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Review Article

2D nanostructures for water purification: Graphene and beyond

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Abstract

Owing to their atomically thin structure, large surface area and mechanical strength, 2D nanoporous materials are considered to be suitable alternatives for existing desalination and water purification membrane materials. Recent progress in the development of nanoporous graphene based materials has generated enormous potential for water purification technologies. Progress in the development of nanoporous graphene and graphene oxide (GO) membranes, mechanism of graphene molecular sieve action, structural design, hydrophilic nature, mechanical strength and antifouling properties and the principal challenges associated with nanopore generation are discussed in detail. Subsequently, the recent applications and performance of newly developed 2D materials such as 2D boron nitride (BN) nanosheets, graphyne, molybdenum disulfide (MoS₂), tungsten chalcogenides (WS₂) and titanium carbide (Ti₃C₂T_x) are highlighted. In addition, the challenges affecting 2D nanostructures for water purification is highlighted and their applications in the water purification industry are discussed. Though only a few 2D materials have been explored so far for water treatment applications, this emerging field of research is set to attract great attention in the near future.

Introduction

The inadequate availability of potable water is an unrelenting issue of global concern. A continuous rise in population has resulted in approximately 750 million people globally lacking access to clean water.

97.5% of the World's water is comprised of salty water, with a mere 2.5% of fresh water remaining for human consumption.^{9, 10} Furthermore, augmented agricultural and industrial activity has yielded increased contamination of our limited water resources due to the widespread dispersion of various

industrial dyes, heavy metal ions, and other aromatic pollutants.^{11, 12} Consequently, an enhanced global endeavour has surfaced in an attempt to develop economical and efficient technologies for disinfection, decontamination and desalination in order to establish water security and create environmental and public health sustainability. Removing the bountiful salt content present in our planet's copious supply of saline water presents a promising opportunity to evade the scarcity of fresh water. Accordingly, desalination, a process which has been exercised for more than 50 years,¹³⁻¹⁷ is predicted to significantly impact the future of the global water supply.¹³ Although the practice of removing salt from water may seem theoretically straightforward; in reality, this challenging task is often exceedingly costly and extremely strenuous.^{13, 16, 18-22} Prevailing reverse osmosis (RO) desalination technologies require approximately 3kWh of energy to force pre-filtered sea water through a series of semi-permeable membranes, under pressure, to produce a mere 1m³ of drinkable water.²³⁻²⁵ Moreover, conventional polymeric membranes are relentlessly defied by fouling.^{16, 26, 27} Impurities and biological materials present in the water feed congregate on the membrane surface^{28, 29} or within the pores of the membrane resulting in poor membrane

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selectivity, listless water flow, reduced membrane resilience and increased energy consumption. As a consequence of this, a greater extent of energy is required to force water through the membrane.²⁶

In order to enhance desalination processes and improve water treatment technologies new classes of membrane systems are continuously being developed, which has also resulted in the application of pressure driven membrane systems for the disinfection, decontamination, and purification of water and waste water. However the need for improved membrane materials remains. In order to significantly reduce the cost and energy demands associated with membrane water treatment technologies, advanced, innovative and inexpensive antifouling membrane materials are required.^{30,31}

A solution to this potentially colossal issue of water scarcity may lie within the new generation of nanoscale materials. Recent developments in environmental technologies have exposed nanomaterials as effective solutions to many on-going issues, including pollution, energy consumption and waste management. The unique properties of nanodimensional materials have stimulated novel and improved technologies in many aspects of environmental conservation and remediation.³²⁻³⁴ Owing to their magnitude, nanoporous materials are considered to be suitable alternatives for existing desalination and water purification membrane materials.^{35,36} New classes of ultra-permeable membrane materials, such as ceramic or advanced inorganic materials,^{31,37} could significantly reduce the energy demand and the pressure vessel requirements of prevailing RO desalination, and enhance separation techniques.^{38,39}

To date, much research has focused on the ability of carbon nanotubes or zeolites to act as nanostructure membranes for ion separation.^{37,40} Recent studies have also attempted to improve water permeability by molecular sieve action of polymers,⁴¹⁻⁴⁵ ceramics⁴⁵⁻⁴⁹ and biological molecules.⁵⁰⁻⁵³ Although these materials are theoretically promising, their practical applications are not yet fully explored. Membranes fabricated from materials such as zeolites and carbon nanotubes, are difficult to shape in a cost effective and scalable manner, and prove somewhat ineffective with regard to the exclusion of salt ions, as well as presenting a low water flux⁵⁴⁻⁵⁸ hence illustrating the need for ultrathin, low cost membranes. The rise in demand for environmental solutions and the urgent need to tackle the water crisis has led to the endless discovery of new classes of nanomaterials.

Two-dimensional (2D) materials were considered non-existent beyond the realm of theory before the rise of graphene, a single layer of carbon atoms arranged in a honeycomb shaped lattice.

Researchers believed that these materials could not exist in a free state, predominantly due to thermodynamic instabilities.^{59,60} However, little more than ten years ago, Nobel Laureates Novoselov and Geim demonstrated the possibility of exfoliating stable, 2D materials from bulk structures through the unexpected isolation of graphene.⁶¹

The discovery of this fascinating material and its exceptional properties⁶² gave rise to a graphene "gold rush,"⁶³ which

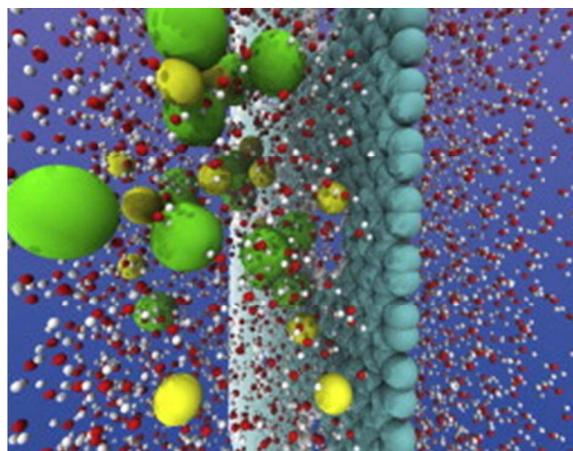


Figure 1 Nanoporous graphene membrane for desalination² Reproduced with permission from Cohen-Tanugi and Grossman (2014); full details are given in the respective publication

subsequently motivated exploration beyond the wonder material, revealing the prospect of isolating 2D layers from an entire range of 3D bulk materials. Alternative graphene-like crystals such as monolayer or few-layer crystals of hexagonal BN (h -BN),⁶⁴ transition metal oxides, chalcogenides, carbide and carbonitrides,⁶⁵⁻⁷⁰ or the more recently discovered silicon- or germanium-based counterparts of graphene,^{71,72} have since been developed and their exotic properties explored. These 2D nanostructures share many of graphene's astonishing properties such as atomic thickness, large surface area (typically over $2500 \text{ m}^2 \text{ g}^{-1}$),⁷³ mechanical strength, ($\sim 2.4 \pm 0.4 \text{ TPa}$),⁷⁴⁻⁷⁶ extreme durability, and the material's strange love affair with water, suggesting they too could act as effective water filtration membranes. However, this area currently requires significant development.

Nanoporous graphene membranes

Due to its atomically thin structure and large surface area, graphene could be considered an ideal separation membrane if it were capable of transporting selected molecules through its carbon planes. However, in its pristine form, graphene is impervious to all gases and liquids,⁷⁷ including molecules as small as helium.⁷⁸

Despite this impassable nature, the ultrathin structure of graphene motivated Suk and Aluru⁷⁹ to consider the possibility of introducing nanopores into graphene's structure to provide the ultimate desalination membrane (Figure 1 & 2).⁸⁰

Subsequently, Nair and his colleagues at the graphene centre in Manchester University revealed that graphene oxide membranes, which are resistant to liquids, vapours, and gases, facilitate unconstrained water permeation.⁸¹ The incomprehensible passage of water was credited to a low-friction flow through 2D capillaries affixed between closely spaced graphene sheets within the membrane. This unusual

activity exposed promise for filtration techniques and also highlighted the need for greater understanding of the design of nanomaterials at a molecular level.

Further to such cutting-edge revelations, David Cohen-Tanugi and Jeffrey Grossman used molecular dynamics to observe the desalination proficiency of graphene membranes revealing that synthetic nanopores present in a monolayer of freestanding graphene can effectively filter NaCl salt from water at permeability greater than conventional RO membranes.⁸⁰ The membrane performance was studied as a function of pore size, chemical functionalization, and applied pressure. The findings suggested that graphene membranes are capable of rejecting 100% of salt ions, simultaneously allowing water passage at remarkable rates ranging from 10–100 L/cm²/day/MPa. This increase in water flux corresponds to the atomic thickness of the membrane and pore dimensions.^{79, 82} The research indicated that the membrane's ability to impede the passing of salt and permit the flow of water significantly depends on pore diameter. Moreover, to warrant successful ion selectivity Cohen-Tanugi and Grossman examined the influence of various chemical functional groups bound to the edges of the graphene pores.⁸⁰ Their investigation revealed that, in addition to pore size, desalination performance is also sensitive to pore chemistry. Hydrophilic hydroxyl groups roughly double the rate at which the water permeates the graphene membrane.⁸³ Consequently, the ability to tune the selectivity of synthetic nanopores in graphene membranes further promotes the use of graphene in desalination technologies.

Graphene molecular sieve action

Earlier computational studies have highlighted the importance of nanopore functionalization in relation to the ion selectivity properties of graphene.⁸⁴ Graphene pores were designed with ion etching and decorated with negatively charged nitrogen, fluorine, and also, positively charged hydrogen atoms. Coulomb coupling between ions and functional groups positioned at the edge of the nanopore influenced pore selectivity. The F-N-pore permitted the passage of Li⁺, Na⁺, and K⁺ ions yet Cl⁻ and Br⁻ ions penetrated the H-pore. Moreover, ion size affected the flow rate of the passing ions. Li⁺, Na⁺, and K⁺ ions passed through the F-N pore in the ratio 9:14:33, while F⁻, Cl⁻, and Br⁻ penetrated the H-pore in the ratio 0:17:33. The findings thus suggested that ion selectivity can be optimized by varying pore size, shape and number of functional ligands attached to the nanopores present in the graphene membrane.

Additionally, more recent molecular dynamic studies have further emphasized the importance of nanopore selectivity properties. Biomimetic ion-selective nanopores in graphene sheets were created through computational design in order to produce graphene nanofiltration membranes capable of separating alkali cations of similar charge, hydration properties, Na⁺ and K⁺.⁸⁵ The bio-inspired nanopores which exhibit stately rates of permeation mimic the biological potassium (KcsA K⁺) and sodium (NavAb Na⁺) protein channels.

⁸⁶ Under predetermined membrane potential, a nanopore containing four carbonyl groups favours the conduction of K⁺ and a nanopore functionalized by four negatively charged carboxylate groups selectively bind and immobilise Na⁺ yet transporting K⁺. The selectivity of smaller diameter pores, containing three carboxylate groups is altered by varying the intensity of applied voltage bias. Low voltage bias exhorts single-file ion transport and approves Na⁺ ions. However, as voltage bias is increased the nanopores become K⁺-selective, as the carboxylate groups tend to withdraw from the graphene plane destabilizing the binding of Na⁺ and allowing a more relaxed passing of K⁺ than Na⁺.

Subsequent to the prominent examination of graphene for desalination, numerous theoretical studies have exposed the potential superiority of graphene membranes to state-of-the-art polymer-based filtration.^{80, 84, 87} Consequently, experimental studies have recently begun exploring their promise, resulting in the rapid progression of research and development in this area.

Nanopore generation

The principal difficulty associated with the design of graphene membranes is the precise generation of sub-nanometer pores on a large surface area.^{1, 40, 88} Simulation and experimental studies have created sub-nanometer pores within graphene sheets using methods such as oxidation, electron beam irradiation,⁸⁹ ion bombardment,⁹⁰ or by doping.^{91, 37} However, O'Hern *et al.*⁹² imaginatively employed low energy ion irradiation and chemical oxidation etching simultaneously to generate high-density nanoscale pores within a monolayer of graphene. Subnanometer pores were created in macroscopic areas of graphene, synthesized by CVD, by first nucleating reactive, isolated defects within the single-layer sheets through ion bombardment. Permeable pores were further developed using oxidative etching. The study illustrated that a variation in etching time resulted in the ability to control pore density. That is, an increase in etching time from 0-120 minutes saw an increase in pore density from 0 - 6x10⁻¹² cm⁻², yet the pore diameter stabilized after 60 minutes of etching. This possibility of control affords selective transit or rejection of ions and organic compounds. However, the ionic flux was poorly refused due to the presence of larger pores resulting from permanganate etching of naturally occurring defects and tears in the graphene sheet. Evidently, the fabrication of large area, defect-free, single-layer graphene is a significant challenge faced in the development of graphene water filtration membranes.^{88, 93, 94}

Attempts have been made to develop facile, reliable processes for producing 2D graphene based membranes. One such method places two layers of optimized CVD cultivated graphene, with minimal defects and good grain connectivity,⁹⁵ consecutively onto a 49 pore puncture, SiNx frame to construct robust, freestanding graphene layers merely 1 nm thick.⁹⁶ Nanopores were subsequently formed *via* a drilling technique completed with a focused ion beam (FIB). The physically perforated double-layer graphene possessed

millions of narrowly distributed pores capable of providing ultimate permeation, exhibiting water transport rates in agreement with 2D.

Rather than focusing solely on the production of unflawed graphene layers, O'Hern, alongside engineers at MIT, Oak Ridge National Laboratory and Saudi Arabia's King Fahd University of Petroleum and Minerals have considered an alternative approach.⁹⁷ Their inventive strategy has allowed the group to construct a relatively defect-free centimeter-scale graphene membrane *via* a multiscale leakage–sealing process. The membrane was fabricated from graphene grown on copper which was subsequently transferred to a surface-modified PCTE membrane with 200 nm pores. Nanometre-scale intrinsic defects within the graphene sheet were then filled with hafnium oxide using atomic layer deposition. Larger holes and tears, formed during the transfer of graphene from the copper substrate used for CVD growth to the PCTE membrane, were sealed with nylon-6, 6 *via* interfacial polymerisation. Following defect repair nanometre scale pores were prepared *via* ion bombardment. The resulting nanoporous, relatively defect free graphene membrane rejected up to 90% of multivalent ions and small molecules and presented a water flux in agreement with previous molecular dynamic simulations, however, salt was transported through the membrane at a rate faster than water. The promising outcomes advocate potential for graphene filtration membranes, although defect sealing techniques require further improvements.

Further attempts to circumvent the challenging preparation of single sheets of pristine graphene examined the desalination proficiency of a multilayer system of nanoporous graphene.⁹⁸ Cohen-Tanugi *et al.* revealed that a bilayer system of NPG offers potential as an efficient RO membrane. The study further revealed however, that the performance of a multilayer NPG membrane is directly affected by the design of the system. The relative placement and number of NPG layers, in addition to pore alignment can affect the membrane properties, highlighting the need for rational consideration and design⁹⁹ before such a system can be relied upon as an energy efficient, cost effective alternative to RO membranes.

Alternatively an oxygen plasma etching process has been employed to fabricate tunable graphene nanopores.¹⁰⁰ This method of pore generation resulted in a suspended monolayer of graphene with tailored nanometre-sized pores of desired dimensions that displayed impressive water molecule selectivity over dissolved ion and exhibited a salt rejection rate of nearly 100% in addition to rapid water transport.¹⁰⁰ The findings once again highlighted the effectiveness and potential of nanoporous graphene for water filtration applications.^{40,101}

The resilience of nanoporous graphene membranes

The development of nanoporous graphene has created great promise for desalination technologies. Pristine graphene demonstrates incomparable strength but as a potential desalination material this resilience will be challenged by the persistently water drenched environment and the high

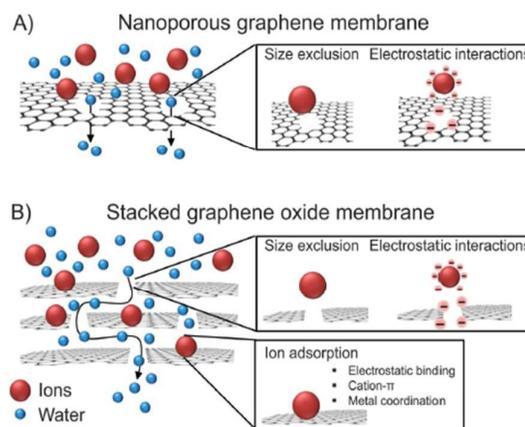


Figure 2 Selective permeation routes in nanoporous graphene and stacked sheets of graphene oxide.¹ Reproduced with permission from Perreault *et al.* (2015); full details are given in the respective publication

pressures associated with RO desalination.^{102, 103} In order to address the uncertainty surrounding the ability of nanoporous graphene to maintain its mechanical integrity Cohen-Tanugi and Jeffrey² employed molecular dynamics and continuum fracture mechanics to determine the mechanical resilience of nanoporous graphene from a desalination perspective. Conventional RO desalination technologies utilise thin film composite membranes which consist of an active layer for salt rejection, often comprised of polyamide, and a highly porous polysulfone support substrate, with a pore size ranging from 0.1–0.5 μm .^{2, 104, 105} Nanoporous graphene, like polyamide, also requires a mechanical support to endure most of the hydraulic load. However, due to the immaturity of the material there remains little information in relation to substrate choice though the use of a polysulfone layer seems reasonable.² Cohen-Tanugi and Jeffrey's computational study focused on an allied system of applied pressure, membrane morphology, elastic properties, fracture stress and the effect of water.² The findings of the study revealed that nanoporous graphene is capable of enduring hydraulic pressures associated with RO desalination technologies, while the choice of substrate is a vital consideration in membrane design, an appropriate substrate with cavities less than 1 μm provides graphene based membranes with the ability to resist pressures greater than 57 MPa.² Though the properties of nanoporous graphene decree the material an ideal filtration membrane there are still various difficulties associated with both the production of large-area, high-quality graphene membranes and also the somewhat undeveloped process of creating nanopores in graphene sheets, both of which often result in the formation of incongruous pores and the subsequent breakdown of membranes during the application of high pressure.¹⁰⁶

Graphene oxide membranes

Graphene oxide's distinct structural design,¹⁰⁷ hydrophilic nature, mechanical strength and antifouling properties impart many prospects for the materials application in advanced

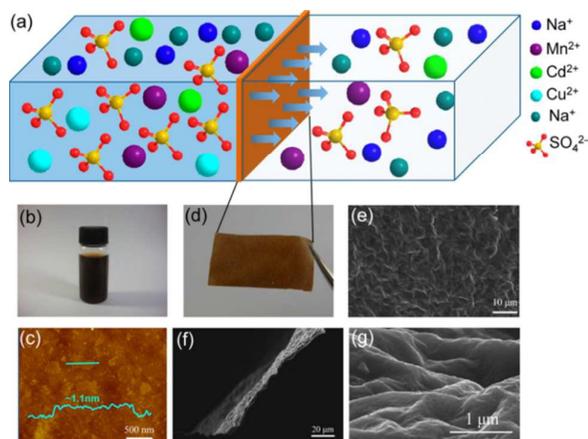


Figure 3 (a) Schematic diagram of the penetration of GO membranes with various ions. (b) 2 mg mL⁻¹ GO aqueous dispersion (c) AFM image of the GO flakes; inset: height profile of a layered GO sheet. (d) Photograph of a freestanding GO membrane prepared via drop-casting. SEM images of (e) the surface and (f) cross-section of freestanding GO membrane. (g) Enlarged view of panel f. ⁸ Reproduced with permission from Sun *et al.* (2012); full details are given in the respective publication

water treatment technologies. Furthermore, graphene oxide can be bulk produced *via* well-established oxidation routes, in comparison to graphene materials which possess properties equivalent to pristine graphene. ¹⁰⁸⁻¹¹⁰

The selective permeation route of graphene membranes which permits separation is through the nanopore structure found within the basal plane of the hexagonal crystalline structure. Alternatively ions or molecules can be selectively transported through the interlayer spacing of multi-layered 2D materials. Stacked nanosheets of GO form a multilayer laminate which exhibits sufficient mechanical strength for utilization in pressure driven water filtration operations ¹¹¹⁻¹¹⁴ due to the strong hydrogen bonds between individual sheets. ⁸ Oxygen-containing functional groups deposited irregularly along the edges of GO sheets retain both considerable interlayer spacing between and empty spaces between non oxidized regions which establishes a network of nanocapillaries within the film. ^{8, 115-119} These nanochannels allow for permeation of water molecules and subsequent transport along the hydrophobic non-oxidised regions of the membrane, which assist a speedy flow of water, ¹²⁰ yet liquids, gases, and vapours are opposed (Figure 2). ⁸¹ The water soluble, oxygen containing functional groups located along the compounds sheets adsorb water molecules, which are then diffused among the non-polar hydrocarbon backbone of GO. This penetration of water increases the interlayer spacing between stacked GO sheets ¹²¹ developing water flux through nanochannels at an elevated flow rate. It has been previously reported that smaller ions penetrate GO membranes at magnitudes much greater than would occur through a simple diffusion process, ¹²² due to the expansion of nanochannels during the hydrated state which only accept ions of similar size.

Despite the hydrophilic nature of GO's oxygen containing functional groups, and the material's succeeding ease of

dispersion in multiple solvents, the stability of GO films in water has been previously examined. ^{114, 122} However, new findings suggest that the reasoning behind this stability may have been overlooked some time. Yeh *et al.* investigated the mechanical properties associated with the ionized oxygen-containing functional affixed to the GO basal plane, ^{112, 114, 123-126} revealing that stiffness of these films is most likely due to multivalent metal cations contamination. ¹²⁷ Porous anodized aluminium oxide (AAO) filter discs are extensively used for the preparation of 2D membranes due to their rigidity, consequently, the mechanical properties and water stability of AAO supported GO membranes vary greatly to films prepared with alternative filter discs such as cellulose nitrate or Teflon. ¹²⁷ Yeh and co-workers discovered that this enhanced stiffness is due to the presence of Al³⁺, released from the filter disc during film production. Furthermore, in comparison to neat GO films, Al³⁺ strengthened films maintain their interlayer spacing upon hydration and present an improved alignment of GO sheets.

Separation performance of graphene oxide membranes

The selective penetration behaviour of a Graphene Oxide membranes prepared by a simple drop-casting method has been investigated (Figure 3). ⁸ The study revealed that sodium salts rapidly penetrated the GO membranes, followed by heavy-metal salts which pervaded the membrane at a much lesser pace. Larger organic contaminants however, such as copper sulphate and rhodamine B, were rejected which suggests that size exclusion is a predominant mechanism involved in GO film filtration. ⁸

Joshi *et al.* ¹²² prepared micrometre-thick laminate membranes *via* the vacuum filtration of graphene oxide suspensions, noting a tightly packed membrane in the dry state which permitted the permeation of water alone.

Upon submerging the membrane in ionic solution, the interlayer spacing between GO sheets increased and the laminate acted as a molecular sieve, allowing small ions with hydrated radii, < 4.5 angstroms, to flow through the nanochannels yet rejecting the penetration of larger solutes. This advantageous characteristic of the hydrated nanocapillary network provides promise for GO membranes in desalination and filtration technologies yet may also pose a challenge for the controlled spacing between the layered sheets in aqueous solutions.

The ability to tune graphene oxide framework (GOF) membranes for water desalination has also been studied, using molecular dynamic simulations. ⁸² GOF materials are nanoporous materials comprised of stacked sheets of graphene oxide covalently bonded to one another by linear boronic acid pillaring units, often termed, linkers. ¹²⁸ It was previously reported that choosing a suitable linker concentration allows for regulation of geometrical parameters of GOF-materials such as the pore size and volume or the accessible surface area. ^{128, 129} Consequently GOF membranes are suitable candidates for water purification. The hydrophobicity of graphene and tunable linker concentration

provide excellent water permeation and filtration respectively.^{82, 130} Computational studies explored the tunability of GOF membranes as a function of linker concentration, GOF-(*n*,*h*) membrane thickness and applied pressure ΔP , finding that these materials exhibit flawless salt rejection and a water permeability a hundred times as great as prevailing RO membranes.⁸² The employed molecular dynamic simulation highlighted that the GOF membrane's water permeability can be adjusted from ~ 5 to 400 L/cm²/day/MPa by altering linker concentration *n* (32–64) and membrane thickness *h* (6.5 nm–2.5 nm). Furthermore, a membrane with specific pore size (*n* = 16 or 32) experiences an increase in water permeability as the pore spacing decreases. However, the water permeability of a membrane with specific pore spacing (*n* = 32 or 64) increased a hundredfold as the pore size increased. Finally, the high water permeability of the GOF membrane with a linker concentrations *n* \leq 32, presents a 100% salt rejection.⁸²

The use of GO membranes also addresses the issues associated with the scale-up of graphene-based membranes. However current techniques employed for the preparation of GO lamellar films, which involve restacking of dispersed GO sheets by filtration and subsequent accumulation of such on a filter support, require the use of large volumes and suffer from potential production issues.

A scalable, liquid film processing approach capable of producing large-area graphene-based membranes has been developed in an attempt to make the industrial production of GO water filters possible.⁷ Rather than focusing on the traditional, often time consuming process, of vacuum filtration the innovative method designed by Akbari *et al.*,⁷ produces concentrated, nematic dispersions of GO by absorbing the water from the initial solution using polymer hydrogel beads. A multi-layered GO thin film can then be prepared on a support using a rigid blade and shear force alignment to thinly spread the viscous, uniformly arranged fluid (Figure 4). The prepared large area (13 \times 14 cm²) membranes exhibit in-plane stacking order superior to GO laminates obtained via vacuum filtration. The structural order of the discotic nematic GO liquid crystal membrane permits the formation of organized channels which results in the significant improvement of water flux.



Figure 4 (Left) Viscoelastic property of (~ 40 mg ml⁻¹) GO nematic liquid crystal. Scale bar, 1 cm. (Right) Gravure printing machine and (inset) 13 \times 14 cm² GO membranes with different thicknesses.⁷ Adapted with permission from Akbari *et al.* (2016); full details are given in the respective publication

The aligned arrangement also facilitates an impressive retention of organic molecules and ions (>90%), in addition to the acceptable retention (30–40%) of monovalent and divalent salts.

Control of GO interlayer spacing

It may be possible to maintain the small spacing between GO sheets which is required for desalination, less than 0.7 nm to sieve with a 0.36 nm hydrated radius to filter the hydrated Na⁺ from water through partial reduction of GO which diminishes hydrated functional groups present on the sheet, or by covalently stacking GO layers with diminutive molecules to ease hydration force.¹²⁰

The interlayer spacing between GO nanosheets can also be increased *via* the insertion of polymeric materials or larger nanoparticles such as nanofibres, creating larger spacing between the layers. Enlarged spacing between the GO nanosheets enhances the formation of nanochannels and also renders the membranes valuable in biomedical applications such as the separation of biomolecules from waste molecules.¹²⁰ Polymer chains inserted between the GO nanosheets can enlarge the interlayer spacing and also create stable bonds between the sheets, enhancing the mechanical stability of the film.^{122, 131}

1, 3, 5-benzenetricarbonyl trichloride crosslinked GO water separation membranes were prepared on a polydopamine-coated polysulfone support, in order to prevent the dispersion of the membranes in water, *via* layer by layer deposition.¹³² Further to enhance the interlayer spacing, combining GO with polymeric materials also increases water flux, as well as mechanical and antimicrobial properties.^{133–136} The 1, 3, 5-benzenetricarbonyl trichloride cross-linked GO membrane's flux was 4–10 times greater than the majority of commercially established nanofiltration membranes, ranging from 80 to 276 L/M/H/MPa. Moreover, the membrane demonstrated a reasonable rejection (46–66%) of methylene blue and considerable rejection (93–95%) of Rhodamine-WT, allowing smaller ions such as monovalent and divalent salts to penetrate the membrane. Therefore, it has been established that polymer cross-linked GO films are model water purification, pharmaceutical and fuel separation membranes.^{137–140}

The interlayer spacing has also been enlarged by constructing a compact and well aligned GO – TiO₂ composite.¹⁴¹ TiO₂ nanoparticles increased the mechanical strength of the GO membrane by acting as a support and also created channels and pores, with an average size of 3.5 nm, within the membrane which facilitated filtration. The composite membrane succeeded in eliminating 100% of Rhodamine B and methyl orange from the water flux.

The introduction of 1D carbon nanotubes (CNTs) amid 2D graphene sheets regulates the interlayer spacing of graphene-based nanofiltration membranes. CNTs have been demonstrated as the ideal nano-wedge for the expansion of the interlayer spacing between adjacent graphene sheets

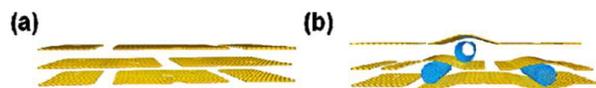


Figure 5 Schematic representation of the enlarged interlayer spacing in (a) CNT intercalated graphene based membranes. ⁶ Reproduced with permission from Han et al. (2015); full details are given in the respective publication

(Figure 5) due to their remarkable properties and compatibility with graphene family materials. ¹⁴²

The formation of enlarged nanochannels, shaped by the inclusion of single-walled carbon nanotubes (SWCNT) amongst GO layers significantly advances water permeation without impeding molecular rejection capability. ⁵ The SWCNT-intercalated GO ultrathin film, with a thickness of 40 nm and a d-spacing of 0.823 nm was prepared by deposition of GO-SWCNT dispersion onto an AAO or mixed cellulose ester (MCE) membrane via vacuum filtration (Figure 6). The ultrafast separation film retained 97.4% to 98.7% of contaminants of various size, including Bovine Serum Albumin (BSA), cytochrome c, Coomassie Brilliant Blue and Rhodamine B while demonstrating a tenfold increase in water flux (660–720 L/m²/h/bar) in comparison to traditional nanofiltration membranes. Further investigation into the potential of the laminar film uncovered the membrane's promise for both drinking water and waste water purification due to exceptional pH stability, superior to most ceramic and polymer based membranes. The intercalation of graphene oxide with multiwalled carbon nanotubes (MWCNTs) has also proven to enhance water flux by increasing the interlayer spacing between sheets. ¹⁴³ The MWCNT-intercalated exhibited enhanced flux of 0 11.3 L/m²/h/bar, rejecting > 96% of organic dyes such as Direct Yellow and Methyl Orange, in addition to 51.4% of NaCl ions and 83.5% for Na₂SO₄. The nanofilter also demonstrated commendable anti-fouling performance against sodium alginate and humic acid, resistance against bovine serum albumin however was subordinate due to the strong interaction between the protein and the graphene sheets. Though both SWCNTs and MWCNTs have successfully been employed to control the interlayer spacing of graphene-based nanofiltration membranes it has been argued that MWCNTs provide greater stability under hydrodynamic flow conditions. ⁶ Reducing GO to fashion rGO 2D films can enhance the pressure stability of the membrane material but often results

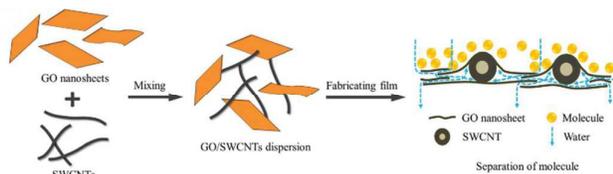


Figure 6 Schematic representation of the preparation of SWCNT intercalated GO membrane and the manner in which the membrane separates molecules. ⁵ Reproduced with permission from Gao et al. (2015); full details are given in the respective publication

in diminished water permeability and flux. ^{144 145}

The assembly of carbon nanostructures comprising of rGO sheets and MWCNTs offers a reinforced architecture with enhanced membrane stability. The MWCNTs improve the membrane mechanical properties by interconnecting the subsequently reduced GO sheets while preventing aggregation after reduction and also provide an adjustable interlayer spacing system between rGO sheets. ⁶ The inclusion of 10 nm diameter MWCNTs between GO sheets facilitated a flux of 52.7 L/m²/h/bar and a rejection rate greater than 99% for methylene blue, acid orange 7, and rhodamine B. The membrane also endured turbulent cross-flows of up to 2000 mL/min and a Reynolds number of 4667. SWCNT intercalated rGO membranes were examined under processing conditions similar to the MWCNT – rGO separation membrane. However SWCNT – rGO film became fractured within a minute due to rapid water penetration of the porous crystalline lattice. ⁶ The inner graphitic walls of the MWCNTs provide greater support to the rGO membrane and prevent rupture. ^{6, 146, 147}

The poor dispersion of CNTs within aqueous and solvent media often impedes the fabrication of CNT intercalated graphene based membranes. Conversely, several dispersion methods with the use of various reagents have been established to facilitate their use, ¹⁴⁸⁻¹⁵¹ with block copolymers (BCPs) showing great promise for water purification applications. ¹⁵² A uniform network of mass transport nanochannels with high permeability and rejection rate was formed by adjusting the interlayer spacing of rGO nanofiltration membranes with well dispersed CNTs. ¹⁵² The hybrid membrane was produced by first dispersing CNTs in BCPs and then loading CNT intercalated rGO onto an AAO filter disc microfiltration via vacuum filtration. The potential of the membrane for drinking water purification was demonstrated through the retention of nanoparticles, dyes, protein, namely BSA, organophosphates, sugars, and humic acid. The hybrid NF membrane presented good antifouling properties and retention efficiencies (typically >99%), and permeabilities as high as 20-30 L/m²/h/bar, once again demonstrate the promise of graphene based-CNT nanofiltration membranes for drinking water purification.

GO enhanced conventional RO membranes

Another yet slightly more economical approach to develop membranes with improved antimicrobial properties is to modify the surface of conventional RO membranes with GO. ^{153, 154} In order to modify the surface of conventional desalination membranes like polysulfonate with GO a smaller amount of material is required thus reducing production cost, in contrast to free standing GO membranes. In an attempt to overcome one of the leading restraints in desalination technologies, the fouling of RO membranes by microorganisms, Perreault *et al*, ¹⁵⁵ covalently attached GO nanosheets to thin-film composite polyamide membranes to reduce the degree of bacterial growth on the surface functionalized membrane in an attempt to evade the fouling of RO membranes by microorganisms. GO functionalization

Table 1 Relevant 2D materials and their various applications in water treatment

| | | Material properties | Recent application in Water treatment | Reference |
|---|---|---|---|--------------------------|
| Group IV Graphene analogues | Graphene | Immense mechanical strength (1.0 TPa), pronounced surface area ($2630 \text{ m}^2 \text{ g}^{-1}$), hydrophobic | Desalination Molecule separation contaminant/pollutant adsorption photocatalytic disinfection | 73, 74, 80, 100, 157-161 |
| | Graphene oxide (GO) | Good mechanical strength (207.6–23.4 GPa), hydrophilic | Desalination Molecule separation Contaminant/pollutant adsorption Co-catalyst for the degradation of contaminants | 120, 122, 158, 162-164 |
| | 2D Boron Nitride nanosheets | Chemically inert, immense mechanical strength (0.81–1.3 TPa), hydrophobic | Contaminant/pollutant adsorption | 3, 165, 166 |
| | Graphyne | Porous nanoweb structure, chemically and thermally stable, good mechanical strength (365–700 GPa) | Molecule separation | 167-169 |
| Chalcogenides | Molybdenum disulfide (MoS_2) | High thermal stability (up to $1,100^\circ\text{C}$), good mechanical strength | Desalination Contaminant/pollutant adsorption Co-catalyst for the degradation of contaminants Antibacterial disinfection | 4, 170-173 |
| | Tungsten chalcogenides (WS_2) | Semiconductor (2.1 eV), electron mobility of $20 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, | Desalination Co-catalyst for the degradation of contaminants | 174-183 |
| MXenes (transition metal carbides & carbonitrides) | Titanium Carbide ($\text{Ti}_3\text{C}_2\text{Tx}$) | Good structural and chemical stability, excellent conductivity, non-toxic, hydrophilic | Molecule separation Contaminant/pollutant adsorption | 69, 70, 184-189 |

resulted in the inactivation of 65% of bacterial cells in contact with the membrane surface after one hour yet neither the permeability nor selectivity of the membrane was hindered. Furthermore, the hydrophilic nature of the membrane was greater due to the presence of oxygen functional groups, provided by GO, on the surface of the nanofiltration membrane. In addition to improving antimicrobial effect, modifying membrane surfaces with GO also enhances chlorine resistance. Kim et al.¹⁵⁶ deposited GO and aminated graphene oxide (aGO) respectively on an amino containing polyarylene ether sulfone (aPES) reinforced by a polysulfone ultrafiltration support membrane using a layer-by-layer self-assembly (LbL-SA) technique. The GO and aGO deposits performed as a protective layer, demonstrating antimicrobial characteristics and amplified chlorine resistance, greater than the resistance of unmodified membranes. The aPES/GO/aGO functionalized membrane also displayed favourable qualities such as a water flux of $28 \text{ L/m}^2/\text{h}$ and a 98% salt rejection. Similarly, LbL-SA was also exercised to apply TiO_2 nanoparticles and GO nanosheets to the surface of a polysulfone membrane,

sequentially.¹⁹⁰ The TiO_2 and GO materials were consecutively embedded on the surface of a polysulfone membrane using a photocatalytic approach and GO was partially reduced via ethanol-UV pre-treatment. The TiO_2 -GO membrane exhibited 60–80% faster UV and 3–4 times faster sunlight photodegradation of methylene blue, rejecting up to 90% of the dye, in addition to an increased water flux of $45 \text{ L/m}^2/\text{h}$, functionalized RO membranes have also presented high levels of selectivity due to the fabrication of a dense GO film which consists of highly ordered and packed laminates as a result of membrane surface modification. A pressure-assisted self-assembly technique facilitated the functionalization of polyacrylonitrile substrates with GO, resulting in a highly ordered and flexible composite membrane, required to separate isopropyl alcohol from water for solvent recycling purposes.¹²¹ The composite membrane performed exceptionally well during partial vaporization separation of a 70 wt. % isopropyl alcohol (IPA)/water mixture imparting 99.5 wt. % water in permeate and a permeation flux of $2047 \text{ L/m}^2/\text{h}$.

Graphene analogues for water purification

Though tens of novel 2D crystals have recently been isolated from bulk structures, few 2D nanosystems have been exploited commercially for water purification (Table 1). However, due to their desirable properties graphene like 2D nanostructures are expected to have a significant influence on a multiplicity of applications and could potentially serve as high-performance membranes. Accordingly, the recent investigation of 2D nanostructured membranes, other than GO, has revealed ultrafast ion and molecule separation. One dimensional boron nitride (BN) nanotubes have been regarded as effective materials for both desalination and decontamination of water.¹⁹¹⁻¹⁹³ However, with the surge in research surrounding 2D materials, the potential of BN nanosheets has also been explored.¹⁶⁵ BN, a compound consisting of equal numbers of boron and nitride atoms, arranged in an sp^2 -bonded honeycomb lattice (Figure 7), can exist in many crystalline forms.¹⁹⁴ The hexagonal form, *h*-BN, also known as white graphene, began to attract attention after the chemically stable insulator surfaced as an excellent substrate for mono- and bilayer graphene devices,^{195, 196} increasing graphene's electronic properties by an order of magnitude.¹⁹⁷ A porous layered BN nanostructure was prepared *via* thermal treatment for removal of oils, organic solvents and dyes from water.¹⁶⁵ The superhydrophobic nanosheets exhibited an exceptional surface area of $1,427 \text{ m}^2 \text{ g}^{-1}$ allowing them to absorb up to 33 times their own weight. Furthermore the highly selective, porous, layered BN nanomaterial can be regenerated upon burning or heating due to its high oxidative resistance which supports reuse of the nanosheets.

MoS_2 is the most widely employed transition metal dichalcogenide (TMD) in a range of applications and has recently been investigated for its potential in separation techniques. MoS_2 , a prototypical TMD, is made up of tungsten disulfide (WS_2), a semiconductor material similar to MoS_2 .^{174, 198} The bulk structure was exfoliated and a thin film constructed *via* filtration. The membrane exhibited a water flux five times greater than GO membranes and two times greater than MoS_2 laminar membranes rejecting 90% Evans Blue molecules. The impressive water permeance further increased from $450 \text{ L/m}^2/\text{h}/\text{bar}$ to $930 \text{ L/m}^2/\text{h}/\text{bar}$ with the addition of metal hydroxide nanostrands. The nanostrands created additional channels between the stacked WS_2 allowing an increased transport of water without degrading the membrane rejection properties. hexagonal layers of Mo and S₂ atoms.¹⁷⁸ TMDs, a family of over 40 materials, are represented by the generalized formula, MX_2 , and consist of a transition metal (M), for example, Mo, W, Nb, Re, Ni, or V, packed between two chalcogens (X) such as S, Se or Te.⁶⁷ A flexible laminar separation membrane prepared from MoS_2 sheets exhibited a water flux 3–5 times higher than that reported for GO and rejected 89% and 98% of Evans blue and cytochrome C molecules, respectively.¹⁷⁰

Advancing their search for high-performance lamellar separation membranes, Sun *et al.* investigated the potential of

Conversely, Heiranian *et al.*⁴ explored a range of atomic thick materials which possess naturally occurring hydrophilic sites for advanced 2D nanostructured desalination membranes. MoSe_2 , MoTe_2 , WS_2 , WSe_2 were examined finding that MoS_2 showed the greatest efficiency. As previously evidenced, positioning hydroxyl groups at the edge of graphene nanopores creates hydrophilic sites which attract water and thus increase flux and permeability. However, the addition of defined functional groups at the pore edge is a complex task, causing the team to investigate the potential of various transition metal dichalcogenide membranes.

Using molecular dynamics simulations, the researchers fashioned a simulation box (figure 8) containing a single layer of MoS_2 , water and ions, in addition to a sheet of graphene, which acted as an unyielding piston capable of enduring external pressure, in order to measure the desalination efficiency of monolayer nanoporous MoS_2 . The study examined the potential of the MoS_2 membrane as a function of pore size, chemistry, geometry and applied hydrostatic pressure. The findings revealed that pore chemistry significantly impacted membrane efficiency. Mo, S and mixed pore architectures were examined respectively revealing that the hydrophobic edges and hydrophilic centre of the Mo only pore presented the proficient ion rejection, in excess of 80%, and encouraged an enhanced water flux 70% better than the nanopores present in state of the art graphene membranes.

Mxenes, a relatively new family of 2D materials which consist of few atom thick layers of transition metal carbides or carbonitrides have also been employed as filtration membranes for the separation of ions and molecules from water.¹⁸⁴ These robust, flexible and hydrophilic $\text{Ti}_3\text{C}_2\text{T}_x$ membranes exhibited a rapid water flux of $37.4 \text{ L/m}^2/\text{h}/\text{Bar}$ and revealed an improved separation performance of higher charge cations in comparison to GO.

Additionally, a naturally porous form of graphene is also set to

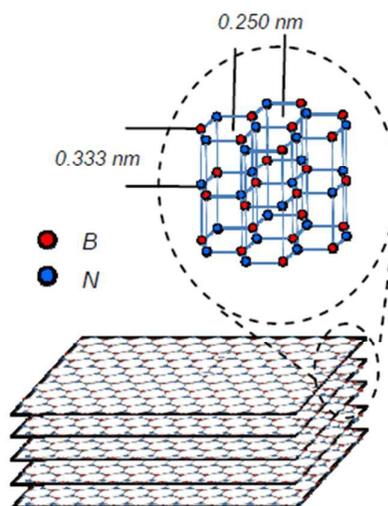


Figure 7 Basic structure of 2D BN³ Reproduced with permission from Lin and Connell (2012); full details are given in the respective publication

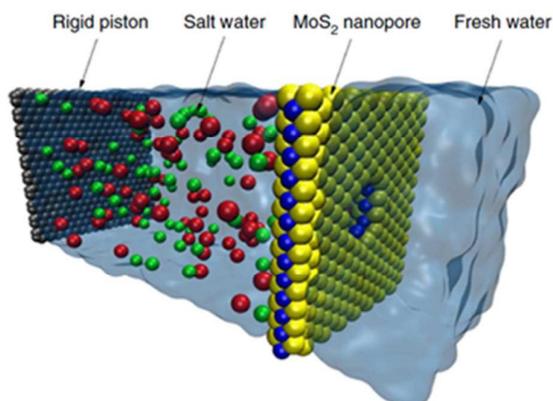


Figure 8 Simulation box comprised of a MoS₂ sheet (yellow), water (transparent blue), ions (red and green) and a graphene sheet (in grey).⁴ Reproduced with permission from Heiranian *et al.* (2015); full details are given in the respective publication

excel within the water purification industry. Molecular dynamics have suggested that graphyne nanoweb membranes demonstrate excellent water permeation and rejection of heavy metal ions, hydrophobic organic chemicals, and monovalent salt ions.^{167, 199} Due to graphyne's naturally occurring nanopores, ultrathin structure, superior mechanical strength and high deformation tolerance the web like membranes present astonishing filtration performance.

The rise of 2D water purification membranes in industry

The recent use of 2D materials for water treatment has also begun to attract attention from industry. Lockheed Martin, a US security and aerospace company, dedicated to the research, design, development and manufacture of technology systems, products and services, has been awarded a patent (US8361321 B2) in 2013 for an advanced material water filtration solution, termed Perforene™. The graphene based molecular filtration solution removes sodium, chlorine and other ions from sea water and other sources, permitting affordable access to clean drinking water. The company have also begun to consider other commercial applications for Perforene™ including purification of oil drilling wastewater. More recently, Arvia Technology, a UK based water and wastewater Treatment Company, is currently attempting to apply its technology a graphene based membrane material, Nyex™, which was developed by Manchester University's School of Chemical Engineering for the treatment of toxic waste water, to large-scale industrial projects. The revolutionizing process separates organic compounds, as well as various contaminants and micro-pollutants from wastewater which is then regenerated using the company's organics destruction cell (ODC) process. The ODC process adsorbs emulsified organics onto dispersed graphene particles, which are later oxidised by subjecting the settled bed of graphene to an electric current.

Moreover, the upsurge in graphene based water treatments has contributed to the establishment of academic and industrial collaborations.

Though graphene is the only analogue yet to make it to industrial level desalination, the scientists from the University of Illinois responsible for the manufacture of the nanoporous MoS₂ membrane maintain they simply require an industrial partner in order to bring their product to market.

Challenges associated with 2D water purification membranes

Though the research on graphene and other 2D crystals is intense the road to industrial scale 2D nanostructured membranes for water purification is at infancy stage. Due to the juvenile nature of many of these materials, synthetic complications and scalable processing issues render their application in industrial practices expensive, and limited to small-scale devices. Moreover, much investment will be required to replace conventional materials typically used within industrial water treatment plants with new 2D nanostructured membrane materials.

Challenges faced by 2D water purification membranes based water purification predominantly correspond to the immature processing routes employed to obtain large area, defect-free single-layers of these materials. The production of pristine graphene and high quality graphene-like 2D crystals still remains a challenge. Furthermore producing such desirable structures on a porous support also presents issues. The reduction of graphene oxide offers a low cost method to produce graphene on a large scale yet reduction pathways require further exploration in order to restore rGO electronic and mechanical properties similar to pristine graphene.

Upon presenting a feasible route for the fabrication of 2D materials, complications may still arise with regard to the controlled formation of pores with precise sizes in the material. It is possible to construct pores of precise size in single layers of graphene using focused electron beam irradiation yet this technology is not practical for creating large area sheets of porous graphene. Chemical or oxidative etching has presented as an alternative for large scale production but difficulty may persist due to the diverse defects found in graphene.^{80, 200} Another possible approach to graphene based water purification is the exploitation of graphene oxide in water treatment rather than pristine graphene. Conversely, the oxidized analogue of graphene too faces complications before ease of use in industry.

The incessant development of new technologies and production techniques has begun to stimulate new phenomena and increase the industrial use of 2D materials. However, uncertainties prevail regarding the health risks and environmental safety of graphene family materials, yet the evolution of graphene within almost all fields of research²⁰¹⁻²⁰⁶ has implored the evaluation of the material's toxicity. Studies examining the cytotoxic effect of graphene suggested the toxicity of graphene is contingent on various parameters

Table 2 The performance of various 2D materials for water purification applications

| Membrane material | Specific conditions | Rejection efficiency | Water flow rate | Reference |
|---|--|--|--|-----------|
| Graphene | Nanoporous graphene membrane for desalination | 100% | 10–100 L/cm ² /day/MPa | 80 |
| Graphene oxide (GO) | graphene oxide framework (GOF) membranes for water desalination | 100% | ~5 to 400 L/cm ² /day/MPa | 82 |
| | Nematic multi-layered GO thin film for selective sieving of 1) charged and uncharged organic probe molecules and 2) monovalent and divalent salts | >90% 30–40% | 71±5 L/m ² /hr/bar | 7 |
| | polymer crosslinked GO membranes for selective sieving of 1) methylene blue and 2) Rhodamine-WT | 46–66% 93–95% | 80 - 276 L/M/H/MPa | 132 |
| | GO – TiO ₂ composite membranes for filtration of methyl orange | 100% | 7 L/m ² /h | 141 |
| | GO – TiO ₂ decorated polysulfone membrane for filtration of methylene blue | 90% | 45 L/m ² /h | 190 |
| | <i>a</i> PES/GO/ <i>a</i> GO functionalized membrane for desalination | 98% | 28 L/m ² /h | 156 |
| | GO-SWCNT membrane for selective sieving of Bovine Serum Albumin (BSA), cytochrome c, Coomassie Brilliant Blue and Rhodamine B | 97.4% - 98.7% | 660–720 L/m ² /h/bar | 5 |
| | MWCNT intercalated rGO membrane for filtration of salt ions and organic dyes | > 96% of organic dyes 51.4% of NaCl ions 83.5% for Na ₂ SO ₄ | 11.3 L/m ² /h/bar | 143 |
| Graphyne | Selective sieving of CuSO ₄ , NaCl, CCl ₄ , C ₆ H ₆ | 100% | 2.9 to 4.5 X 10 ⁻⁹ m ² /Pa/s | 167 |
| Molybdenum disulphide (MoS ₂) | Selective sieving of Evans blue and Cytochrome C molecules. | 89% 98% | 245 L/ m ² / h/bar | 170 |
| | Molecular dynamic investigation of water desalination potential | > 88% | ~70% greater than graphene nanopores | 4 |
| Tungsten chalcogenides (WS ₂) | Selective sieving of Evans Blue molecules | 90% | 930 L/m ² /h/bar | 175 |
| Titanium Carbide (Ti ₃ C ₂ T _x) | Selective sieving of Li ⁺ , Na ⁺ , K ⁺ , Mg ²⁺ , Ca ²⁺ , Ni ²⁺ , Al ³⁺ , methylthioninium ⁺ and MB dye cations | Differential sieving of ions depending on hydration radius and charge of the ions | 37.4 L/ m ² / h/ Bar | 184 |

including chemical structure²⁰⁷ and surface functionalization,²⁰⁸⁻²¹³ size and dose,²¹⁴⁻²¹⁶ and time of exposure.²¹⁷ In addition to the type of graphene, for instance, graphene oxide, reduced graphene oxide, few layer graphene and graphene nanosheets, the number of layers, the manner in which the materials was

synthesized, the type of cell exposed and in some cases the route of administration.²¹⁸ However, recent in vitro and in vivo studies have observed contradictory toxic and nontoxic effects of the material simultaneously, due to the various forms of graphene which can be present.²¹⁹ Such findings

demonstrate a gap in research which must be bridged before it is possible to industrially employ graphene based technologies.
218, 220

Though the toxicity of graphene has begun to receive attention, to date, there has been little examination of the health and environmental impact of other 2D crystals due to their emerging nature. In order to ensure the safe design, production and use of 2D nanomembranes it is essential to investigate their potential toxicity and environmental risks. It is necessary to understand the manner in which these nanostructures react with cells and tissues, with a particular focus on exposure routes such as the lungs and skin, and also the immune system and nervous system in order to minimize the health and environment risks of 2D materials. In addition, the potential impact on terrestrial and aquatic organisms and microorganisms must also be investigated. Consequently, the Scientific Committee on Emerging and Newly Identified Health Risks, in addition to various other groups, have highlighted the urgent need for the risk assessment of graphene and its related 2D materials.²²¹⁻²²³

In addition, there is limited knowledge of graphene and other 2D materials post treatment recovery recycling and disposal. If the correct measures to salvage and dispose of graphene family materials are not exercised, further water pollution may result.

With the continuous exposure of new nanomaterials and the employment of nanomaterials in new fields of technology it is imperative researchers devote their attention to the study of their effects on the environment and establish appropriated means of disposal.

Conclusions

Conventional means of water purification such as boiling, sedimentation, distillation and oxidation, in addition to solar and chemical disinfection are currently incapable of providing the globe's population with an economical or satisfactory supply of potable water.⁹ In order to provide each individual of the earth's population with basic rights to safe drinking water, improved technologies must be established and industrialized. Pressure driven, membrane based, water purification technologies such as ultrafiltration, nanofiltration and reverse osmosis have subsequently surfaced as promising solutions for the large scale production of potable water.^{224, 225} Such technologies circumvent the use of chemical additives, thermal inputs and spent media regeneration thus providing an encouraging opportunity for water purification.⁵³ However, due to the aforementioned demerits associated with techniques like reverse osmosis, including poor selectivity, amplified energy demands and increased costs, membrane-assisted technologies require much improvement in order to radically challenge the potential water crisis currently faced by humanity.

Substantial advances have recently been made in understanding the possibility of confronting the shortcomings of established membrane technologies with cutting edge nanomaterials.^{53, 226} The progression of nanotechnology

within the field of water purification, amongst others, has seen focus shift from the use of conventional non porous RO polymeric membranes to quasi-2D nanomembranes. The unique properties of such intricate nanosystems separate inorganic salts and organic compounds of low molecular weight based on the mechanisms of nanopore size exclusion and surface charge interaction, thus facilitating lower energy consumption and higher flux rates in comparison to traditional ultrafiltration or reverse osmosis.

2D graphene like crystals demonstrate great potential in the field of membrane assisted water purification (Table 2).^{93, 227}

The unique properties of such state of the art materials can enhance the performance of conventional membrane separation techniques in terms of water flux, salt rejection and fouling resistance thus reducing the costs of many processes used extensively throughout industry. The atomic thinness, large surface area and synthetic pores or naturally occurring nanochannels of 2D material based membranes, effortlessly facilitate selective permeation, high water flux and effective contaminant rejection (Table 2) without the requirement of high pressure necessitated by current technologies.

Indeed, many restrictions surrounding industrial scale 2D materials prevail, however, once addressed 2D nanostructured membranes have the ability to provide a solution to the potential water crisis by improving the performance and commercial viability of current water treatment performances. As a result it is imperative that the research and development should be focused on further advancing these materials.

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