# Recent Advances in Graphene Oxide Membranes for Water desalination

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**Abstract.** Freshwater is one of the most important sources in daily life. However, freshwater resources are very scarce at present. As a consequence, water desalination remains an important challenge in solving the problem of the shortage of freshwater resources. As an effective technique, membrane-based desalination has been developed to be a mature solution to solve the problem of water desalination. Graphene oxide membranes have been considered important membrane materials for water desalination due to their high stability and high hydrophilicity. In such review, this paper will introduce three kinds of recently-developed graphene oxide membranes for water desalination, which respectively are mixed matrix membrane, reduced nanoporous graphene oxide membrane, and GO/C60 membrane. Firstly, the structure and characteristics of each membrane are introduced; then, the processes of how to make these membranes are described. Additionally, this study compares them with other novel methods for water desalination. In the end, on the basis of graphene oxide membranes, it could be seen that these three membranes are more promising.

## 1 Introduction

Nowadays the scarcity of fresh water is becoming a worldwide challenge. The unprecedented pace of economic progress, population growth, and industry development boost the water demand, while human activities simultaneously pose a significant threat to the quality and quantity of freshwater resources [1-3]. Since saltwater makes up roughly 97% of water resources on earth, while ice and groundwater account for only 3% [4], it is extremely essential to develop desalination methods that can process saltwater on a larger scale, so that future needs can be fulfilled.

For all the desalination methods, 63.7% of the total desalinated water is produced by membrane processes and 34.2% by thermal processes [5]. The membrane technology has shown its great potential for its high efficiency, lower energy consumption, and ease of integration; thus, it is considered a promising material for desalination [6,7]. One of the most typical ways of water desalination using membrane technology is called reverse osmosis (RO), which utilizes the pressure difference between a dilute solution and a concentrated solution to promote the flow of solvent through a membrane. An increase in pressure on the concentrated solution forces the solvent to pass through the membrane in response to the change, leaving the solute intercepted by the membrane [8]. Besides, pervaporation (PV) is a newly-developed method driven by a chemical potential gradient from the heat at one side and low pressure at the other side, which is ideal for desalinating high-saline water [9].

There is research focusing on external conditions to increase the desalination rate of membrane methods. Mortazavi et al. [10] studied the effect of oscillating electrical fields on the enhancement of desalination efficiency. Delpisheh and coworkers developed a creative desalination unit that can simultaneously produce hydrogen [11]. However, the desalination membrane itself has always been the key component. By applying the membrane method, the hydrate of ions in the saltwater can be intercepted by the nanochannels in the membrane, while these channels are still large enough for water molecules to pass through [12]. The application of graphene, a revolutionary material in several fields, in the desalination membrane has attracted attention. By studying its mechanical strength, it is proven that graphene with nanopores exhibits outstanding desalination capacities [12]. The graphite oxide (GO) membrane, fabricated by oxidizing graphite or graphene, is considered to have a satisfactory water permeance and gas separation capacity superior to the commonly-used polymeric membranes [13]. Graphene oxide can also be modified through a variety of methods to adapt to different methods and conditions. Sun et al. studied the enhancement of desalination capacity of the GO membrane through poly (vinyl-alcohol)-intercalation [9].

This paper will focus on the three approaches of GO membranes in desalination methods and compare several factors to evaluate the potential strengths and weaknesses of these methods.

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# 2 Structure, synthesis and application of graphene oxide membrane for desalination

## 2.1 Structure of Graphene Oxide Membrane

### 2.1.1 Mixed matrix membrane (MMM)

While considering the desalination method of pervaporation, the mixed matrix membrane (MMM), the membrane that combines inorganic moieties with polymer matrix, inherits the advantages of both materials, guaranteeing a relatively higher chemical and thermal stability and hydrophilicity. In the first method, chitosan (CS), a material that guarantees high hydrophilicity, non-toxicity, and distinctive biomedical properties, is incorporated with graphene oxide to form the MMM [14].

### 2.1.2 Reduced nanoporous graphene oxide membranes (rNPGO)

As a class of graphene oxide membranes, reduced graphene oxide membranes (rGO) have high stability in solutions, but its water permeability is not very high. To solve this weakness, researchers optimized it into a reduced nanoporous graphene oxide membrane (rNPGO) by $H_2O_2$ oxidation, which has the characteristics of providing more channels for transportation and shortening the distance for the transportation of water molecules. In addition, by adjusting the thermal treatment time and membrane thickness, rNPGO's water permeability and salt rejection can be controlled [15].

### 2.1.3 GO/C60 membrane

GO membranes have relatively high water permeability compared to other membranes, which is very beneficial for water desalination [16]. However, it remains a great challenge to fix its interlayer spacing within 1 nm. To solve this difficult problem, researchers grafted C60 molecules on the surface of GO sheets through a lithium reaction and successfully achieved a fixed interlayer spacing of 1.25 nm [17]. This GO/C60 membrane has not only long-term stability but also a high rejection rate of NaCl under electrostatic and spatial effects. In addition, filtering cross section by encapsulating GO/C60 membranes with epoxy can also increase the effective area of desalination. [17]

## 2.2 Synthesis of Graphene Oxide Membrane

### 2.2.1 Mixed matrix membrane (MMM)

A unique method to graphene oxide membrane synthesis was adopted by Qian et al. to synthesize a mixed matrix membrane (MMM) with good hydrophilicity performance [14]. This approach is based on the modification of a traditional graphene oxide where defects that weaken the desalination capability are observed. Often, graphene oxide was obtained by oxidizing graphite with potassium permanganate. Then, the synthetic GO was dispersed to HAc solution by sonication, after which CS was added to form a 3% CS casting solution. In this way, a MMM was obtained successfully. Based on X-ray results, it is observed that the original interlayer in GO was expanded. It was also inferred that the covalent bonds, electrostatic interactions, and hydrogen bonds contributed to the compatibility between GO and CS, resulting in fewer interfacial defects.

### 2.2.2 Reduced nanoporous graphene oxide membranes (rNPGO)

To improve the low water permeability of GO membranes, the $H_2O_2$ oxidation method can modify GO membranes into NPGO membrane, which has a higher water permeability [15]. Researchers firstly mixed the prepared GO powder with $H_2O_2$ solution and treated it with ultrasonic baths to achieve a better dispersion[15]. Then, they heated this solution to 70 degrees and cooled it for 10 hours. Next, the mixture was put into a cellulose dialysis bag and purified with Milli-Q water so that a stable NPGO solution was obtained. To fabricate rNPRO membranes, researchers used a method called thermal reduction. In the beginning, they filtered the NPGO solution with a poly (PES) filter in a vacuum to assemble the NPGO membrane. Then, they thermally reduced the NPGO membranes in a predetermined period in an oven at 150 °C. Finally, they got rNPRO membranes, which have high porosity and hydrophilicity that can make water molecules penetrate quickly [15].

### 2.2.3 GO/C60 membrane

Due to the diameter of about 0.7-1 nm, C60 becomes an ideal material for adjusting the spacing between graphene oxide layers [18]. When compared with other materials, C60 molecules also show its ideal rigidity, which is critical to its stability. Before preparing GO/C60 membrane, researchers followed the processes as reported to prepare C60-grafted GO first [19]. Then, they dispersed the prepared C60 grafted GO in toluene. After acoustic bath treatment, they got GO/C60 suspension, which needed to be vacuumed through an Anodisc alumina filter membrane and dried overnight in a 60°C vacuum oven. Next, they cut this membrane into rectangular strips and encapsulated it with epoxy. In the end, they bonded GO/C60 laminates into a groove in a plastic sheet and obtained the GO/C60 membrane successfully. With C60-grafted GO, it's much easier to control the interlayer spacing of GO membranes [17].

## 2.3 Applications of graphene oxide membranes

Evaluation of the desalination performance of the membrane focuses most often on two basic indexes: water flux and salt rejection rate. Water flux, the rate of feed solution passing through the membrane, is dependent on the three factors of volume of solution passing the membrane, the cross-sectional area of the membrane, and

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the time period [15,17]. Salt rejection rate, the rate of salt ions intercepted by the membrane, is obtained by calculating the salt concentration of the solution on both sides [15,17].

### *2.3.1 Mixed matrix membrane (MMM)*

The MMM membranes with CS incorporation synthesized in the first method are tested. As is shown in Fig. 1, the water flux through the membrane increases and then decreases as the GO constant increases from 0 to 2 wt% under the condition of 60 ºC, and it is hardly affected by the concentration rate of the solution. The highest water flux of approximately 17 kg $m^{-2}$ $h^{-1}$ is achieved roughly at 1 wt% GO constant when tested by NaCl solution with concentration ranging from 3.5% to 10%. Since hydrophilicity directly affects the water adsorption rate on the membrane, it is estimated that the increase of water flux at a lower rate of GO results from the increased hydrophilicity brought by the hydrophilic GO. However, this advantage of further added GO is cancelled by the strong interaction between GO and CS, causing the adsorption rate to decrease. Additionally, the higher possibility of cross-link, a phenomenon that is beneficial to the membrane's stability [13] but reduces the water diffusion rate [14], also contributes to the decrease of water flux when the GO content is raised from 1 to 2 wt%. In all cases, the salt rejection rate maintains over 99.99% with various contents of GO. It can be concluded that the CS-mixed MMM membrane exhibits an acceptable water flux and a satisfactorily high salt rejection rate while reducing the number of interfacial defects that can degrade the rejection rate [20].

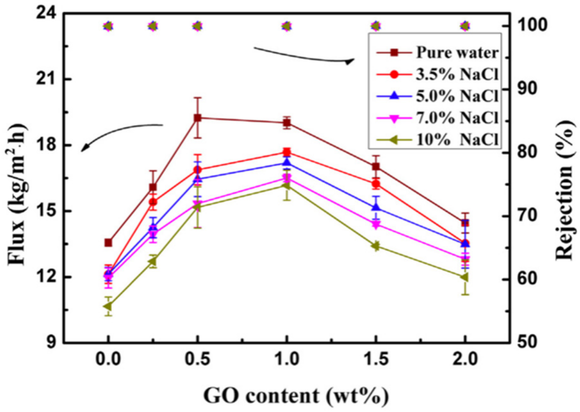


**Fig. 1.** PV desalination performance of CS/GO MMMs with different GO content at 70 °C [14].

### *2.3.2 Reduced nanoporous graphene oxide membranes (rNPGO)*

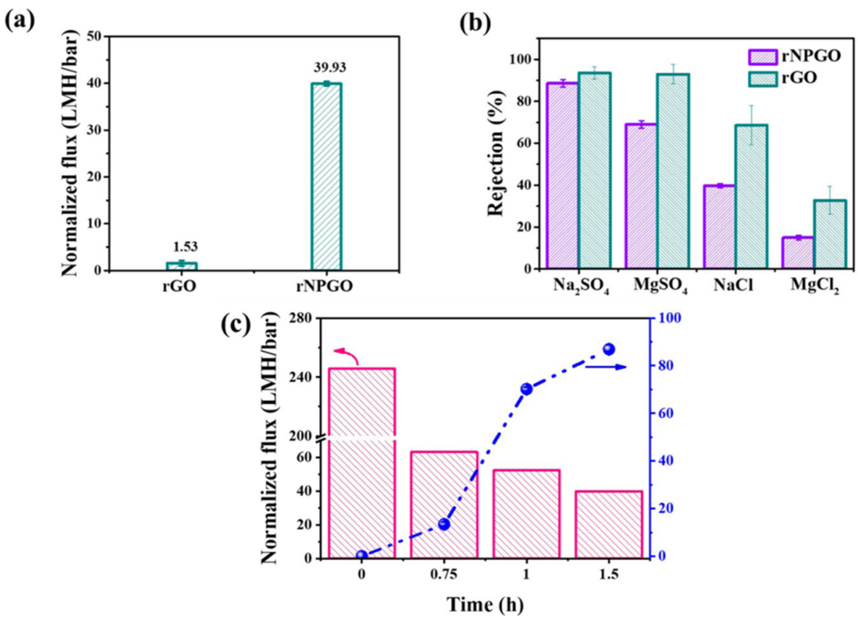


**Fig. 2.** (a) Water permeability and (b) salt rejection of rGO and rNPGO membranes at the same loading of 55.73 mg/$m^2$. (c) Thermal treatment time of the resultant rNPGO membranes [15].

Synthetic rNPGO membranes with dead-end filtration systems are tested. As shown in Fig. 2a, at the same loading of 55.73 mg/$m^2$, the water flux of rNPGO membrane is 39.93 ± 0.46 LMH/bar, while that of rGO membrane is only 1.53 ± 0.59 LMH/bar. By comparing the magnitude of water flux, it has been found that the water permeability of rNPGO membrane is almost 26 times that of rGO membrane. These data indicate that nanopores can greatly improve the permeability of membranes. Although rNPGO and rGO membranes show similar rejection to $Na_2SO_4$ in Fig. 2b, the high-water permeability of rNPGO membranes is an absolute advantage in the comparison of the two membranes [15].

In addition to comparing the water permeability and salt resistance of the two membranes, it is necessary to understand how thermal reduction will affect the performance of rNPGO membranes. After thermal treatment for different times, the water permeability of the rNPGO membrane decreased. Especially after being heated for 0.75 h, the water permeability decreased sharply from 268.51 LMH/bar to 63.06 LMH/bar. Besides, when the heat treatment time lasted for 1.5 h, the rejection rate of $Na_2SO_4$ increased from 0 to about 90%. This result demonstrates that adjusting the thermal treatment time can change the performance of rNPGO membranes effectively. Referring to the relevant articles, rNPGO membrane obtained through hydrogen $H_2O_2$ and thermal reduction have better water permeability, and its performance can be adjusted by adjusting the time of thermal reduction [15].

### *2.3.3 GO/C60 membrane*

Fullerene-tailored GO membranes with different GO:C60 rates (1:2, 1:1 and 2:1 respectively) are fabricated and tested. The results are presented in Fig. 3. The ion rejection rate shows a linear relation with the change of pressure between the two sides for all membranes tested. With the increase in pressure from 1 to 5 bar, the ion rejection rate of GO:C60 1:1 membrane decreases from roughly 90% to 83%, because the increased pressure imposes a larger force on the ions to overcome the kinetic barriers that retain them on the membrane. The other two membranes also present a similar trend. Comparing the three membranes, the membrane with a relatively higher rate of C60 shows a slightly higher rate of salt rejection.

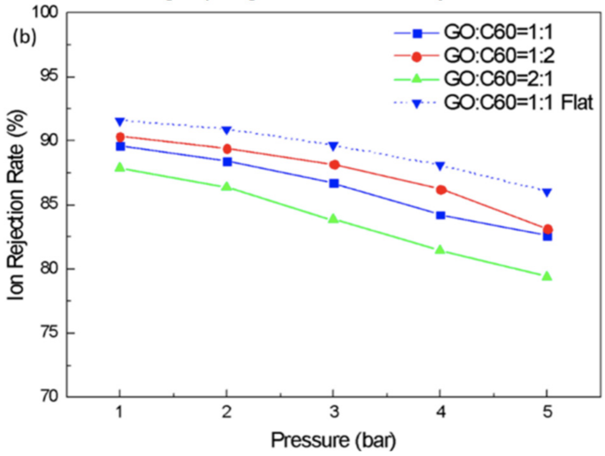


**Fig. 3.** Ion rejection rate through GO/C60 membrane with different pressure applied [17].

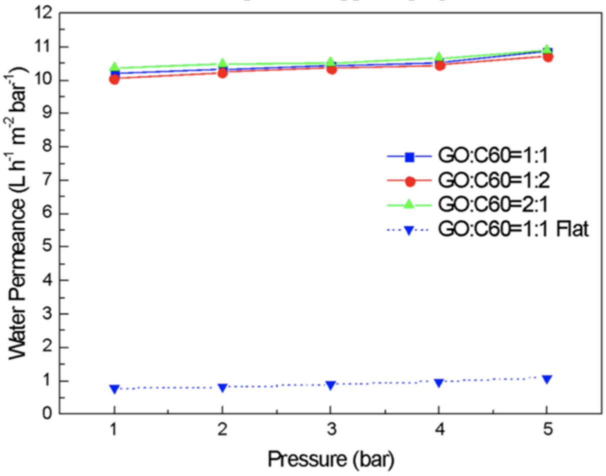


**Fig. 4.** Water permeation rate through GO/C60 membrane with different pressure applied [17].

The water permeation flux is also considered to have a linear relation with the increase in pressure, as is shown in Fig. 4. All three membranes present a slight increase between 11 and 12 L $h^{-1}$ $m^{-2}$ $bar^{-1}$ (this unit is similar to kg $h^{-1}$ $m^{-2}$ $bar^{-1}$ when saline water is tested) when pressure increases from 1 to 5 bar. Similar to the pressure effect on the ions, the increased pressure strengthens the capacity of the water molecules to overcome the membrane energy barrier.

### 2.4 Evaluation

Based on the above findings in 2.3, it can be seen that the MMM fabricated as a pervaporation membrane exhibits the highest salt rejection rate, while the rejection rate of GO/C60 membrane ranges from roughly 80% to 90% given different pressures. The rejection rate of the rNPRO membrane is similar to that of the rGO membrane, and it will increase with the increase of heat treatment time. On the other hand, the GO/C60 membrane is expected to have a higher water flux than the MMM when the pressure added is over 2 bars. The water flux of the rNPRO membrane is much higher than that of rGO membrane. However, since these membranes are utilized in different methods and occasions, more controlled experiments are to be designed to accurately compare the desalination capacity of the GO membranes fabricated by different methods.

## 3 Conclusion

In a world lacking freshwater seriously, graphene oxide membrane, a novel material, plays an important role in water desalination. Through focusing on three kinds of graphene oxide membranes in desalination, and comparing and evaluating their strengths and weaknesses, the main conclusion that can be drawn is that mixed matrix membrane has high chemical and thermal stability and hydrophilicity; reduced nanoporous graphene oxide membrane has a higher water permeability than reduced graphene oxide membrane; GO/C60 membrane has long-term stability and good salt rejection. With these advantages, the three membranes possess great potentials to solve the freshwater shortage in future. Nevertheless, the processes of making those membranes are not very mature and they require many elaborate steps due to the extremely small membrane gaps, so mass production of membranes is a big problem for researchers. All in all, enhancing the understanding of graphene's properties and developing novel methods to make graphene-based membranes will certainly lead to some greater improvements in the field of water desalination.

## References

1. S.P. Surwade, S.N. Smirnov, I.V. Vlassiouk, R.R. Unocic, G.M. Veith, S. Dai, S. M. Mahurin, Water desalination using nanoporous single-layer graphene, *Nat. Nanotechnol.* **10** 459–464 (2015)
2. S.F. Anis, R. Hashaikeh, N. Hilal, Functional materials in desalination: a review, *Desalination* **468** (2019)
3. P.J.J. Alvarez, C.K. Chan, M. Elimelech, N.J. Halas, D. Villagran, Emerging opportunities for nanotechnology to enhance water security, *Nat. Nanotechnol.* **13** 634–64 (2018)

4. Earth's Water Resources https://www.aslo.org/what-is-aquatic-science/earths-water-resources/
5. Global Water Intelligence (GWI/IDA DesalData), Market profile and desalination markets, 2009–2012 yearbooks and GWI website, http://www.desaldata.com/.
6. E. Drioli, A.I. Stankiewicz, F. Macedonio, Membrane engineering in process intensification—an overview, J. Membr. Sci. 380 (2011) 1–8.
7. L.F. Greenlee, D.F. Lawler, B.D. Freeman, B. Marrot, P. Moulin, Reverse osmosis desalination: water sources, technology, and today's challenges, Water Res. 43 (2009) 2317–2348.
8. A. Boretti, S. Al-Zubaidy, M. Vaclavikova, M. Al-Abri, S. Castelletto, S. Mikhalovsky, Outlook for graphene-based desalination membranes, *Npj Clean Water* 1:5; doi:10.1038/s41545-018-0004-z (2018)
9. J. Sun, X. Qian, Z. Wang, F. Zeng, H. Bai, N. Li, Tailoring the microstructure of poly (vinyl alcohol)-intercalated graphene oxide membranes for enhanced desalination performance of high-salinity water by pervaporation, *Journal of Membrane Science* **599** 117838 (2020)
10. V. Mortazavi, A. Moosavi, A. Nouri-Borujerdi, Enhancing water desalination in graphene-based membranes via an oscillating electric field, *Desalination* **495** 114672 (2020)
11. M. Delpisheh, M. A. Haghghi, H. Athari, M. Mehrpooya, Desalinated water and hydrogen generation from seawater via a desalination unit and a low temperature electrolysis using a novel solar-based setup, *international journal of hydrogen energy* **46** 7211e7229 (2021)
12. D. Cohen-Tanugi & J. C. Grossman, Mechanical strength of nanoporous graphene as a desalination membrane, *Nano Letters* **14** 6171–6178. doi:10.1021/nl502399y (2014)
13. D. I. Petukhov, O. O. Kapitanova, E. A. Eremina and E. A. Goodilin, Preparation, chemical features, structure and applications of membrane materials based on graphene oxide, *Mendeleev Communications* **Volume 31**, Issue 2, Pages 137-148, (2021)
14. X. Qian, N. Li, Q. Wang, S. Ji, Chitosan/graphene oxide mixed matrix membrane with enhanced water permeability for high-salinity water desalination by pervaporation, *Desalination* **438** 83–96 (2018)
15. Y. Li, W. Zhao, M. Weyland, S. Yuan, Y. Xia, H. Liu, J. Yang, C. D. Easton, C. Selomulya, and X. Zhang, Thermally Reduced Nanoporous Graphene Oxide Membrane for Desalination, *Environmental Science & Technology* **53** 8314−8323 (2019)
16. J. Lyu, X. Wen, U. Kumar, Y. You, V. Chen and R. K. Joshi, Separation and purification using GO and r-GO membranes, *RSC Advances*, **8**, 23130–23151.doi:10.1039/c8ra03156h. (2018)
17. Y. Liu, B. Phillips, W. Li, Z. Zhang, L. Fang, J. Qiu, and S. Wang, Fullerene-Tailored Graphene Oxide Interlayer Spacing for Energy- Efficient Water Desalination, *ACS Applied Nano Materials* **1** 6168−6175 (2018)
18. A. G. Nasibulin, P. V. Pikhitsa, H. Jiang, D. P. Brown, A. V. Krasheninnikov, A. S. Anisimov, P. Queipo, A. Moisala, D. Gonzalez, G. Lientschnig, et al, A Novel Hybrid Carbon Material, *Nat. Nanotechnol.* **2** 156−161 (2007)
19. D. Yu, K. Park, M. Durstock, L. Dai, Fullerene-Grafted Graphene for Efficient Bulk Heterojunction Polymer Photovoltaic Devices, *J. Phys. Chem. Lett* **2** 1113−1118 (2011)
20. Lin Li, Jingwei Hou, Yun Ye, Jaleh Mansouri, Vicki Chen, Composite PVA/PVDF pervaporation membrane for concentrated brine desalination: Salt rejection, membrane fouling and defect control, *Desalination* **422** 49-58 (2017)