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Review

A review of performance improvement strategies for graphene oxide-based and graphene-based membranes in water treatment

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ABSTRACT

In the past few decades, due to the rapid development of industry and the rapid growth of population, emissions of pollutants to the environment have increased dramatically, and the demand for drinking water is also increasing. Water treatment is a matter of concern because it is directly related to the health of humans and wildlife. Graphene and its derivatives have potential applications in seawater desalination and wastewater treatment due to their unique pore structure and ionic molecular sieving separation capabilities. Graphene, graphene oxide (GO), and reduced graphene oxide (rGO) can be formulated into nanoporous materials and composites with tunable properties that can be optimized for water filtration. Methods for perforating graphene include ion etching/ion bombardment and electron beam nanometer engraving, which are briefly introduced in this paper. Graphene-based composites further expand the capabilities of graphene in seawater desalination and wastewater treatment, by introducing new features and properties. In this review, the performance improvement of graphene-based separation membranes in decontamination and desalination in recent years is reviewed in detail. This review focuses on improving the performance of graphene-based membranes for separation, decontamination, and seawater desalination applications, by discussing how various modifications and preparation methods impact important performance properties, including water permeance, selectivity, rejection of solutes, membrane mechanical strength, and antifouling characteristics. We also discuss the outlook for future development of graphene-based membranes.

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Introduction

Two-dimensional (2D) materials with excellent chemical stability, advantageous dimensional selection characteristics and high aspect ratio are often used in the manufacture of filtration membranes. [1] Graphene is a two-dimensional material with carbon atoms in the sp^2 hybridization, which has extremely high thermal conductivity and stiffness, and is able to reconcile the contradictory properties of brittleness and ductility. [2, 3] Graphene oxide (GO) is an oxidized derivative of graphene, which maintains the unique two-dimensional structure, and is rich in oxygen-containing functional groups, such as hydroxyl, epoxy, and carboxyl groups. [4] GO has chemical stability and convenient size control characteristics [5], high mechanical strength, and chemical adaptability. [6, 7] GO has been widely used as a material for membrane manufacture. [8] GO-containing membranes have been proposed for a wide range applications, such as water desalination [9–14], dye removal [15–19], oil–water separation [20–22], gas separations [23–27], luminescence [28], and electrochemical applications [29–31]. Graphene materials can perform as molecular sieves if pore sizes can be controlled through perforation or through preparing intercalated layers and composite membranes. [5]

High-performance membranes for water purification should achieve high flux, high rejection, high stability in aqueous media, mechanical strength, and high fouling resistance. GO membranes have desirable ion selectivity, but suffer from poor structural stability and low flux. [32] Their stability can be improved through strong interactions, such as chemical cross-linking, but these modifications greatly affect the water permeability of dense GO membranes. On the other hand, GO membranes with weak and stable interactions (hydrophobic or π–π interactions) may not be strong enough to withstand actual water filtration operation. [11] Therefore, combining GO with nanoparticles and polymer carriers to prepare GO-based composite membranes is an attractive approach. [33–35] In fact, these strategies can improve the water flux while also improving mechanical strength and preserving the screening performance of the GO membrane. [36–38]

In our previous reviews [39–42], we summarized the status of GO-based composite membranes and the manufacture and application of graphene-based materials in membrane science. We also provided a summary of the theory and simulation of restricted substance transport. As sketched in Fig. 1, a single layer of perfect graphene can be used to form GO and porous graphene composites by a variety of strategies. [43] Methods for perforating graphene include ion etching/ion bombardment and electron beam nanometer engraving, which are briefly introduced in this paper. Graphene-based composites further expand the capabilities of graphene in seawater desalination and wastewater treatment, by introducing new features and properties. Graphene-based composites contain metal–organic frameworks (MOF), nanotubes and other nanomaterials intercalated into layers of graphene oxide (GO) and can achieve the effect of sieving molecules of different sizes by regulating the layer spacing of GO. Composites with polymers can improve the membrane strength and desalination performance. The performance of GO-based membranes can be improved by adjusting the membrane spacing and membrane surface functional groups. This article reviews the performance improvement of GO-based composite membranes for desalination and decontamination applications. The most important forms of GO-based membranes include composites of GO with nanoparticles and polymers.

Improved strategies for preparation of graphene separation membranes

Graphene-based materials include both nanoporous graphene and membranes in which GO and various materials are compounded with each other. [44] Based on the resulting microstructure, graphene-based membranes can be broadly classified into three types, as shown in Fig. 2.

The preparation technology of graphene is relatively mature, with low cost and high yield, so that graphene can be widely used. There are many ways to prepare graphene, such as liquid-phase exfoliation [45], mechanical exfoliation [46], epitaxial growth [47], chemical vapor deposition, and decomposition of carbon nanotubes to obtain two-dimensional graphene sheets. [48] [49] In recent years, the most commonly used method for preparing large-area high-quality graphene is chemical vapor deposition (CVD). CVD uses hydrocarbon gas as the main carbon source to grow graphene on a metal substrate.

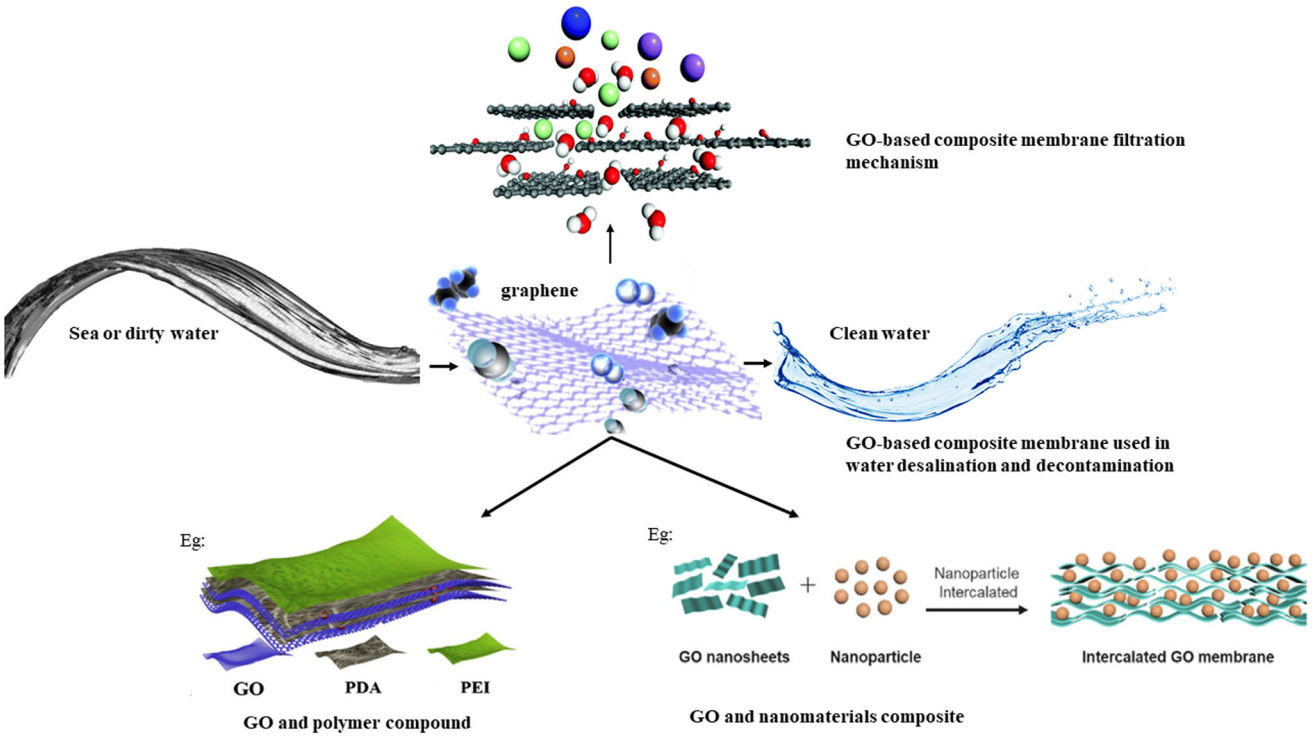

Figure 1 Schematic diagram of graphene-based materials used for water desalination and decontamination.

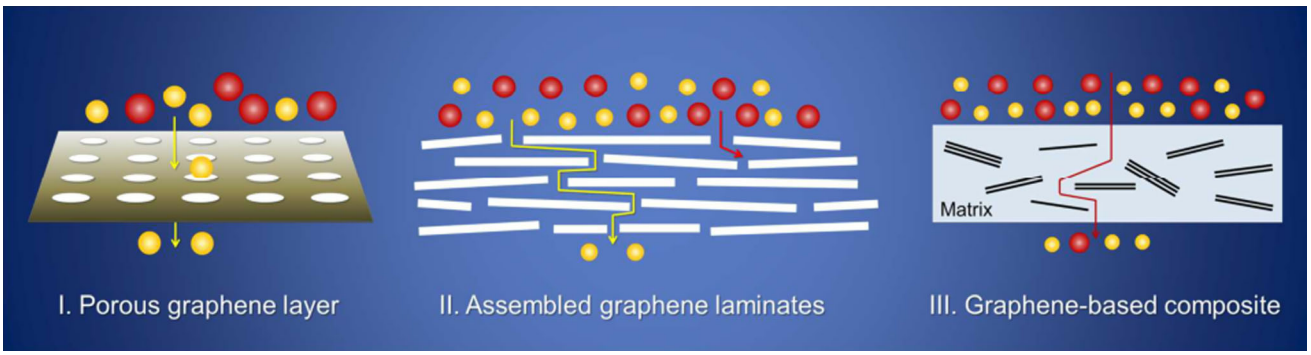

Figure 2 Main types of graphene-based membranes: type I. single porous graphene layers; type II. assembled graphene laminates; type III. graphene-based composites. [5].

Different reaction pressures and temperatures are selected according to the different properties of the carbon source to prepare large-area high-quality graphene. [50, 51]

The sp^2 electronic structure of graphene provides a high electron density and enables graphene to strongly repel both water molecules and many other molecules in the gas phase. [52] Therefore, there are basically only three methods to achieve molecular sieving for graphene-based membranes as shown in Fig. 2. For type I, the graphene sheet is perforated to form nanopores, and the sieving of different molecules can be achieved by controlling the pore size. For type II, graphene sheets are stacked or laminated. For type III, the graphene serves as a composite filler combined with other matrix materials. The filtration mechanism of the latter two methods is the same, both of which achieve the sieving of different molecules by changing the interlayer distance of the graphene-based membrane. Because GO contains more oxidized groups, is more hydrophilic, and has improved chemical properties, GO is also commonly used to form the type II and type III composite materials. [53]

Porous graphene membranes

By controlling the introduction of defects into graphene through physical and chemical methods, uniform nanoscale pores can be formed on the surface of the graphene membrane, resulting in excellent selectivity in gas mixture separation, seawater desalination, and other applications. In addition, porous graphene, with its ultra-thin membrane thickness and unique pore structure, obtains a very high permeability compared to other materials. The pore size is a critical design parameter for desalination applications. As shown in Fig. 3a, a suitable pore size can exclude ions, allowing only water to pass through. [54] In recent years, several methods of introducing nanopores into graphene have been studied and reported.

Ion etching/ Ion bombardment

For practical applications permeability and selectivity must be imparted by introducing many pores at sufficient density acting in parallel over macroscopic areas of graphene. To form porous membranes by ion etching or ion bombardment, graphene first undergoes ion bombardment to form defects and is then oxidized and etched. The etching reagents preferentially corrode the defects, so as to achieve controllable pore size. [55] Figure 3b shows the simple process of preparing nanopores. Kemal et al. [57] developed an effective method of drilling quickly without etching through physical methods. As shown in Fig. 4, the researchers first overlap the two graphene layers by a special method and then drill using a focused ion beam. This method is fast and accurate and also prevents the formation of cracks.

Block copolymer lithography

Bai et al. [56] used block copolymer photolithography to prepare graphene nanomeshes with high-density nanohole arrays, which can withstand large currents and have improved electronic properties. Figure 3c shows the preparation process of the nanomesh. The initial preparation of graphene sheets is similar to CVD. The graphene sheets are then placed in a template, and holes are etched by oxygen ions. It is worth noting that in this method, the size of the graphene network only depends on the size of the graphene nanosheets, and theoretically, a large amount of porous graphene can be prepared.

Electron Beam Nanosculpting

Electron beam nanoengraving can also be used to prepare nanoholes. In this method, a suspended multilayer graphene sheet is nanoengraved by a focused electron beam in a transmission electron microscope (TEM), which can prepare nanoholes in a short time. [58] Figure 3d is a TEM image of a nanohole engraved by an electron beam, with a diameter of about 8 nm and a thickness of about 2 nm. Conductivity measurements on membranes prepared with electron beam methods demonstrate that ions can pass through the pores of graphene. [59]

Assembled graphene or GO laminates

A more common method than perforation is to use stacked GO nanosheets to form membranes. In this method, the interlayer spacing between the sheets is controlled to achieve molecular sieving. The thickness of the graphene nanoflake itself is only on the order of a single atom, but the tile size is as high as tens of microns. When the graphene is oxidized to GO, its original sp^2 structure is destroyed. This causes the GO layers to adopt wrinkles, making them easier to stack with increased layer spacing, [4, 60], resulting in the type II membrane shown in Fig. 2. When the GO membrane is used for water treatment, this layer spacing plays a role in sieving molecules. Furthermore, the charge on the GO can repel charged dyes and other pollutants. [61]

Vacuum-assisted filtration

The vacuum filtration method, shown in Fig. 5a, is the most widely used method for preparing graphene-based membranes. In this method, a solution of graphene nanosheets is forced through a microfiltration support membrane using a filter suction apparatus under vacuum. [62] The vacuum suction method produces a thin membrane with a layered structure of ordered lamella, with a very high degree of orientation. The π–π interactions between graphene sheets provide mechanical stability to the resulting membrane. When GO is used, the resulting membrane contains a very high density of oxygen-functional groups. The vacuum suction method is

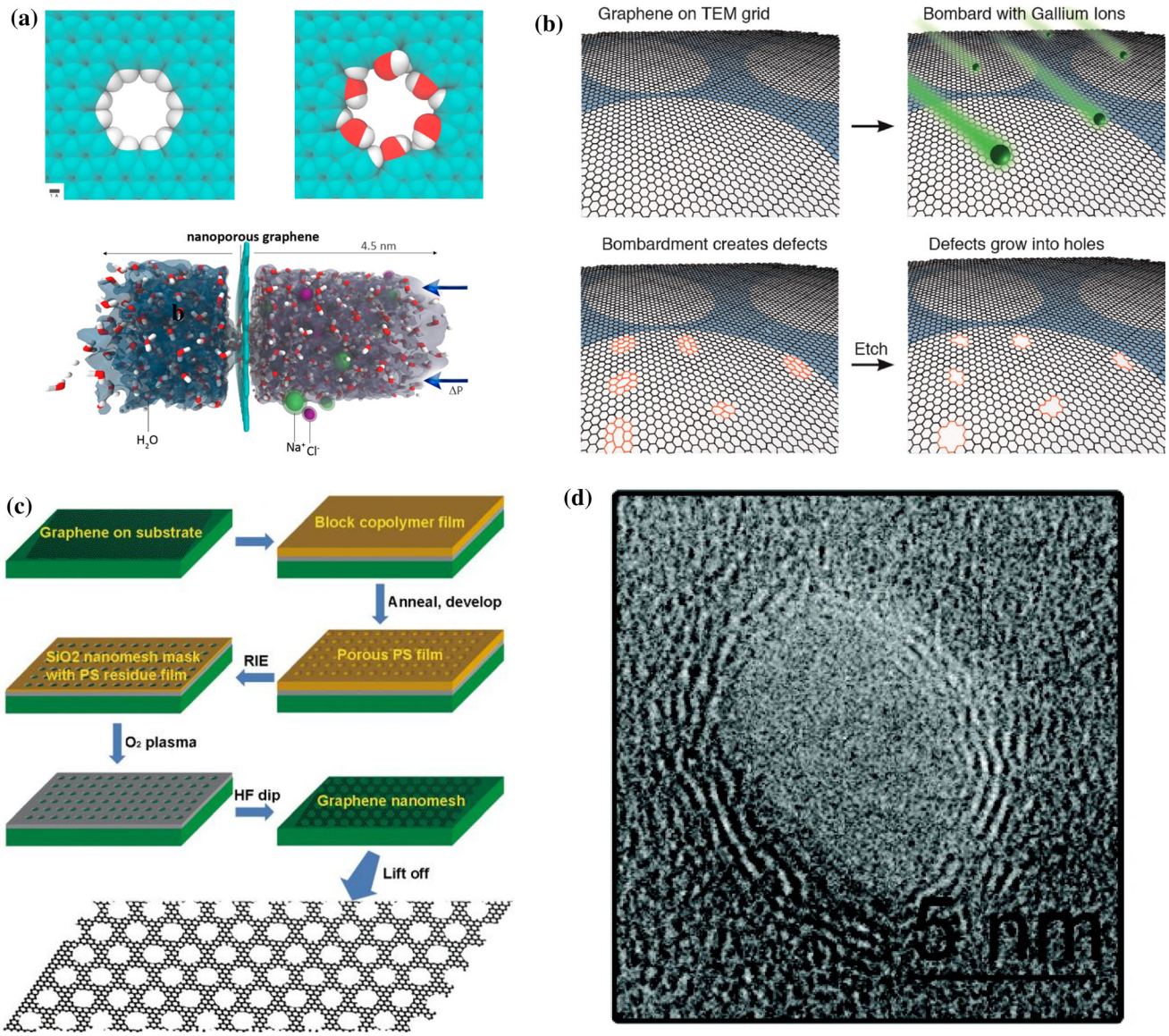

Figure 3 Schematic diagram of porous nanofilm sieve separator. **a** [54] Preparation of controllable graphene nanopores by ion bombardment and etching. **b** [55] Schematic of fabrication of a graphene nanomesh. **c** [56] TEM image of nanohole engraved in graphene by an electron beam. **d**.

very simple to perform and can produce membranes ranging in thickness from transparent membranes only a few nanometers thick to membranes that are tens of microns thick.

Layer-by-layer assembly

Layer assembly methods include the layer-by-layer (LbL) self-assembly and Langmuir–Blodgett (LB) self-assembly methods. High-quality and large-area graphene sheets can be assembled by both LbL and LB methods. In the LbL method, layers are deposited sequentially and are stabilized by hydrogen bond, electrostatic, dipole–dipole, or covalent bond interactions. Because the surface of GO is rich in negatively charged functional groups, LbL assembly using GO can be achieved by combining GO with cationic small molecules and with cationic polymers. GO membranes prepared by the LbL method have high toughness and elastic modulus. Different microstructures of the resulting GO sheets are obtained depending upon the forces used to stabilize the LbL assembly (Fig. 5b). [63] LB technology has also been proposed for the production of GO sheets

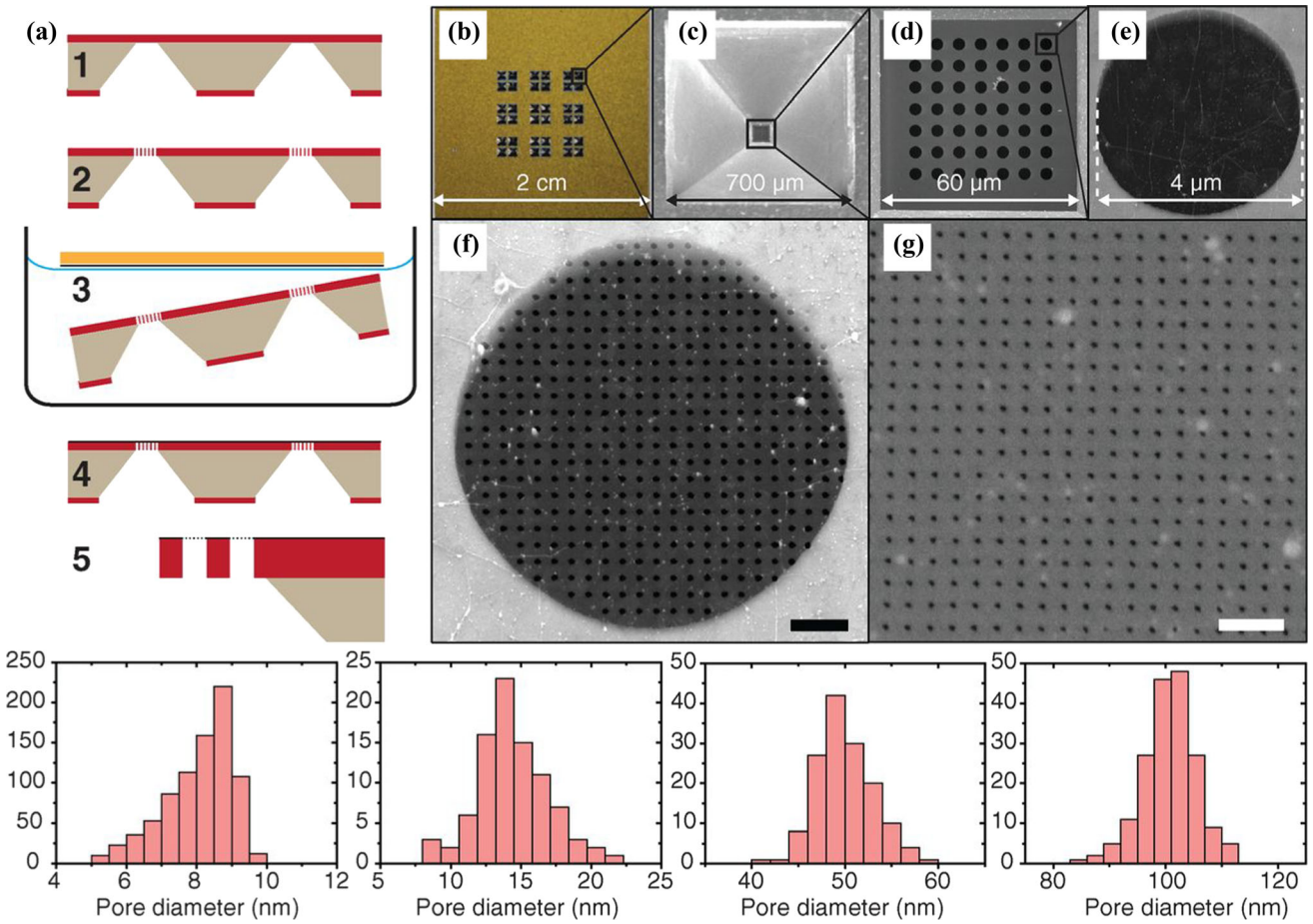

Figure 4 Membrane fabrication and pore diameter distribution, achieved using drilling with a focused ion beam. [57].

and results in membranes that contain fewer wrinkles [64, 65].

Continuous centrifugal casting (CCC)

Continuous centrifugal casting (CCC) is an efficient method for preparing GO nanosheets. Zhong et al. prepared dense GO membranes in a short time through CCC. The membranes produced have a thickness on the order of 10 μm, which is generally thicker than the membranes produced by other methods. Figure 5a depicts the CCC process for preparation of GO nanosheets. The centrifugal force and shear force generated during the rotation process are transferred into the GO dispersion, so that the GO membrane is compressed both in the radial direction and the tangential direction, thereby obtaining a smooth and dense GO membrane (Fig. 5d, e). [66]

The methods described above may all be classified as lamination methods, as they are various approaches for generating laminated graphene or GO structures. These methods have shortcomings with respect to their ability to provide control of the pore structure and surface chemistry. GO membranes formed by lamination methods are susceptible to disintegration in contact with aqueous environments, due to poor bonding between GO sheets within the membrane. Several methods described below have been developed to further enhance the stability, improve the mechanical properties, and/or provide greater control of the pore size.

Weak reduction

Weak reduction methods change the surface chemistry of GO, by reducing the oxygen-containing functional groups, to form rGO. This moderates the hydrophilicity of the membrane. Weak reduction also inhibits the dissociation of the membrane in solution and thereby increases membrane stability. However, reduction can also damage the membrane, so appropriate reductants must be carefully chosen. [67]

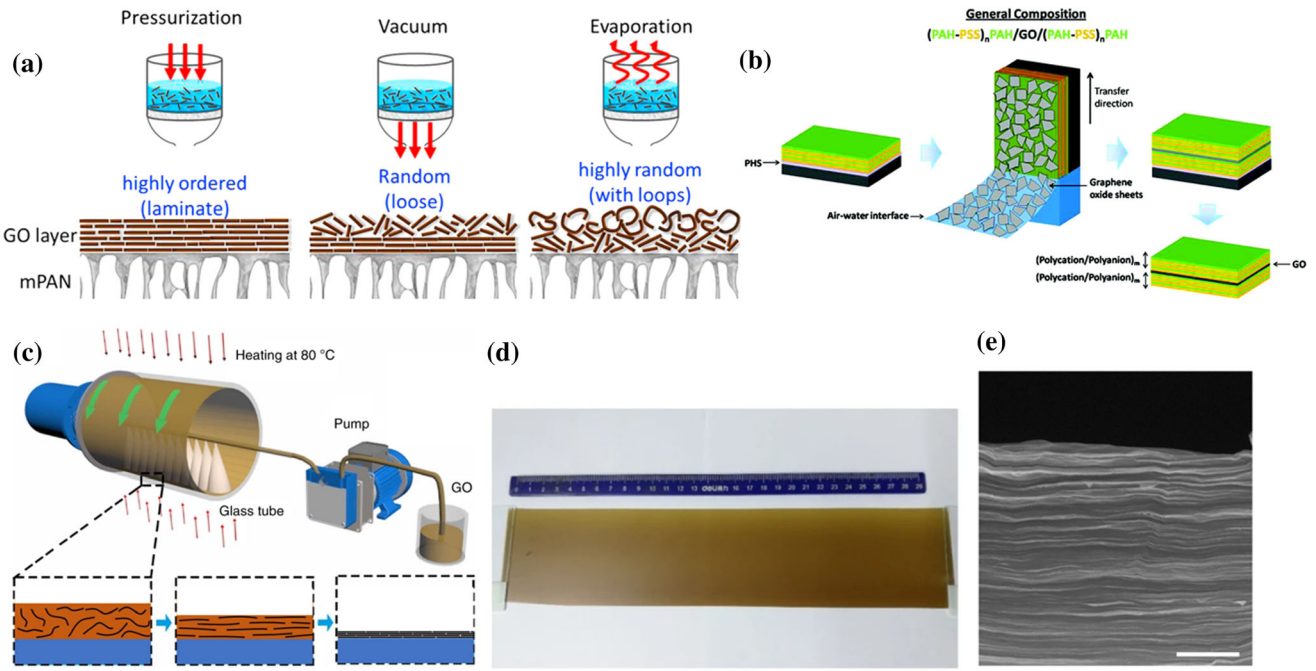

Figure 5 Schematic diagram of GO membrane preparation by vacuum-assisted filtration **a** [62]; schematic representation of fabrication and assembly of freestanding GO-LBL membrane **b** [63]; schematic of the CCC production process **c**; a GO film with a thickness of ~ 100 μm and size of ~ 30 × 10 cm^2 **d**; cross-sectional scanning electron microscopy (SEM) image of a GO film, showing highly aligned and compact layered structure **e**. [66].

Proper weak reduction treatment can not only increase the number of sp^2 regions in GO and thus improve the water flux of the membrane, but also effectively improve the structural stability of the membrane upon exposure to aqueous solutions.

Cross-linking methods

Cross-linking can suppress GO membrane swelling and dissociation in solution and improve structural stability. Cross-linking methods include both covalent and non-covalent methods. Covalent cross-linking can enhance the stability and sieving ability of graphene-based membranes, while non-covalent cross-linking generally helps the dispersion of graphene-based materials [68–70]. Non-covalent cross-linking can maintain the inherent properties of graphene-based materials, and the modification of graphene-based materials is mainly achieved through the interaction of anion and cation, hydrogen bonds, surfactants, and stacking interactions [68]. Covalent methods include the use of UV activation chemistry, small molecule cross-linking agents and thermally induced reactions, etc. [71]. Covalent cross-linking can cause defects in graphene, reduce the inherent properties of graphene-based materials [72], and bring many different properties to graphene-based films. For example, the hydrophobicity of the graphene-based film can be greatly enhanced by the amidation reaction of the coupling agent [73], and the graphene-based material functionalized by amine and carboxyl groups is covalently attached to the polymer matrix containing anhydride; the film is realized Super hydrophilic. [74] Or the conjugated structure modification of graphene itself realizes the preparation of amphiphilic materials. The coordination of divalent metal ions with oxygen-containing functional groups in GO can greatly improve the mechanical properties of the membrane [75]. And, Cross-linking using small molecules can reduce the internal concentration polarization that occurs during forward osmosis and can greatly improve the flexibility of the membrane synthesis process. [76] Thermal annealing can induce cross-polymerization of acetylene groups. [77] When heated, the ethynyl group has an exothermic transformation, and the isoimide in the ethynyl group is rearranged into imide. The mechanism of cross-linking reaction is very complex, most of the acetylene dimer becomes enyne structure, and a small part trimerizes to form

benzene ring. [78, 79] Typically, cross-linking increases the solvent stability, but has no effect on gas separation performance [80].

Large molecule intercalation

Since GO nanosheets have very high specific surface area, the electrostatic repulsion between layers can generate strong destabilizing forces within GO membranes. The addition of large molecules that intercalate between layers can effectively reduce the electrostatic repulsion within the GO membrane, thereby stabilizing the structure. Large molecule intercalation can also be used to modify membrane performance by controlling interlayer spacing to enhance molecular separation [81].

Graphene-based and GO-based composites

The combination of GO with nanoparticles to form composite membranes can achieve both excellent permeability and selectivity. The oxygen-containing functional groups in GO can be used to bind nanomaterials between layers of GO through coordination forces, forming submicron GO composites with excellent mechanical stability and precise molecular sieve properties [82]. Polymers can also be used to adjust layer spacing in GO membranes. GO/polymer membranes have been proposed for use in seawater desalination and wastewater treatment and may contribute to alleviating water shortages and environmental problems. GO/polymer composite membranes are often impermeable to water in the dry state, making them also suitable for gas sieving applications [83].

Significant advances in next-generation separation membranes based on graphene and GO take advantage of a number of novel transport properties of these materials. [84, 85] GO fragments are stacked layer-by-layer to form a compact stacked structure. Although there are gaps between the layers, these are not sufficient to achieve selectivity in separations. However, by rebuilding two-dimensional nanochannels between graphene sheets, the separation ability can be effectively improved, to enable sieving of molecules of specific sizes. [86, 87] Graphene-based membranes, including GO, rGO, and doped graphene, have also been used for catalytic degradation of harmful pollutants and dyes. [88–91]

Table 1 summarizes the modification methods of some graphene-based membranes and their properties after modification. Composite membranes from graphene and its derivatives have led to new applications in water purification and desalination. Although most graphene-based water membrane technologies are still in the development stage, they have promising prospects for the future. In particular, the GO-based membranes are expected to have greater direct market potential due to their relatively low cost and the ease with which they can be implemented in existing membrane-based operations. The combination of GO with macromolecules, such as polymers, makes the GO membrane more ductile while increasing water flux. The combination with nanoparticles, such as nanotubes, TiO_2 nanoparticles, and MOF, can also improve the water flux, desalination rate and decontamination capabilities of GO-based membranes.[92–95]

Improved performance of graphene-based membranes in decontamination applications

Compared with the pure GO water purification membranes with fixed layer spacing, composite membranes formed by combining GO with various materials have important enhancements in properties and performance. Performance enhancements are achieved by changing the GO membrane layer spacing, the membrane surface charge, and the chemistry of the oxygen-containing groups on the membrane. Decontamination performance is often demonstrated by the removal a model dye compound from water. Commonly used cationic dyes include methylene blue (MB) and rhodamine B (RB); anionic dyes include methyl orange (MO), rhodamine WT (R-WT).

Nanomaterial intercalation to modify GO membranes

The nanomaterials used for intercalation can be divided into three categories, based on their dimensionality. Zero-dimensional nanoparticles include MOFs [107] and carbon quantum dots [108], one-dimensional nanoparticles include carbon nanotubes [109], and two-dimensional nanomaterials include WS_2 nanosheets [110].

Table 1 Examples of performance of graphene-, GO- and rGO-based composite separation membranes

Materials[a]	Preparation methods	Water permeance (L m^{-2} h^{-1} bar^{-1})	Salt rejection (%) NaCl	Ref.
PVDF/graphene	Electrospun nanofibrous	150 kg $\cdot m^{-2} \cdot h^{-1}$		[96]
PMMA/graphene/PET	Ion-track nanotechnology chemical etching	5.4 ± 2.3		[97]
GO/graphene (80wt%)	Vacuum-assisted filter	7.2	88.3%	[98]
LIG/PVA	Cross-link\	225		[99]
GO-TFN (0.015 wt%)	Coating method	2.871	93.8 ± 0.6	[100]
GO-PSBMA/PES (22.0 wt%)	Interfacial polymerization	11.98	4.3 ± 0.3	[101]
GO@PAN	Filter method	8.20	9.8	[102]
PSF-GO (0.30 wt%)	Coating method	2.45	59.5	[103]
rGO–CNT-AAO	Vacuum-assisted filter	31.5	42 ± 0.6	[95]
GO − OCMC/PSF	LbL self-assembly	1.78 ± 0.02	62	[104]
GO-PSf	Coating method	5.47	33.01	[92]
rGO/TiO_2-PSf (0.01 wt%)	Coating method	6.14	36.61	[92]
rGO/TiO_2 (0.02 wt%)	Interfacial polymerization	3.42	99.45	[93]
GO-TFC	Interfacial polymerization	1.07	99.5 ± 0.3	[105]
GO-ZIF8/PEI	Vacuum-assisted assembly	3.5	99.1	[106]

[a]PVDF—polyvinylidene fluoride; LIG—laser-induced graphene; PVA—polyvinyl alcohol; TFN—thin-film nanocomposite; PSBMA —poly(sulfobetaine methacrylate); PES—polyethersulfone; PAN—polyacrylonitrile; PSF—polysulfone; AAO—anodic aluminum oxide; OCMC—O-(carboxymethyl)-chitosan; TFC—thin-film composite; PEI—polyethyleneimine

Nanoparticles

Liangliang Dong et al. [111] introduced NH_2-Fe_3O_4 through the vacuum filtration strategy to prepare high water flux GO/NH_2-Fe_3O_4 nanofiltration membranes (Fig. 6a). Addition of the NH_2-Fe_3O_4 nanoparticles increases the GO layer spacing significantly, thus sacrificing ion sieving performance, but at the same time, the water flux and dye rejection increase (Fig. 6b). The NH_2-Fe_3O_4 also acts as a cross-linking agent to stabilize the composite membrane. Therefore, GO/NH_2-Fe_3O_4 composite membranes may be used in the treatment of dye/salt mixed wastewater.

Nanoporous MOFs have attracted increased attention in the field of decontamination and desalination due to their special porous structures. [112] Guanet et al. [94] produced rGO, which increases the stability, and reduces the interlayer spacing and water flux, compared to GO. They then formed rGO composite membranes containing nanoporous crystals of UIO-66 and Prussian blue (PB). The prepared composite membranes have increased interlayer spacing, and screening performance. The pore size of UIO-66 is between 0.6 and 1.1 nm, the pore size of PB is around 0.4 nm, and the average diameter of water is 0.32 nm. The composite containing the porous MOF nanoparticles has greatly increased the water flux. Figure 7a-c illustrates the transmission path of water in the composite membrane. Two screenings, provided by both the rGO layer spacing and the intercalating MOF, also greatly increase the rejection of the a model dye compound. As shown in Fig. 7d, as the content of UIO-66 increases the rejection remains above 90%. Increasing the nanoparticle content will not continuously increase the interlayer spacing of rGO, but will result in more densely packed nanoparticles. Thus, the increase in water flux is also due in part to the better water permeability of porous MOF materials. [94]

Other MOFs have been used as intercalation materials to control the interlayer spacing of GO membranes. Calculations have predicted good compatibility between GO and ZIF-8. [114] As a porous nanomaterial, ZIF-8 also has the advantages of high specific surface area and large functional pore size. MOF grown on the GO membrane can effectively improve the weak compatibility between the

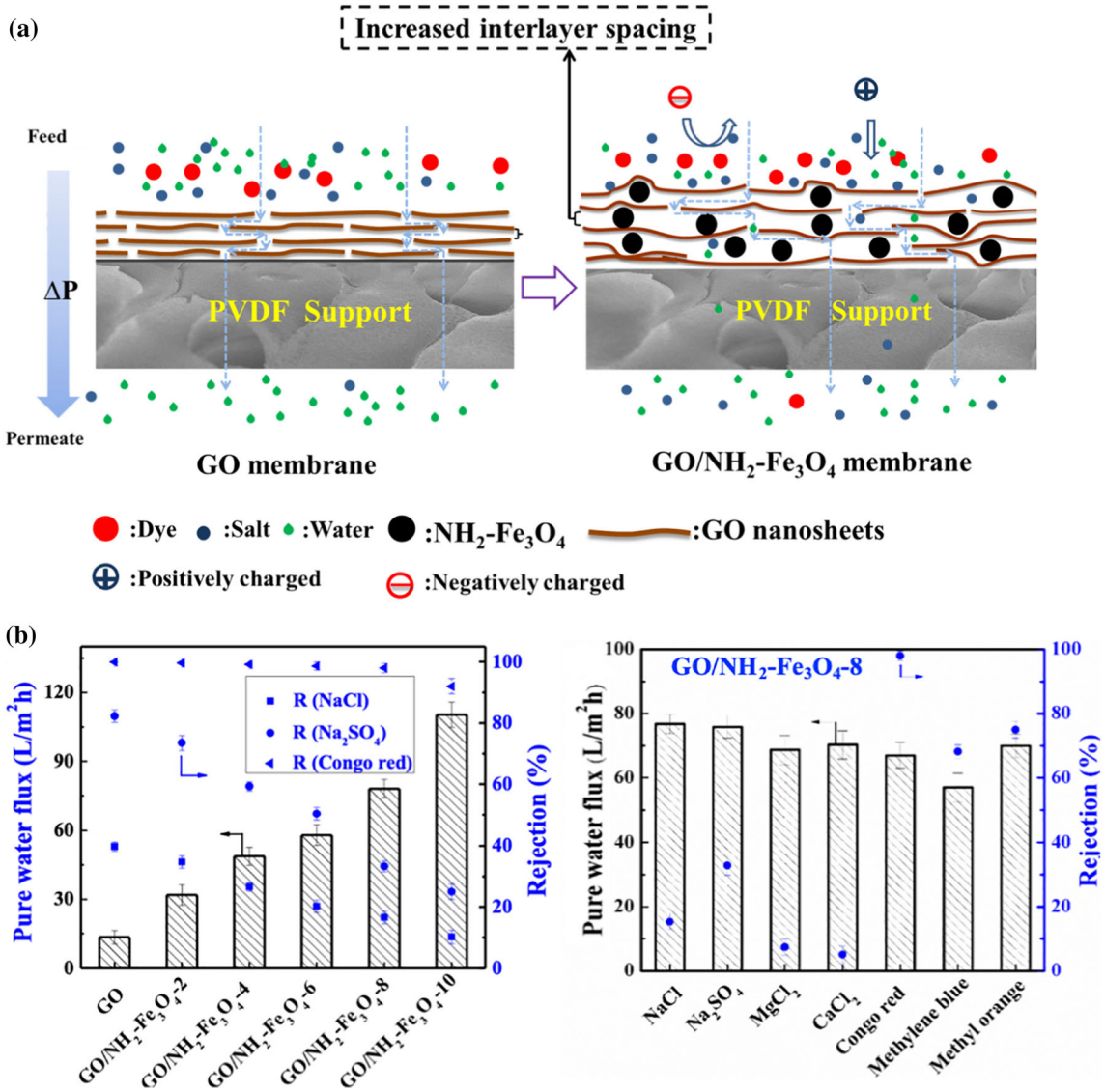

Figure 6 Mechanisms of transport process of GO and GO/NH_2-Fe_3O_4membranes. **a**. Water flux and single dye and salt rejection of GO/NH2-Fe3O4 membranes. **b** [111].

nanoparticles and the polymer and prevent the aggregation of MOF on the polymer. [106, 113] Figure 7e is a schematic diagram of ZIF-8 growing on GO.

In addition to porous nanomaterials, other nanoparticles can also be used as intercalation materials to compound with GO. Zhao et al. [108] prepared GO composite membranes containing GO quantum dots (GO QDs). Compounding with GO QDs improves the hydrophilicity and water flux without affecting the rejection of pollutants. Figure 8a illustrates the preparation of the composite membrane, which is prepared into a membrane by a the vacuum filtration method. When the content of GO QDs increases, the interlayer spacing also increases, and the quantum dots scattered on the outer surface of the membrane can improve the membrane hydrophilicity, thereby improving the water flux. The left picture in Fig. 8b shows the test of the composite film on MO, and the right picture shows the test on DY. It can be clearly seen that as the content of GO QDs increases, the water permeability increases steadily and the rejection rate can be well maintained. Similarly, Peng et al. [115] used a simple deposition method to compound rGO with SiO_2 (Fig. 8c) which improved the water permeability of GO base film and retained the high rejection rate. In order to solve the problem of the stability of GO base

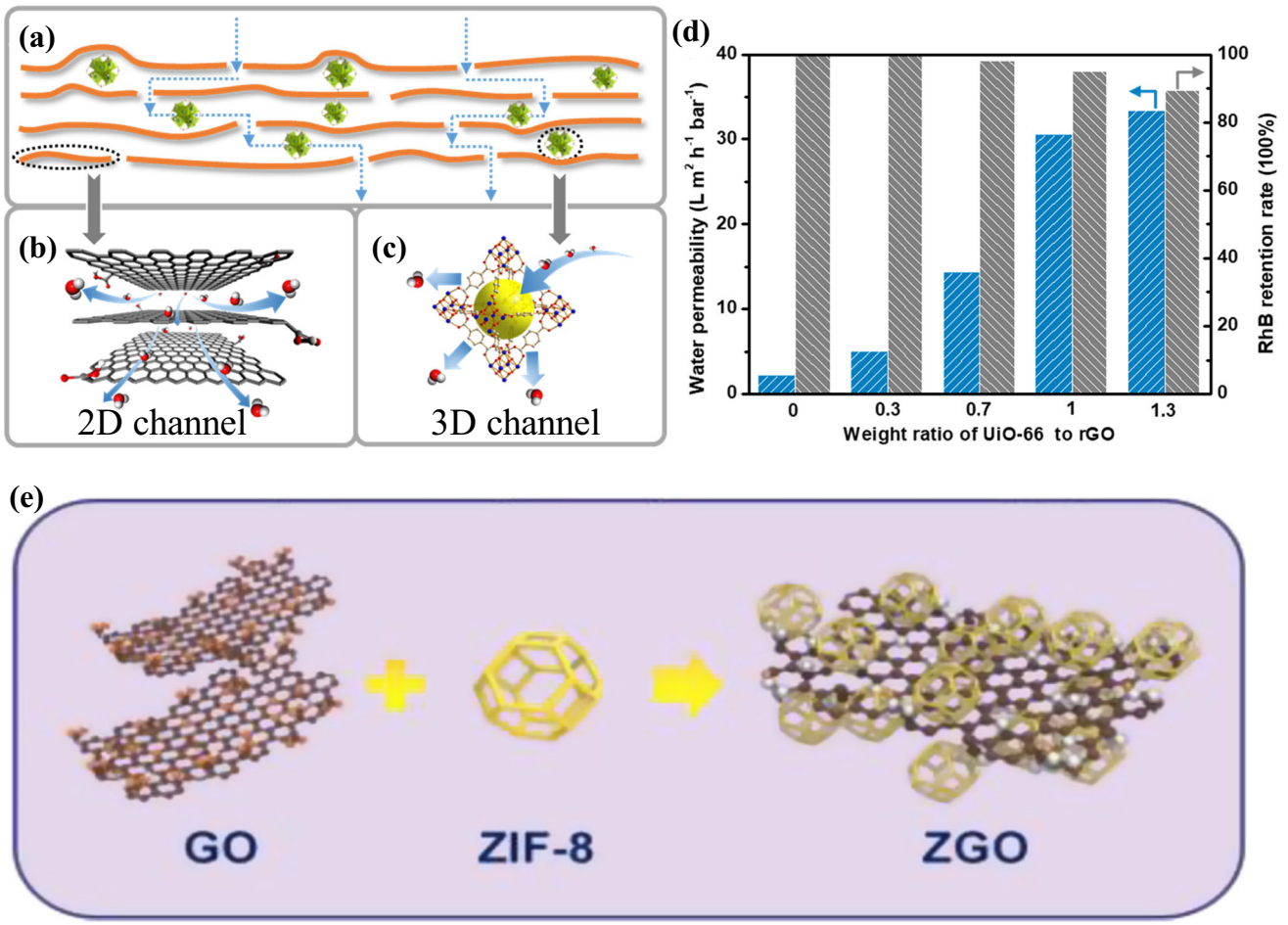

Figure 7 Schematics of water transport through **a** nanocrystals rGO composite membranes, **b** stacked rGO sheets, and **c** nanoporous crystal. **d** Filtration performance of UiO-66-rGO membranes with different amounts of the MOF. [94] Schematic diagram of fabrication of ZGO/ polyether block amide (PEBA) membranes. **e** [113].

membrane, the author also introduced PDA, which not only made the composite membrane strong, but also improved its hydrophilicity. And, as shown in Fig. 8d, as the ratio of GO to SiO_2 increases, the water permeability greatly increases and the MB rejection rate is not significantly affected.

Nanotubes

Two-dimensional carbon nanotubes have good compatibility with GO and precise diameter. Han et al. [116] combined rGO with multi-walled carbon nanotubes (MWCNTs) on a porous substrate to obtain a composite membrane. The addition of the nanotubes doubles water permeability while maintaining the dye rejection above 95%. Figure 9 shows a schematic diagram of the GO-MWNTs composite membrane. MWNTs widen the interlayer spacing and increase the membrane roughness. The resulting membrane is hydrophilic, with improved resistance to fouling. The improved antifouling performance greatly increases the value of the composite membrane. After discovering the antifouling property of the composite of GO-MWNT, Yuan et al. [117] modified PVDF membranes by a facile phase inversion method. The composite PVDF/MWCNT/GO mixed matrix membrane not only exhibited increased the water flux, but also permitted electrical conductivity measurements for real-time monitoring of the degree of membrane pollution. While these modifications reduced the mechanical strength of the original PVDF membrane, these new membranes still have good application potential.

In addition to carbon nanotubes, other nanotubes can also be used to compound with GO. Zhan et al. [118] embedded halloysite nanotubes (HNTs) in GO

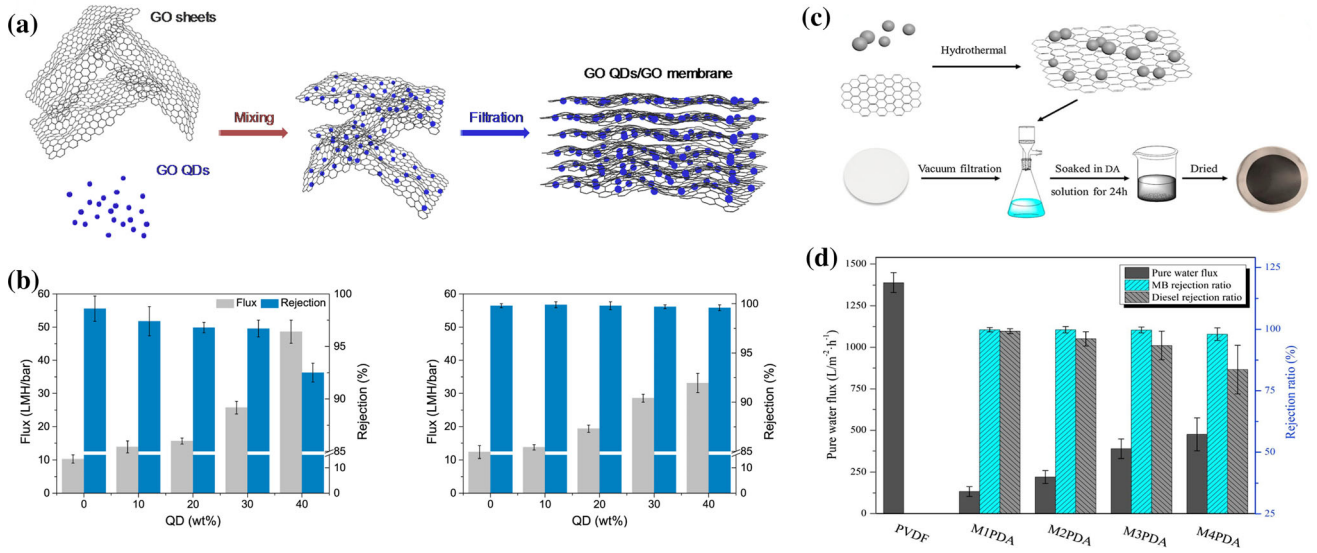

Figure 8 Schematic illustration of the preparation process of GO QDs-intercalated GO membranes. **a** Water flux and rejection rates when separating two model dye aqueous solutions by the membranes fabricated with varying GO QDs contents. **b** [108] Schematic depiction of the preparation of PVDF/RGO@SiO2/PDA membrane. **c** Pure water flux and removal ratio. **d** [115].

Figure 9 Schematic representation of the structure and water transport path for (left) graphene nanomembrane (GNm) and (right) graphene–carbon nanotube membrane (G-CNTm). [116].

to obtain a high-throughput, high-rejection antifouling composite membrane, for oil–water separation. HNTs are low-cost and environmentally friendly nanomaterials. [119] HNTs increase the layer spacing of the GO membrane, reduce the roughness, and significantly improve the antifouling performance. In the same year, Liu et al. [120] also published an article on HNT modified GO. As shown in Fig. 10, the rGO/HNTs composite membrane is vacuum filtered to a support membrane with the help of polydopamine, and the performance in oil–water separation is improved.

After GO is compounded with nanotubes, the general antifouling performance has been improved. This may be because commonly used nanotubes MWCNT and HNT have many hydrophilic groups that improve the membrane hydrophilicity. In addition, reports mention that the insertion of nanotubes can reduce the surface roughness of the membrane. It is generally believed that lower roughness imparts improved antifouling performance.

Nanosheets

2D nanomaterials have large specific surface area, stability after membrane formation, and both edge-to-edge and face-to-face interactions. These properties make 2D nanomaterials ideal for preparing various functional membranes. Incorporation of 2D nanosheets into graphene-based membranes can achieve property and performance enhancements. Misato et al. [121] mixed niobate nanosheets (NbNs) and GO to prepare NbN-GO composite membranes by vacuum filtration. As can be seen from Fig. 11a, based on the tight channel structure of NbN, the loose accumulation of voids after mixing with a small amount of GO forms a larger nanochannel, resulting in high porosity and high water permeability of the

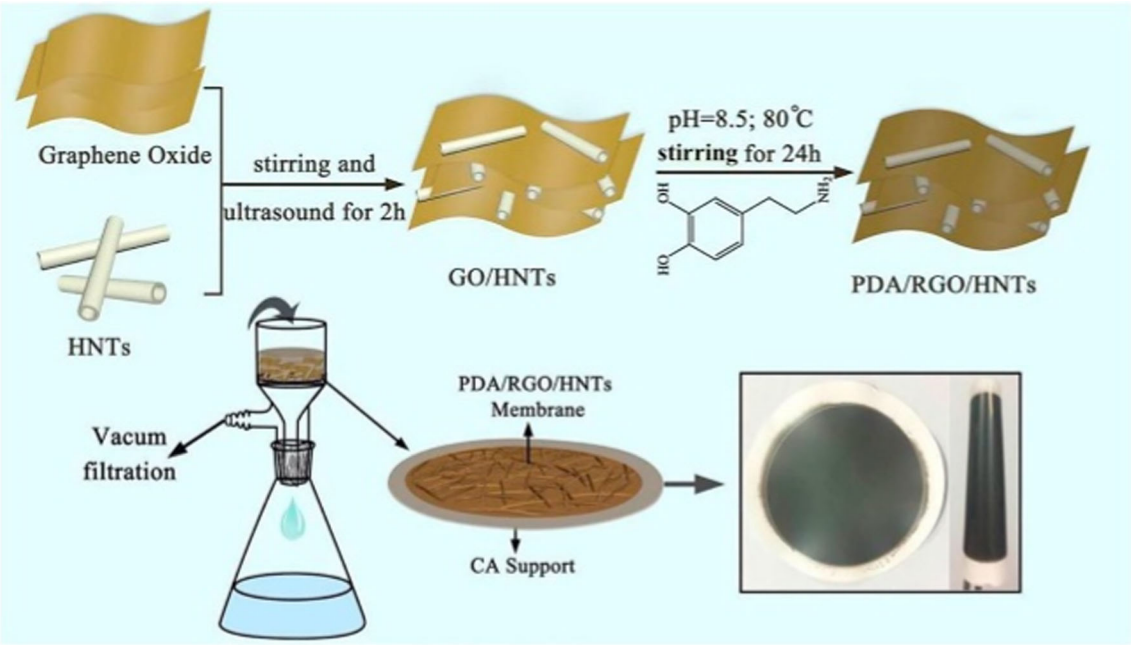

Figure 10 The preparation procedures of polydopamine (PDA)/RGO/HNTs membranes [120].

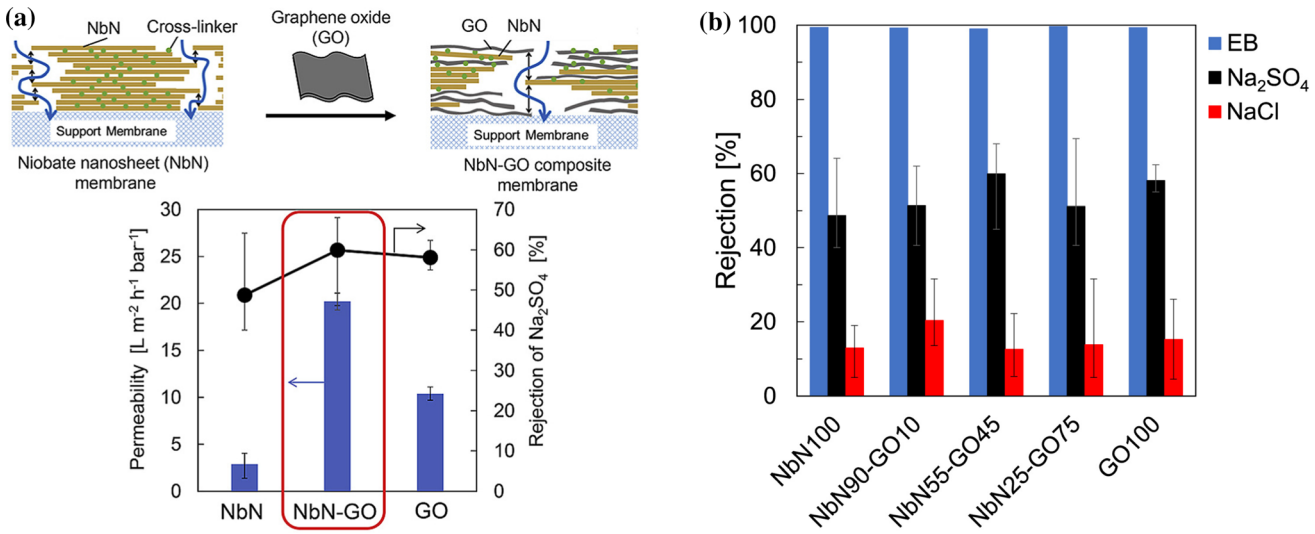

Figure 11 Schematic diagram of channel structures in NbN-GO composite membranes. **a** Permeability and rejection of EB, Na_2SO_4 and NaCl for NbN100, GO100 and NbN-GO composite membranes. **b** [121].

membrane structure of NbN-GO. When the mass ratio of NbN to GO is 55:45, the composite achieves a higher water flux and particle retention, with no effect on the rejection of a model dye (Fig. 11b). Chen et al. [110] also reported that transition metal dihalide, (TMDs) WS_2 was compounded with GO, and a hybrid membrane with high flux and high rejection was prepared by simple vacuum filtration (Fig. 12a). The unmodified GO membrane is easy to swell, but has good retention function, while WS_2 has the advantages of good stability, and high flux, but poor retention performance. When GO is compounded with WS_2, the performance is best when the mass fraction of GO is 15%, and the rejection of dye is more than doubled.

The GO and nanosheet composite membranes mentioned above are all prepared with GO as the filler. Ma et al. [122] used MoS_2 as the filler to

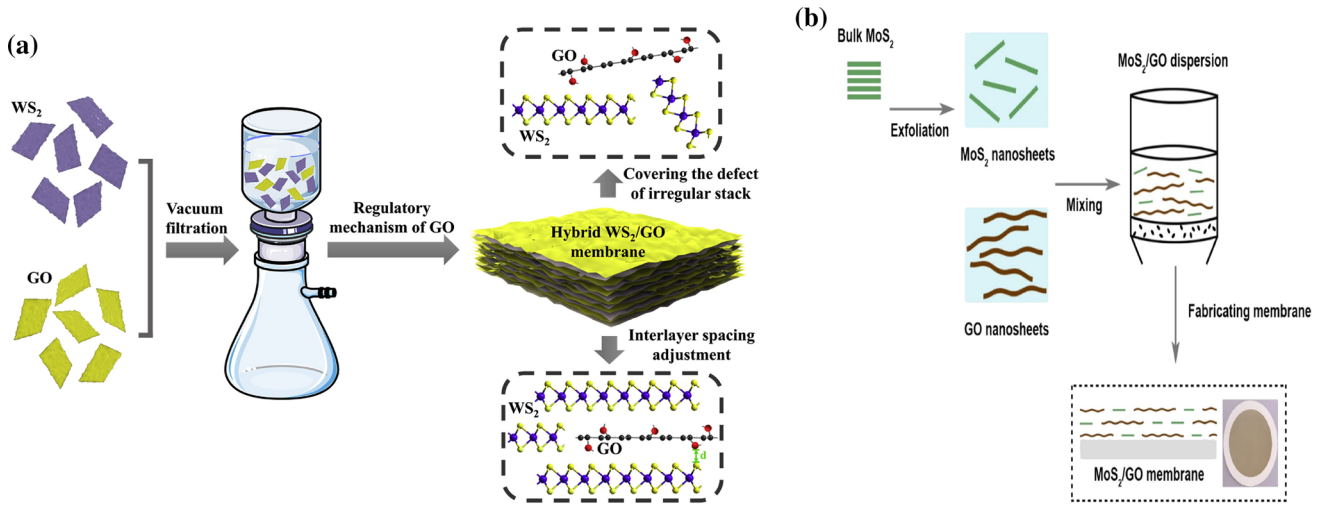

Figure 12 Illustration of the fabrication process of hybrid WS_2/GO membrane and its regulatory mechanism. **a** [110] Preparation of MoS2/GO composite membranes. **b** [122].

compound with GO. As shown in Fig. 12b, a stable GO/MoS_2 composite membrane was prepared. MoS_2 is hydrophobic and can promote strong van der Waals interactions between MoS_2 and GO, so the stability of the composite membrane in water increases. Moreover, the expansion of the interlayer spacing by MoS_2 still increases the flux of the composite membrane.

Other methods to modify GO membranes

The performance of GO-based membranes can be improved by adjusting the properties via alternative preparation techniques. Potential improvement strategies include designing the spacing between GO layers by incorporating cross-linking agents of different sizes and modifying membrane charges by functionalizing GO. As shown in Fig. 13, 1, 3, 5-benzenetricarbonyl trichloride (TMC)-cross-linked GO has improved water flux and dye rejection. Furthermore, cross-linking greatly improves the stability of GO membrane. [61] In this work, the authors also considered the adsorption performance of GO when testing dye rejection. Before collecting the trapped dye, the experimental samples were equilibrated for two hours to completely eliminate the influence of adsorption.

Swelling of GO membranes in water is a persistent problem, as it increases the layer spacing, thereby reducing retention performance. [123, 124] Jingqiu Sun et al. [125] reduced the oxygen-containing functional groups of GO to form rGO and then subsequently modified the surfaces with additional GO, to obtain a layered structure of O-rGO membranes (Fig. 14a). These layered membranes have improved hydrophilicity and water permeability, compared to rGO membranes. Reduction of the oxygen-containing functional groups reduces the swelling, while addition of GO further alters charge density on the surface, thereby improving antifouling performance. As shown in Fig. 14b, the resulting modified O-rGO membrane has improved rejection of dye molecules with different charges.

For decontamination, the adsorption effect, the electrostatic repulsion effect, and the physical sieving effect of the nanochannels are all phenomena that can be improved. The adsorption of contaminants is most frequently ignored or not evaluated in many reports. The inherent adsorption capacity of GO may affect the retention performance of composite membranes. The intercalation of nanomaterials mainly achieves the effect of increasing flux and rejection by changing the interlayer spacing. Nanotubes can also improve the antifouling performance when used as intercalation materials. However, in most cases, the improvement of flux is accompanied by a decrease in retention, or it is difficult to greatly improve both the flux and the retention performance at the same time. Table 2 summarizes the water flux and retention of modified GO substrates after modification.

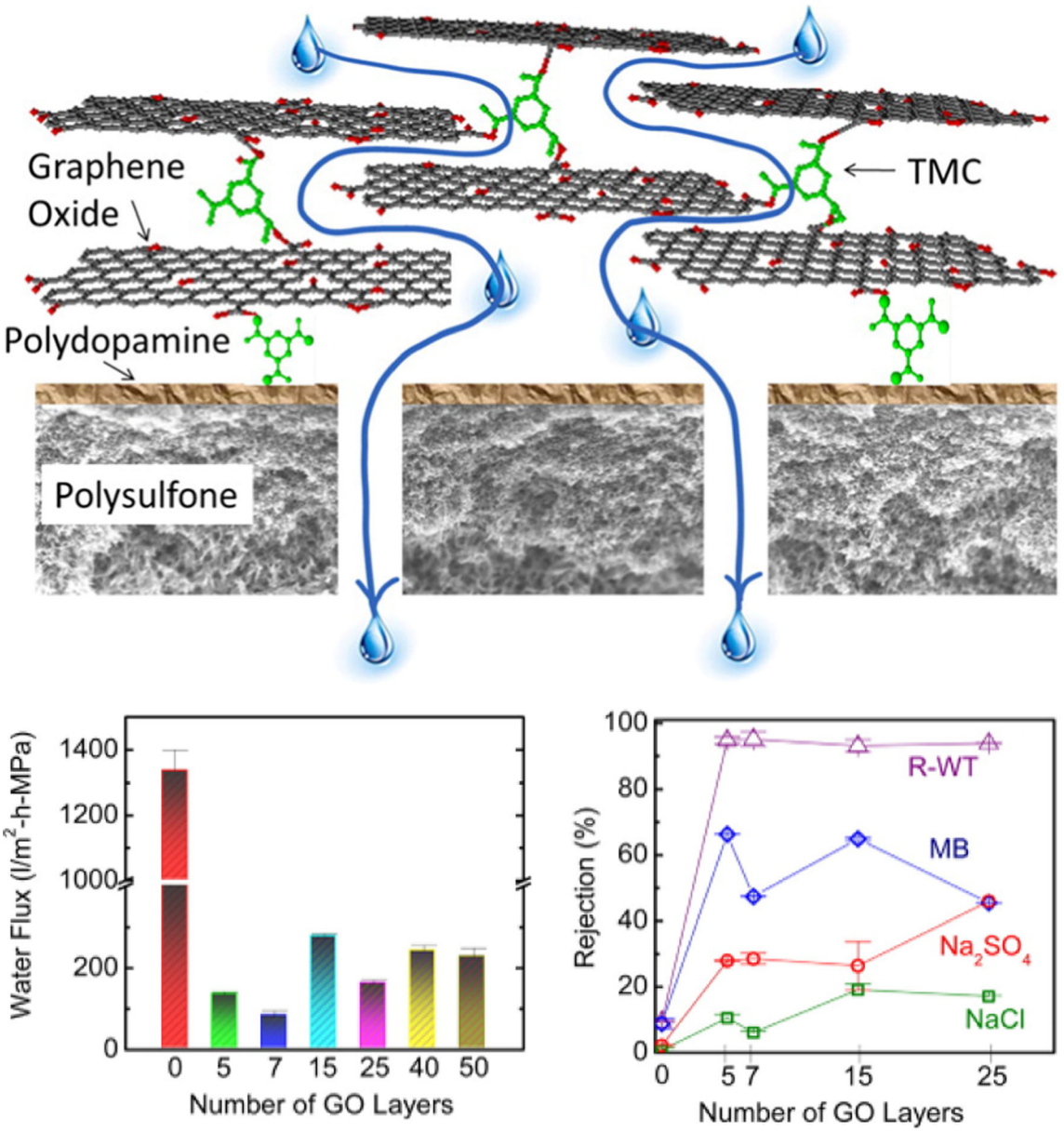

Figure 13 Schematic diagram of TMC-cross-linked separation membrane and water flux of different GO layers and rejection rate of organic dyes. [61].

Improved performance of graphene-based membranes in seawater desalination applications

Membrane technology has become one of the important means of water purification and desalination. Desalination technology can contribute solutions to water shortages in coastal areas. [132] Membrane technology can be classified according to the pore size of membrane materials, and commonly used commercial membranes can be divided into reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF). The interception of various membranes for different solutes in water is shown in Fig. 15. RO can achieve 98–99.8% interception of Na^+ and Cl^- monovalent ions in solution. [133] The rejection of larger ions such as Ca^{2+}, Mg^{2+}, and other divalent ions exceeds 90% for NF membranes. So NF membranes can soften water quality, but the rejection of smaller ions such as Na^+ will be reduced. [134] Table 3 summarizes the pore sizes of different types of membranes and the

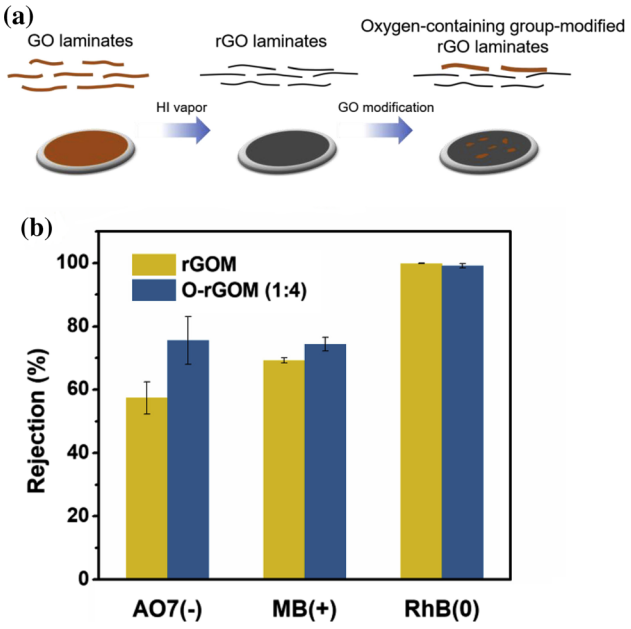

Figure 14 Schematic of the O-rGOM fabrication strategy. **a** O-rGOM on the rejection of dyes with different charges. **b** [125].

corresponding materials and solutes that can be screened by microfiltration (MF), ultrafiltration (UF), reverse osmosis (RO), forward osmosis (FO), and nanofiltration (NF) membranes.

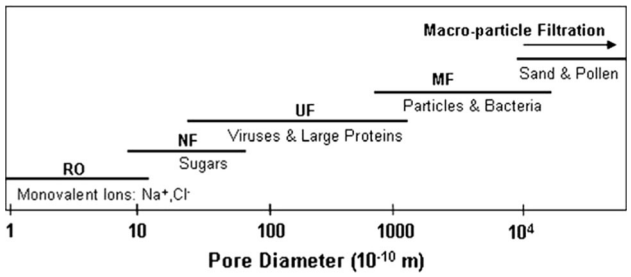

Figure 15 Range of nominal pore diameters for commercially available membranes. [135].

Surwade et al. [54] prepared nanoscale holes in a graphene layer with a thickness of one atom by an oxygen plasma etching process and showed that the size of the holes can be adjusted (Fig. 16a). Experiments demonstrated that porous graphene is capable of desalination while maintaining high permeability. They demonstrated that it is possible to precisely control the pore size of the graphene membrane to achieve selective screening of different ions (Fig. 16b).

The salt rejection of nanoporous graphene can reach 100%. [54] Most GO membranes achieve ion sieving by adjusting the layer spacing. If the advantages of nanoporous graphene and GO membranes

Table 2 Performance of modified GO membranes for decontamination

Materials[a]	Water permeance ($L/m^2 \cdot h \cdot bar$)	Rejection performance							Ref
		NaCl	Na_2SO_4	MB (+)	MO(-)	R-WT(-)	EBT	RB (+)	
GO/TMC	8–27.6	6–19%	26–46%	46–66%		93–95%	……	……	[61]
GO/nylon 6–13	11.15	27.6%	56.5%	> 95%	> 99%	……	……	……	[126]
GO/TiO_2/CA	68.1	33.0%	57.1%	99.3%	99.3%	……	……	……	[127]
GO/MB	7.67	……	> 70%	……	93.3%	……	……	82.6%	[128]
SG/GO	33	……	……	……	……	……	98.0%	……	[129]
GO/PBI (coated with a PDA layer)	91.3 ± 3.4	The oil removal efficiency: 100%							[20]
NbN/GO45	20	15.0%	60.0%	Evans blue: nearly 100%		……	……	……	[121]
GO15WS_2/Nylon	156.3	……	……	96.3%	……	……	……	97.7%	[110]
rPGMs	5.3	……	71.2%	……	> 97.5%	……	……	……	[130]
GO/GO QD	48.59	28.4%	74.9%	……	98.6%	……	……	……	[108]
SiO_2-GO/psf 0.3wt%	185	……	……	……	……	……	……	……	[131]
rGO/UiO-66	27	……	……	98.7%	……	……	……	95.0%	[94]
O-rGOM	3.22	……	……	74.4%	……	……	……	98.2%	[125]
GO/TiO_2	68.1	33.0%	57.1%	99.3%	99.3%	……	……	99.4%	[127]

[a]CA— cellulose acetate); SG—solvent green; PBI—polybenzimidazole; QD—quantum dots;

Table 3 Categorization of membranes according to mean pore radius and molecular weight cut-off

Process	Mean pore radius (nm)	Molecular weight cut-off	Intercepted materials	Ref
MF	0.1-1 μm	…	Suspended solids, bacteria, microparticles	[53]
UF	20–50	> 500 Da	Protein, enzyme, bacteria latex, microparticles, viruses	[53]
FO	0.25–0.37	…	Inorganic salts, sugars, amino acids, etc.	[53, 136]
RO	0.5–10	> 100 Da	Inorganic salts, sugars, amino acids, etc.	[53]
NF	≈1	150-500 Da	Inorganic salts, sugars, amino acids, etc.	[53, 137]

are combined, this could lead to substantial improvements in water purification. [138]

Nanomaterial/GO composite membranes

The oxygen-containing groups on the surface of GO introduce multiple functionalities. Adjusting the oxygen-containing groups on GO can alter the performance of the membrane without addition of other materials. Yuan et al. [139] mixed glycine with GO under alkaline conditions and irreversibly bound carboxylic acids to the surface of GO films by nucleophilic substitution, and formed membranes by vacuum filtration (Fig. 17a). As shown in Fig. 17b the permeability and salt rejection of the membrane is improved by introducing a large number of carboxyl groups. The high permeability may be attributed to the increase in hydrophilicity. The introduction of a large number of carboxyl groups makes the membrane more negatively charged, resulting in a higher salt rejection rate. The rejection of divalent anions in Fig. 17b is twice that of monovalent anions, which also illustrates the enhancement of electronegativity of the carboxylated GO.

Porous reduced graphene oxide (PRGO) formed by perforating GO after reduction can solve the problem of GO aggregation while maintaining its flux and retention performance. PRGO has been used in dye removal, desalination and other fields. [95, 140] Zhu et al. [141] used poly (sodium-p-styrenesulfonate) (PSS) and modified halloysite nanotubes (HNTs) intercalated PRGO to obtain a composite membrane with significantly improved flux. Figure 18 is a schematic diagram of the composite membrane preparation and filtration simulation. After intercalation, the interlayer spacing of PRGO increases, and the removal rate of dye is over 97%. The removal rate of monovalent and divalent ions is less than 10%. The composite membranes can therefore be used for separations of dye form salt in mixed solutions.

The rigid nanosphere NH_2-Fe_3O_4 intercalated GO mentioned above also achieves separation of mixed dye/salt solutions. [111] The nanomaterial composite GO membrane can separate molecules with a larger size than the salt ions due to the increase of the interlayer spacing. To achieve the removal of salt ions in water, composites are formed with polymers, which will be discussed below.

Polymer/GO composite membranes

Anion exchange membranes (AEM) are commonly used in desalination. [142] Li et al. [143] modified AEM with polydopamine and GO composite not only

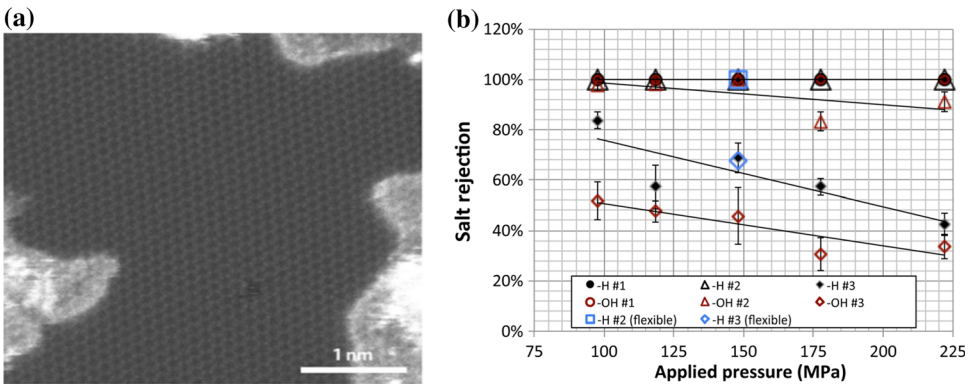

Figure 16 Characterization of nanoporous graphene. **a** Average salt rejection as a function of pore type and pressure differential. **b** [54].

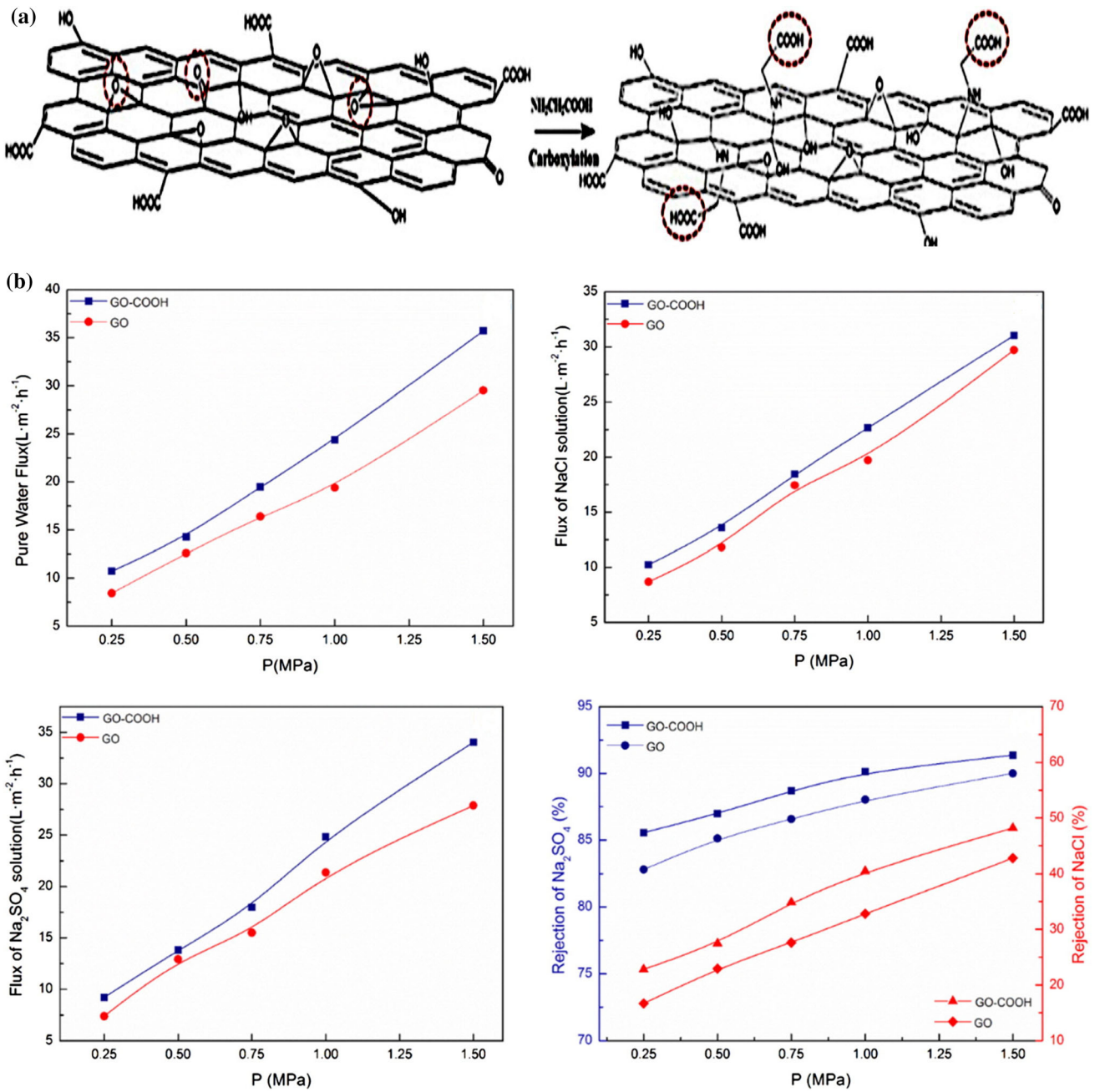

Figure 17 Schematic illustration of carboxylation reaction. **a** Performance comparisons of GO and GO-COOH membranes. **b** [139].

to increase the salt rejection but also to greatly increase the antifouling performance. The hydrophilicity, electronegativity, and surface roughness of the membrane are all related to the antifouling performance of the membrane. [144] The GO imparts excellent hydrophilicity, electronegativity, and screening performance to AEM, but its stability is poor. The introduction of polydopamine acts as a cross-linking agent to enhance the stability of the membrane and provide a degree of hydrophilicity. Polydopamine also provides electronegativity when pH > 4. The modified membrane has increased hydrophilicity, increased electronegativity, and reduced roughness, achieving a dual improvement in desalination performance and antifouling performance.

Karkooti et al. used the non-solvent induced phase separation (NIPS) method to prepare GO/

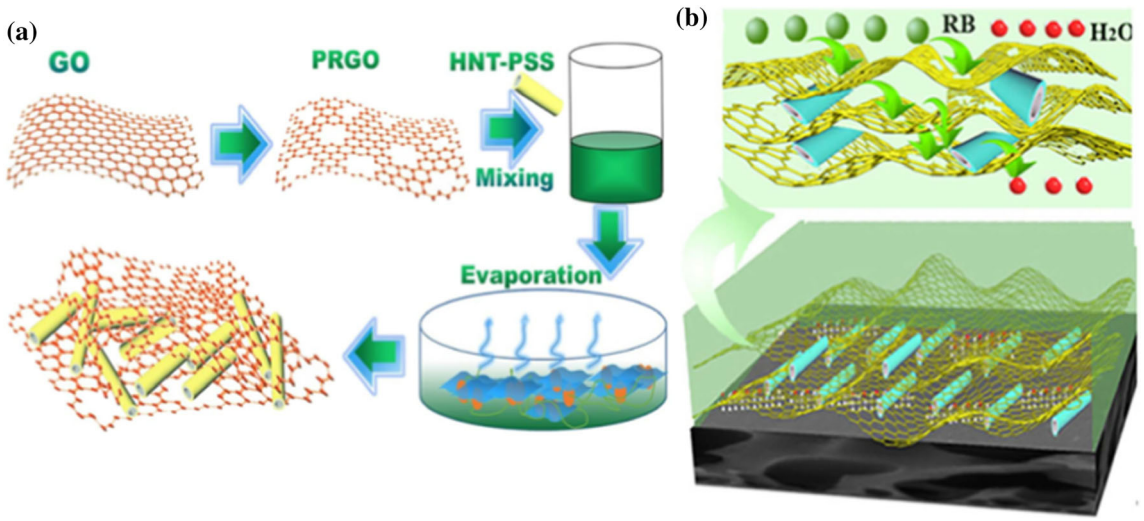

Figure 18 Schematic diagram of the preparation and retention of PRGO/HNTs-PSS composite membrane. [141].

polyethersulfone (GO/PES) composite membranes, which exploit the hydrophilicity and electronegative properties of GO, and greatly improve the membrane performance, while maintaining desalination performance and antifouling performance. [145]

GO nanocomposites are also often used to optimize polymer-based membranes. For example, Safarpour et al. [93] reported a new type of RO membrane. They interfacially polymerize and insert nano-rGO and TiO_2 into the polyamide (PA) layer. Due to the uneven structure of GO, TiO_2 is uniformly distributed on the surface of the GO film, and the exposed RO film is not affected by the embedded rGO/TiO_2 nanocomposite material (Fig. 19a). The hydrophilicity and electronegativity introduced by the composite material greatly improve the flux and antifouling performance of the PA membrane. Figure 19b shows the flux and desalination results of the prepared new reverse osmosis membrane. The water flux and desalination performance of the membrane reach the maximum when the mass ratio of nanocomposite material is 0.02 wt%. However, only monovalent salt ions were tested in the article, and the salt solution concentration used for testing was low, so the desalination performance of the new membrane was not fully demonstrated.

Interfacial polymerization is a mature method for the preparation of NF membranes. Wang et al. [146] used the interfacial polymerization method with polyethyleneimine (PEI) as the water phase monomer and trimesoyl chloride (TMC) as the organic phase monomer to incorporate exfoliated hydrotalcite/graphene oxide (EHT/GO) hybrid nanosheets into a polyamide (PA) membrane. Both flux and desalination performance are improved (Fig. 20b). It is worth noting that EHT/GO will positively charge the membrane, which can effectively intercept Mg^{2+}, which is important for water softening. Figure 20a is a diagram of the electrostatic repulsion mechanism of the membrane.

Composite membranes used for desalination are mostly polymer membranes doped with GO or GO composite materials, but the polymer can also be used as an intercalation material inserted between GO layers. As mentioned earlier, when GO is compounded with nanomaterials, the layer spacing is too large for desalination; although there is a large water flux, small ion rejection cannot be obtained. However, when polymer intercalation is used, while obtaining high nanometer-scale water channels, the cross-linked network of the polymer can also prevent the passage of salt ions. Jiawei Sun et al. [147] prepared GO membranes embedded with and cross-linked by PVA and supported on cellulose microfiltration membranes, by pressure-assisted filtration for total evaporative desalination of high-salinity water. Figure 21 is a schematic diagram of the preparation of the GO-based composite membrane. The authors demonstrated adjusting the transmission channel by appropriately adjusting the intercalation of the PVA, to achieve excellent stability of the membrane through covalent cross-linking.

In addition, the selection of a supporting substrate can improve desalination performance. For example,

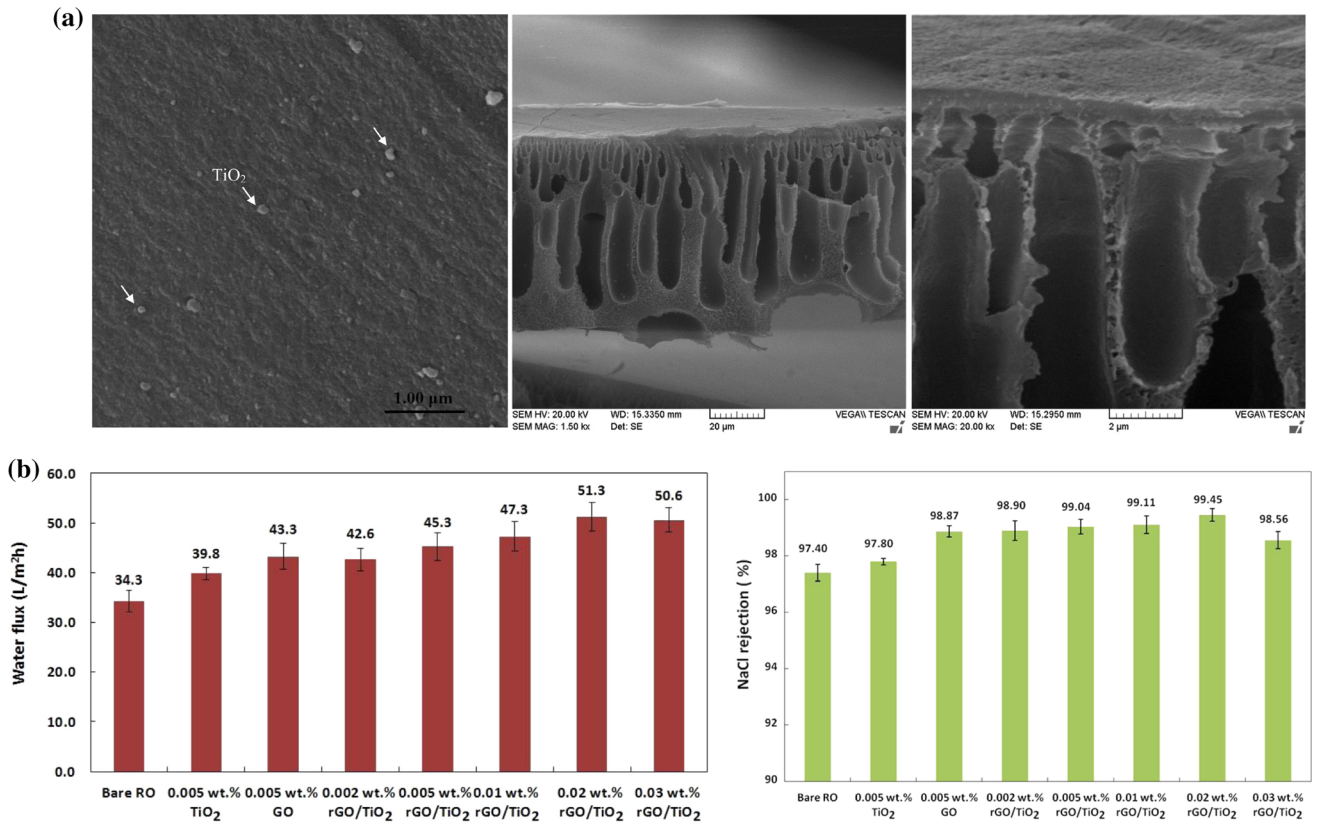

Figure 19 rGO / TiO_2 EDX image and rGO / TiO $_2$ / RO scan cross-section image. **a** Water flux and salt rejection of the rGO/TiO_2 membranes. **b** [93].

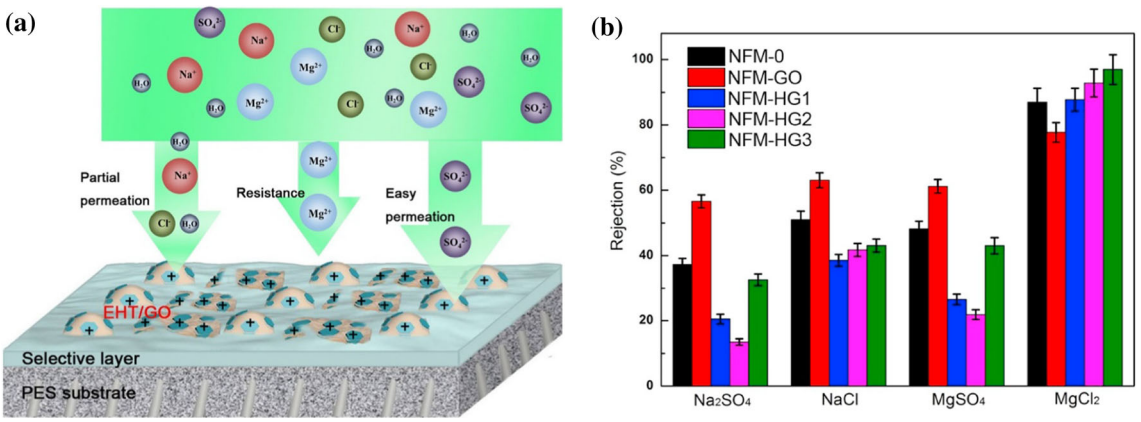

Figure 20 Separation schematic diagram of EHT/GO nanofiltration membranes. [146].

the performance of a PSF substrate has been improved by adding highly hydrophilic and negatively charged graphene oxide nanosheets. Several studies have demonstrated high water permeance and desalination by combination of GO and PSF membranes. [103, 148, 149]

For desalination applications, multiple polymers have been combined with GO-based materials. Compared with nanoparticle composites, which may be useful for dye/ion separations, polymer-based GO composite membranes are more suitable for desalination due to their control over the interlayer spacing, and the ability of the polymer network to provide additional screening. Polymer/GO composites can also achieve similar stability and antifouling properties as nanoparticle/GO composites. However,

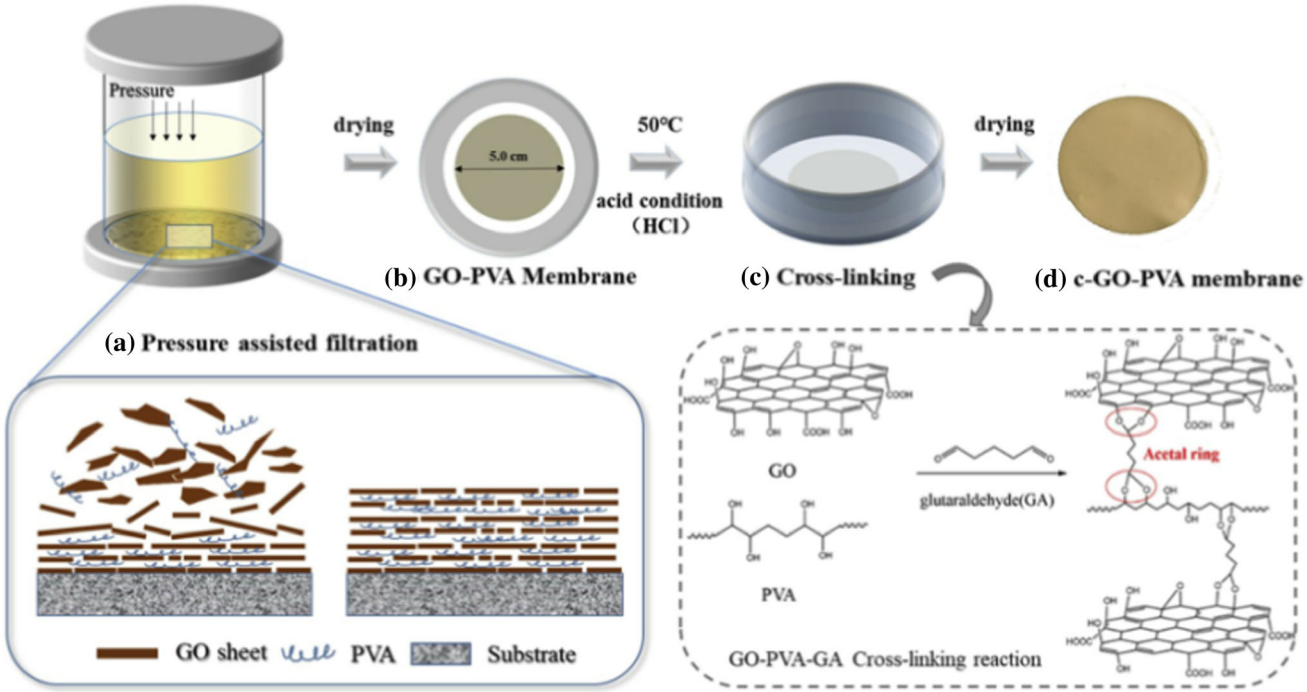

Figure 21 Schematic diagram of PVA/GO composite membrane fabrication. [147].

by comparing Table 3 and Table 4, we find, not surprisingly, that performance for desalination may sacrifice water flux. Table 4 summarizes some GO/polymer and GO/nanoparticle/polymer composite materials with improved desalination performance and their performance parameters.

Conclusions and outlook

Graphene-based and GO-based membranes exhibit extraordinary permeability properties, opening the door to the ultra-fast and highly selective transport of water and gas molecules. Graphene and its derivatives have excellent mechanical properties, single atomic layer structure, large specific surface area, and abundant modification methods which provide many opportunities for separations, desalination, and water purification.,

The modification of graphene-based membranes can be divided into three methods. The first is to directly perforate the graphene and to achieve particle screening performance by controlling the size of the holes. Perforation methods have been briefly reviewed: drilling holes in graphene membranes is a difficult process making it is expensive and complicated. Drilling may result in uneven pores and is not easy to scale to large quantities of material or large surface areas.

The second category of methods is embedding of nanomaterial and polymers between graphene and GO sheets. This intercalating method is used to control the interlayer spacing of the GO membrane to realize the screening of different substances. The primary nanomaterials used for intercalation include nanoparticles (e.g., MOF, COF, NH_2-Fe_3O_4, and Ag nanoparticles) and nanotubes (carbon nanotubes, TiO_2 nanotubes, and HNT). When forming GO/polymer composites, composite materials are usually doped with polymer membranes as fillers. GO-based polymer composites impart high hydrophilicity, high electronegativity, and unexpected antifouling properties. When the polymer is used as an intercalation material between GO layers, its unique cross-linking characteristics greatly improve the stability of the GO membrane.

The third method is to modify GO or graphene itself through introduction of charged and oxygen-containing functional groups to achieve performance enhancement. While, this method has poor scalability, it is a relatively simple method to improve performance.

On the basis of this review, these following four points should be addressed in future research on

Table 4 Performance of GO/polymer and GO/nanoparticle/polymer composite membranes for desalination

Materials[a]	Water permeance (l/m^2•h•bar)	Rejection performance				Ref
		NaCl	Na_2SO_4	$MgCl_2$	Mg_2SO_4	
GO-PVA	98.1 kg/m^2·h	99.99%	……	……	……	[147]
PES-GO	16.9		……	……	……	[145]
CDA-GOCM	20.1	99.90%	……	……	……	[150]
pPDA-GOCM	10.7	99.80%	……	……	……	[150]
GO-PSS/PAN	16.8		97.10%	……	……	[151]
GO-TiO_2-PSS/PAN	56.8		93.90%	……	……	[151]
GO-TMC/PDA-PSf	30	29.00%	26.00%	……	……	[61]
GO-PAN	1.8	9.80%	56.70%	……	……	[102]
GO/PSf	11	25.00%	65.00%	……	……	[148]
GO-MWCNT/PVDF	11.3	39.70%	81.00%	……	……	[116]
GO-MoS_2/PVDF	10.2	43.20%	65.20%	……	……	[152]
GO-PDA/PSf	18.5	4.00%	28.00%	……	……	[153]
GO/PSf	2.5	58.00%	72.00%	……	……	[149]
PVDF-f-G	< 1	99.0%	……	……	……	[154]
Psf/GO 0.3wt%	353	59.50%	95.20%	62.10%	91.10%	[103]
GO/PA	2.97	93.80%	97.30%	……		[100]
PRGO-HNT(PSS)	8.8	6.80%	14.30%	4.70%	4.70%	[141]
CFGO/PA	11.2	28.70%	≈83%	≈20%	≈70%	[155]
RGO/TiO_2/PA	3.42	99.45%				
GO/EHT/PA	15	≈40%	≈30%	≈90%	≈40%	
GQDs/PEI	12.9 L/m^2•h	……	……	……	……	[156]

[a]CDA—1, 4-cyclohyxanediamine; pPDA—p-phenylenediamine;

improving the performance of GO-based materials for desalination and decontamination:

1. When preparing GO-based composite membrane materials, while improving water flux and solute rejection, the membrane mechanical strength cannot be ignored. This important property determines whether the prepared membrane will survive practical application. This is particularly important when GO is compounded with nanomaterials. Although a higher water flux and rejection rate are often obtained, this should not require compromising the strength of the membrane. When a polymer substrate is added or when GO is compounded with a polymer, although the strength of the membrane may be increased, this should not be at the expense of water flux and rejection properties. Cross-linking using small-molecule chemistries may provide better way to provide simultaneous control over size exclusion and membrane durability. Suitable cross-linking methods that can improve stability without affecting flux and retention remain an open area of exploration.
2. In most solvents, GO spontaneously aggregates, and it is difficult to obtain effective dispersion. Researchers are working hard to overcome these difficulties. However, the impact of graphene-based membranes will continue to be at the forefront of research because of the potential for further development.
3. In rejection tests, the rejection of anionic dyes is generally better than the rejection of cationic dyes, which may be attributed to the negative surface charge of GO. Some researchers have addressed this by changing the surface charge of the membrane, which affects other performance properties. Additional strategies aimed at addressing this issue should be pursued.
4. Membrane fouling remains as a persistent challenge for the successful application of membrane technology in the field of water treatment. Without major breakthroughs in prevention of membrane fouling, many otherwise promising

technologies may never be translated from laboratory development to industrial application.

Acknowledgements

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Compliance with ethical standards

Conflicts of interest There are no conflicts of interest to declare.

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