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Enhanced Separation Performance of Graphene Oxide Membrane through Modification with Graphitic Carbon Nitride

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Abstract: The treatment of tritiated nuclear wastewater is facing greater challenges with the continuous expansion of the nuclear industry. The key to solving the issue of detritium in low-abundance tritium water lies in developing highly efficient and cost-effective hydrogen isotope separation technology. Graphene oxide (GO) membrane separation method exhibits greater potential compared to other existing energy-intensive technologies for the challenging task of hydrogen isotope separation in nuclear wastewater. In recent years, researchers have explored few strategies to enhance the performance of graphene oxide (GO) membranes in hydrogen isotope water treatment, recognizing the current limitations in separation efficiency. In this study, the GO/g-C₃N₄ composite membrane has been successfully employed for the first time in the separation of hydrogen isotopes in water. A series of GO membranes were prepared and their performances were tested by a self-made experimental device. As a result, the separation performance of the GO membrane was enhanced by the modification with graphitic carbon nitride (g-C₃N₄). The permeation rate of the GO/g-C₃N₄ membrane was higher than that of the GO membrane, while maintaining a high separation factor. Our study also demonstrated that this phenomenon can be attributed to the changes in membrane structure at the microscopic scale. The H/D separation factor and the permeate flux of the composite membrane containing g-C₃N₄ of 6.7% by mass were 1.10 and $7.2 \times 10^{-5} \text{ g} \cdot \text{min}^{-1} \cdot \text{cm}^{-2}$ are both higher than that of the GO membrane under the same experimental conditions, which is promising for the isotope treatment.

Keywords: graphene oxide; hydrogen isotope; separation membrane; nanomaterial



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1. Introduction

Tritium (T) is a radioactive isotope of hydrogen that can enter the human body through inhalation and skin absorption, posing internal radiation hazards [1]. It occurs in minute quantities in nature and is primarily generated through nuclear reactions, particularly in heavy water reactors (HWRs) where heavy water is used for moderation and cooling purposes [2]. The current primary approach for tritium management in nuclear power plants involves its controlled release into the environment, such as discharging into the sea after dilution with a significant volume of seawater [3].

In the foreseeable future, the expansion of the nuclear industry presents significant challenges regarding the management and treatment of tritium-containing nuclear wastewater. Therefore, the application of tritium extraction or tritium separation technology is imperative in the treatment of nuclear wastewater containing tritium. However, the existing tritium separation techniques such as cryogenic distillation [4] and combined electrolysis catalytic exchange [5,6] are relatively energy-intensive, complex, and unfriendly to the environment. On the contrary, the membrane separation process exhibits significant potential for tritium treatment owing to its low energy consumption, exceptional selectivity, and high operational efficiency. Moreover, it has already gained widespread application in

the field of industrial wastewater treatment [7]. As a result, it is necessary to explore an appropriate separation membrane and analyze its working principle and feasibility before designing a complete industrial facility.

Two-dimensional materials have gained significant attention from the public since the discovery of graphene [8]. Graphene's unique atomic-level thickness, high mechanical strength, stable physical and chemical properties, and impermeability caused by dense atomic arrangement make its derivatives worthy of attention as membrane separation materials, such as porous graphene and graphene oxide [9,10]. In the past decade, numerous researchers have dedicated their efforts to investigating the preparation methods [11], mass transfer mechanisms [12], and separation performance [13,14] of graphene-based two-dimensional separation membranes. These endeavors have greatly advanced scientific progress in this field.

Porous graphene can be prepared by focused ion beam and can be used for hydrogen purification [15,16]. However, the filtration performance of this membrane entirely depends on the pore size, and since the kinetic diameters of different hydrogen isotope molecules vary little, and porous graphene films are not suitable for hydrogen isotope separation. Graphene oxide has become the most promising material for two-dimensional hydrogen isotope separation membranes due to its strong mechanical strength, excellent purification and separation performance, and suitability for large-scale production [17]. Laminar GO membrane contains hydroxyl and epoxy groups that maintain a greater spacing between the graphene layers in the unoxidized regions of the film [18]. Moreover, these groups tend to cluster together, creating a large network of unoxidized capillary channels for particles to pass through. Due to the unique hydrophilicity of oxygen-containing groups and capillary pressure generated by graphene's hydrophobic layer, water molecules can rapidly penetrate through the capillaries network, achieving a perfect GO membrane penetration of water [19].

Currently, extensive research has been conducted to investigate the transport mechanism of gas, water, and solution ions across the GO membrane [20,21], as well as the water molecular arrangement between the interfaces of two graphene layers, particularly within the capillaries in the GO membrane [22]. Water is transported in the form of double-layer ice in the unoxidized region between the two nanosheets in the GO film, that is, inside the nanoscale capillary [23]. It is destroyed (melted) as it passes through the oxygen-containing groups at the edge of the nanosheet, after which the water molecules penetrate into the next capillary layer and recombine into a double-layer ice structure to continue its transport [24]. The GO membrane exhibits a remarkable ion screening capability in solution desalination experiments that smaller ions (with a hydration radius of less than 4.5 Å) can rapidly permeate through the membrane, while larger and organic molecules are virtually impermeable [18].

The hydrophilic nature of the GO membrane makes it a promising candidate for isotope water separation technology. An experiment proved that the content of heavy isotopes (deuterium and tritium) would be significantly reduced after hydrogen isotope water passed through the GO membrane [25]. In recent years, a large number of researchers have invested in the study of the optimization of the separation performance of GO membranes. Compared to GO membranes, various separation membranes optimized based on GO materials show better separation properties, such as higher penetration rates or higher separation factors. These modification methods of the GO membrane include the reduction method [26], surface modification method [27], intercalation method [28], and so on. RGO membranes exhibited a comparable D₂O blocking rate to GO membranes while demonstrating superior mechanical stability and serving as an effective material for the separation of hydrogen isotope water mixtures [29]. A research team employed perfluoroalkyl substances [30] or fluorinated silica nanoparticles [31] to modify one side of the GO membrane forming a hydrophobic or super-hydrophobic surface, resulting in modified GO membranes exhibiting enhanced separation factors.

It is worth mentioning that researchers commonly employ heavy water instead of tritium to analyze the separation of hydrogen isotopes in water, primarily due to the potential radiation hazards involved. The H/D separation factors can reflect the H/T separation factors with some theoretical calculations [25].

In this study, GO membranes were modified with graphitic-phase carbon nitride ($g\text{-C}_3\text{N}_4$) and tested using self-made distillation equipment to demonstrate that this intercalation method can enhance the performance of the GO membranes in separating hydrogen isotopes. The impact of intercalating different quantities of $g\text{-C}_3\text{N}_4$ on the selective separation of GO membranes was also investigated.

2. Materials and Methods

2.1. Materials

The nature graphite powder was purchased from Tianjin Damao Co., Ltd. (Tianjin, China). The $g\text{-C}_3\text{N}_4$ dispersion was supplied by Nanjing XFNANO Technology Co., Ltd. (Nanjing, China). Potassium permanganate (KMnO_4), concentrated sulfuric acid (H_2SO_4 , 98%), hydrogen peroxide (H_2O_2 , 30%), and hydrochloric acid (HCl , 37%) were supplied from Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). PC (polycarbonate) membranes and AAO (anodic aluminum oxide) membranes with 0.22 μm pore size were obtained from Whatman Co., Maidstone, UK. Hydrophobic PTFE membranes (tetrafluoroethylene, ϕ 47 mm, pore size ~ 1 μm , Millipore Co., Billerica, MA, USA) were used as the support in the distillation tests. The heavy water (99.9 at. % D) was purchased from Energy Chemical Co., Ltd. (Anqing, China). Deionized water (18.25 M Ω) was produced by Ultra-pure Water Purifiers (Ulupure UPR-II, Chengdu, China) in the lab.

2.2. Fabrication of Membranes

The GO nanosheets were synthesized from graphite powder using the improved Hummers method [32]. GO dispersion solution was prepared by the ultrasonic dispersing of dry GO in deionized water. The GO membrane was fabricated on a PC substrate through vacuum filtration. In this study, 0.2 g of dried GO solid was sonicated in 100 mL of deionized water to make 2 mg/mL of GO dispersion. After that, 5 mL, 7.5 mL, 10 mL, and 15 mL GO dispersion solutions were taken and prepared into GO membranes of varying thicknesses by vacuum filtration.

The preparation of the GO/ $g\text{-C}_3\text{N}_4$ composite membrane followed a similar procedure as that of the GO membrane. The mass concentrations of GO and $g\text{-C}_3\text{N}_4$ suspensions were 2 mg/mL and 0.18 mg/mL, respectively. In this work, 2 mL, 4 mL, 6 mL, 8 mL, and 10 mL $g\text{-C}_3\text{N}_4$ suspensions were added into 5 mL GO suspensions. The suspension of GO and $g\text{-C}_3\text{N}_4$ was intensively mixed by ultrasonication for 2 h and then filtered on the AAO substrate to form a membrane. Following a 24 h drying period at room temperature, the independent membrane could be easily detached from the substrate.

2.3. Characterization of the Membranes

The surface and cross-section morphology of membranes were studied by a field emission scanning electron microscope (FE-SEM, JEOL JSM-7900F, Yamagata, Japan). The gold-coated membranes were soaked in liquid nitrogen to make them easier to tear. The observation of GO nanosheets was supplied by a tunneling electron microscope (TEM, Hitachi H-7650, Marunouchi, Japan). X-ray diffraction (XRD, Bruker D8 ADVANCE, Karlsruhe, Germany) equipped with Cu $K\alpha$ radiation ($\lambda = 0.154$ nm) was applied to measure the d-spacing of the prepared membranes. X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB QXi, Morecambe, UK) and Raman spectra (Horiba Jobin Yvon LabRam HR800, Palaiseau, France) were used to recognize the chemical composition of the membrane surface.

2.4. Selective Separation Tests

2.4.1. Static Diffusion Experiment

The static diffusion experiment used a 50 mL glass sample bottle, which was filled with 20 mL H₂O or D₂O (99.9%) liquid. The GO membrane was covered at the opening of the sample bottle, and the place where the mouth of the bottle contacted the membrane was sealed using an O-type silicone ring. The experiment was carried out at room temperature, and the weight of bottles was weighed every 24 h, based on which the amount of liquid lost was calculated. The experiment was conducted for a total of 43 days. The permeate flux (J) was calculated by equation:

$$J_i = \frac{m_i}{At} \quad (1)$$

where m , A , and t represent the mass loss of liquid in the bottle, the membrane area, and the experiment time.

2.4.2. Distillation Tests

To analyze the differences in the performance of GO membranes with different properties in the separation of hydrogen isotope water, a custom-made experimental device for the separation of hydrogen isotope water was established. As shown in Figure S1, the device is divided into three sections: the feed section consists of an evaporation chamber with a capacity of approximately 100 mL and a pressure-reducing valve; the middle section comprises a membrane carrier; and the collect section is connected to a sample bottle for collecting the filtered liquid.

In the test, the evaporation chamber was loaded into a resistance oven and insulated with thermal insulation cotton. All stainless steel components, except for the evaporation chamber and pressure-reducing valve, were covered with a glass fiber heating sleeve to prevent the condensation of water vapor and heavy water vapor within the apparatus. Two temperature controllers were used to regulate the temperature of the resistance furnace and heating sleeve, respectively. A sample collection bottle was positioned on the collection side and connected to the stainless steel tube via a high-temperature-resistant silicone hose. The GO membrane was sealed in the middle section between the silicone and stainless steel gaskets to make sure the whole device was airtight during the process. Considering the vapor pressure on the feed side can reach 0.14 MPa at 110 °C, a support PTFE membrane was attached to the permeate side of the GO membrane to prevent it from being ruptured by the high pressure.

The molar concentration of heavy water in the chamber of 10% was achieved by mixing pure D₂O with deionized water. The deuterium and hydrogen abundance of the permeated water were measured by NMR (Bruker AVANCE III 400 MHz, Karlsruhe, Germany). The heavy water samples, each with concentrations of 6%, 8%, 10%, 12%, and 14%, were combined in a 1:1 ratio with pure acetone solution. A small quantity of the resulting mixture was then transferred into an NMR tube for analysis. Two distinct peaks would appear in the ¹H NMR spectrum, namely the water peak caused by the vibrations of hydrogen in water and the acetone peak caused by vibrations of hydrogen in methyl groups in acetone. Figure S2 shows a ¹H NMR spectroscopy of a mixture of 10% heavy water and acetone with a 1:1 volume ratio. The left peak represents the water peak and the right peak represents the acetone peak, respectively. The area ratio of the two peaks is $I_{\text{H}_2\text{O}}/I_{\text{acetone}} = 1.182$. The area ratio of the two peaks was positively correlated with their contents. Finally, a graphical representation illustrating the relationship between the concentration of heavy water and the corresponding ratio is presented, revealing a linear correlation upon fitting, thus establishing a standard curve, as shown in Figure S3. To obtain the concentrations of heavy water in distillation tests, the unknown concentration of heavy water to be analyzed was mixed with an acetone solution in a 1:1 ratio, and a portion of the resulting mixture was introduced into the NMR tube. By comparing the peak area ratio of the two observed peaks in the test results with a standard curve, the heavy water concentration of the sample under investigation was determined.

The separation factor q can be calculated by equation:

$$q = \frac{C_H/C_D}{C'_H/C'_D} \quad (2)$$

where C_H and C_D represent the hydrogen and deuterium abundance of permeated water, and C'_H and C'_D denote the hydrogen and deuterium abundance of feed water. The deuterium abundance C_D is equal to the concentration of heavy water which is given by NMR results and the hydrogen abundance is equal to $1 - C_D$.

3. Results

3.1. The Characteristics of the Membranes

The GO membrane was peeled off from the AAO base membrane, immersed in liquid nitrogen, fractured, and affixed onto the front or side of the sample stage. Subsequently, it was subjected to SEM characterization following gold spraying. As depicted in Figure 1a,b, a disparity in flatness is observed between the top and bottom surfaces of the GO membrane. Herein, the top surface denotes the side exposed to air during vacuum filtration for membrane formation, while the bottom surface refers to its contact with the AAO substrate. The image reveals that the upper surface exhibits roughness and more pronounced wrinkling compared to its relatively flat counterpart on the lower surface. This phenomenon can be attributed to self-assembly occurring primarily in proximity to the AAO filter membrane on its bottom surface, resulting in a highly ordered stratified structure conducive to a flatter morphology. Conversely, due to solution evaporation effects during exposure to air, inadequate arrangement leads to wrinkling [33].

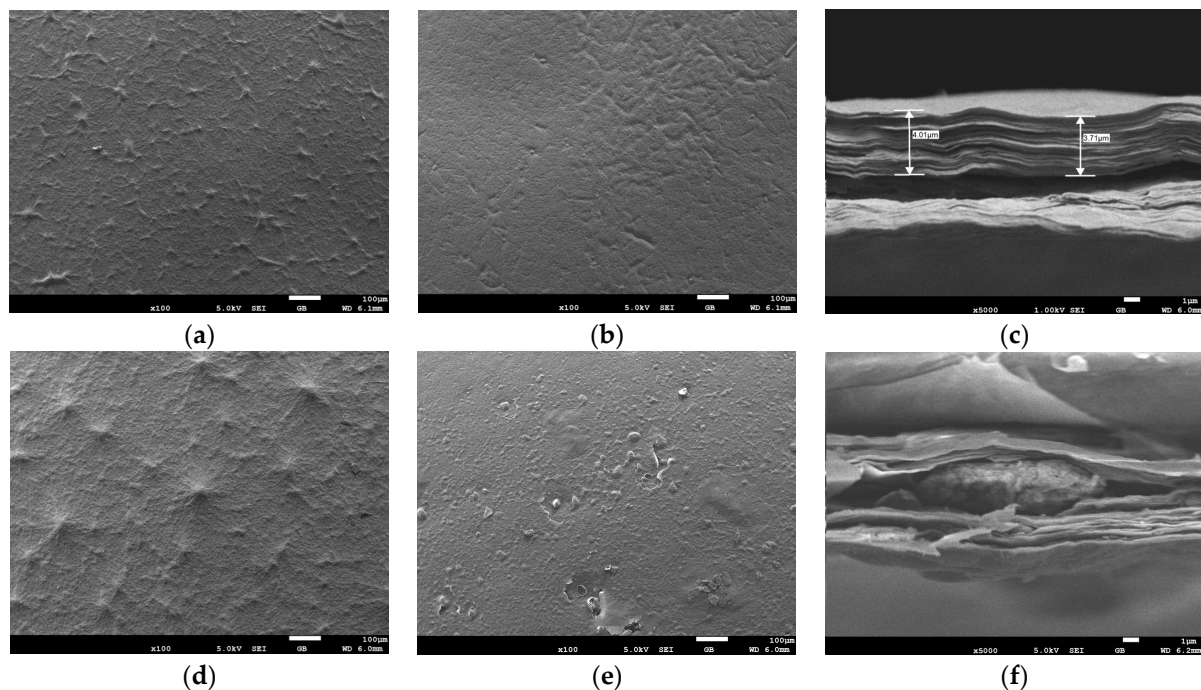


Figure 1. SEM images of (a) the top surface of the GO membrane, (b) the bottom surface of the GO membrane, (c) the cross-section of the GO membrane prepared by 10 mg dried GO, (d) the top surface of the GO/g-C₃N₄ membrane, (e) the bottom surface of the GO/g-C₃N₄ membrane, and (f) the cross-section of the GO/g-C₃N₄ membrane.

The clear laminated structure can be seen in the cross-section SEM image of the GO membrane, as shown in Figure 1c. When the amount of GO is 10 mg, the average thickness of the GO membrane is 4 μm, and the surface area of the membrane is 12.56 cm². The relationship between the amount of GO and the membrane thickness in this experiment

is 2 g/cm^3 . Compared with the GO membrane, the GO/g- C_3N_4 (the mass of GO and g- C_3N_4 was 10 mg and 0.9 mg) membrane has more bulges on the top surface (Figure 1d); correspondingly, more particles can be observed on the bottom surface (Figure 1e), and the presence of these particles increases the local roughness. In the cross-sectional SEM image of the GO/g- C_3N_4 membrane, as shown in Figure 1f, a smaller particle is observed within the interlayer region. This observation is absent in the GO membranes, suggesting the inadequate stripping of small g- C_3N_4 bulks during membrane fabrication.

The 10 mg/mL GO dispersion was diluted by a factor of 100 and subsequently dropped onto the copper net for transmission electron microscopy (TEM) characterization following a 15 min ultrasound treatment. At the edge of the copper mesh, single- or few-layer GO nanosheets were observed. Figure 2 shows a single-layer GO nanosheet whose size is about $0.2 \mu\text{m}$ in the lateral dimension, which can prove that the GO nanosheets can be striped well by the ultrasound process.

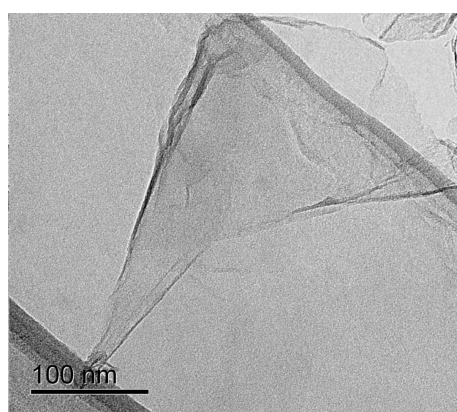


Figure 2. TEM image of a GO nanosheet.

The XRD was used to verify the effect of the intercalation of g- C_3N_4 on the structure of GO, the peaks correspond to the conjugated aromatic (001) planes. As shown in Figure 2, the characteristic peak of the GO appears at $2\theta = 11.7^\circ$, corresponding to $7.6 \text{ \AA}$ d-spacing. The characteristic peak of the GO/g- C_3N_4 appears at $2\theta = 11.24^\circ$, corresponding to a d-spacing of $7.9 \text{ \AA}$. The increase in the d-spacing was attributed to the intercalation of g- C_3N_4 nanosheets into the GO nanosheets and caused the peaks shifting in XRD.

The structural transformation of the GO membrane was confirmed by Raman analysis after modification with g- C_3N_4 . GO exhibits two absorption peaks at 1340 cm^{-1} and 1580 cm^{-1} , corresponding to the presence of disordered carbon and sp^2 hybridized planar carbon in graphene or graphite, respectively [34]. The peak at 1340 cm^{-1} (peak D) represents the vibrational disorder of carbon atoms, indicating structural defects in the aromatic ring where some sp^2 carbon atoms are transformed into sp^3 hybrid structures. Conversely, the peak at 1580 cm^{-1} (peak G) arises from the in-plane vibrations of sp^2 carbon atoms, symbolizing the symmetry and order of the aromatic ring structure. Furthermore, the I_D/I_G ratio can be employed to characterize the proportion of disordered carbon to sp^2 carbon atoms and objectively evaluate the degree of graphitization in graphene samples. The I_D/I_G ratios for the GO/g- C_3N_4 membrane, commercial GO membrane (the GO dispersion was purchased from XFNANO), and lab-made GO membrane were determined as 0.73, 0.58, and 0.59, respectively. These results indicate a lower abundance of perfect graphene layers (sp^2 hybridized carbon structure) in the GO/g- C_3N_4 membrane than that of the GO membranes.

The C1s XPS spectra of the GO membrane and GO/g- C_3N_4 membrane are shown in Figures 3c and 3d, respectively. There are five main peaks: sp^2 carbon (C–C bond) at 284 eV, sp^3 carbon (C=C bond) at 284.77 eV, hydroxyl or epoxy groups (C–O bond) at 286.17 eV, carbonyl groups (C=O bond), at 287.48 eV, carboxyl groups (O–C=O bond) at 288.77 eV [35]. The C–O/C–N peak at 286.17 eV in the GO/g- C_3N_4 spectrum is significantly

higher compared to that of the GO spectrum, indicating the successful intercalation of g-C₃N₄ into the GO membrane. Meanwhile, the combined area proportion of sp² and sp³ peaks in GO/g-C₃N₄ is 45.6%, whereas it reaches 53% in the GO spectrum.

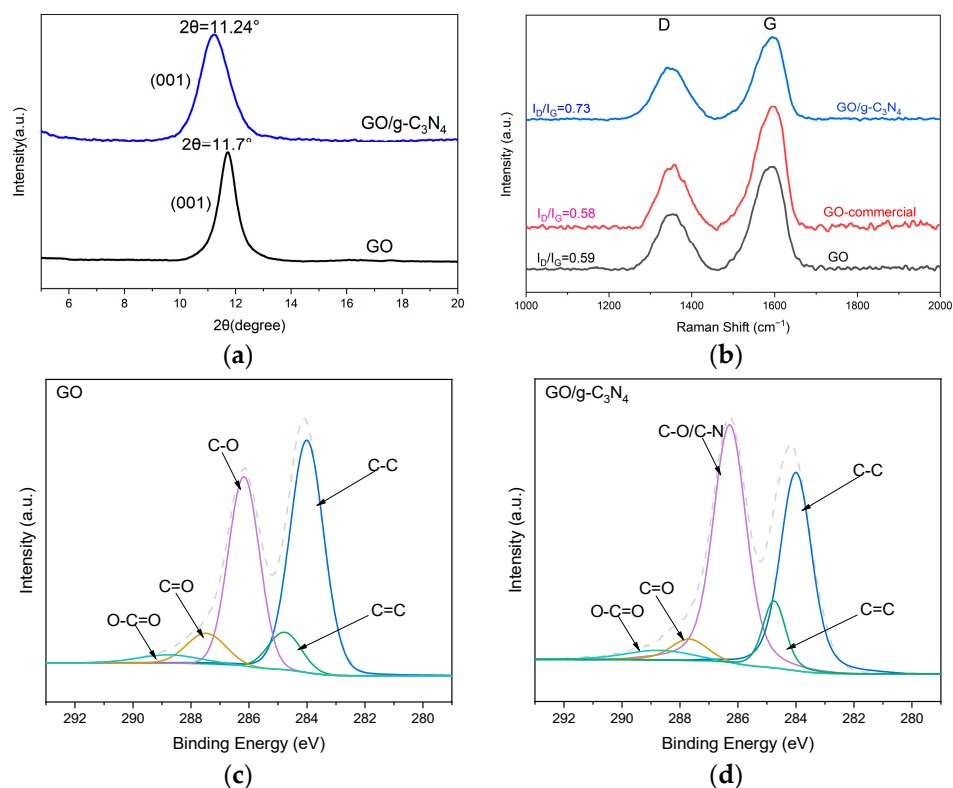


Figure 3. (a) XRD spectra of GO and GO/g-C₃N₄; (b) Raman spectra of GO, GO-commercial, and GO/g-C₃N₄; C1s XPS spectrum of (c) GO membrane and (d) GO/g-C₃N₄ membrane. The grey dashed lines represent the XPS spectral lines.

3.2. Static Diffusion Experiment

In the previously described static diffusion experiment, GO membranes of varying thicknesses were prepared by the vacuum filtration of 5 mL, 7.5 mL, 10 mL, and 15 mL GO dispersions (2 mg/mL) on PC substrate membranes. The mass of GO used was 10 mg, 15 mg, 20 mg, and 30 mg, respectively, resulting in membrane thicknesses of 4 μm, 6 μm, 8 μm, and 12 μm. The area of the membranes utilized in this experiment is approximately 2 cm². The experiment was conducted at room temperature for 43 days, the relationship between the mass loss of the samples and time is shown in Figure S4, and the evident correlation between the two variables is readily apparent. Figure 4 illustrates the permeate flux of H₂O or D₂O through these membranes. It should be noted that the data for the membrane with no added GO (0 mg) represents a control where only the PC substrate membrane was sealed at the top of the bottle. The trend evidence that the permeability of both water and heavy water decreases as the membrane thickness increases. As shown in Table 1, for the PC membrane, the D₂O permeate flux was 10.22% lower than that of H₂O, which was less than any other GO membrane. The most significant disparity was observed at a membrane thickness of 4 μm when the amount of GO was 10 mg and the permeance of D₂O was 14.73% less than that of H₂O.

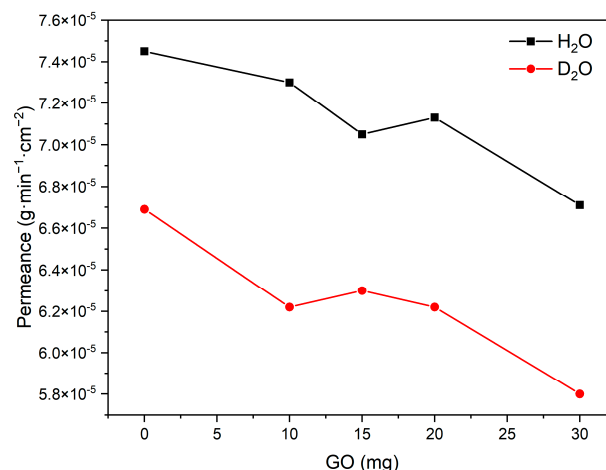


Figure 4. Permeance of H₂O and D₂O for different amounts of GO used in the fabrication of membranes in the static diffusion experiment.

Table 1. The results of the static diffusion experiment.

GO (mg)	H ₂ O Permeance (10 ⁻⁵ g/min·cm ²)	D ₂ O Permeance (10 ⁻⁵ g/min·cm ²)	Difference (10 ⁻⁵ g/min·cm ²)	Reduction
0	7.45	6.69	0.761	10.22%
10	7.30	6.22	1.07	14.73%
15	7.05	6.30	0.738	10.48%
20	7.13	6.22	0.900	12.64%
30	6.71	5.80	0.905	13.48%

3.3. Distillation Tests

For the distillation tests, the mixed suspensions of GO/g-C₃N₄ for vacuum filtration were prepared by combining 2 mg/mL dispersions of GO with 0.18 mg/mL g-C₃N₄ dispersions, followed by subjecting them to ultrasound treatment for 2 h. The volume of g-C₃N₄ dispersion was 2 mL, 4 mL, 6 mL, 8 mL, and 10 mL, corresponding to the mass of g-C₃N₄ intercalated in the GO membrane as follows: 0.18 mg, 0.36 mg, 0.54 mg, 0.72 mg, and 0.9 mg shown on the X axis in Figure 5. During the experiments, 10% D₂O was evaporated by heating the chamber to 110 °C and subsequently permeating through the membrane. The results of the distillation tests was listed in Table 2. The mass increase in the collected sample bottle was measured, and the permeate flux was calculated using Equation (1), the area of membrane in the tests is about 2 cm² and the test time is 2880 min. The integral area ratio was given by the NMR spectrum and the deuterium concentration can be obtained by comparing with standard curve shown in Figure S3. The separation factor was calculated by Equation (2).

The separation factor and permeate flux for the GO membrane, as shown in Table 2 with g-C₃N₄ mass of 0, is 1.06 and 5.6×10^{-5} g·min⁻¹·cm⁻². Additionally, the PTFE support membrane, an advanced commercial micro-filtration membrane with 0.22 µm pore size, was also tested and the separation factor is 1.02. The separation factor of GO/g-C₃N₄ composite membranes ranges from 1.04 to 1.1, which exhibits a comparable performance to that of the GO membrane. The permeability of all the composite membranes is larger than that of the GO membrane. The optimal performance is achieved with a mass of g-C₃N₄ at 0.72 mg, accounting for 6.7%. The permeate flux reaches up to 7.2×10^{-5} g·min⁻¹·cm⁻², which is 29% higher than that of the GO membrane, while maintaining a separation factor of 1.1.

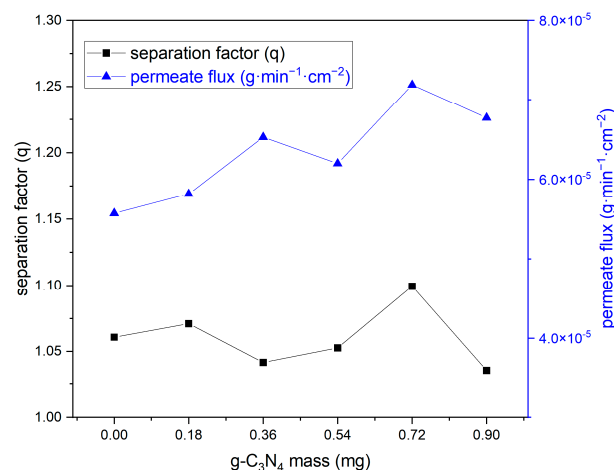


Figure 5. The separation factor and permeate flux of GO membranes with varying masses of g-C₃N₄ intercalation in the distillation tests.

Table 2. The results of the distillation tests.

g-C ₃ N ₄ Mass (mg)	Integral Area Ratio in NMR	Deuterium Concentration	Separation Factors	Permeate Mass (mg)	Permeate Flux (10 ⁻⁵ g·min ⁻¹ ·cm ⁻²)
0	1.189	9.48%	1.06	0.321	5.57
0.18	1.191	9.40%	1.07	0.335	5.82
0.36	1.187	9.64%	1.04	0.376	6.53
0.54	1.189	9.55%	1.05	0.357	6.20
0.72	1.194	9.18%	1.10	0.414	7.19
0.9	1.187	9.69%	1.04	0.390	6.77

4. Discussion

The separation factors of the GO/g-C₃N₄ membranes were similar to the GO membrane. The collective migration of water molecules in the GO membrane and the resulting hydrogen isotope separation performance are attributed to the unique structure of the GO membrane. The oxygen-containing groups located at the edges of GO nanosheets provide support for interlayer spacing, allowing water molecules to pass through and enter subsequent layers via structural defects within or at the edge of the membrane [36]. Due to its triazine or heptazine structure [37], two-dimensional g-C₃N₄ possesses an ample number of molecular-level pores for water molecules to pass through, while amino groups are present at the edges, resembling oxygen-containing groups in GO and capable of forming hydrogen bonds with water. The chemical properties of carbon nitride nanosheets closely resemble those of GO nanosheets, thereby preserving the separation efficiency of GO membranes towards hydrogen isotope water.

The permeate flux of the composite membranes exhibited an obvious increase after being modified with g-C₃N₄. Three contributing factors are postulated to account for this result:

- Large barely stripped g-C₃N₄ bulks are first deposited at the bottom of the membrane in the vacuum filtration process, as shown in Figure 1d. These particles contribute to an increased surface roughness of the membrane. A study has demonstrated that the high permeability of GO membranes observed may be attributed to the disordered microstructure of the membrane [38];
- Smaller particles of partially stripped g-C₃N₄ with a transverse size of 10 μm and height of 3 μm can be observed to be inserted between the laminates, as illustrated in Figure 1f. The I_D/I_G ratio of the GO/g-C₃N₄ membrane is larger than the GO membrane in the Raman analysis, indicating that the interlayer particles disrupt the

originally relatively complete structure and result in more defects within the composite membrane.

- The shift of the peak in the XRD pattern can prove that single or fewer layers of g-C₃N₄ nanosheets are inserted between the layers of GO nanosheets and the layer d-spacing of the GO membrane is modified [37]. The increase in d-spacing from 7.6 Å to 7.9 Å contributes to the higher permeability [39].

Moreover, the static diffusion test was carried out at room temperature for 43 days, during which the permeation rate of the membranes was maintained as time went by. In the distillation experiment, the temperature of the film is maintained at 110 °C under the action of the glass fiber heating jacket. At this temperature, the permeability rate of the GO membrane will decrease with the increase in time [29], which may be attributed to the membrane being reduced at high temperatures. This results in a slightly lower permeation rate of the GO membrane in the distillation experiment than in the static diffusion experiment performed at room temperature.

The outstanding performance of the GO/g-C₃N₄ membrane in heavy water separation suggests its potential application in the treatment of tritiated wastewater in the future nuclear industry.

5. Conclusions

In this work, we have successfully fabricated a GO membrane by the Hummers method and modified it with g-C₃N₄. Static diffusion experiments have proved that there is a difference in the penetration rate between water and heavy water through GO membrane which indicate that the GO membrane separation technology is a possible application used in a stage of nuclear wastewater treatment. A device was designed and customized to make the heavy water vapor permeate the membrane. A series of repeatable experiments were conducted to investigate the impact of the intercalation of g-C₃N₄ in the GO membrane on the separation performance. The result is the permeation rate of the GO membrane, which was modified with g-C₃N₄, which is higher than that of the GO membrane, while maintaining a high separation factor. This improvement may be attributed to changes in the membrane structure at the microscopic scale. Based on the results of the characterization experiments, we presented a comprehensive analysis from three perspectives; however, the primary determinant remains inconclusive. The mechanism remains to be fully elucidated through simulation experiments. Compared to energy-intensive technologies, GO membranes have the potential to purify low-concentration tritiated wastewater. This study demonstrates that modifying the membrane through intercalation is a feasible approach. In the future, further investigation into the different intercalating materials should be conducted to enhance the membrane separation performance and make the utilization of GO membranes in industrial-scale nuclear wastewater treatment possible.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/w16070967/s1>, Figure S1: The custom-made device for the isotope separation experiment; Figure S2: The 1H NMR spectroscopy of a mixture of 10% heavy water and acetone by 1:1 volume ratio; Figure S3: The linear relation between the area ratio of the two peaks in the NMR spectra and the heavy water concentration; Figure S4: The relationship between the mass loss of H₂O (a) or D₂O (b) and time.

Author Contributions: Conceptualization, Y.H.; investigation, Z.L. and R.F.; methodology, L.C.; data curation, S.L. and X.L.; writing—original draft preparation, Z.L.; writing—review and editing, Y.H. All authors have read and agreed to the published version of the manuscript.

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