1959 titled “Plenty of Room at the Bottom”. In his talk Feynman anticipated the peculiar properties that would likely exist at this intermediate scale, unlike either bulk or atomic and molecular properties, which could potentially lead to new understanding of matter and new applications in technology. At nanoscales, surface tension and van der Waals interactions play an inordinately large role; gravity is less important. Interest in nanoscience was subsequently galvanized by the advent of scanning tunneling and atomic force microscopes which allowed imaging at the molecular level. It is now this potential for new and

useful properties of materials at nanometer length scales, and new techniques for fabricating and testing structures at this length scale that are driving developments in nanoscience and technology.

How does this relate to desalination? In essence, desalination is a problem at the atomic and molecular length scales. Salts dissolved in water can be adequately described by the properties of individual atoms and molecules of salt ions and the bulk properties of water. However, the methods we use to desalinate water—membrane and distillation processes—involve transport and other properties that are inherently nanoscale. Water interaction with surfaces that determine partitioning of water and dissolved salts at membrane interfaces, nucleation of mineral scale formation on membrane or heat exchanger surfaces, and transport of ions in ion exchange membranes are all processes that involve larger aggregations of molecules, exhibiting distinct properties from either the molecular or bulk scale.

Membranes are complex structures that contain active elements on the nanometer scale. Modern day reverse osmosis membranes are typically homogeneous polymer thin films supported by a porous support structure. Partitioning of water and dissolved salts between membrane and bulk solution, and transport of water and salts across the membrane, depend on the chemical properties of the membrane as well as physical structures at nano- to microscale. While we usually think of chemical properties of a material as homogeneous, the membrane-water interface can significantly affect the properties of the water layer in the ‘interphase’ region which may be nanometers thick. The density and distribution of ionic charges in the membrane material can influence the partitioning of charged ions into the membrane material. Thickness and dynamic free volume in the active homogeneous polymer layer, as well as pore size and pore distribution in the support structure, determine transport rates through the membrane. In ion exchange membranes, it is the charge density and charge distribution that determines the ionic transport in the membrane, as well as its mechanical stability in an aqueous environment. And in certain ion exchange materials, such as Nafion™, it is conjectured that charge-induced segregation within the material creates nanometer-scale void spaces or hydrophilic regions which facilitate ion sorption and transport.

Surfaces of membranes and heat exchangers have structures on the nanoscale that may play an active role in desalination processes. Surface roughness can affect the mixing and transport of components in the contacting liquid through hydrodynamic effects, nucleation of scale deposits, adhesion of particulates, and the hydrophobic or hydrophilic nature of the surface. Thin film coatings applied to these surfaces can be used to alter adhesion of foulants, incorporate biocides into the surface, or change the surface tension to control fouling.

These are examples of known properties of membranes and surfaces where nanometer-scale structures have significant effects on the performance of desalination processes. For the most part, these structures are present not by design, but are intrinsic properties of the materials that have been found to work in membrane or other desalination processes. The promise and potential of nanometer scale science and technology for new applications and improved processes is not so much due to the recognition that nano-scale effects are important, but rather the new found ability to use this knowledge to construct materials on the nanoscale to take advantage of favorable aspects or optimize the performance of processes used in desalination. The technological strategy is to recognize what are the limiting factors in performance of current desalination processes and how the new toolbox of nanometer scale science and technology can be put to use to improve this performance. The discussion below first outlines the physical chemistry of water at the nanoscale, then considers specific applications of nanotechnology to desalination, and concludes by trying to anticipate what the impacts of nanotechnology on water treatment will be in the future.

## **Water at the Nanoscale**

The nanometer length scale defined above lies between the scale of macroscopic particles suspended in water and dissolved atomic and molecular species. From a filtration perspective, this intermediate range contains species such as colloidal solids, large organic and biological molecules, polymers, and viruses. It also corresponds to the dimensions at which we recognize distinct modes of material transport across a membrane. For the larger dimensions of porous membranes (ultrafiltration, microfiltration) transport is described in terms of convective flow through pores

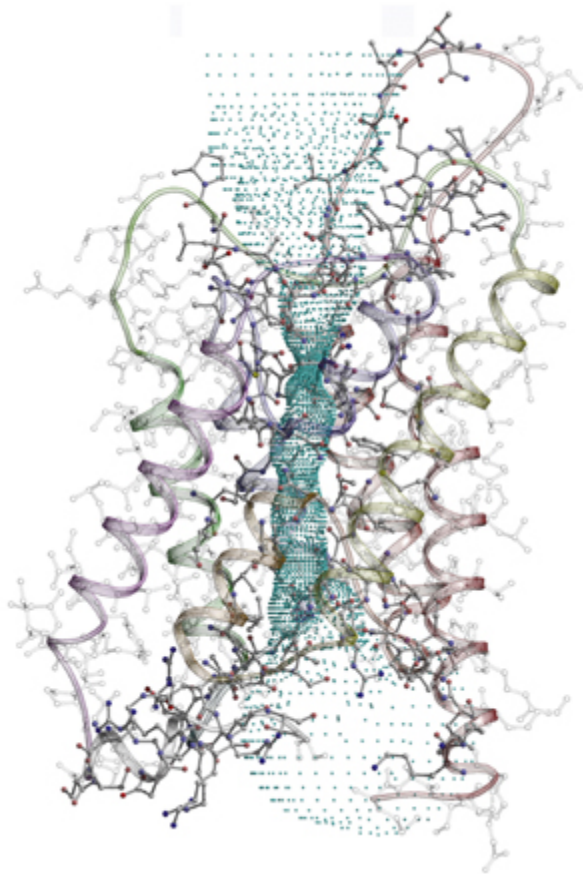
described by the Hagen-Poiseuille equation. On the other hand, transport in dense reverse osmosis membranes is typically described in terms of diffusive flow through a homogeneous material. The intermediate range of 1-100 nm length scale is somewhat less clearly defined, where pore sizes approach the typical boundary conditions applied to bulk fluid dynamic formulas. It is not clear that bulk fluid dynamics is applicable in this range, nor is the description of random interactions of atoms or molecules dissolved in a homogeneous material appropriate. Hydrogen bonding and van der Waals forces probably both play an important role. Several recent studies have addressed these specific molecular issues as they pertain to understanding the fundamental interactions of water treatment materials and how to improve their efficiencies (e.g. Orendorff, Huber et al. 2009; Zhang, Singh et al. 2009).

Conventional RO membranes are dense polymer films without macroscopic pores. Transport of water through the membrane is by diffusion, with molecules executing a tortuous path through 'free volume' in the polymer matrix. Solute ions also diffuse across the membrane, and selectivity is achieved through optimization of the density, composition, and thickness of the polymer to maximize the ratio of transport rates of water to those of salt ions. While pressure-driven RO is likely to remain the dominant desalination technology, further improvements in conventional polymer membrane performance are likely to be incremental.

Membranes with pores or channels specifically engineered to maximize water transport or ion selectivity offer the potential for dramatically more efficient operation compared to conventional polymer membranes. Some of these concepts are based on the function of biological membranes, and all take advantage of recent developments in nanofabrication techniques.

## Aquaporins

Peter Agre received the Nobel Prize in Chemistry in 2003 for his co-discovery of aquaporins “the plumbing system for cells”. Cell walls of most organisms contain specialized protein channels that quickly transport water or ions selectively across the cell membrane (Borgnia, Nielsen et al. 1999). The function of these ‘water channels’ (aquaporins) or ‘ion channels’ is only now becoming understood. In the case of aquaporins, water is transported in a hydrophobic channel a few Ångströms (1 Ångström = 0.1 nm) in diameter, while hydrogen bonding interactions with functional groups on the channel walls preferentially orient the molecules in single-file fashion inside the pore (see Figure 2). Ions are effectively excluded because of the large increase in free energy associated with penetrating a channel due to loss of its hydration sphere and the associated decrease in entropy. High water transport coefficients of  $\sim 10^{-16} \text{ cm}^3 \text{ s}^{-1} \text{ bar}^{-1}$  for a pore have been measured for natural aquaporin channels (Walz, Smith et al. 1994).

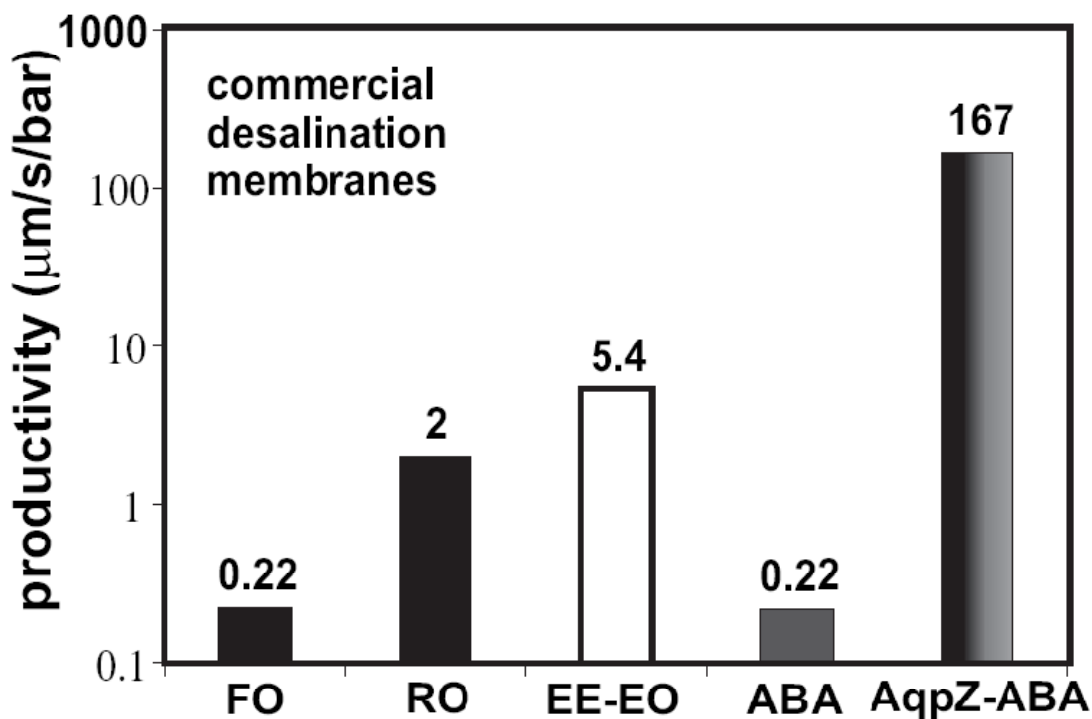


**Figure 2.** The structure of one of the four subunits of the water-channel protein AQP1, embedded in a cell membrane. Pore waters are marked by blue dots. A wide "vestibule" outside the cell (top) leads to the pore, which is about 2.8 Ångstroms across at its narrowest, just wide enough to admit water molecules. The pore widens into another vestibule inside the cell (bottom) (Reproduced with permission from the publisher. Source: <http://www.lbl.gov/Science-Articles/Research-Review/Highlights/2002/stories/biosciences/watergate.html>).

The effectiveness of aquaporins in shuttling water through cell membranes has motivated the search for aquaporin-assisted membranes, and for synthetic analogues. For example, Kumar et al. (2007) made amphiphilic triblock polymer vesicles that contained the bacterial water-channel protein Aquaporin Z (AqpZ) and found that the presence of the aquaporin imparted an 800-fold increase in water permeability (see Figure 3; note logarithmic vertical axis). While allowing water to pass, the polymer



rejected glycerol, glucose, salt, and urea. The AqpZ-incorporated membranes were found to perform roughly an order of magnitude better performance than existing membranes.

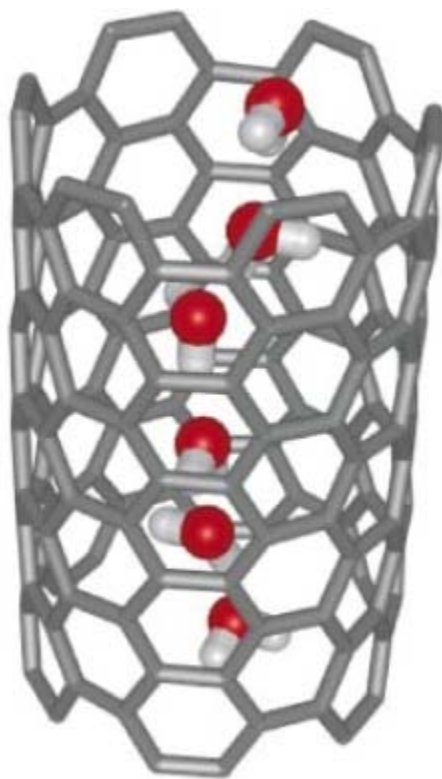


**Figure 3.** Comparison of reported permeability values for AqpZ-containing polymer membrane (AqpZ-ABA) with non-AqpZ ABA, FO, a commercial forward-osmosis membrane, RO, a commercial reverse-osmosis desalination membrane, and EE-EO a polyethylethylenepolyethylene oxide diblock polymer (from Kumar, Grzelakowski et al. 2007) Copyright 2007 National Academy of Sciences, U.S.A. Reproduced with permission from the publisher.

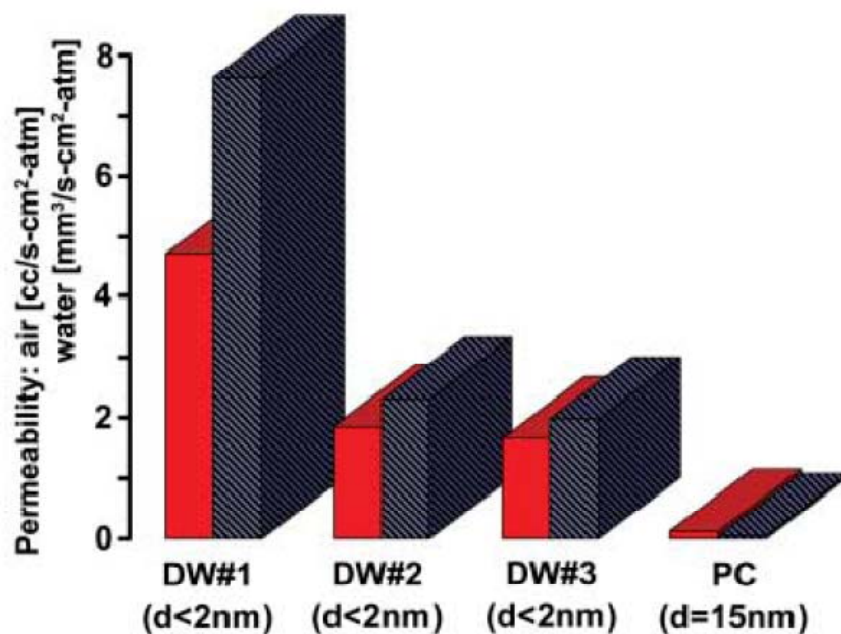
## Carbon Nanotubes, Oxide Membranes, and Nanocomposite Membranes

A number of approaches have been proposed for building a synthetic analog to aquaporin. While natural aquaporin proteins extracted from living organisms can be

incorporated into a lipid bilayer membrane or a synthetic polymer matrix (Walz, Smith et al. 1994), porous inorganic membranes modified to provide aquaporin-like function may provide a more robust alternative. These include carbon nanotubes (CNTs), double-walled carbon nanotubes (DWNTs), and metal oxide frameworks. CNTs have been grown and assembled into a dense array supported by a polymer matrix (Hinds, Chopra et al. 2004) as have DWNTs. Molecular simulations suggest that water transport in carbon nanotubes occurs in single-file fashion (see Figure 4), similar to aquaporins (Hummer, Rasalah et al. 2001).

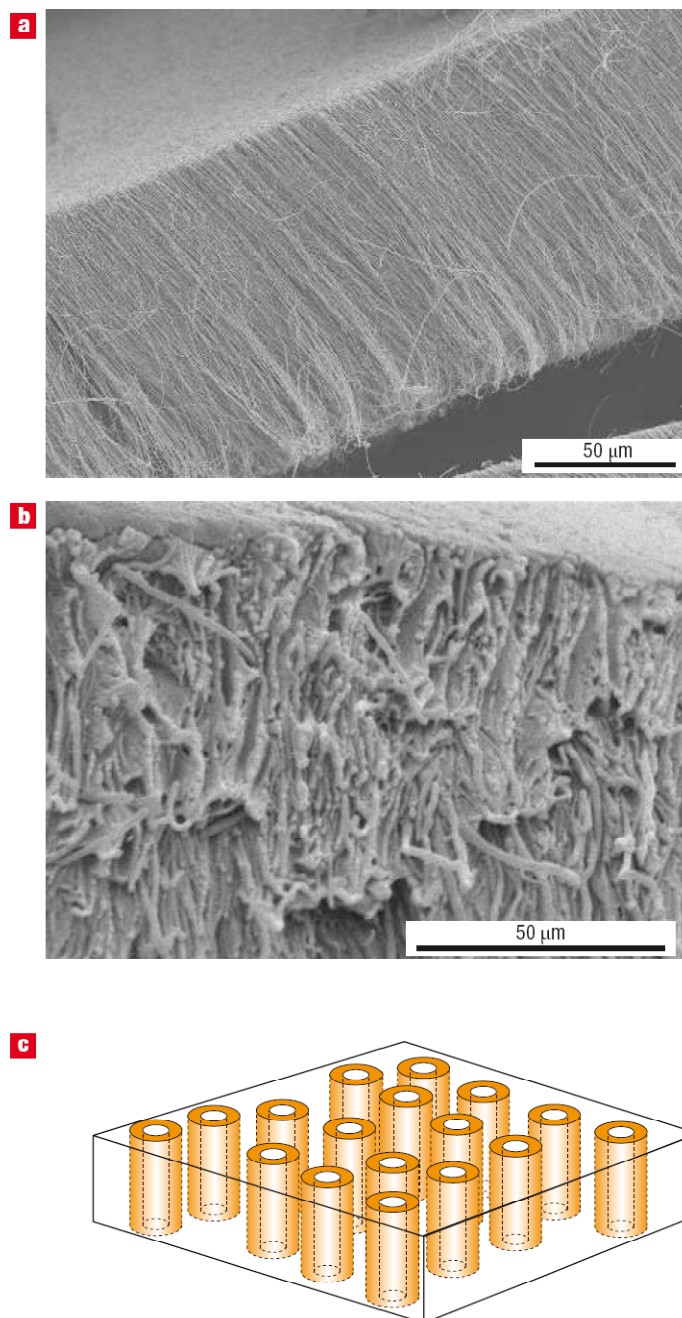


**Figure 4.** Water moving single-file through a carbon nanotube (Hummer, Rasalah et al. 2001). Reproduced with permission of the publisher.



**Figure 5.** Air (red) and water (blue) permeability as measured for three DWNT membranes (DW#1, 2, and 3) and a polycarbonate membrane (PC). Despite considerably smaller pore sizes, the permeabilities for all DWNT membranes greatly exceed those of the polycarbonate membrane (from Holt, Park et al. 2006). Reproduced with permission of the publisher.

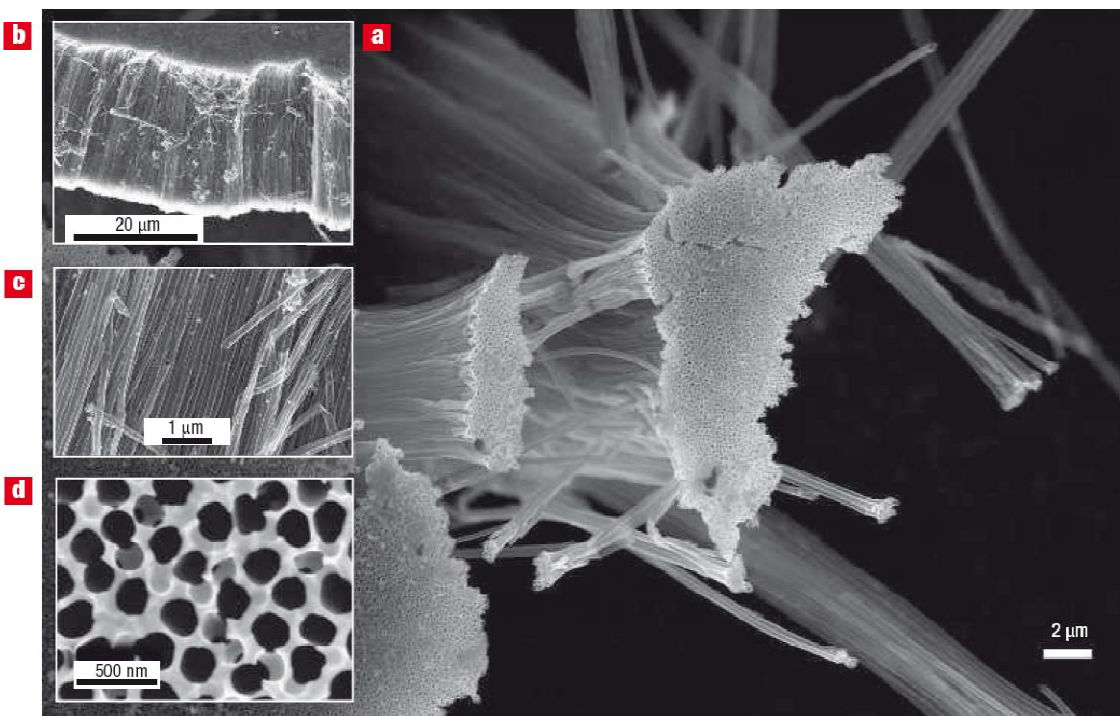
Keep in mind that making CNTs is an involved technical process. Typically a substrate containing metal seeds of the same diameter as the nanotubes are heated to 600 to 900°C, and then a carbon-containing gas such as methane or alcohol is added. Nanotubes then grow from the metal seeds. The metal from the seeds are problematic in that the metal can later occlude nanotubes. Figure 6 gives an idea of the steps involved in the process.



**Figure 6.** Carbon nanotube arrays and membranes. a) An as-grown, dense, multiwalled carbon nanotube array produced with a Fe-catalyzed chemical vapor deposition process. b) The cleaved edge of the nanotube-polystyrene membrane after exposure to  $\text{H}_2\text{O}$  plasma oxidation. The polystyrene matrix is slightly removed to contrast the alignment of the nanotubes across the membrane. c) Schematic of the

target membrane structure. With a polymer embedded between the nanotubes, a viable membrane structure can be readily produced, with the pore being the rigid inner-tube diameter of the nanotube (from Hinds, Chopra et al. 2004). Reproduced with permission from the publisher.

Nanopipes are made by chemical vapor deposition of carbon onto alumina templates. Unlike nanotubes, nanopipes tend to be made up of amorphous, as opposed to ordered, carbon (Whitby and Quirke 2007). Reproduced with permission of the publisher.

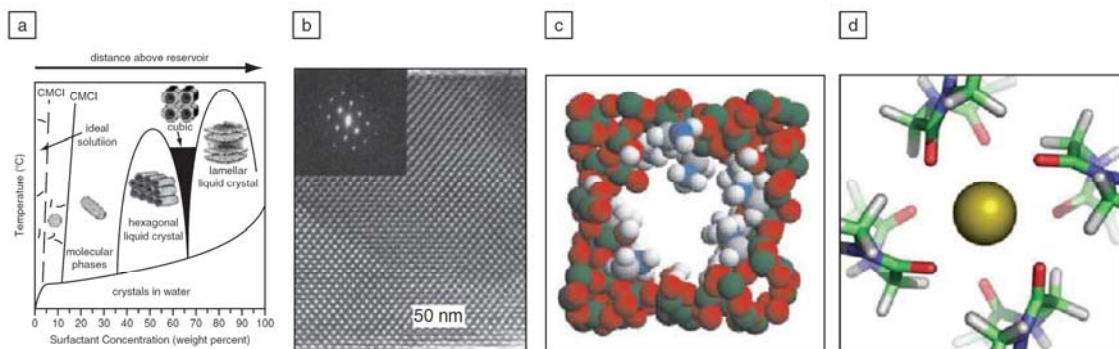


**Figure 7.** Scanning electron microscope images of carbon nanopipes produced using standard chemical vapour deposition (Whitby and Quirke 2007). a) Nanopipes partially released from an anodic aluminum oxide template following sonication in NaOH. b) Cross section of intact carbon coated membrane. c) Higher magnification view of individual aligned carbon pipes. d) Surface of carbon membrane showing open pores (diameter ~160 nm). Reproduced with permission of the publisher.

Nanofibrous materials, in general, are expected to see significant improvements in development and processing as the fundamental science of these nanomaterials is better understood. Electrospinning methods using an electrically charged jet of polymer solution or melt, in particular, are expected to achieve new nanofiber morphologies, including yarns and a variety of beaded, porous, hollow, ribbon, branched, and helical fibers (Kaur, Gopal et al. 2008). Additionally, the development of ceramic-based nanofibers involving carbon and various oxides (alumina, silica, etc.) will provide filtration materials having high selectivity and versatile adsorption properties. The impact of such new materials design on a new generation of water treatment media from nanofiltration to RO membranes will be significant.

Self-assembly and template directed synthesis techniques have been used to make porous materials that might ultimately mimic aquaporins from carbon, silicon dioxide, and polymers. Evaporation-induced self-assembly (Doshi, Huesing et al. 2000; Gibaud, Grosso et al. 2003) has produced  $\text{SiO}_2$  structures with ~40% porosity (Figure 8), which can be produced over large areas on a supporting substrate with a pore density of  $5 \times 10^{12} \text{ cm}^{-2}$ . Surface modification of the pore interiors to produce aquaporin-like function can potentially produce a membrane with a water transport coefficient of  $5 \times 10^{-4} \text{ cm}^3 \text{ cm}^{-2} \text{ s}^{-1} \text{ bar}^{-1}$ , or a factor of ~25 higher than conventional RO membranes. Recent advances in understanding the complex mechanisms of ion selectivity and transport in these types of nanomaterials have benefited by high fidelity molecular simulations (Leung and Rempe 2009).





**Figure 8.** a) Synthetic phase diagram for porous silica membranes (Brinker, Lu et al. 1999). b) Transmission electron micrographs of nanoporous silica thin films depicting the highly ordered 2-nm-diameter pore structure (Brinker, Lu et al. 1999). c) Snapshot of *ab initio* molecular dynamics simulation of  $-\text{CH}_2\text{NH}_2$  functionalized silica nanopore; protons are almost quantitatively transferred from silanol to the amine groups;  $\text{H}_2\text{O}$  molecules omitted for clarity (Leung, Rempe et al. 2006). d) 8-carbonyl binding site made of diglycine molecules and occupied by a  $\text{K}^+$  ion from quantum chemical study of a biological potassium channel (Varma and Rempe 2007). Reproduced with permission of the publisher.

Nanofabrication approaches have also been applied to ion-selective membranes incorporating fixed ionic charge in the pore walls, or externally biased to provide control of ion transport (Schaldach, Bourcier et al. 2004; Schaldach, Bourcier et al. 2004). In this case, pore diameter is controlled to be of the order of the electric double layer formed at the interface of a charged surface with an electrolyte, providing electrostatic exclusion of ions from the pore interior, and control of ion transport. Prototypes of this type of membrane have been fabricated from track-etched polycarbonate films (Martin, Nishizawa et al. 2001; Bourcier 2005), and methods of making similar pores in polymer membranes have been proposed.

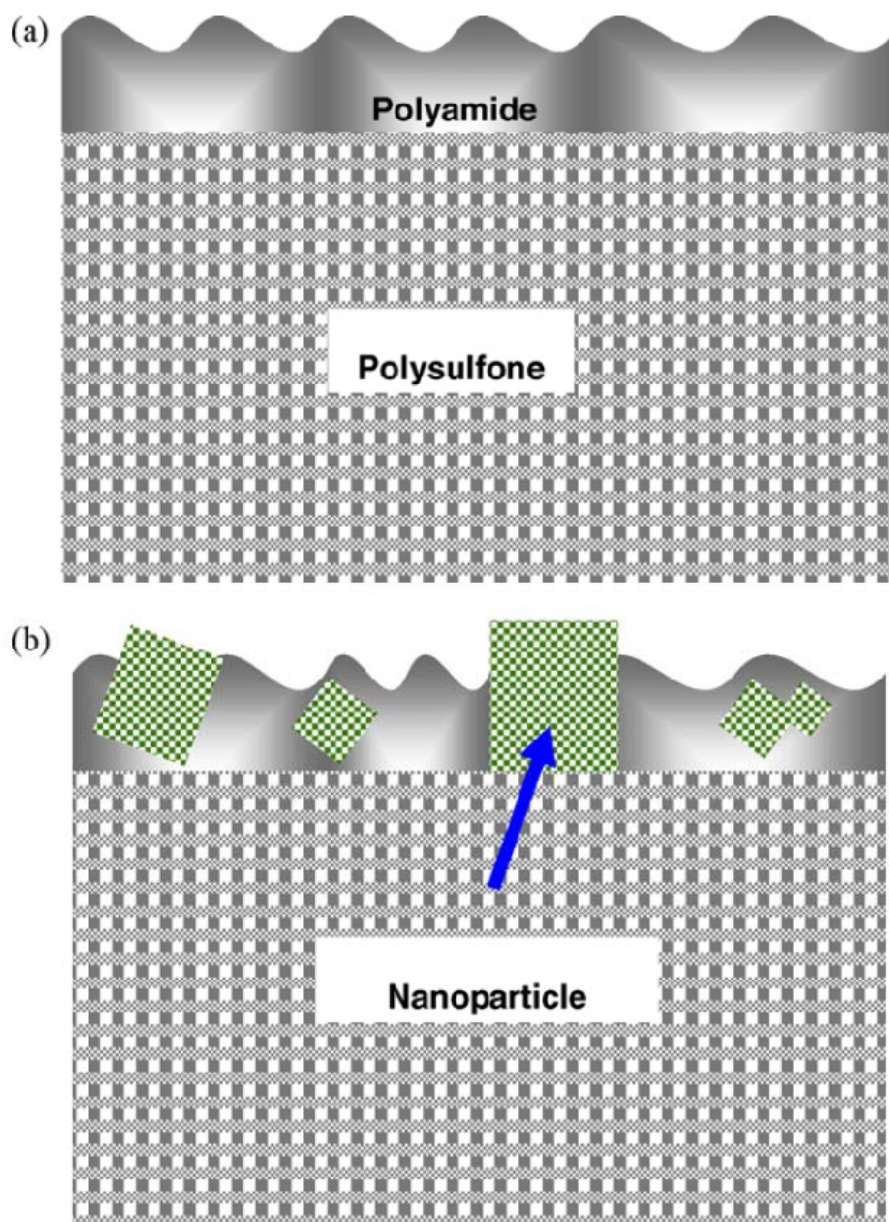
Self-assembly techniques have also been applied to fabrication of high-efficiency proton exchange membranes for fuel cells, using diblock copolymer phase separation techniques to construct high conductivity ion channels in a rigid polymer matrix (Won,

Park et al. 2003) (Wiles, Wang et al. 2005). Attempts to apply this technique to high conductivity electrodialysis membranes are underway (Hibbs, Fujimoto et al. 2005).

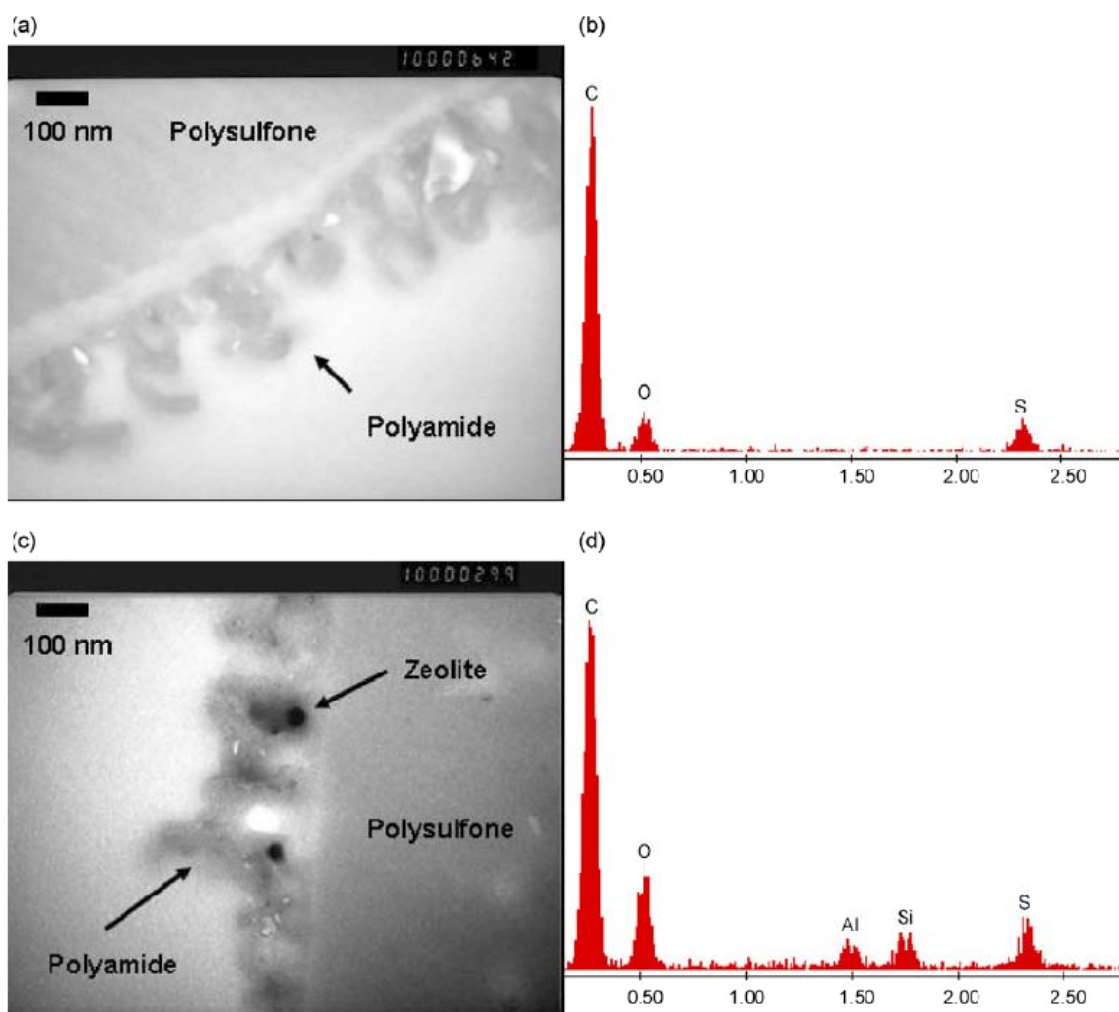
## **Nanocomposite Membranes**

Nanocomposite membranes consist of nanoparticles embedded in a thin-film composite membrane (see Figure 9). Jeong et al. (2007) dispersed zeolite nanoparticles onto polyamide films to produce relatively smooth and hydrophilic, negatively-charged surfaces that could be optimized to produce more effective membranes.





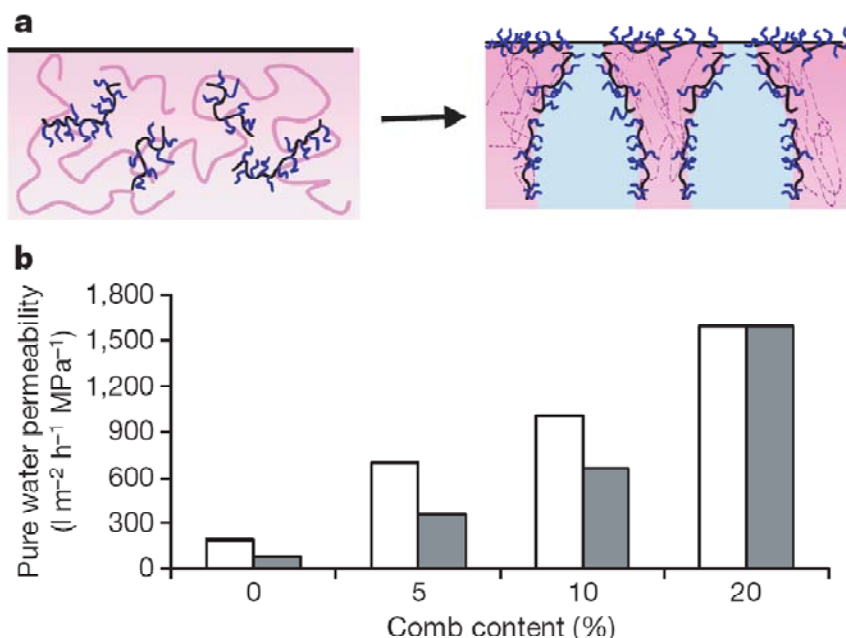
**Figure 9.** Schematic of (a) thin-film composite membrane and (b) thin-film nanocomposite membrane (from Jeong, Hoek et al. 2007). Reproduced with permission of the publisher.



**Figure 10.** Characterization of hand-cast thin film properties by TEM and EDX for (a–b) pure polyamide membrane and (c–d) nanocomposite membranes. Magnification is 100,000× in TEM images (from Jeong, Hoek et al. 2007). Reproduced with permission of the publisher.

## Amphiphilic Membrane Coatings

Another application of nanotechnology to membrane filtration is the anchoring of amphiphilic ‘combs’ to membrane surfaces to prevent biofouling. By extending a polar, hydrophilic headgroup into solution, amphiphiles bound to a membrane surface apparently are able to prevent biofouling (see Figure 11).



**Figure 11.** Comb copolymer amphiphiles for fouling-resistant membranes (from Shannon, Bohn et al. 2008). a) Schematic illustration of in situ approach using comb copolymer amphiphiles to modify ultrafiltration membrane surfaces and internal pores during membrane casting. b) Pure water permeability of polyacrylonitrile ultrafiltration membranes incorporating 0-20% comb copolymer additive having a polyacrylonitrile backbone and polyethylene oxide side chains. White bars show the initial pure water permeability, and grey bars show the pure water permeability after 24 hr of dead-end filtration of 1,000 mg per liter of bovine serum albumin in phosphate buffered saline, followed by a deionized water rinse. Initial flux and flux recovery increase with comb additive content. Membranes exhibit complete resistance to irreversible fouling at 20% comb content (from Asatekin, Kang et al. 2007). Reproduced with permission of the publisher.

## The Future

We tempt fate by stating that in the coming decades there does not appear to be any fundamentally new approach to desalination likely to supplant the established desalination technologies. Forward osmosis processes for desalination remain at present just a curiosity

because of significant problems with separation and recycling of the draw solute, and cross contamination of solutes through the membrane. Although the energy requirement of pressurized water feed in RO is eliminated, this savings may well be offset by the cost of unit operations to separate and recycle the draw agent. Electrodialysis and its cousin capacitive deionization are currently only economical for relatively dilute solutions due to that energy demands are a function of solution concentration. Unless this critical limitation can be addressed, these technologies will only contribute marginally to the growth in desalination. Energy recovery schemes appear to be most feasible with the capacitor arrangement, for example, through coupled or oscillating systems.

There is potential for significantly improving the efficiency of membrane processes, however, through novel nanostructured materials that mimic the function of natural systems, or otherwise take advantage of unique thermodynamics and transport properties of water in confined spaces (Donnan exclusion). To take full advantage of the promise of these super-efficient membranes, we will need to develop more efficient methods of reducing fouling and concentration polarization. Many of the potential improvements in RO membranes will likely also be applicable to ED in the form of high-conductivity, nanostructured ion-exchange membranes. New techniques will be needed to fabricate such membranes. All of the nanofabricated membrane efforts described above are still currently in the research laboratory. It is difficult to anticipate their future performance, manufacturability, and costs.

As for the future of nanotechnology, in 2004, M.C. Roco, Senior Advisor for Nanotechnology at the National Science Foundation, projected nanotechnology to evolve over four generations (Roco 2004):

***Passive nanostructures (~2001)***, illustrated by nanostructured coatings, dispersion of nanoparticles, and bulk materials—nanostructured metals, polymers, and ceramics. The primary research focus is on nanostructured materials and tools for measurement and control of nanoscale processes. Examples are research on nanobiomaterials, nanomechanics, nanoparticle synthesis and processing, nanolayers and nanocoatings, various catalysts, nanomanufacturing of advanced materials, and interdisciplinary simulation and experimental tools. Most of the industrialized countries have introduced products in the last 2–3 years, from

paints and cosmetics (Australia) to car components (Germany, Japan, U.S.) and nanostructured hard coating and filters (U.S.).

**Active nanostructures (~2005)**, illustrated by transistors, amplifiers, targeted drugs and chemicals, actuators, and adaptive structures. An increased research focus will be on novel devices and device system architectures. Key areas of research include nanobiosensors and devices, tools for molecular medicine and food systems, multiscale hierarchical modeling and simulation, energy conversion and storage, nanoelectronics beyond CMOS, 3-D nanoscale instrumentation and nanomanufacturing, R&D networking for remote measurement and manufacturing, converging technologies (nano-bio-info-cogno) and their societal implications.

**3-D nanosystems and systems of nanosystems (~2010)**, with various syntheses and assembling techniques, such as bioassembling; networking at the nanoscale and multiscale architectures. Research focus will shift toward heterogeneous nanostructures and supramolecular system engineering. This includes directed multiscale self-assembling, artificial tissues and sensorial systems, quantum interactions within nanoscale systems, nanostructured photonic devices, scalable plasmonic devices, chemico-mechanical processing, and nanoscale electromechanical systems (NEMS), and targeted cell therapy with nanodevices.

**Heterogeneous molecular nanosystems (~2015)**, where each molecule in the nanosystem has a specific structure and plays a different role. Molecules will be used as devices and from their engineered structures and architectures will emerge fundamentally new functions. This is approaching the way biological systems work, but biological systems are in water, process the information relatively slow, and generally have more hierarchical scales. Research focus will be on atomic manipulation for design of molecules and supramolecular systems, dynamics of

single molecule, molecular machines, design of large heterogeneous molecular systems, controlled interaction between light and matter with relevance to energy conversion among others, exploiting quantum control, emerging behavior of complex macromolecular assemblies, nanosystem biology.

Present day nanotechnology falls somewhere between Generation 2 and Generation 3 in Roco's scheme. If nanotechnology progresses in the direction outlined above towards active nanostructures, systems of nanostructures, and heterogeneous nanostructures, we can expect water treatment spinoffs such as self-healing and/or self-monitoring membranes, membranes that possess useful catalytic properties (e.g. membranes that also break down specific contaminants), and/or membranes that assemble themselves. Again, a critical unknown remains the speed at which manufacturing techniques are developed to convert largely laboratory-scale phenomena to industrial products.

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