New Materials for Emerging Desalination Technologies

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Desalination as a Solution to Water Shortage

The global water shortage caused by dwindling fresh water resources and increasing water demand, compounded by extreme climate conditions (less precipitation), has highlighted the very importance of treating unconventional waters for ensuring sustainable economic and societal growth in water-stressed regions.[1] Desalination, a process originally referred to as the removal of salts and minerals from saline water but herein broadly including brackish/seawater desalination and wastewater reuse, likely offers a long-term strategy for augmenting water supply. This technology is widely used in many parts of the world especially in the arid Middle East. For example, Israel has been heavily relying on wastewater reuse and seawater desalination to meet much of its water needs. Currently, this country has 86% of its wastewater recycled and 60% of drinking water produced by desalination. As a sharp contrast, such numbers are only 7% and <1%, respectively, for California, which has recently suffered from a severe state-wise drought.[2]

The state-of-the-art desalination technologies include (i) thermal processes such as multi-stage flash (MSF) and multi-effect distillation (MED) and (ii) membrane-based processes such as reverse osmosis (RO) and electrodialysis (ED). The RO technology, a hydraulic pressure-driven filtration process that removes contaminants from water mainly by size exclusion and charge repulsion, takes around 60% of the market due to its relative advantages in the capital cost, energy consumption, and ease of operation. Many other processes, including forward osmosis (FO), membrane distillation (MD), capacitive deionization (CDI), pressure retarded osmosis (PRO), and enhanced solar evaporation, have recently emerged as attractive alternatives in view of their great promise for addressing the water-energy nexus by satisfactorily reducing the operational energy consumption and capably using sustainable energy sources such as solar, geothermal or waste heat.

Producing water by desalination at the current development stage is more expensive than treating conventional water sources. For example, the unit cost of RO seawater desalination in the U.S. is now about \$2.0/m^3 on average (which may go down to \$1.1/m^3 when it is scaled up), compared to a typical wholesale water price in the range of \$0.1 to 0.5/m^3. [3] The high cost is mainly because desalination requires the removal of small, soluble contaminants (e.g., salts and inorganic/organic micropollutants such as pharmaceuticals and endocrine disrupting compounds) that are generally not a concern in conventional water treatment. Additionally, the high salt concentration in seawater imposes a thermodynamic limit of 1.1 kWh/m^3 as the theoretical minimum energy consumption at 50% recovery, significantly contributing to the overall cost of seawater desalination. Therefore, a prominent task for improving the desalination technology is to more effectively and energy-efficiently separate the target contaminants from water. In particular, development of high-performance desalination membranes using the emerging two-dimensional (2D) nanomaterials plays a key role in revolutionizing the membrane-based desalination technology.[2]

New Desalination Membranes Made of 2D Nanomaterials

Membranes made of conventional materials (e.g., polyamide) have inherent limitations in permeability, selectivity, chemical stability, and antifouling properties, severely affecting their separation performance in desalination. Recent advances in 2D nanomaterials have offered an unprecedented opportunity to help overcome these limitations by fabricating a new class of filtration membranes for desalination applications. In particular, the emerging graphene-based nanomaterials possess a unique 2D structure and highly tunable physicochemical properties as well as exceptional mechanical, electrical, and biological characteristics, all of which can be advantageously leveraged to significantly improve the separation efficiency of desalination membranes.[4] Expected to be in par with carbon nanotube membranes [5] and biomimetic aquaporin membranes [6] in terms of excellent separation capability, graphene-based membranes are much easier to scale up thanks to the use of graphite as low-cost raw materials and membrane synthesis via facile, scalable routes.

There are two general types of graphene-based membranes, made via drastically different approaches and having fundamentally different separation mechanisms. The first type is a porous graphene membrane made by punching nanometer pores through the ultrathin, super-strong, and impermeable graphene monolayer, as illustrated in Fig. 1(a). By precisely controlling the size and manipulating functional groups (that dictate the critical entrance properties) of the punched pores, the resulting nanopore membrane only allows molecules smaller in size than the pores to permeate through the membrane while larger molecules are ideally rejected.[7, 8] The single-carbon-atom thickness (~0.3 nm) of this super-strong membrane is almost three orders of magnitude less than the thickness (typically a few hundred nanometers) of traditional desalination membranes, thereby extremely improving the water permeability, which is inversely proportional to membrane thickness. However, bottle-neck challenges of making such a monolayer graphene membrane include the enormous difficulties in preparing a large-area, defect-free monolayer graphene sheet and in creating high-density pores of controllable, relatively uniform sizes on the graphene sheet.

The second type of graphene-based membrane is made of mass-producible graphene oxide (GO) nanosheets. As illustrated in Fig. 1(b), the unique 2D structure of GO nanosheets makes it ideal to synthesize a membrane via a simple, scalable layer-stacking technique.[9, 10] The nanochannels formed between the layer-stacked GO nanosheets, functionally equivalent to nanopores in the monolayer graphene membrane, provide a zigzag water transport path while rejecting unwanted ions and molecules that are larger in size than the inter-GO-layer spacing (Fig. 1(c)). Simulation and experimental evidence has indicated that due to the very large slip length (i.e., low friction) of water molecules on a graphene surface, water can flow at an extremely high rate in the planar graphene nanochannels,[11, 12] a property that could perfectly lead to the formation of highly permeable membranes for desalination. Besides, the layer-stacking synthesis approach lends much flexibility to adjusting the spacing and functionalities of GO nanosheets so that membrane permeability and selectivity can be optimized. Additionally, it has recently been discovered that the 2D carbon-walled channel surface leads to stronger carbon-organic interactions and thus hinders the diffusion of organic molecules inside the membrane. As a result, the GO membrane can efficiently remove neutral organic contaminants,[13] a unique feature when compared to traditional polymeric RO membranes, which are typically charged and have a relatively poor removal rate for neutral molecules.

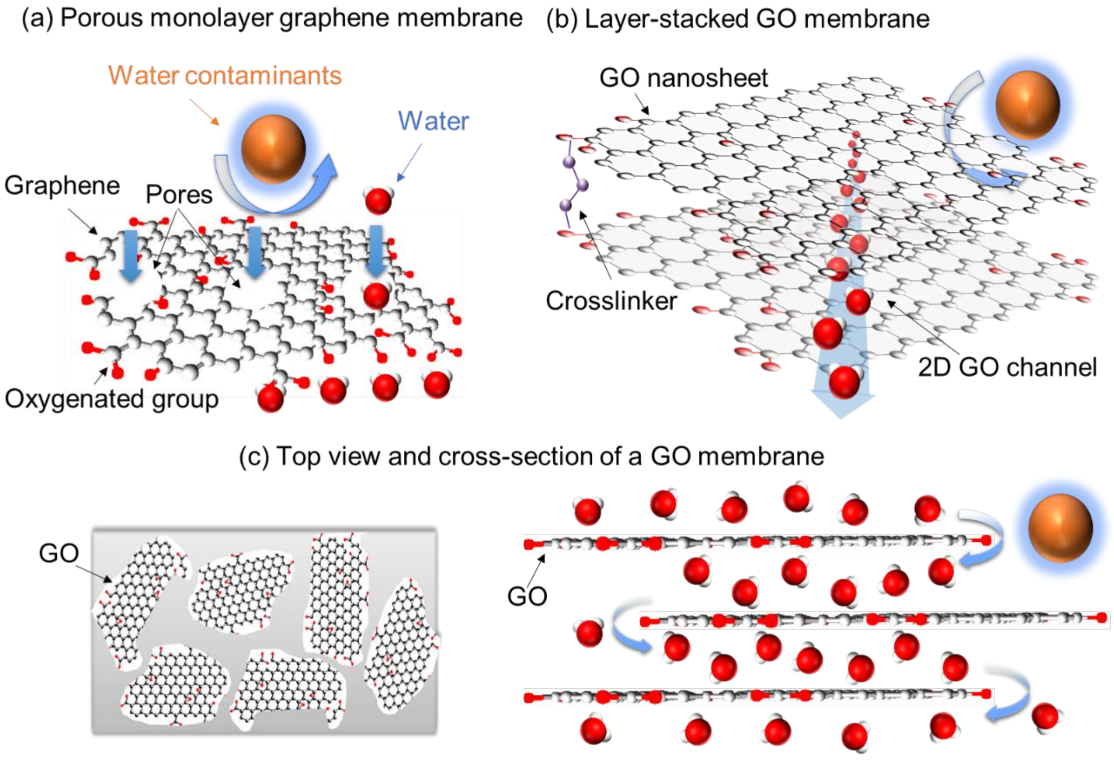

Figure 1. Two major types of graphene-based membranes.

In addition to being directly used as building blocks for membrane synthesis, graphene-based nanomaterials can be exploited to modify existing membranes for improved performance or multifunctionality. For example, the semiconducting property of GO nanosheets and their composites (e.g., GO-TiO_2) makes GO photoactive under both ultraviolet and visible lights, a salient property for developing photocatalytic membranes.[14] Another example is to use the conveniences of GO nanosheet assembly to form a dense barrier layer on the back (i.e., porous) side of a traditional asymmetric membrane for fouling control in the PRO process, which is a desalination-related, energy-production process yet its advancement has been much hindered by the severe irreversible fouling that occurs as foulants accumulate inside the porous membrane support.[15]

Major Challenges in GO Membrane Development

The high water permeability of a GO membrane relies on the hypothetical existence of a continuous, nearly frictionless path for water flow within the extremely smooth graphitic (i.e., non-oxidized) regions of GO nanochannels. However, the heavily oxidized GO regions, which represent a large portion of the GO basal plane but do not provide a frictionless pathway, could significantly affect such water flow. As illustrated in Figure 2(a), a GO nanosheet is composed of three distinct regions: graphitic, oxidized, and defect. The total graphitic region typically occupies less than half of the total area of a GO nanosheet prepared by using the widely used Hummers method.[16, 17] Additionally, because graphitic regions even with the same overall area ratio could be distributed quite differently in GO nanosheets, as illustrated in Figure 2(b-c), the resulting water transport paths and boundary effects can be dramatically different, so are the corresponding membrane properties. So far, the true microstructure of GO nanochannels as well as the associated dominant water and molecular transport mechanisms have not been clearly understood. Significant efforts are thus needed to precisely control the size of GO nanochannels, accurately characterize the transport length and channel width, and comprehensively build mechanistic models to correlate such characteristics to membrane performance.

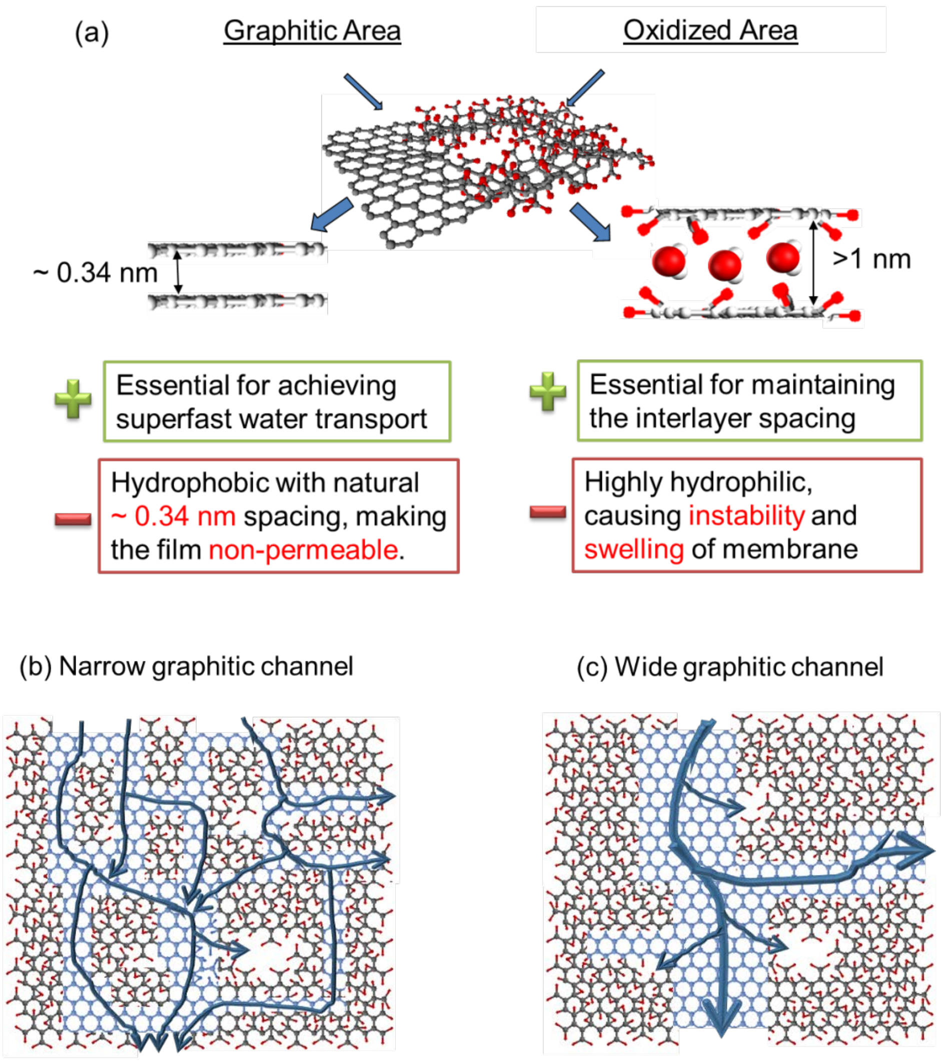

Figure 2. Effects of GO nanostructure on water and molecular transport.

Controlling the interlayer spacing in a GO membrane is another critical challenge to making successful desalination membranes. Previous studies[9, 10, 13] have shown that it is relatively straightforward to construct a membrane with GO interlayer spacing of above 1 nm. However, it becomes challenging to further reduce the spacing to less than 0.8 nm (a critical value for desalination membranes to achieve high removal of sodium chloride by size exclusion) because the oxidized region in GO starts to create strong hydration forces and charge repulsion that cause membrane swelling and thus increase interlayer spacing. To accurately quantify the degree of swelling and interlayer spacing, a protocol has recently been established to simultaneously measure the mass of GO thin film by quartz crystal microbalance with dissipation (OCM-D) and film thickness by ellipsometer (Fig. 3). It is found that a GO film can swell by about three times when it changes from dry to wet. Potential strategies to overcome such swelling include creating short covalent bonds, crosslinking out of aqueous solution, and inserting appropriately sized spacer between GO layers.

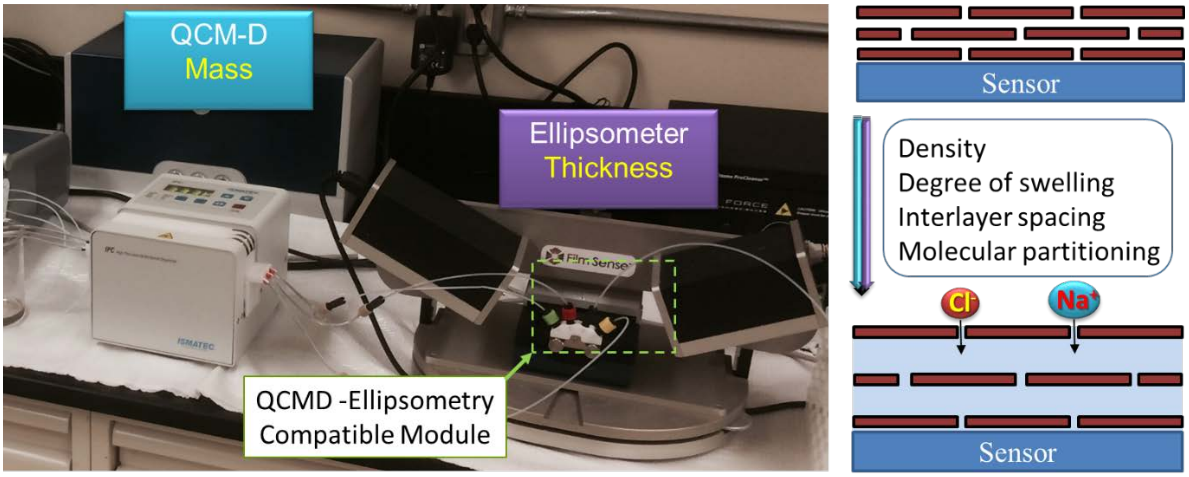

Figure 3. Simultaneous measurement of membrane mass and thickness by QCM-D and ellipsometer.

Concluding Remarks

Despite of the above-discussed challenges, 2D graphene-based nanomaterials hold great promise for revolutionizing the membrane-based desalination technology, due to their salient advantages over traditional materials in synthesizing a desalination membrane via simple, scalable layer-stacking techniques, and in flexibly manipulating the membrane permeability and selectivity for target contaminants. Other 2D materials (e.g., zeolite, MoS_2), in view of their unique configurations that could help control the interlayer spacing, are also attracting research interest in making high-performance membranes. [18] Besides, 2D nanomaterials can be innovatively constructed into a 3D structure and thus function as a nanosized reactor to further enhance membrane selectivity and minimize membrane fouling. [19] Finally, it is worth noting that 2D nanomaterials are also finding their potential applications in non-membrane-based desalination technologies. For example, 2D graphene material-enabled thin films may be effectively used to enhance solar evaporation [20] and thus efficiently help desalinate water by directly using the sustainable solar energy.

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