

Graphene-Based Membranes for Water and Wastewater Treatment: A Review

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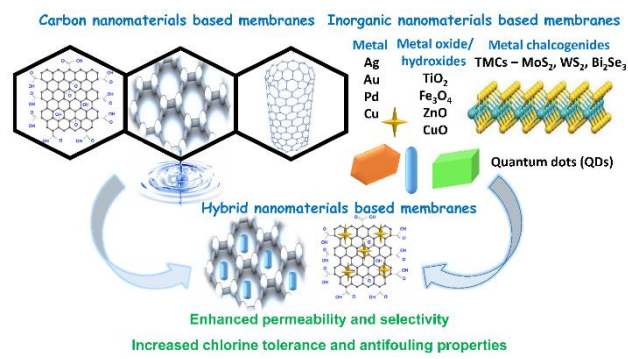
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Graphical Abstract



Abstract

Increasing population and industrial growth, combined with climate change, led to global water problems. This review paper summarises the next-generation hybrid graphene-based membrane materials that are used for water purification to meet global freshwater supplies. Graphene-based membrane materials are believed to be the advanced materials for the desalination process due to their atomic thickness and tunable functionalities. The effect of membrane fabrication techniques and operating conditions on separation and membrane fouling mechanisms are discussed in depth. The present study discusses the development, advantages, and shortcomings of using hybrid graphene membranes compared to traditional polymeric membranes. To extend the applications of graphene membranes, more attention should be paid to the water permeability and membrane selectivity in long term operation at conditions similar to the field for performance analysis. While literature reviews have mainly concerned the ability of graphene materials to adsorb water contaminants, there is very limited updated information related to its sieving properties. Moreover, the literature lacks on comparative discussion of graphene-based membranes with other hybrid membrane materials. Thus, a profound understanding of graphene-based membranes is much needed to unlock the potential for graphene materials. Also, the research interest in preparation of hybrid graphene membrane is expected to be explored in the future.

Keywords: Graphene-based membranes; Conventional polymeric membranes; Hybrid membrane materials; Nanoparticles and Desalination

1. Introduction

Water is one of the valuable resources that improve the sustainability of life on earth. The rapid growth of the world's population and the depletion of natural water resources have worsened the problem of water scarcity.¹ The global water demand has been estimated to continue at a similar growth rate until 2040, projecting 20 to 30% increase from existing water consumption (Figure 1).^{2,3} There are various physical and chemical technologies for water and wastewater treatment such as gravity separation, membrane filtration technologies, air flotation, absorption materials, chemical vapour deposition, coating mesh, carbon-based materials, hydrophobic aerogels, sol-gel process, and sponges.^{4,5} These technologies can remove a large proportion of dissolved ions.⁶ Still, they have some inherent limitations such as low separation or rejection rate, fouling, high energy consumption, reusability, and recyclability of the filtration media.⁷

Further, conventional filtration methods, including distillation, adsorption, chlorination, coagulation, and flocculation, are incapable of producing high-quality water to meet the global demands of the 21st century.^{8,9} Compared to the conventional filtration methods, membrane filtration enables continuous operation with lower energy consumption at an affordable price.^{5,10} Several materials and developments have been adopted to design membranes in recent years. Since in the early 1960's, organic polymers are dominating the membrane industry. However, most of the membrane process for water and wastewater treatment relies on a polyamide thin-film composite (TFC) membrane, which was developed four decades ago (Figure 2).¹¹

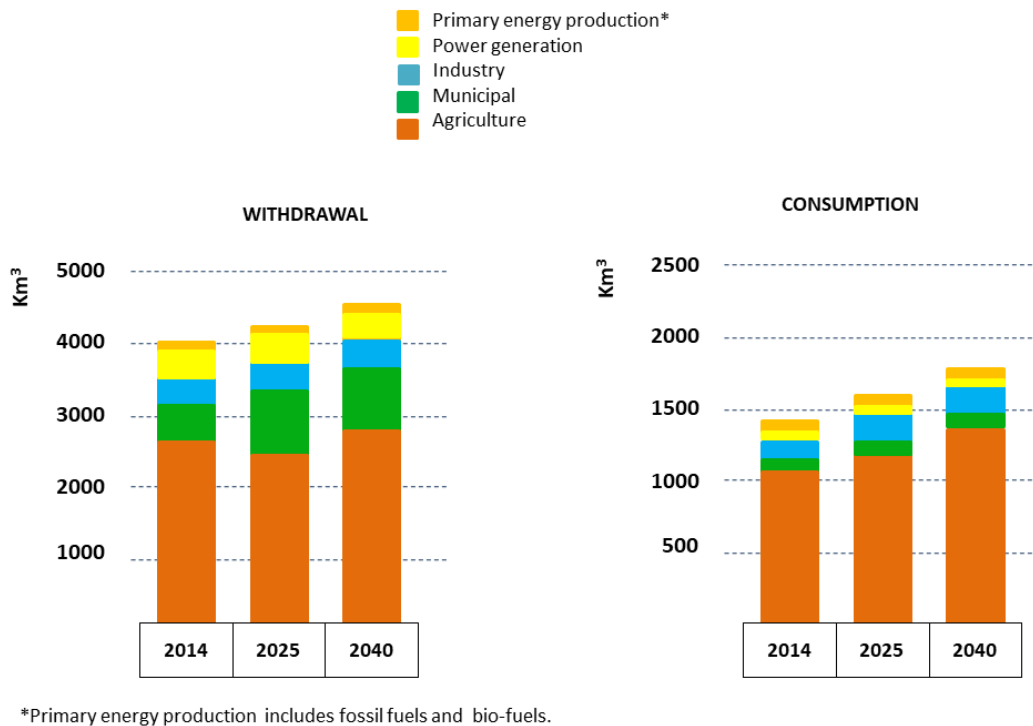


Figure 1 Global water demand by various sectors from 2014 to 2040 is projected. Modified by authors and reproduced with permission from ref 3. Copyright 2019 International Energy Agency (IEA).

Unfortunately, low chlorine tolerance, fouling, limited water flux, and separation efficiency are some of the major drawbacks of traditional polymeric membranes.^{6,12} The drawbacks of conventional polymeric membranes can be eliminated by the hybrid nanoporous membrane because it has continuous channels that allows a high volume of water to pass at low operational pressure.⁹ With the integration of nanoparticles, the permeability and selectivity trade-off for polymeric membranes could be eliminated; for instance, an increase in the permeability rate for gas separation was observed for silica nanoparticle incorporated polysulfone (PSf) membranes.¹³ The addition of nanoparticles within the polymer matrix could improve the

stability of the polymer membrane's perm selectivity at high temperature.¹⁴ However, the fine dispersion of nanoparticles in the vicinity of polymers is the main drawback of these hybrid polymer membranes.¹⁵ Therefore, a breakthrough in membrane development is much needed for resolving the water challenges of the 21st century.¹²

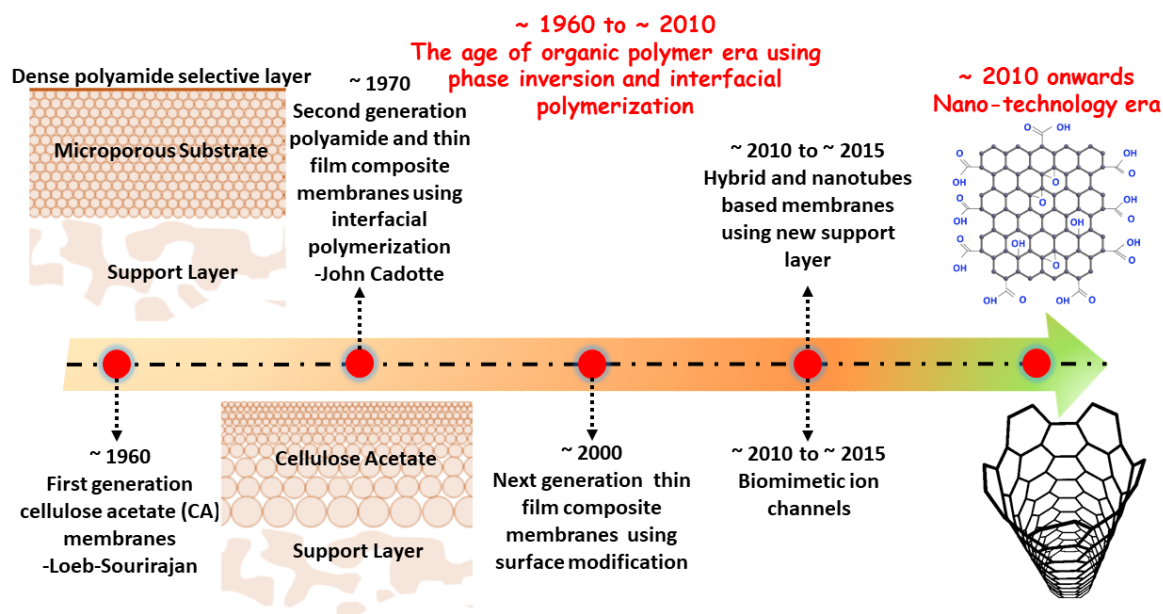


Figure 2 Trends and developments in membrane materials from 1960 to the present.

Two-dimensional graphene materials have excellent mechanical strength, thermal conductivity, and electrical properties. Further, due to unique lattice structure graphene has become a fascinating functional membrane material for water purification.^{16, 17} In addition, a broad range of graphene derivatives have been studied to improve the graphene material capability further. Graphene oxide (GO) has become one of the main derivatives of graphene that retains a substantial portion of the graphene characteristics.¹⁸ Owing to presence of polar oxygen-containing functional groups, GO is water dispersible. During the preparation, the degree of oxidation in GO can be customized, which is crucial for a successive alteration of the graphene derivatives.¹⁹

Specifically, functionalization implies the covalent bonding of functional groups on the surface of the graphene sheet. Whereas doping is the introduction of heteroatoms like nitrogen (N), sulphur (S), and fluorine (F) into the carbon lattice of graphene.^{20, 21} Both functionalization and doping will tailor the properties of graphene for a wide variety of high-performance applications, including membrane technology.²² Furthermore, GO derivatives show

exceptional membrane properties such as antifouling, high chlorine tolerance, and antimicrobial activity thus improving membrane lifetime.⁴ Fouling resistant membranes with tunable surface functionalities have an enormous potential to eliminate the pre-treatment process, which decreases the energy consumption of desalination plants to a greater extent.²³ Currently, graphene membranes have shown huge potential for brackish water treatment using nanofiltration (NF) membrane.^{24, 25} Molecular simulations and theoretical studies show the applicability of graphene membranes for reverse osmosis (RO) desalination.¹¹

This review summarizes the most recent developments of fabrication methods for preparing graphene-based membranes of the existing literature. Initially, the study briefly introduced GO and carbon nanotubes (CNTs) membrane materials. Then, factors governing the transport mechanism in graphene materials are reviewed. The major objective of this article is to discuss the hybrid graphene membrane performance as compared to other advanced nanomaterials and polymeric nanocomposite with exemplified illustrations. Finally, the future research directions and bottleneck challenges of graphene membranes are discussed in detail.

2. Graphene-based nanomaterials

The two-dimensional graphene and its derivative are building blocks for advanced membranes. The graphene consists of sp^2 -hybridized carbon atoms positioned in a hexagonal honeycomb lattice.¹⁶ Recently, graphene-based nanomaterials like zero-dimensional carbon quantum dots, one-dimensional CNTs, two-dimensional GO, and reduced graphene oxide (rGO) have drawn incredible consideration from researchers around the globe.²³⁻²⁷ In addition to that when these are assembled into multilayered structures, it enhances the separation efficiency.

2.1 Graphene oxide-based membranes

The presence of sp^2 (aromatic) and sp^3 (aliphatic) carbon with oxygen contain functional groups in the GO structure allows chemical reaction and surface modification to form distinct assembly morphologies for specific application of separation performance.²⁸ The existence of polar functional groups allow GO better hydrophilicity and stable dispersion in aqueous medium.¹⁷ The possible production of large-scale GO, and its inexpensiveness makes GO to study effectively. Controlling the degree of oxidation, size, and functional groups in the controlled synthesis of GO helps to study and understand the separation mechanism of lamella arrangement resulting in high separation efficiency.²⁹

Recent studies depicted that graphene has a potential for application for fabrication of highly selective and permeable separation membrane with better performance for water purification as compared to inorganic filtration membrane or polymer-based membrane. Nevertheless, major graphene-based membranes showing high permeation flux were prepared by decreasing their thickness to the extent of < 50 nm. Astonishingly, to enhance the permeability of membranes, graphene-based materials are modified using nanomaterials and have become a promising alternative. The nanomaterials can range from inorganic nanoparticles to organic molecules.^{30, 31} Above-mentioned low-dimensional graphene nanomaterials with tunable functionalities and enhanced surface properties facilitate the membrane modification as a trade-off between the permeability and the selectivity properties. Graphene-based frameworks with polar functional groups have been considered as a key property of nanotechnology to obtain an ideal membrane.^{32, 33} Further, incorporation of these nanomaterials provides frictionless capillary channels, which further enhances the permeability speed within the membranes.

2.1.1. Fabrication and functionalization of graphene oxide-based membranes

GO membranes tends to self-assemble by simple filtration with GO solutions, layer-by-layer (LBL), drop-casting, dip coating.³⁴ The packing structure of GO laminates can be tuned depending upon the assembly using different methods. The filtration method is considered to be one of the simple and common approach where a hydraulic pressure or vacuum is applied on GO nanosheets to narrow down the inter layer spacing. GO paper via filtering out GO solution through a microfiltration membrane was engineered³⁵ and X-ray diffraction (XRD) patterns show 0.83 nm of layer-to-layer d-spacing of the GO paper was confirmed. The interlayer spacing (d-spacing) increases with an increase in the degree of oxidation and reaches around 1 nm.³⁶ The pure graphene poses interlayer spacing of 0.34 nm, which is sufficient to allow a single layer of water in-between.³⁷ Further, the d-spacing may change in GO, upon hydration or provided an environment with high humidity.³⁸ Water transport channels are supplied by d-spacing with a size-exclusion property for small size molecules. A chemically converted method is followed to fabricate graphene-based membranes for studying the corrugation of GO nanosheets and conclude GO nanosheets possibly can be used to fabricate nanofiltration membranes.³⁹ The rejection rate of 67% was achieved for direct yellow dye. Hence, the nanofiltration membrane is possible to prepare by simply filtering out a GO solution from a microporous membrane. GO membrane were studied to determine the permeability of the membrane and found to be unhindered during permeation of water while it was highly blocking hydrogen, nitrogen, argon, and helium.³⁷ The cause for fast water penetration into the

multilayered GO membranes was due to the channels opposing the slower solution-diffusion water transport mechanism in membranes. Numerous methods were developed for fabricating GO separation membranes, out of which most common methods such as casting/coating method, layer-by-layer method, and vacuum/pressure-assisted self-assembly method have been discussed in further section.

2.1.1.1 Casting/coating-based method

The direct and simple approach in the deposition process makes cast and coating methods the most common method for fabricating GO membranes. The cast/coating process has a broad variety of options on a substrate, particularly in the designing of freestanding GO membranes. GO laminates over the copper foils using coating process and carving them out produces a freestanding GO membrane.³⁷ GO membranes were fabricated through drop-casting over a portion of smooth paper. Then the freestanding GO membrane stripped out from the supported paper. Additionally, based on charged hollow membranes, the deep coating can be employed for fabricating selective thin barriers.⁴⁰ A comparative study of two coating methods for the testing the relative effect of electrostatic repulsion and immersion capillary force over the stacking GO configuration was carried out.⁴¹ During the process the base membrane was kept in contact with the interface of air-liquid in GO solution, where GO membranes were synthesized via direct spin coating. Highly dense GO deposition occurred in the spin-coating process because attractive capillary forces surmount the repulsive interactions.

2.1.1.2. Layer-by-layer self-assembly method

The layer-by-layer (LBL) self-assembly method can generate thin-film charged at the molecular level by accumulating polyelectrolytes of opposite charge.⁴² LBL membranes consist of polycations and polyanions that deposit over the substrate via electrostatic interaction. For LBL self-assembly technique, GO can be an appropriate choice since it poses a laminar configuration as well as a functional group with charged oxygen. In the process first, the substrate is modified to become a charged surface then LBL process starts. Zhang et al. cross-linked the substrate layer by hyperbranched polyethyleneimine (HPEI) along with repeatedly dipped and soaked the membrane in GO and ethylenediamine (EDA) solution for further deposition cycles of GO and EDA (Figure 3a).⁴³ Positively charged HPEI alters the surface property. A similar LBL self-assembly technique is also useful for assembling two nanomaterials to form a multilayered configuration. GO membranes into a sandwich structure were produced⁴⁴ and successfully altered the d-spacing in the GO LBL membrane. In the

process, an alternative layer of GO and oxidized CNTs were stacked on one another to form sandwich morphology which was afterward cross-linked with the help of polyelectrolyte (Figure 3b). The presence of oxidized CNTs highly accelerates the permeability and roughness on the membrane surface. In addition to electrostatic attraction, the cross-linking and electric field has also been utilized to fabricate LBL GO membranes. Further, Hu et al. produced GO membrane of cross-linked morphology with fine mechanical strength by depositing GO and 1,3,5-benzenetricarbonyl trichloride (TMC) over polydopamine-coated polysulfone support.¹⁶

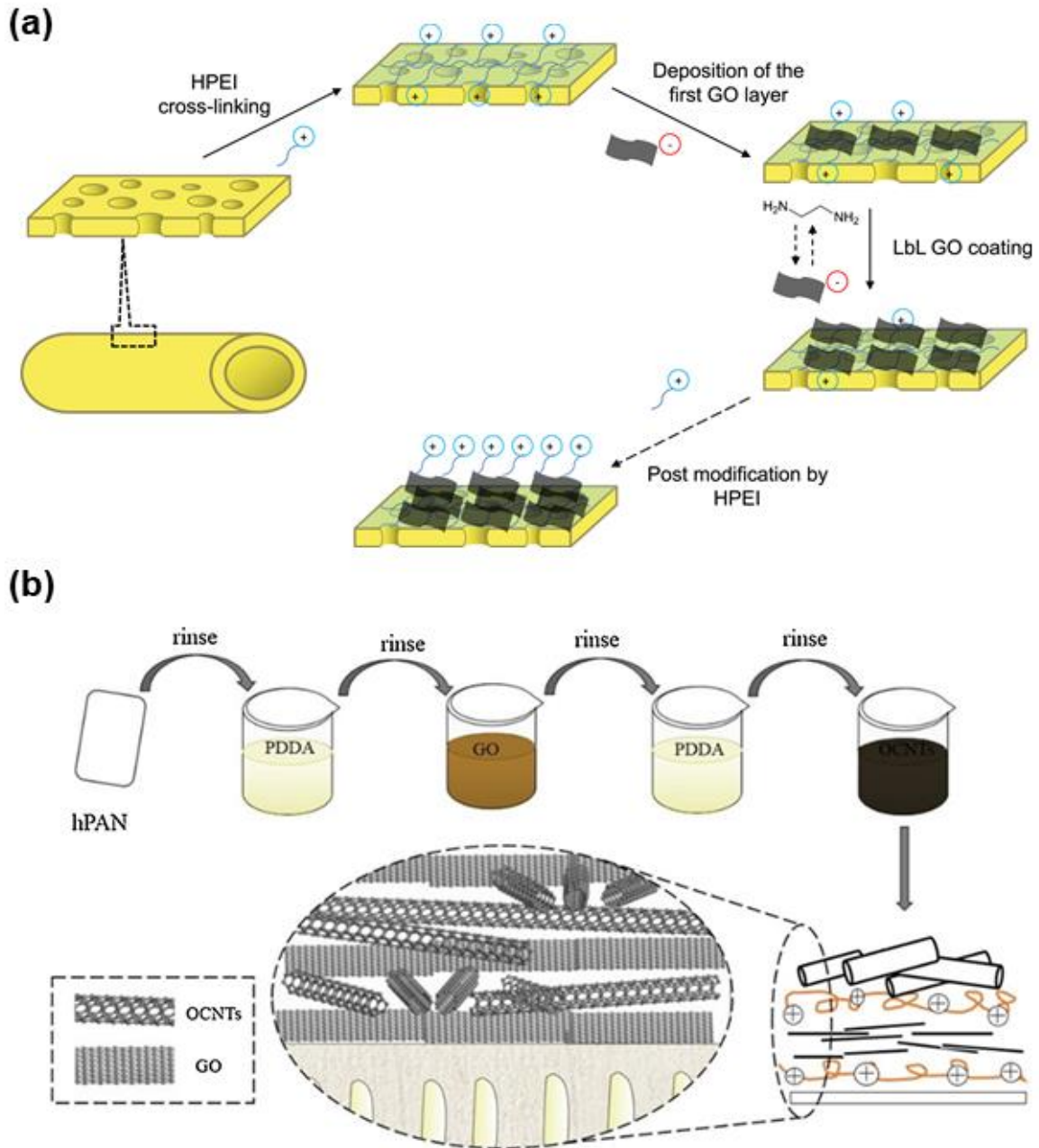


Figure 3 Schematics illustration of different methods for designing the layer-by-layer (LBL) GO membrane. (a) Alternatively, dipping into two solutions for the production of LBL GO

membrane. Reproduced with permission from ref 43. Copyright 2016 Elsevier. (b) Designing LBL GO membrane of sandwich structure by using polyelectrolyte as cross-linker between GO and CNT. Reproduced with permission from ref 44. Copyright 2018 Elsevier.

2.1.1.3. Vacuum/pressure-assisted method

GO material possesses hydrophilic and negatively charged oxygen functional groups like epoxy, hydroxyl, and carboxyl groups that are well dispersed in the aqueous medium without aggregation, because of which vacuum/pressure-assisted method is suitable to design GO membranes with multilayer. Both vacuum as well as pressure-assisted methods, are filtration technique wherein simultaneous deposition of GO nanosheets in a parallel manner on the base membranes, counting the ultrafiltration and microfiltration membranes. The alteration of volume or concentration of the GO precursor solution, the thickness of GO membranes can be tuned in the vacuum/pressure-assisted method. A comparative study of GO microstructures was designed using pressure-, vacuum-, and evaporation-assisted self-assembly methods and concluded that GO membranes formed from pressure-assisted fabrication method exhibited highly controlled laminar morphology with the lowest surface roughness.³⁴ For instance, Cheng and co-workers prepared GO/polyacrylamide membranes for organic dyes separation using vacuum filtration method. GO/polyacrylamide membrane shows 0.68 nm interlayer spacing, with 95.43 % rejection for rhodamine B (RhB) dye solution.⁴⁵ Whereas, GO membranes formed from evaporation-assisted fabrication method displayed maximum roughness and water contact angle as compared to the other two methods.

Transmission electron microscopy (TEM) image shows that the orientation of the pressure-assisted GO membrane is highly organized (Figure 4a). In contrast, an evaporation-assisted membrane possessed ring morphology with random orientation (Figure 4c). The formation of ring morphology in evaporation-assisted membrane indicates the hydrophobic nature of the membrane. Controlling the deposition rate can improvise the channel structure in the pressure-assisted GO membranes. When the deposition rate is reduced, it results in more oxidized patches, consequently forming spots free of the functionalized group. The highly ordered GO membranes displayed simultaneously high rejection and flux (Figure 4d).⁴⁶ Some of the recent studies and performance of the GO based membranes are tabulated in Table 1.

Table 1: Summary of properties and performance for graphene oxide membranes

GO properties		Substrate			Membrane performance		References
O/C	Interlayer space (nm)	Type	Pore size	Thickness	Water permeance (LMH/bar)	Rejection	
NA	NA	PVDF	50 nm	44.1 mg/m ²	7.64	98.3% Na ₂ SO ₄	47
NA	0.86-1.12	Nylon	0.22 μm	NA	51 - 60	99% MB 99.82 CR	48
~2.39	0.76	PES	NA	1.36 μm	13.4	~80% MB ~80% RhB 89.8% MR, 99.4% MB,	49
NA	0.65-0.75	PES	0.03– 0.2 μm	NA	~30	96.8 BBG, 72.6% EB, 63.9% RhB	50
NA	0.766	MCE	0.2 μm	478 mg/m ² , 86.5 nm	10.7	~35% NaCl	51
NA	0.64	CA	0.2 μm	NA	0.592-1.416	~89% NaCl	25
~0.5	0.9	MCE	0.2 μm	478 mg/m ² , 330 nm	11.0	~30% NaCl	52
0.4	NA	PC	NA	69.41±3.85 nm	~5	~70% Na ₂ SO ₄	7
1.61	0.82-0.84	AAO	NA	4.7nm, 23.6 nm	7 - 20	MgSO ₄ ~60%, NaCl ~30%	46
NA	0.899	PC	200 nm	~20 nm	6.3	20% NaCl	53
0.4	0.796	PES	30 nm	~20 nm	7.37	57.73% Na ₂ SO ₄	54

[NA: Not available; CA: Cellulose acetate; AAO: Anodic Aluminium Oxide; PVDF: Polyvinylidene fluoride; PES: Polyethersulfone; MCE: Mixed cellulose esters; PC: Polycarbonate; Na₂SO₄: Sodium sulphate; MgSO₄: Magnesium sulphate; NaCl: Sodium chloride; MB: Methylene blue; CR: Congo red; RhB: Rhodamine B; MR: Methyl red; BBG: Brilliant Blue G; EB: Evans blue]

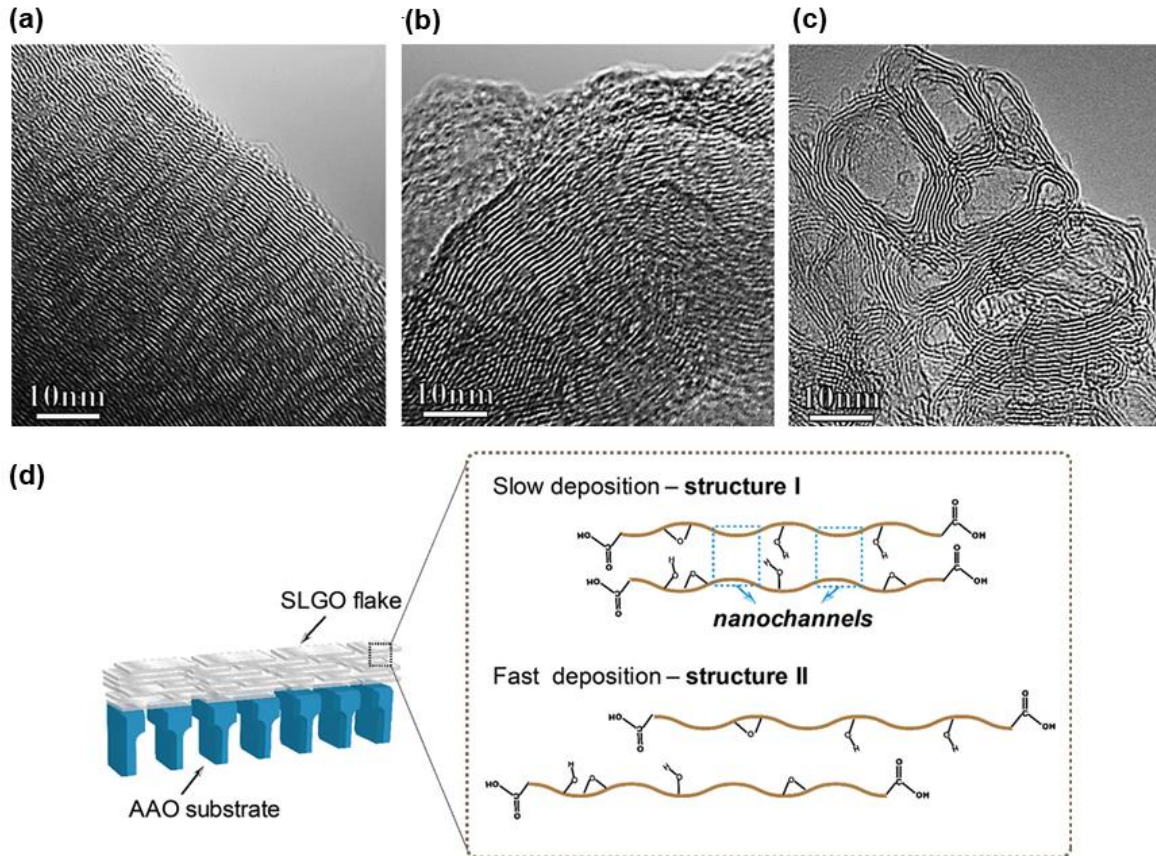


Figure 4 (a-c) TEM morphology of GO membrane synthesized via (a) pressure-, (b) vacuum- and (c) evaporation-assisted methods. Reproduced with permission from ref 34. Copyright 2015 Elsevier. (d) Interlayer nanostructures of GO membranes fabricated by slow and fast deposition rates. Reproduced with permission from ref 46. Copyright 2017 American Chemical Society.

From the above, it is observed that the versatile techniques and strategies exist to design GO-based membranes have certain advantages and disadvantages in real-time applications, depending on mechanical strength, porosity, nano channel type, and chemical inertness. GO membranes prepared by pressure-, evaporation- and vacuum-assisted method may result in the roughness on the nanosheets. The evaporation-induced self-assembly method utilizes the π - π stacking interaction among of GO primitives to form thin and large graphene-based films. Highly ordered GO membranes can be prepared following the evaporation-induced self-assembly method. The pros and cons of various fabrication techniques for graphene-based membranes are shown in Figure 5. Further, capillary-force-assisted self-assembly helps to form highly packed with well-ordered dense morphology and enhances conductivity compared

to vacuum filtration prepared membranes. Thus, a higher rejection rate is expected for various contaminants compared to the less ordered vacuum filtration membranes. Stacked GO membranes with lamellar morphology possess extreme advantages like ease of scalability, high separation efficiency, water permeability and can be intensely applied for nanofiltration and reverse osmosis. However, depending on the preparation technique desired GO membranes can be developed for specific application for liquid separation.

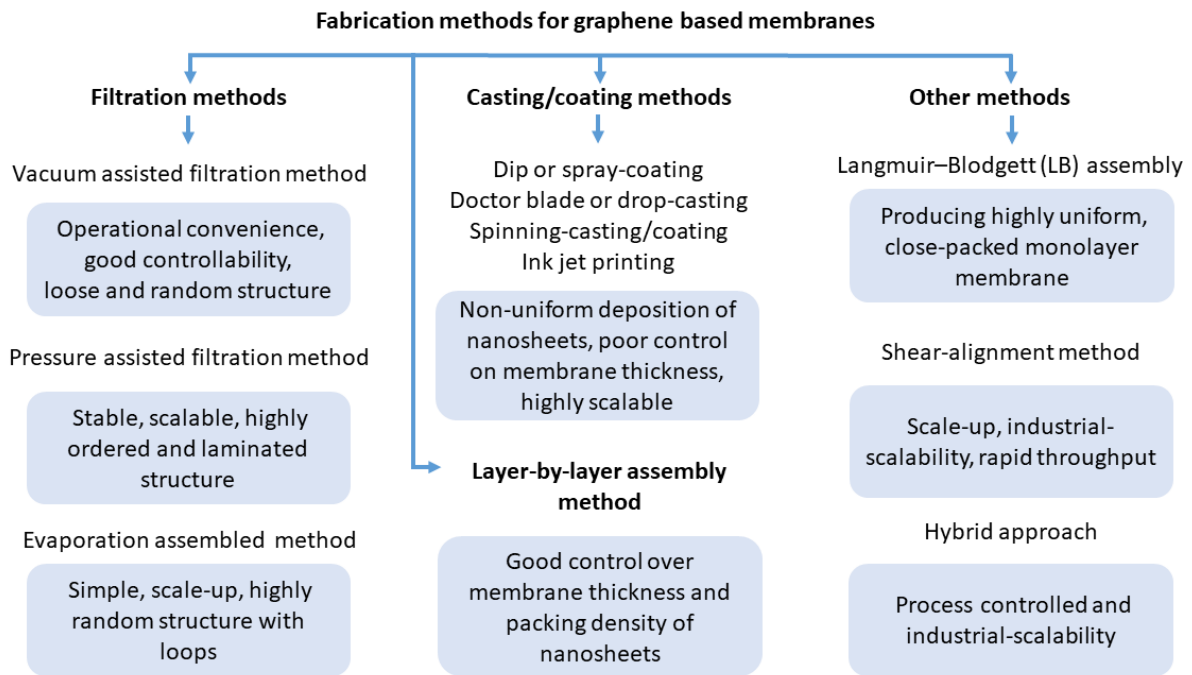


Figure 5 Schematic representation of pros and cons of various fabrication techniques for the preparation of graphene-based membranes.

2.1.2. Transport mechanism for graphene oxide-based membranes

To understand the mechanism of GO separation, several studies were carried out on GO membranes. In GO-based nanofiltration membranes (Figure 6II) due to the size barring effect the large size, organic molecules were blocked by the nano-channels inside the GO membranes.⁸ Water molecules can pass through GO by taking a tortuous pathway (dotted line) inside the vacant space of oxidized regions among GO sheets (with a thin d-spacing). The water molecules move across all over the oxidized regions (from top view) and to reach the next interlayer space (from side view) and it moves around the GO sheets (with longer dimensions L) (Figure 6I).³⁷

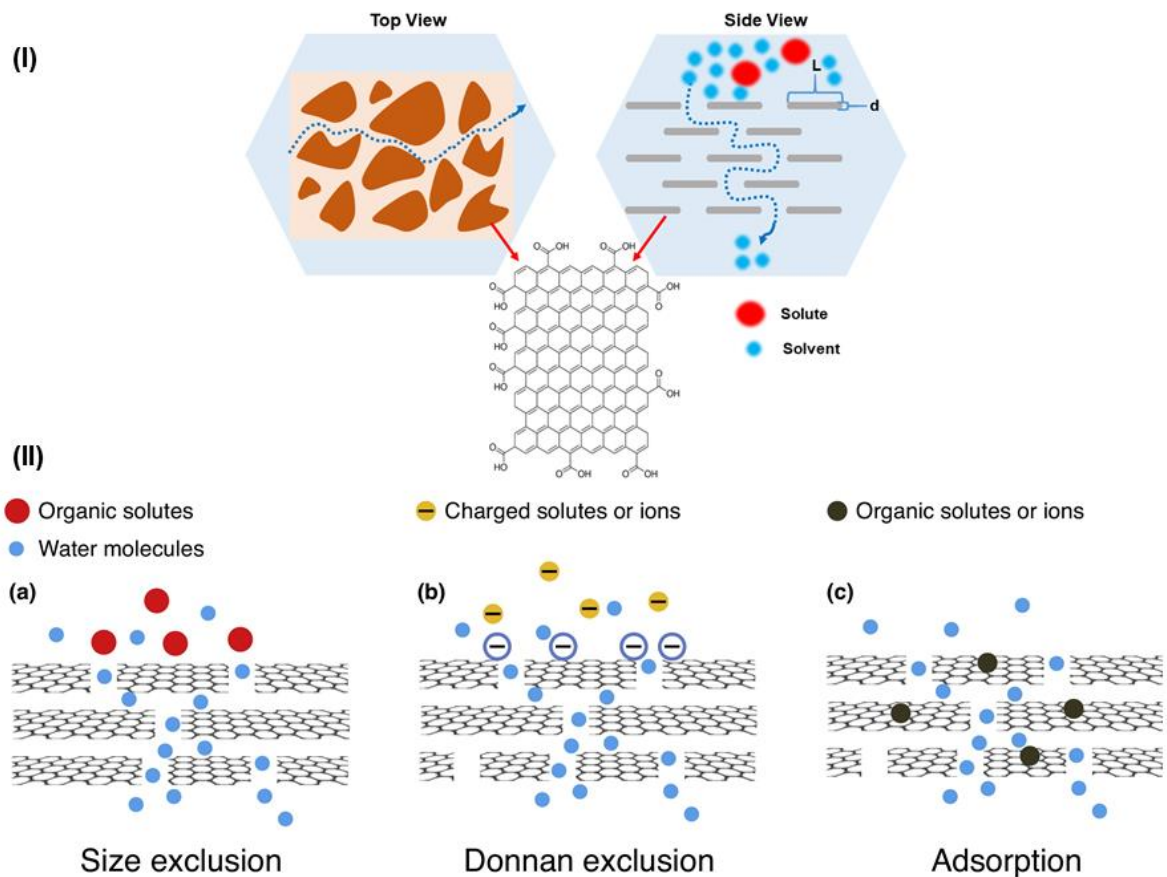


Figure 6 (I) Transport channels in GO membranes. (II) GO membranes separation mechanism by (a) size exclusion, (b) Donnan exclusion, and (c) adsorption. Reproduced with permission from ref 8. Copyright 2017 Elsevier.

Particular size exclusion to ionic and bigger molecules can be obtained by tuning the spacing of GO nano-channels.⁵⁵ Because of which GO membranes are mostly used to design membranes with fine inter-layer spacing with the insertion of cross-linkers or nano-fillers of a particular size for the water purification, pharmaceutical separation, and wastewater reuse. The GO membranes are reduced with the help of reducing agents providing small-sized nano-channels and better membrane hydrophobicity. The passage of smaller molecules and charged ions can also be restricted by following the Donnan exclusion of GO membranes.^{56,57} The GO is negatively charged in the broad pH range since the carboxyl groups undergo deprotonation from the edges of GO nanosheets. This makes GO membranes efficient to separate with high rejection for negatively charged organic molecules as well as divalent ions.²⁷ The negatively charged features of GO membranes were altered by incorporating amine-abundant molecules such as PAMAM dendrimer and hyperbranched polyethylenimine (HPEI),⁷ to produce positively charged GO framework membranes for heavy metal rejection which displays an

efficiency of 95 %. Various smaller hydrate ions adsorb strongly on different regions of GO sheets through various interactions leading to excellent selectivity with GO membranes. It is possible due to the transition metal cations could co-ordinately interact with oxygen-containing functional groups and blocked by GO membranes.⁴⁰ Likewise the interaction of alkali and alkaline earth cations with the sp^2 cluster of GO via cation- π interactions can decrease the permeability of alkali and alkaline earth cations across GO membranes.⁵⁸

2.2. Carbon nanotube-based membranes

Graphene layers rolled up to form thin hollow cylinders with open or capped end are known as CNTs. CNTs exhibit outstanding properties like high aspect ratio, high mechanical strength, large specific surface area, low tortuosity, and smooth morphology. The diameter of CNTs can be tuned, offering controllable porosity in the structure that can be employed for various separation activities.⁵⁹ CNTs exhibit excellent thermal and electrical conductivity and considered as one of the strongest fibers. Membranes based on CNTs can be designed into variant structures which could offer unlimited advantages in the membrane performance. For instance, cylinders formed by multiple layers are referred to as multiwall CNTs (MWCNTs), while few layers (1-10) of graphene form single-walled CNTs (SWCNTs). SWCNTs possess a diameter of up to 1-3 nm and inner diameters of 0.4–2.4 nm. MWCNTs possess outer diameter varying from ~2 nm (double-walled nanotubes) to ~100 nm consisting of tens of walls.¹⁹ MWCNTs are coaxially arranged, and the d-spacing between graphene layers is found to be similar to that of graphene is about $\sim 3.4 \text{ \AA}$.⁶⁰

Based on the orientation of graphene layers, several configurations are possible for CNTs like a chiral, armchair, and zigzag. Inner hollow cavities with nanoscale diameters make CNTs an ideal candidate for several applications including membrane-based separations.^{61, 62} Due to the presence of rolled graphene and lamellae columns, water molecules can travel at a higher magnitude compared to other materials with similar pore size. Molecularly smooth hydrophobic graphene surface provides frictionless capillaries for water permeability.⁶³

2.2.1. Fabrication of carbon nanotube-based membranes

Based on the fabrication technique, CNTs are classified into three classes such as mixed matrix (MM-CNT), vertically aligned (VA-CNT), and self-standing CNT bucky paper membranes (Figure 7). MM-CNT and CNT-BP membranes hold a random distribution of CNTs on a huge porous structure whereas, in VA-CNT membranes, the CNTs are perpendicularly arranged in

a line over a substrate for the passage of fluid through the interior of CNT or among the CNT bundles.⁵⁹ CNT-BP membranes are produced into a paper-like morphology of CNT mat using self-assembly method. The stability of the CNT mat is due to the presence of Van der Waals forces as well as π - π interactions among the attached nanotube which offers a highly porous 3D network and large specific area.⁶⁴ Further, the CNT membranes can be aligned horizontally over a substrate during the fabrication technique forming horizontally aligned CNT membranes (HA-CNT).^{65, 66}

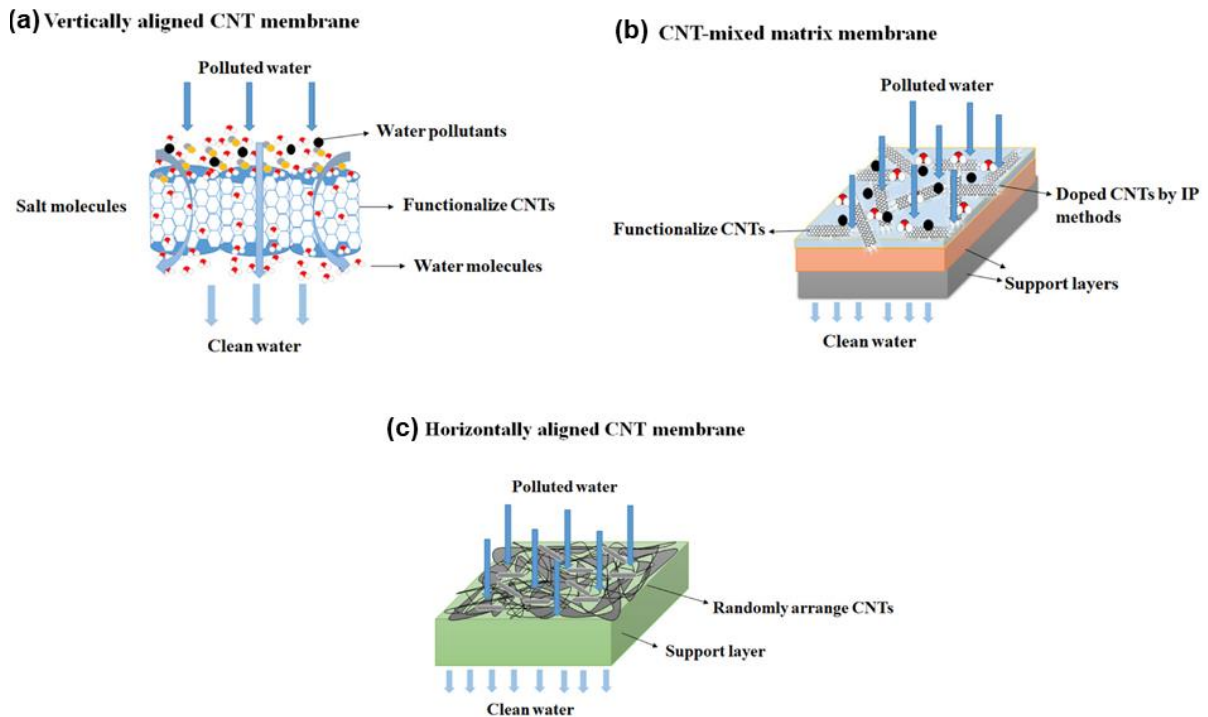


Figure 7 Water transport and rejection mechanism of current state-of-the-art f-CNT membranes: (a) VA-CNT membrane, (b) MM-CNT membrane, (c) HA-CNT membrane. Reproduced with permission from ref 66. Copyright 2019 Elsevier.

2.2.1.1. Vertical aligned (VA)-CNT membrane

CNT with hollow morphology can be utilized to remove various emerging pollutants from wastewater.⁶⁷ Hind and group developed multiwall VA-CNT membrane consisting pore diameter of 6 nm with CNT incorporated fillers into polystyrene film.⁶⁸ In general, manufacturing VA-CNT membranes require the organization of CNTs perpendicularly to the organic or inorganic support layer as shown in Figure 7a.²⁷ Chemical vapour deposition (CVD) technique facilitates the vertically aligned growth of CNT forest over the support layer, which is useful for designing fine membrane structure. Afterward, polystyrene, parylene, or epoxies

are filled in the space between the nanotubes to restrict the water leakage.⁶⁹ Afterwards the extra fillers are removed from the surface via etching method to open the CNT tips forming fine porous CNT membranes. The membranes possess high sieving capacity for various pollutants present in water. However, large scale production of VA-CNT is difficult since it requires alignment of CNT in larger surface area, restricting its real-time application in large scale water treatment processes. This can be overcome by following the electro-casting technique for fine alignment of MWCNTs over the substrate.⁷⁰ Wu and group developed this approach for aligning MWCNTs on a polystyrene membrane using an alternating electric field of 2000 V cm^{-1} .⁷⁰ The MWCNTs/PS nanocomposite membranes were prepared using newly developed electro-casting method. The analysis was carried out in different frequency ranges (from 1 Hz to 100 Hz) and achieved the highest MWCNT dispersion and good VACNT membrane permeability. Further, Lee and group developed a new VACNT membrane in which interstices between CNT fillers are used to eliminate the contaminants instead of void channels of CNT and termed as outer wall- CNT membrane.⁷¹

2.2.1.2. Mixed matrix (MM)-CNT membranes

Randomly aligned CNTs into the polymeric matrix are known as mixed matrix (MM)-CNT membranes in which CNT serves as the inorganic filler.⁷² Such heterogeneous morphology provides excellent permeability and selectivity due to the combined characteristics of CNT and polymeric membranes that result in high permeability and selective membranes.⁷³ The greater anti-fouling propensity and filtration capacity of MM membranes have made researchers to focus more on its water treatment process.⁷⁴ Fabrication of MM-CNT membranes involves interfacial polymerization (IP) process or phase inversion process (Figure 7b) in which the functional CNTs are straightly added to the polymeric membranes.^{75, 76} These membranes are outstanding in the ultrafiltration, forward osmosis, or in the RO process.⁶⁹ However, this method involves certain drawback that is the dispersion of CNTs over the support membrane matrix, which is being dominated by employing functional CNTs with good dispersion properties over membrane substrate.⁷⁷

A new sulfonated MWCNT (S-MWCNT) membrane was developed by Zheng and group by IP method.⁷⁸ To prepare S-MWCNT, hydroxylated MWCNT was used to disperse in solvent. The addition of 0.01 % of S-MWCNTs to the membrane exhibited maximum salt rejection of 96.8 % with an outstanding water permeability of $13.2 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$. The presence of free

amine, carboxyl and other negatively charged functional groups on the surface of polyamide membrane acts as binding sites for CNT when loaded on polyamide membranes.⁷⁹

2.2.1.3. Horizontally aligned (HA)-CNT membranes

HA-CNT membranes require horizontal placement of CNTs on the support layer, which often results in the random orientation of CNT materials on the porous active layer (Figure 7c). Two steps are followed for the fabrication of HA-CNT membrane in which functionalization of CNTs and the manufacture of HA-CNT structure via vacuum filtration of CNT dispersion is used. Step one involves the employment of functional CNT to enhance the homogeneous dispersion of CNTs in the solvent via ultra-sonication. In step two, dispersed functional CNTs is fabricated over a substrate membrane followed by drying out the solvent in the oven.⁶⁹ The random orientation of CNT over HGA-CNT membrane generates good porous morphology and high SSA,⁷⁷ resulting in greater adsorption capacity for natural organic pollutant⁸⁰ and strong antimicrobial activity.⁸¹

2.2.2. Functionalization of carbon nanotube-based membranes

CNT membrane functionalization is indeed a precondition for CNT membrane-based desalination and wastewater treatment. Pristine CNTs are hydrophobic and tend to accumulate on the surface, which results in the perm-selectivity trade-off. The poor stabilization and dispersion of CNTs in solvent media limit their application in water purification. However, these are very much compatible with hydrophilic graphene-based materials to form a hybrid membrane. When employed for water purification, it has shown greater adsorption capacities and high filtration efficiency for the elimination of pollutants from water. In general, metal catalysts are used for the CNT functionalization.⁸² Further, capping agents are used to facilitate the selective functionalization of capped CNTs. Surface charge and properties can be tuned with the help of functionalization.⁸³ Functionalized CNT membranes show better activity such as permeability, selectivity, and fouling resistance.⁸⁴

Hybrid membrane compiled of 2D GO sheets, 1D CNTs, and activated carbon (AC) for removal of tetracycline hydrochloride (TCH) antibiotics from water were studied.⁸⁵ A freestanding and flexible membranes were produced from GO, GO/CNT, and GO/AC by following a facile vacuum filtration method. The GO membrane possessed a dense structure with uniform dispersity of CNTs within GO flakes which might be due to Van der Waals force

of interaction between them. Due to which GO/CNT exhibited maximum porosity as compared to pure GO (Figure 8).

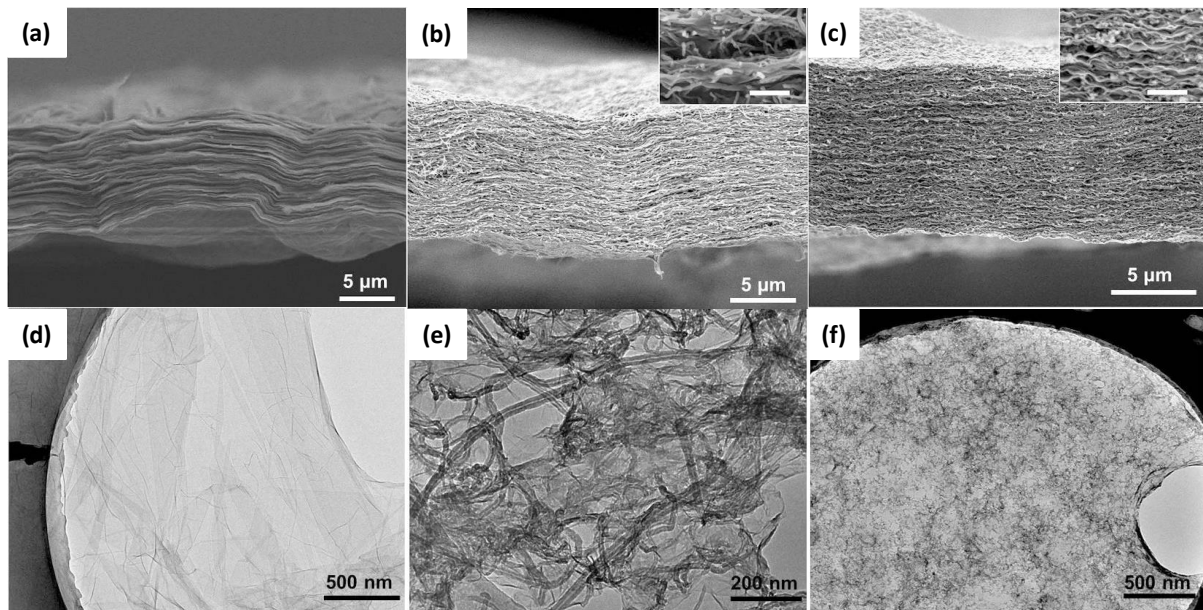


Figure 8 Cross-sectional scanning electron microscopy (SEM) morphology of (a) GO, (b) GO/CNT and (c) GO/AC membranes, and TEM images of (d) GO, (e) GO/CNT, and (f) GO/AC membranes. Reproduced with permission from ref 85. Copyright 2017 Nature Research.

The absorption capacity of membranes was studied using UV-Visible spectra of TCH solution (20 mL, 1 mg/mL) and residue solutions of TCH (Figure 9a) after filtration with GO, GO/CNT, CNT/AC, and GO/AC membranes. The TCH solution displayed a strong absorption band in the UV region. While GO membrane filtered TCH residue solution displayed a huge fall in the absorption peak as compared to TCH solution. Whereas GO/CNT and GO/AC TCH residue solution showed even more fall in absorption intensity as compared to TCH and GO filtered TCH residue which depicts the higher adsorption ability of GO/CNTs as compared to GO/AC and GO for TCH. The enhancement in the adsorption ability arises due to the porous structure that emerged within GO when CNTs and ACs are incorporated into the interstitial sites of GO nanoflakes. The addition of CNTs and AC develops micro-channels in the hybrids resulting an acceleration in the water flow through the membrane. Hence, better permeability and selectivity were achieved by hybridizing with CNTs. Figure 9b-f illustrates the mechanism for acceleration of GO/NT and GO/AC membranes. Better performance of GO/CNT and GO/AC was obtained as compared to pristine GO membrane because GO possesses strong π - π stacking as shown in Figure 9b. When pure GO was incorporated with CNTs and ACs in the interstitial

sites, a porous structure rises in the vicinity of hybrid membranes as shown in Figure 9c and d. But CNT/AC possesses poor mechanical strength and develops cracks and gaps within few minutes after formation. Figure 9f shows the water permeation route for TCH solution. Since there is an increase in porous structure with insertion of ACs and CNTs, the micro channels in the hybrid membrane formed accelerating the water flow across the membranes. Therefore, the hybridization approach leads to an improvement in separation efficiency and permeability.

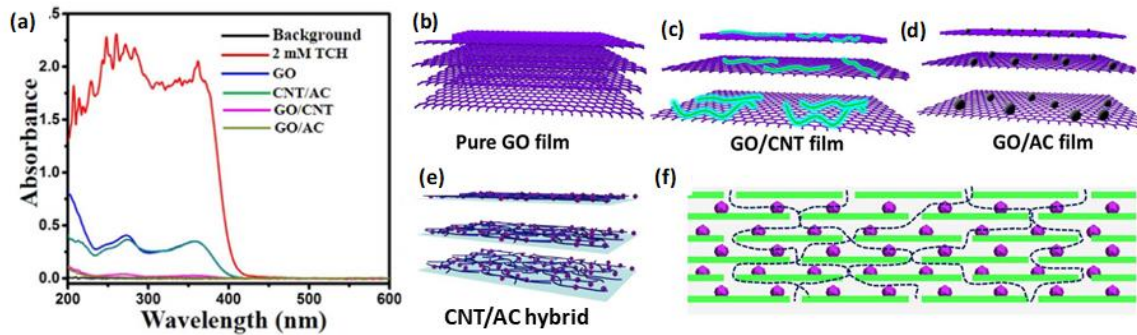


Figure 9 (a) UV-Vis absorption spectra of the GO, GO/CNT, and GO/AC membranes filtered initial TCH and residue solutions. (b) Pure GO, (c) GO/CNT, (d) GO/AC membranes and (e) the CNT/AC hybrid. (f) Transport mechanism route for the TCH solution through contact with the GO/AC membrane. Reproduced with permission from ref 85. Copyright 2017 Nature Research.

In another study, CNTs were made dispersible with the help of F127 surfactant.²² The finely dispersed 1D CNTs were incorporated into 2D graphene sheets to shape a homogeneous network. The dispersed CNTs remarkably affected the rGO-CNTs hybrid NF membrane performance. When the hybrid membrane was subjected to drinking water, it shows excellent retention efficiencies (more than 99 %) and permeability of 20-30 $\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$ of dyes, bovine serum albumin (BSA), nanoparticles, humic acid, and sugars. The NF displayed nice retention and high flux for Au nanoparticles, BSA, and phoxim with retention 99.2 %, 99.5 %, and 99.8 % respectively. Hence, the rGO-CNTs are effective hybrid NF membranes for drinking water purification. Further, TiO_2 is one of the promising semiconducting materials that promote advanced oxidation processes in the water treatment process. TiO_2 are inexpensive, catalyst inert in nature, and are photostable.⁸⁶ Titania possess a bandgap of 3.2 eV in its anatase phase and can produce e^-/h^+ pair when the light of wavelength below 380 nm is absorbed.^{87,88} Polymer membranes impregnated with TiO_2 are more hydrophilic as compared to unaltered polymer membrane and shows improved antifouling characteristics. For example, PAA grafted PVDF

with TiO₂ has contact angle lesser than the pure PVDF membrane.⁸⁹ However, the degree of antifouling was not proportional to the degree of hydrophilicity of the membrane.

When nanofiltration membrane coated with 0.01 wt.% of TiO₂ showed greater flux as compared to 0.03 wt.% coating of TiO₂, even though the 0.03 wt.% TiO₂ coating enhances the hydrophilicity. A hybrid polysulfone/nano-TiO₂/multiwalled CNT (MWCNT) ultrafiltration membranes incorporating variable nanoparticle ratios (total filler content at 1%(w/w)) were produced and were fabricated using phase inversion method.⁹⁰ The study showed the effects of TiO₂/MWCNT nanoparticles ratio on the pore size of the membrane, membrane morphology, rejection of humic acid, and permeation fouling. The addition of TiO₂ and MWCNT generates finger-like interconnected pores forming a greater number of pores on the surface of the membrane. The study revealed higher TiO₂ composition displayed a lower flux decline in the presence of humic acid. While a higher amount of MWCNT in the membrane also enhances the pore size with greater pure water flux. When the two nanostructures of TiO₂ and MWCNT are combined (e.g., 0.5% TiO₂ and 0.5% MWCNT (w/w)) displayed moderate permeation and rejection rate for 2ppm humic acid feed solution. When two nanomaterials are present in equivalent percentage (e.g., the 0.5%/0.5% mixture), it offers flexibility and improves the membrane characteristics.⁹⁰

2.2.3. Transport mechanism for carbon nanotube-based membranes

The non-polar inner shell of the hollow cylinder consisting of carbon molecules provides spontaneous and unbridled passage of water molecules with low adsorption. VA-CNT membranes are predominantly studied for membrane fabrication. The pore radius plays a key role in the perm selectivity trade-off consisting of aligned CNTs.⁹¹ Previous studies based on molecular dynamics simulations have suggested the direct correlation between low surface friction and permeability of CNT membranes.^{92,93} Longhurst et al.⁹² observed an upshift in the radial breathing mode frequency when CNT surface interacts with water molecules. Hummer et al.⁹⁴ studied the pulse-like transmission of water through the CNT channels because of the formation of strong intramolecular hydrogen bonding between water molecules. Besides, the interaction between water molecules and the inner CNT shell has a huge influence on pore hydration of rigid hydrophobic hollow cylinders.⁹⁴ The observations suggest new research directions to unlock the molecular sieve mechanism of CNT membranes.

2.3 Hybrid graphene-based membranes

2.3.1. Graphene oxide/TiO₂ hybrid membranes

TiO₂ exhibits excellent photocatalytic oxidation and antifouling characteristics when it is subjected to organic wastewater treatment and exhibited remarkable performance. For example, Gao and co-workers synthesized GO-TiO₂ microsphere hierarchical membrane (Figure 10) by accumulating the GO-TiO₂ microsphere composite over the polymer filtration membrane surface for simultaneous photo-degradation as well as water filtration.³⁰ GO-TiO₂ reached a permeate flux up to 60 LMH, 9 times higher than the performance of the commercial membrane. In addition to that, when the membrane is kept under UV radiation, TiO₂ is excited. It generates highly oxidative species, hydroxyl radicals, and electron hole pair which can help in the degradation of organic moieties. The GO-TiO₂ with dual performance effect can remove more than 90 % of dyes (acid orange 7, RhB) and humic acid from water under UV irradiation. Hence, GO-TiO₂ based membranes possess an excellent future in the research of water treatment.

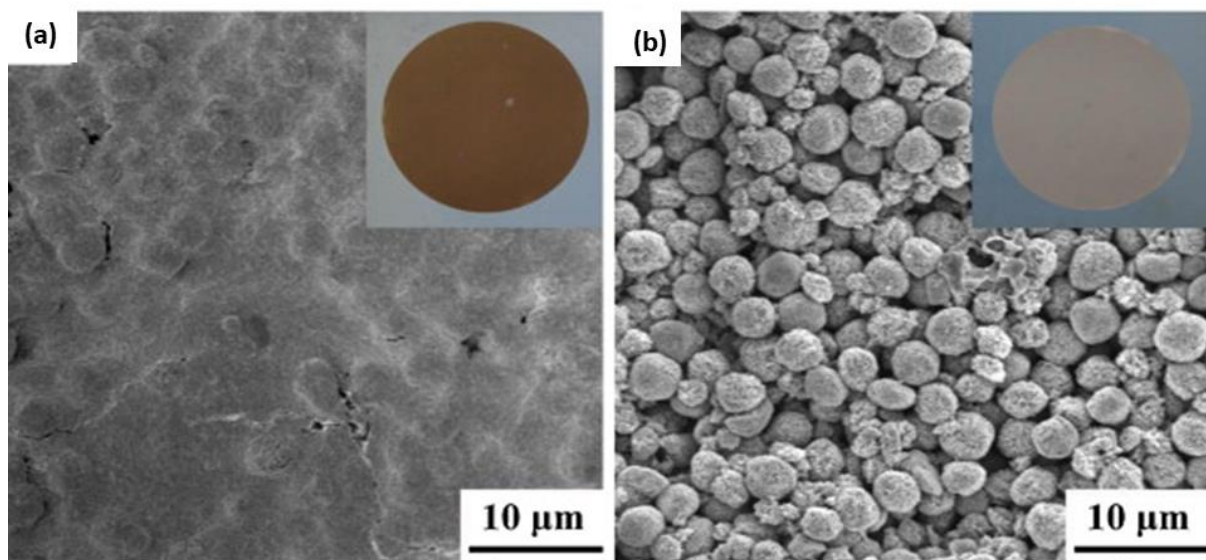


Figure 10 FESEM image of GO-TiO₂ membrane surface after filtration: (a) without UV irradiation surface of the membrane (inset: digital photo of GO-TiO₂ membrane) and (b) membrane surface with UV irradiation (inset: digital photo of GO-TiO₂ membrane). Reproduced with permission from ref 30. Copyright 2017 Elsevier.

Filice and co-workers prepared hybrid Nafion composite membrane and studied their application in the degradation of water pollutants.⁸⁶ The membrane properties were tuned using some suitable fillers such as organo-modified GO (GO_{SULF}), GO and TiO₂ nanoparticles

associating the advantage of membrane application and photocatalysis. The photocatalytic and adsorption property of the membrane was studied using azo dye, methyl orange (MO). MO dipped into the membranes shows a decrease in its concentration in both dark and irradiation conditions, but a stronger effect was observed in the case of irradiation. Nafion-TiO₂ and Nafion-GO_{SULF} performance were greater compared to the photocatalytic performance of fillers dispersed directly into the MO solution. Under irradiation, Nafion-TiO₂ degrades MO to form by-products. Nafion GO_{SULF} was very much efficient in the removal of dye, and even after 3 h UVA/blue lamp the concentration of residual MO was lower than 30 % from its starting value without forming any toxic by-products in the solution (Figure 11).

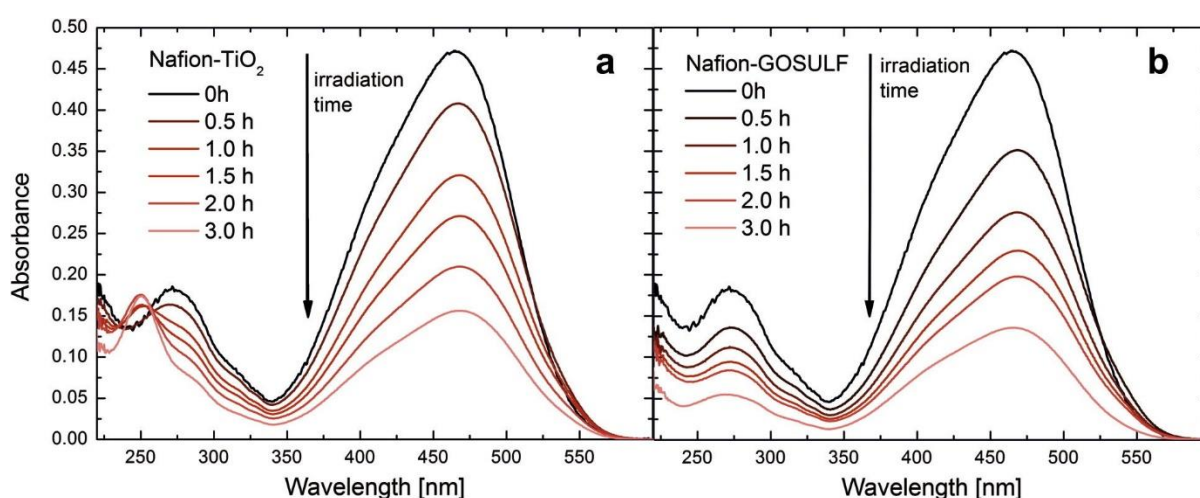


Figure 11 UV–Vis absorbance spectra of MO solution after irradiation for 3 h in the presence of (a) Nafion TiO₂ and (b) Nafion GO_{SULF}. Reproduced with permission from ref 86. Copyright 2015 Elsevier.

2.2.2. Graphene oxide/polymer hybrid membrane

GO consists of lamellar morphology with a thickness of about 1-30 μm with polar functional groups of carboxyl and hydroxyl-containing negative charged oxygen.⁹⁵ The presence of polar functional groups allows it to disperse stably in water without any addition of stabilizer.⁹⁶ The interlayer spacing of GO membranes can be easily tuned with the insertion of organic polymers such as water-soluble polyacrylamide. Polyacrylamide being polycation can be used as a binder and to synthesize hybrid membrane with negatively charged GO. Cheng and co-worker prepared GO/polyacrylamide membrane by following vacuum filtration method.⁴⁵ A stacked multilayer morphology consisting numerous channels in the cross-sectional layers of GO membrane were obtained. Further, the inter layer spacing was tuned by incorporating organic

polymer PAM. From the performance studies it was observed that water flux was inversely related with to the thickness of membranes and the retention was directly related with to the thickness of membrane. The 95.43 % of rejection rate was obtained by GO/ polyacrylamide membrane whereas pristine GO membrane showed 85.03 % rejection for RhB dye. Since, RhB is an anionic dye and the GO membrane is negatively charged, thus, it is difficult to adsorb anionic dye by GO membrane, but when it is hybridized with polyacrylamide, the surface negative charge reduces as a result of decreasing the inhibition effect for adsorbing anionic dye.⁴⁵

Wang and co-worker were successful in preparation of large lateral size (>200 μm) GO based nanofiltration membrane over a polyacrylonitrile (PAN) nanofibrous mat (GO/PAN) using vacuum filtration method.⁹⁷ Concentration of the GO solution could manipulate the thickness of uniformly arranged GO layers. Even at a low external pressure of 1.0 bar, the unique structure allows high water flux, and further support of the porous nanofibrous mat also contributes to water flux. Prepared GO/PAN membranes obtained 99% rejection for Congo red dye solution due to physical sieving and electrostatic repulsion effect. In addition, prepared GO/PAN membranes were also effective in removing salts, such as 56.7 % for Na_2SO_4 and 9.8 % for NaCl. GO nanofilms with 2D channels were fabricated over PAN by vacuum filtration method.⁹⁸ The GO/PAN displayed excellent water flux up to $65.1 \text{ Lm}^{-2}\text{h}^{-1}$ and high rejection of 99.8 % for desalinating by pervaporation at 90 °C. The GO/PAN composite membrane could treat even high saline water with salt concentration up to 100,000 ppm. Thus, hybrid GO membrane could be used for the brackish water desalination.

2.2.3. Graphene oxide/ nanoparticle hybrid membrane

Compared to other nanoparticles, silver (Ag) nanoparticle has shown promising performance in water purification as it limits the growth of microorganisms such as algae, bacteria, and fungi.⁹⁹ Research has focused on inducing its property by manufacturing it with a graphene-based membrane in the development of the antibacterial membrane for wastewater treatment. Yang and coworkers developed composite membranes of graphene oxide/silver nanoparticles (GO/Ag) and studied the size effect of Ag in nanofiltration performance.¹⁰⁰ The group has studied the membrane performance for the rejection of RhB dye by tuning the size of Ag nanoparticles (8, 20, and 33 nm) in the membrane matrix. The incorporation of 20 nm of Ag nanoparticle into the GO membrane showed the highest flux ($106.1 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$) with 97.73

% rejection compared to the other two sizes of Ag nanoparticle. The results were supported by both interlayer spacing and defect size of GO. The interlayer spacing increases with an increase in nanoparticle size, and the size of the defects decreases with an increase in the size of the Ag nanoparticle. Due to the solution diffusion effect, the rejection of RhB was inversely correlated with the feed concentration of the RhB solution. The reduced graphene oxide/gold (rGO/Au) hybridized membrane observed a similar observation.¹⁰¹ The rGO/Au membrane showed a water flux of $204.1 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$ with 99.79 % rejection for RhB dye solution. In addition, to the silver and gold nanoparticles, silica referred to as an excellent host for membrane matrix, owing to its high thermal and chemical stability.¹⁰² Electrostatic stabilization of the silica surface in the aqueous medium facilitates the dispersion of nanoparticles, allowing for high miscibility in the solution phase. Experimentally proven that GO/SiO₂ composite membrane synthesized by vacuum filtration method allows rapid passage to water molecules where membrane thickness and permeation were negatively correlated.¹⁰³ Prepared GO/SiO₂ composite membrane showed high water permeability ($229.15 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$) with excellent rejection rate of 99 % for RhB dye solution. From the above, mentioned literature it is worth to explore the potential of nanoparticles with graphene-based membranes to overcome the inherent limitation of low water permeability.

3. Conventional nanoparticles and polymeric membranes

Various conventional membranes such as polymeric, metal/metal oxide have been approached for water purification. However, their application till now limits with laboratory scale due to membrane fouling, high hydrophobicity, low fluxes which makes researchers more intriguing to overcome the disadvantages. Designing hybrid-based membranes based on polymeric, metal/metal oxide nanoparticle, and fibrous material could unlock its potential application in water purification on large scale. This section provides overview of hybrid nanomaterials which can be incorporated with graphene-based membranes to overcome the existing drawbacks of pristine graphene membranes. For instance, GO membranes have low operational time due to hydration effect, however chemical modification of GO with other nanomaterials reduces the swelling of GO membranes during operation. Additionally, the role of nanoparticle incorporation in developing synergistic properties in the polymeric and nanofibrous membranes is discussed briefly.

3.1 Nanofibrous membranes

Nanofibrous with one-dimensional morphology offers specialized characteristics like high mechanical strength, high aspect ratio, and large surface area, which could have a potential role in membrane technology like CNT-based membranes. The availability of large surface area to volume ratio is the key requirement for an efficient membrane. The electrospinning technique is the most common method to design nanofibrous membrane resulting in uniform pore size, counting significant characteristics of membranes.^{104, 105} In addition to that, electrospun nanofibrous membranes offer considerably elevated flux and high rejection rates. TiO₂ nanofibre membrane is designed by the electrospinning method with the incorporation of Ag nanoparticle¹⁰⁶ degraded methylene blue under solar light radiation. In the Ag/TiO₂ nanofibers the Ag nanoparticles were grown on the surface of nanofibre. The membrane was prepared from synthesized Ag/TiO₂ nanofibre by simply dipping it into a surfactant solution followed by sonication. After that, the suspension was filtered with the help of a vacuum filtration setup through a glass filter. The membrane was cleaned with distilled water followed by drying and pressurization. The Ag/TiO₂ displayed higher permeate flux as compared to pure TiO₂ and P25 deposited membrane, providing the same transmembrane pressure.

Proficient removal of fluoride ion from polluted water streams by employing carbon-based hybrid membrane made of amyloid fibrils-ZrO₂ nanoparticle (<10 nm) nucleated and grown in-situ over the surface of amyloid fibrils using chemical deposition method reported.¹⁰⁷ Amyloid fibrils functions as a template to grow ZrO₂ nanoparticle through in-situ reaction forming ZrO₂ nanoparticle coated amyloid fibrils. Later, hybrid membrane (referred to CAF-Zr) was synthesized by simply mixing hybrid nanocolloids along with activated carbon for purification and removal of fluoride ions from polluted water. The presence of carbon offers large surface area generating high permeability through the membrane. The hybrid membrane CAF-Zr exhibited an effective fluoride hunt with a removal efficiency of 95.5 % in a wide pH range (2-10). The presence of additional competitive anionic species such as SO₄²⁻/Cl⁻/NO₃⁻ could affect the adsorption efficiency vary slightly only at high concentration. A powerful selectivity of CAF-Zr towards fluoride against other competitive anions was achieved with a distribution coefficient K_d of 6820 mL/g even 180 times better than the commercial ion exchange resins (IRA-900) in wide pH range. The wide range adsorption capability of the CAF-Zr membrane was due to the strong affinity of small sized ZrO₂ nanoparticles. The membrane exhibited 99.5% removal efficiency equally in low (several mg/L) and high (up to 200 mg/L) fluoride concentrations, representative neutral tap-water, and different concentrations of acidic

wastewater were taken as supplying source. The membrane was employed with real untreated municipal tap water (~2.8 mg/L) under nonstop working mode and revealed ~1750 Kg water/m² membrane can be treated with maintaining water quality above the drinking threshold standardized by WHO with multiple reusability. A facile and efficient hybrid membrane based on metallic 2D molybdenum disulfide (MoS₂) nanosheets and 1D silk nanofibrils (SNF) for water purification was designed.¹⁰⁸ The hybrid membrane acquired a multilayer structure, similar to shell nacre, with a negative surface charge and sufficient interaction sites due to which it facilitates favourable separation performance for organic dyes and metal ions from water. The separation efficiency was altered by tuning feed ratio of two nanomaterials. When the membrane was subjected to filtration, because of the reducing ability of MoS₂ nanosheets, it reduces the precious metals ions into their respective nanoparticle, excluding further chemical and thermal treatment. Hence, the hybrid membrane is efficient for single-step removal and recovery of precious metal ions.

In addition to that, it displayed outstanding performance for the simultaneous purification and determination of dyes from water. The surface and cross-sectional SEM images of the hybrid membrane MoS₂-SNF after filtration along with EDS mappings and the adsorption capacities for metal ions confirms the MoS₂-SNF hybrid membrane has the adsorption capacity for all six metal ions. The three possible factors responsible in the separation mechanism are (1) complexation of heavy metal ions with exposed S atoms on the surface of hybrid membrane through soft-soft interaction because S-Mo-S sandwiched architect of MoS₂.^{109, 110} (2) Presence of different amino acids in silk nanofibrils forms metal-ligand pairs aiding adsorption of heavy metal ions.¹¹¹ (3) The negative surface charge of the hybrid membrane attracting positively charged metal ions through electrostatic attraction could further promote the adsorption.

3.2 Polymeric nanocomposite membrane

Polymeric material has been frequently utilized for membrane fabrication because of its excellent chemical and thermal stability, fine control of the pore-forming mechanism, higher flexibility, and low cost.¹¹² Polysulfone, polyvinylidene fluoride (PVDF), polyurethane (PU), Polyamide, sulfonated polyethersulfone (SPES), polyethersulfone (PES), polyethylene terephthalate (PET), polyester, polyacrylonitrile (PAN) and polytetrafluoroethylene (PTFE) are majorly investigated and fabricated as membranes for wastewater treatment due to these excellent properties.^{90, 113, 114} Amongst all the polymer present, polysulfone possess highest

mechanical strength and maximum resistance to temperature.^{90, 113} Even if polymeric membranes comprise these characteristics and become a preferential choice for membrane fabrication, these have certain pitfalls hindering its efficient performance. The drawbacks faced by polymeric membranes are exposure to biofouling, low fluxes, high hydrophobicity, membrane crack, pore blocking, and low mechanical strength which could be overcome with the incorporation of various nanoparticle or nanotubes developing synergistic effect, strength, selectivity, permeability, and enhances their hydrophilicity.¹¹⁵ The inclusion of nanoparticles to the vicinity of polymeric membranes has become a recent trend for developing membranes. For instance, when PVDF membranes are incorporated with silica nanoparticles, the temperature resistance of the membrane increase with greater selectivity and diffusivity.¹¹⁶ Zinc oxide (ZnO) incorporated chitosan membrane developed strong mechanical properties with high antibacterial activity.¹³ Silica nanoparticle is incorporated into polysulfone demonstrated an increase in the gas permeability.¹¹⁷ Higher porosity, a low rejection in flux and a pseudo-steady-state permeability of polyethersulfone membranes were achieved by incorporating aluminium oxide nanoparticle.¹¹⁸ Whereas silica nanoparticle incorporated into polybenzimidazole membranes delivered greater selectivity in the gas separation with enhanced permeability.¹⁴

3.2.1 Incorporation of iron oxide nanoparticles

Iron, the most omnipresent and abundantly available element among all transition metals in the earth's crust and is the backbone of material research. Iron oxide (FeO) nanoparticle is referred to as one of the promising materials for water purification due to its high availability, surface area, magnetic properties, catalytic activity, low cost, low or no toxicity, and hydrophilic nature. Polyethersulfone (PES)-FeO composites nanofiltration membrane used for removal of copper.¹¹⁹ The membrane showed the highest Cu removal (92 %) with the presence of 0.1 wt.% of FeO. The presence of ethylenediaminetetraacetic acid (EDTA) polyethersulfone (PES)-FeO displayed the best result at 0.1 wt.% FeO. Shahwan et al. studied polysulfone (PSf) membrane and achieved low membrane fouling because of the development of bio-films.¹²⁰ Incorporation of FeO nanoparticles had drastically improvised the eradication of hydrophobic contaminants and antifouling in the seawater treatment. Iron-carbon hybrid materials have been successfully used for removal of organic contaminants from water.¹²¹

3.2.2 Incorporation of silica nanoparticles

Silica referred to as an excellent host, owing to its thermal and chemical stability, possess large surface area, stable dispersion in an aqueous medium, and is inert.¹²² Electrostatic stabilization of silica surface in the aqueous medium facilitates nanoparticle dispersion enabling high miscibility in the solution phase. Wastewater consisting of oil is difficult to separate using polymeric membranes when present on large-scale since the polymeric membranes are easily fouled with oil. Research is going on to alter the polymeric membranes, so that it could be employed on a large scale for wastewater treatment containing oil. The excellent physicochemical stability, oxidation resistance, and chlorine makes polysulfone a good candidate for membrane material. However, their surface energy is low with strong hydrophobicity resulting in weaker anti-fouling ability. Numerous efforts have been put to improve the hydrophilicity of membrane.¹²³⁻¹²⁵ Among which inorganic oxide doping to polymer to produce an organic-inorganic composite membrane solves the issue. Ce-doped non-stoichiometric nano-silica (modified nano-silica) and combined it with PSF to engineer a new type of composite membrane was developed.¹²⁶ The composition of silica nanoparticle was kept constant 10 wt. % in PSF to differentiate the performance and its effect of modified and unmodified silica nanoparticle, without incorporating nanoparticle into PSF membranes. The addition of nanoparticle enhanced the membrane performance concerning its permeability, mechanical strength, etc. However, the concentration of nanoparticle should be limited, as increasing the weight of nanoparticle in the membrane could be harmful in membrane activity. Average transmembrane pressure (TMP) is 0.05 MPa; a collection of permeate to be examined and undertaken less than 90 min after the operation.

A comparative study of separation efficiency for membranes synthesized with different casting solution. Modified nanosilica/PSF composite membrane when employed, permeate flux flattened out after 90 min is 80 L/(m²h) and pure water flux levelled off after 90 min is 120 L/(m²h) during oil-water separation procedure. Addition of modified inorganic oxide nanoparticle with the help of novel Ce-doped nonstoichiometric, the tensile strength could be improved to a certain degree. Reports propose the intermolecular forces between polymeric chain and incorporated inorganic oxide nanoparticles dispersed uniformly in PSF partly checks the polymeric chain resulting in the sequential improvement of the membranes tensile strength. In addition to that, the inorganic oxides are very well packed by polymeric chains twisting mutually that further enhance the membrane's tensile strength.¹²⁷ The hydrophilicity of the

membrane is enhanced with doping of inorganic oxide nanoparticle because of the presence of surface hydrophilic hydroxide radicals on the inorganic oxide nanoparticle.¹²⁸

3.2.3. Incorporation of silver nanoparticles

Silver (Ag) has been most remarkable for designing tableware and coinage from ancient times because of its high resistance to corrosion, low toxicity, and antibacterial property.¹²⁹ Moreover, Ag nanoparticle has shown promising performance in water purification since it restricts the growth of microorganisms like algae, bacteria, and fungi. Research has been focused on inducing its property in the growth of the antibacterial membrane for wastewater treatment by fabricating it with polymer membrane. The interaction of silver with sulphur and phosphorous, mainly with thiol groups (S-H) which mainly present in cysteine.¹³⁰ The Ag nanoparticle association with thiol group destructs the bacterial proteins, dimerize the DNA, and affects the transport chain of electrons.¹³¹ Various polymer membrane has been incorporated with Ag nanoparticles such as polyamide, Poly(2-ethyl-2-oxazoline), cellulose acetate, and polyimide to improve the membrane performance.¹³²⁻¹³⁴ Li et al. produced a superhydrophobic/superoleophilic NF membrane by incorporating Ag nanoclusters into the polyacrylonitrile (APAN) nanofibers.¹³⁵ The fabricated APAN-Ag membrane displayed a high water contact angle of $162.4 \pm 1.9^\circ$, a low oil contact angle of 0° , a self-cleaning surface holding water contact-angle hysteresis of $3.4 \pm 0.9^\circ$, and a smaller water-adhesion propensity. The synthesized APAN-Ag membrane efficiently separated oil/water mixtures in both hypersaline and at different pH medium. Zdrovet and co-workers reported impregnation of 0.9 wt.% nAg into polysulfone does not affect the permeability or surface charge of the membrane. However, the composite membrane showed an improved hydrophilic property as compared to pristine polysulfone membrane with 10 % drop in contact angle.¹³⁶ The asymmetric arrangement of silver-impregnated membranes was evident. Change in the membrane structure with impregnation of nAg couldn't be identified visually. Still, its presence adversely affected in the number of growths of *Escherichia coli* on the membrane surface after filtrating out the dilute bacteria suspension, which is indicated by the number of colonies forming units (CFU) per 9.35 cm^2 membrane coupons.

Even incorporation of Ag nanoparticle into polymeric membrane exhibits a huge number of advantages still researcher hesitate its use in wastewater treatment because of its high reactivity which is a nanoparticle characteristic. The presence of excessive Ag nanoparticles can develop

an environmental and health risk.¹³⁷ When silver nanoparticles are incorporated in the polymeric membrane for drinking water filtration system, it may cause leaching of Ag nanoparticles in the drinking water. The leaching out of Ag nanoparticle could happen due to improper impregnation technique or due to any physical damage. Further, exposure to the high concentration of Ag for a longer period could result in diseases like argyria, a blue-grey discoloration of the skin and other organs.¹³⁸ Reports also depicts Ag nanoparticle could damage the DNA and apoptosis in mouse embryonic stem cells and fibroblasts.¹³⁹ List of various studies and their performance is tabulated in Table 2 for nanoparticles incorporated membranes.

Table 2: Summary of various nanoparticles incorporated membranes and their performance.

Name of the experiment	Materials used	Method of preparation	Water flux (LMH)	Rejection (%)	Reference
Polyethersulfone membrane enhanced with iron oxide nanoparticles for copper removal from water: application of new functionalized Fe ₃ O ₄ nanoparticles	Fe ₃ O ₄ nanoparticles; Support: PES	Non-solvent induced phase inversion method	41.5	92 % Cu	119
Zirconia nanofibers incorporated polysulfone nanocomposite membrane: Towards overcoming the permeance-selectivity trade-off	ZrO ₂ nanofibers, Support: PSf	Non-solvent induced phase inversion method	339.3	84 % BSA	140
Effect of nano-TiO ₂ loading in polysulfone membranes on the removal of pollutant following natural-rubber wastewater treatment	nano-TiO ₂ ; Support: PSf	Non-solvent induced phase inversion method	2.1	14.03 % TDS; 87.88 % COD; 99 % Turbidity	141
Preparation of a Novel Polyvinyl Chloride (PVC) Ultrafiltration Membrane Modified with Ag/TiO ₂ Nanoparticle with Enhanced Hydrophilicity and Antibacterial Activities	Ag/TiO ₂ , Support: PVC	Non-solvent induced phase inversion method	58.6	98.6 % Lanasol blue 3R dye; 98.02 % BSA	142

Novel poly(vinyl alcohol) nanofiltration membrane modified with dopamine coated anatase TiO ₂ core shell nanoparticles	TiO ₂ nanoparticle, Support: PVA	Non-solvent induced phase inversion method	27	80 % Microorganism; 85 % Sulphate; 70 % Chloride;	143
Synthesis of polyethersulfone (PES)/GO-SiO ₂ mixed matrix membranes for oily wastewater treatment	SiO ₂ /GO Support: PES	Non-solvent induced phase inversion method	2561	30% Oily-wastewater sample containing Ca, Mg, and K ions	144
Biocompatible Fe ₃ O ₄ @SiO ₂ -NH ₂ nanocomposite as a green nanofiller embedded in PES–nanofiltration membrane matrix for salts, heavy metal ion and dye removal: Long–term operation and reusability tests	Fe ₃ O ₄ /SiO ₂ -NH ₂ nanocomposite Support: PES	Non-solvent induced phase inversion method	65	93 % Cd(II); 97 % MR dye	145
Electrospinning superhydrophobic–superoleophilic PVDF-SiO ₂ nanofibers membrane for oil–water separation	SiO ₂ nanofibers, Support: PVDF	Electrospinning method	1857 ± 101	99 ± 0.1 % Oil-water separation	146
Facile Immobilization of Ag Nanocluster on Nanofibrous Membrane for Oil/Water Separation	Ag nanocluster; Support: APAN	Electrospinning method	447.5 ± 100.3	99 ± 0.1 % Oil-water separation	135
Polyacrylonitrile Nanofiber Membrane Modified with Ag/GO Composite for Water Purification System	(Ag/GO); Support: PAN	Electrospinning method	390	30 % Bacteria	147

[PES: Polyethersulfone; PSf: Polysulfone; PVDF: Polyvinylidene difluoride; PVA: Polyvinyl alcohol; APAN: Activated polyacrylonitrile; PAN: Polyacrylonitrile; Ag: Silver; GO: Graphene oxide; Cu: Copper; Cd (II): Cadmium (II) cation; Ca: Calcium; Mg: Magnesium; K: Potassium and BSA: Bovine serum albumin]

4. Current challenges and future research directions

The graphene-based membranes for wastewater treatment have been successfully synthesized using different techniques such as casting/coating method, layer-by-layer self-assembly method, or vacuum/pressure-assisted method. However, there exist certain challenges that are being prevailed by continuous research and study. In the GO membranes reduction of interlayer spacing and maintenance of the structural stability at a particular level for the exclusion of small-sized ions is the major challenge. Further, maintaining the same spacing without swelling of GO membranes when dispersed in the aqueous medium is another concern that could limit its potential application for ion filtration.

Current efforts for designing the ultrathin separation layer of GO membranes enhance its application scale from water separation to organic solvent nanofiltration, including gas separation. In the pressure filtration method, effective desalination of water via GO membranes is hard to achieve, claiming a requirement of sub nanosized channels in GO membrane structure. Hence, pore channels of GO membranes should be carefully prepared so that it can restrict the small-sized ions passage through it. Reproduction of GO nanoporous membranes revealed that they it allows fast convective water flow through the channels opposing to the slower solution-diffusion water transport mechanism in RO membranes. While significant progress has been made on the separation mechanisms of graphene-based membranes and great potential for their liquid and gas separation applications has been demonstrated.

There are few significant challenges before graphene-based membranes are completely commercialised.

- a) Firstly, the graphene-based membranes long-term stability remains a major concern. For practical applications, the testing period for the stability of graphene-based membranes is only from several hours to a few days, which is far below the duration for industrial applications. The long-term stability of the graphene-based membranes need to be further studied.
- b) Secondly, graphene-based membranes must be resilient towards backwash and chemical cleaning as these are applied to overcome membrane fouling. However, there are still limited graphene-based membranes that can withstand backwashing and chemical cleaning.
- c) Finally, it is still challenging to stabilise the effective separation of graphene-based membranes in liquid separations. It has been reported that d-spacing of graphene

nanosheets changes during operation due to the hydration effect generated by water molecules.

Further, in CNT membranes have some inherent limitations such as poor dispersion, high cost, large scale production, functionalization, exact loading of material, preservation of alignment, and integration of CNTs materials with support is still needed to outshine. A chemical oxidation process is followed for functionalization of CNTs that could enhance the adsorption capacity and dispersity of CNTs. However, this requires an extreme reaction environment that could result in the production of chemical waste. Further, it ruptures the sidewalls and tips of CNT that could affect the structural stability as well as electrical and thermal property.

Hence, studies are needed to develop a novel approach for facile synthesis of graphene-based membranes that could be inexpensive and large-scale production. A deeper understanding of structural properties and mechanisms for the elimination of water pollutants should be investigated more. Further, the toxicity of membrane should be studied thoroughly to avoid health hazard issues. The real-time application and utilization of graphene-based membranes for water purification can be achieved with future research.

- a) Functionalization of nanoparticle or design hybrid mix-matrix membranes for enhancing water treatment performance.
- b) Adapt novel routes for utilizing renewable sources for generating cost-effective graphene-based membranes.
- c) Integration of conventional techniques with graphene-based membranes for advanced water treatment process.

It is necessary to develop a method with scalable and reproducible membrane fabrication. Membranes with accurate material load is also a challenge and can be overcome with a proper strategy that can integrate the graphene materials with other matrix or nanoparticle developing synergistic effect and high performance in the water treatment process. Overcoming these drawbacks will make graphene as a potential candidate for water and wastewater treatment.

5. Summary

In this review, we explicitly discuss the achievements of graphene-based membranes. The rapid interest and research achievements made graphene membranes is the key material for the water treatment process. Here, we highlight various approaches in the development of graphene-based membranes, from fabrication techniques to functionalization and hybridizing methods. GO separation mechanism and transport channels within the membranes, including size

exclusion, Donnan exclusion, and adsorption have been discussed briefly. Considerable growth in designing CNT-based membranes (VA-CNT, MM-CNT, HA-CNT, and CNT-BP) offers excellent achievement in the membrane characteristic, selectivity, and performance ranging its potential application from liquid separation to gas separation. Furthermore, other conventional membranes comprising polymeric materials (PSf, PAA, APAN, PVDF), metal/ metal oxide nanoparticles such as TiO₂, FeO, silica nanoparticle, Ag nanoparticle, ZnO have been discussed. However, pristine polymeric membranes performance limits in their industrial application. Alteration of polymeric membrane material with the incorporation of nanoparticle forming complex and offers certain advantages such as high selectivity, high diffusion rate, permeability, better tensile strength, low fouling, resistance to high temperature, and pressure as compared to the pure polymeric materials. Nevertheless, these materials are far from the results of graphene-based membranes for water purification, and thus further research and understanding are needed for advanced membrane materials.

Author Contributions

† Prangya Bhol and Sudesh Yadav contributed equally. The review has been written through the contributions of all authors. All authors have approved the final version of the review.

Conflicts of interest

The authors declare no competing financial interest.

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