Dehydration of C₂–C₄ alcohol/water mixtures via electrostatically enhanced graphene oxide laminar membranes

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Abstract
The dehydration of alcohol/water mixtures using pervaporation membranes requires less energy than is required by conventional separation technologies. In this paper, we report electrostatically enhanced graphene oxide (GO) membranes for the highly efficient pervaporation dehydration of C₂–C₄ alcohol/water mixtures. Positively charged molecules were introduced as the interlayer of negatively charged GO layers via layer-by-layer assembly, thereby creating an electrostatic attraction that drives the assembly of GO nanosheets into ordered interlayer channels. The effects of the feed temperature, water concentration, and continuous operation on the membrane transport behavior were systematically investigated. In the dehydration of 90 wt% alcohol/water mixtures at 70°C, the membrane exhibited ethanol/water, isopropanol/water, and n-butanol/water fluxes of 2.35, 2.98, and 4.69 kg/(m² hr), respectively, as well as separation factors for the same mixtures of 3,390, 5,790, and 4,680, respectively. This excellent alcohol/water dehydration performance outperforms those of state-of-the-art polymeric membranes and GO-based membranes.

KEYWORDS
butanol, ethanol, graphene oxide membrane, isopropanol, pervaporation dehydration

1 | INTRODUCTION

Pervaporation is a membrane-based process that has been widely used for the selective permeation and separation of water1,2 or volatile organic compounds3-5 from mixtures. There is particular interest in applying pervaporation technology for the dehydration of azeotropic mixtures, such as C₂–C₄ alcohol/water mixtures, because of the lower energy consumption compared to that with traditional distillation processes. There are two critical points for the development of pervaporation technology2: (a) developing novel membrane materials to improve the permeate flux and separation factor; (b) process design that often combines pervaporation with one or more other separation technologies.3 The first point is the focus of this work. Traditional membrane materials for solvent dehydration are mainly polymers, which suffer a general trade-off between permeability and selectivity.5-7 Inorganic materials such as zeolites8 and metal-organic frameworks9 have shown excellent separation performance for solvent dehydration, and the large-scale fabrication of defect-free membranes would further promote the use of inorganic membranes in the chemical industry.10 As an emerging alternative membrane material, graphene oxide (GO), which has a single-layer structure offers great potential to minimize the membrane thickness and, thus, maximize the permeance.1,11-13 Moreover, the functional groups (e.g., epoxy groups, hydroxyl groups, and carboxyl groups) of GO can be chemically modified14 during membrane fabrication, thus forming water transport channels between the GO nanosheets.15

Despite their great potential for water separation, GO membranes suffer from some practical problems, including relatively low separation performance and structural instability in water.13,16 Thus, there is much scope for improving the separation performance of GO.
membranes for practical use. Laminar GO membranes are based on weak interlayer interactions, which result in a low binding force between the GO nanosheets and, thus, excessive swelling of the GO membranes in water as well as stability issues. The interlayer channels are considered to be the main transport pathways of water through GO membranes. Thus, precision assembling and tuning of the interlayer structure of GO membranes are critical to improve the membrane stability and separation performance.

Various strategies have been proposed to regulate the interlayer structure of GO membranes to achieve selective water transport and improve their structural stability in water. Among them, crosslinking is the most widely studied approach. Hung et al. used a diamine monomer to crosslink GO frameworks with interlayer spacings varying from 0.87 to 1.04 nm. The resulting diamine-crosslinked GO membranes showed highly improved selectivity for ethanol dehydration via pervaporation. Sun and co-workers found that the mechanical stability of GO membranes can be improved by incorporating diboronic acids to form covalent bonds with GO nanosheets. Apparently, the strong covalent bonds endow the GO membranes with enhanced selectivity and stability but reduce the permeance because of the reduction in the size of the interlayer channels.

Intuitively, introducing molecular interactions that are weaker than covalent bonds, for example, electrostatic interactions, could enable the formation of selective and stable interlayer channels while preventing the excessive reduction in the number and size of the channels within the GO membranes. In fact, the assembly of polyelectrolytes and GO nanosheets via electrostatic interaction has been demonstrated to be a feasible strategy to improve the separation performance of GO membranes for water filtration processes including nanofiltration and forward osmosis. However, to date, the potential of this technique for enhancing the pervaporation performance of GO membranes has not fully been explored.

In this work, we introduced a typical polycation, chitosan (CS), as a modifier to tune the interlayer structure of GO membranes to achieve highly efficient pervaporation dehydration of alcohol–water mixtures. Our earlier work proposed coating one CS layer on the surface of GO laminate, thereby reaching a high flux of 10.0 kg/(m² hr) and moderate separation factor of 1,520 for dehydration of 10 wt% n-butanol/water mixtures at 70°C. The high flux was attributed to the highly enhanced water sorption from the CS layer and molecular channels from the GO laminates. However, highly selective dehydration of alcohols with smaller molecular size than butanol (e.g., ethanol, isopropanol) were not realized in this CS@GO membrane, due to the large interlayer height (~1.02 nm) of the GO layer. By contrast, this work focused on utilizing the electrostatic features of CS to drive the assembly of GO nanosheets into ordered interlayer channels with remarkably enhanced molecular sieving effects and suppressed swelling in water. Specifically, CS is positively charged via the protonation of the amine functional groups in acidic solution, thereby resulting in electrostatic attraction with the negatively charged GO nanosheets during layer-by-layer assembly of the laminar GO membrane. The resulting CS/GO membranes exhibited high fluxes and excellent separation factors for the pervaporation dehydration of C₂–C₄ alcohol/water mixtures.

2 | EXPERIMENTAL SECTION

2.1 | Materials

CS, acetic acid, sodium hydroxide, and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd. Polyacrylonitrile (PAN) ultrafiltration membranes with a nominal pore size of 20 nm were purchased from Shandong Lanjing Trading Co., Ltd. The molecular weight cutoff is about 50,000 Da. Deionized water was prepared before use. The GO dispersion was purchased from Nanjing Jicang Nano Technology Co., Ltd.

2.2 | Membrane fabrication

A dispersion of 0.5 wt% GO was diluted with water to 0.01 wt%, sonicated for 60 min, and centrifuged for 10 min to form a uniform GO dispersion. Then, 2 wt% acetic acid solution was used as a solvent to dissolve CS powder with stirring at 40°C for 24 hr to prepare a CS solution. A hydrolyzed PAN support (prepared by soaking PAN in 1.5 M NaOH at 55°C for 30 min) was fixed to a glass plate that was placed on the turntable of a spin coater. After the hydrolysis process, the nitrile groups decreased and the hydroxyl groups increased, which can generate more hydrogen bonds with CS to enhance the interfacial adhesion. Then a few drops of the CS solution were added to the center of the support, and rotation was turned on. After the turntable had stopped rotating, a few drops of GO dispersion were dropped onto the turntable in the same manner, and the rotation was started again. The spin casting of the CS solution followed by that of the GO dispersion was recorded as the formation of one bilayer. A certain number of bilayers were formed on the PAN substrate by repeating the spin-coating process, in which the out layer of the final membrane was set as GO. The prepared CS/GO membrane was placed in a drying oven and dried at room temperature for more than 24 hr. The heat treatment might be also performed after each bilayer coating. However, it would result in a denser membrane structure that is not favorable for the permeation flux.

2.3 | Characterization

The morphologies and energy dispersive spectroscopy (EDS) analysis of the membrane samples were obtained by field-emission scanning electron microscopy (S4800, Hitachi, Japan). The roughness values (10 μm × 10 μm), as well as the height profiles, of the GO nanosheets were obtained by atomic force microscopy (AFM, Bruker Dimension Icon, Germany). X-ray diffraction (XRD, Bruker D8 Advance, Germany) measurements were performed at room temperature in the range of 5° ≤ 2θ ≤ 40° in increments of 0.02°/s. X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250) was used to determine the chemical compositions of the sample surfaces. Zeta potential analysis (Zetasizer Nano ZS90, Malvern,
UK) was carried out to characterize the charge of the coating solution at different pH values.

2.4 | Pervaporation measurements

The pervaporation dehydration of alcohol/water mixtures was used to analyze the separation performance of the membrane. The method can be found in our previous work.30 The effective membrane area for pervaporation operation is 2.2 cm². The permeation flux (J) and separation factor (β) are two key parameters that reflect the separation performance of a membrane, as defined by Equations (1) and (2).

\[
J = \frac{W}{AT} \tag{1}
\]

\[
\beta = \frac{Y_A}{Y_B} \tag{2}
\]

Here, \(W\) is the mass of permeate (g), \(A\) is the membrane area (m²), \(t\) is the operation interval (hr), \(X_A\) and \(Y_A\) are the mass fractions of water in the feed and permeate, respectively, and \(X_B\) and \(Y_B\) are the mass fractions of alcohol in the feed and permeate, respectively.

The relationship between operating temperature and permeance can be determined using the Arrhenius equation.31 The activation energy for water and alcohol permeation can be calculated by fitting the slope of the line using Equation (3).

\[
P_1 = A_1 \exp\left(-\frac{E_1}{RT}\right). \tag{3}
\]

Here, \(P_1\), \(A_1\), \(E_1\), \(R\), and \(T\) represent the permeance (1 GPU = 3.33 x 10⁻¹⁰ mol/[m² s Pa]), gas permeation unit, pre-exponential factor (GPU), activation energy (J/mol), gas constant (8.314 J/[mol K]), and operating temperature (K), respectively.

To explore the influence of temperature on the flux and separation factor, the driving-force-normalized permeance and selectivity32 can be calculated using Equations (4) and (5).

\[
\left(\frac{P}{I}\right)_i = \frac{J_i}{P_{x0} - P_i} = \frac{J_i}{\alpha_0 Y_0 P_{x0}^\text{sat} - P_i}, \tag{4}
\]

\[
\alpha = \left(\frac{P}{I}\right)_A / \left(\frac{P}{I}\right)_B. \tag{5}
\]

Here, \((P/I)_i\) is the permeance of component \(i\), and \((P/I)_A\) and \((P/I)_B\) represent the permeances of water and alcohol, respectively. \(P_{x0} - P_i\) is the total driving force for the transport of component \(i\), \(P_{x0}\) and \(P_i\) are the vapor pressures of component \(i\) on the feed and permeate sides, respectively. \(P_i\) is 0 because of the low pressure on the permeate side (close to vacuum, ~160 Pa). \(x_0\) and \(y_0\) represent the activity coefficient and mole fraction of component \(i\) of the feed, respectively, and \(P_{x0}^\text{sat}\) is the saturated vapor pressure (Pa) of pure component \(i\) at a set temperature.

3 | RESULTS AND DISCUSSION

3.1 | Membrane fabrication

The molecular interactions between CS and GO were studied using zeta potential measurements and XPS analysis. The zeta potential of GO dispersions (0.01 wt%) and CS solutions (0.05 wt%) at different pH values were measured to determine the electrostatic interactions (Figure 1b). Because of the ionization of COOH to COO⁻ in water, the zeta potential of the GO dispersion ranged from ~37.83 to ~60.03 mV. The GO dispersion showed a strong negative surface charge over a wide range of pH values (2.3–10.0). Meanwhile, the CS was positively charged because of the protonation of the amine functional groups in the acidic solution, as confirmed by the zeta potential increasing from 3.62 to 56.63 mV as the pH increased from 7.1 to 2.0. Under alkaline conditions, the CS solution was slightly negatively charged, and the zeta potential decreased from ~0.69 to ~2.89 mV as the pH increased from 8.1 to 10.0. On preparing the CS/GO membrane, the 0.01 wt% GO dispersion of pH 3.7 had a zeta potential of ~60.03 mV, whereas the 0.05 wt% CS solution at pH 2.7 exhibited a zeta potential of 50.8 mV. Thus, strong electrostatic interactions should be formed between GO and CS.

Figure 1b shows images of the GO dispersion, CS solution, and mixtures of the GO dispersion and CS solution. As shown, a CS/GO complex forms and precipitates in water upon mixing the GO dispersion and CS solution, which is not favorable for the formation of CS/GO membranes with ordered interlayer channels.33 Thus, in this study, we used the layer-by-layer assembly approach to introduce the positively charged CS into the negatively charged GO interlayer. Using this method, effective electrostatic interactions can be easily formed between CS and GO without aggregation or precipitation. As expected, the zeta potential of the CS/GO membrane was much higher than that of the GO membrane over the whole pH range studied (2.5–10). This suggests that the introduction of CS reduced the negative charge of the GO membrane, thereby inhibiting the repulsive force between the negatively charged GO nanosheets and inducing the formation of more ordered interlayer channels, as discussed later.

FTIR analysis was carried out to understand the interaction between CS and GO. As shown in Figure S1, compared with pure CS and GO membrane, no new peaks were revealed in the FTIR spectra of CS/GO membrane, which probably due to the absence of covalent bonding between CS and GO. XPS analysis was further employed to explore the specific interaction sites between CS and GO further. As shown in Figure 1c,d, the peaks of GO could be deconvoluted into four components with binding energies at approximately 284.7, 287.0, 288.4, and 289.5 eV, which are attributed to the C=O, C–O–C, C=O, and O–C–O bonds, respectively.1 The C=O peak in the CS/GO membrane shifted to 288.1 eV, probably because of the electrostatic effect between COOH⁻ (in GO) and NH₄⁺ (in CS).34 At the same time, we found that the positions of the C–O–C and C–OH peaks remained almost unchanged, suggesting that the hydrogen bonding between the epoxy and hydroxyl groups on GO and carboxyl and hydroxyl groups on CS might be relatively weak. Based on the
XPS analysis, as we envisioned, the molecular interactions between CS and GO are mainly dominated by electrostatic interactions. Unlike the formation of stronger bonds (such as covalent bonds by chemical cross-linking), the use of electrostatic interactions could reduce the possibility of sacrificing the number and size of interlayer channels caused by the stronger interactions, meanwhile construct a regular and stable interlayer structure.

Because of the electrostatic interactions between GO and CS, the amount of added CS dopant (controlled by varying the CS solution concentration) should have a significant influence on the formation of the CS/GO membrane. The properties of GO and CS are different in aqueous solution with the same concentration. For instance, 0.5 wt% GO solution can be easily transformed into a gel, while 0.5 wt% CS solution exhibits very low viscosity. Thus, different concentrations were used for GO and CS when assembling the CS/GO membrane. The CS/GO membranes prepared with CS solution concentrations of 0–0.1 wt% were tested for the pervaporation separation of 90 wt% ethanol/water mixtures, and the results are shown in Figure 2a. On increasing the CS concentration to 0.05 wt%, the permeation flux decreased, but the water content in the permeate increased gradually.

**FIGURE 1** (a) Schematic of possible molecular interactions between CS and GO; (b) zeta potentials of 0.05 wt% CS solution, 0.01 wt% GO dispersion, CS/GO membrane, and GO membrane at different pH values. The inset shows digital photographs of the CS solution, GO dispersion, and CS/GO mixed solution. C1s spectra of (c) GO membrane and (d) CS/GO membrane. CS, chitosan; GO, graphene oxide [Color figure can be viewed at wileyonlinelibrary.com]

**FIGURE 2** Separation performance of CS/GO membranes prepared with (a) different concentrations of the CS solution and (b) different numbers of bilayers (feed conditions: 90 wt% ethanol/water mixtures at 70°C). CS, chitosan; GO, graphene oxide [Color figure can be viewed at wileyonlinelibrary.com]
This result suggests that a denser GO membrane structure with fewer defects was formed on the introduction of more CS into the GO laminate, thus enhancing the attractive forces between the GO nanosheets. However, increasing the amount of CS to 0.1 wt% produced excessively strong electrostatic interactions in the CS/GO membrane, as shown by the visible agglomeration on the membrane surface (Figure S2). This agglomeration phenomenon could cause the formation of non-selective defects in the membrane and result in lower selectivity and higher flux. Therefore, 0.05 wt% was chosen as the optimal CS concentration for the fabrication of the CS/GO membranes.

The number of deposited nanosheets also has a critical effect on the formation of the GO membrane. While maintaining the concentration of the GO solution constant, we varied the number of CS/GO bilayers by spin-coating to control the deposition of the nanosheets. As shown in Figure 2b, the permeation flux decreased, but the separation factor increased with increase in the number of bilayers, and the spin-coating of more bilayers would produce thicker CS/GO membranes. The membrane thickness-dependent selectivity indicates that an integrated separation layer was gradually formed with the deposition of more CS/GO bilayers on the porous substrate. The optimal number of bilayers would be that providing a defect-free membrane layer with minimal thickness. In our case, as the number of spin-coating cycles reached 30, the water content in the permeate exceeded 99.5 wt%, and the total flux was over 2.00 kg/(m²·hr). Thus, we considered this the optimal bilayer number for preparing the CS/GO membranes because, although further increasing the membrane thickness would increase the separation factor, it would significantly reduce the flux because of greater transport resistance.

To explore the roles of CS and GO in membrane formation, pristine CS membranes and pristine GO membranes were prepared using the optimal concentration of the CS solution (0.1 wt%) and spin-coating layers for the CS/GO membrane. As shown in Figure 3, the water contents in the permeates (water/ethanol separation factor) of both the pristine GO membrane and the pristine CS membrane were very low, indicating the presence of large defects in the membrane layer. We hypothesize that the low-concentration CS solution used here was difficult to form a selective layer on the surface of the support having pores with diameters of tens of nanometers. Although GO nanosheets with a lateral size of a few micrometer can be easily deposited on the porous substrate, a high-quality GO membrane with orderly stacking was not formed without the introduction of an electrostatically attractive layer (i.e., the addition of CS) between each spin-coated GO layer. By combining the dilute CS solution with the GO coating solution via the layer-by-layer assembly approach, the electrostatic attraction between CS and GO enabled the formation of a well-stacked and defect-free laminar separation layer showing the highly selective permeation of water molecules over ethanol molecules during the pervaporation separation of 90 wt% ethanol/water mixtures at 70 °C.

### 3.2 Membrane characterization

The morphologies of the pristine GO membrane and CS/GO membranes were characterized using scanning electron microscopy (SEM) and AFM. Figure 4a,b show surface and cross-section SEM images of the pristine GO membrane, revealing a typical wrinkled morphology and a membrane thickness of approximately 70 nm. In comparison, Figures 4d,e and S3 show that the CS/GO membrane is less wrinkled but has a slightly thicker membrane layer (~100 nm). This indicates that the introduction of positively charged CS chains results in an increased stacking density of the negatively charged GO nanosheets. This phenomenon was further confirmed by the AFM images shown in Figure 4c,f. The surface roughness of the CS/GO membrane (Rq of 37.9 nm; Rz of 37.1 nm) is much lower than that of the pristine GO membrane (Rq of 69.3 nm; Rz of 59.3 nm).

EDS elemental analysis was further performed on the surfaces of the CS/GO membranes. As shown in Figure 4g, the distribution of C and O on the membrane surface can be attributed to either the GO nanosheets or CS chains. Moreover, the N (a major component of CS) distribution over the CS/GO membrane surface was even. The EDS results are consistent with the XPS analysis, indicating that CS had been successfully and uniformly introduced into the GO membrane.

The transport of CS/GO pervaporation membrane was controlled by the solution–diffusion model. To study the surface hydrophilicity, we measured the water contact angle on the surfaces of GO membrane and CS/CS membrane. As shown in Figure 5, the water contact angle of the GO membrane surface was enhanced by introducing CS, presumably due to the reduced surface roughness indicated by AFM analysis shown in Figure 4c.f. The result suggests that the introduction of CS played a negative effect on the hydrophilicity and thus solubility of the membrane, which also accounted for the reduced water flux compared with GO membrane shown in Figures 2 and 3.

XRD measurements were used to study the laminar structures of the pristine GO and the CS/GO membranes. As shown in Figure 6, the peak in the XRD pattern of the CS/GO membrane is sharper than that in the XRD pattern of the pristine GO membrane, confirming that the laminar stacking of the GO nanosheets induced by the

![FIGURE 3](http://wileyonlinelibrary.com)  
Separation performance of pure CS, pure GO, and CS/GO membranes (feed conditions: 90 wt% ethanol/water mixtures at 70 °C); CS, chitosan; GO, graphene oxide [Color figure can be viewed at wileyonlinelibrary.com]
electrostatic interactions with CS was more orderly. In addition, the XRD pattern of the GO membrane exhibits a reflection at 2θ = 10.16° with an interlayer d-spacing of 0.87 nm, calculated using the Bragg equation: 2dsinθ = nλ, where d is the d-spacing, n is 1, and λ is 0.15406 nm. The thickness of a graphene sheet is 0.34 nm,35 and the interlayer height (h) for molecular transport was calculated to be 0.53 nm. In comparison, the orderly stacked CS/GO laminar membrane exhibited a smaller d-spacing of 0.77 nm, and thus, a narrower interlayer height of 0.43 nm. This indicates that the electrostatic attraction between CS and GO also led to a smaller interlayer separation between GO nanosheets.

We further analyzed the laminar structure of the pristine GO membrane and CS/GO membrane after 10-hr soaking in 90 wt% ethanol/water, which was used to evaluate the separation performance. The characteristic peak (2θ = 8.93°) of the pristine GO membrane was shifted to lower angles, and the peak broadened. Thus, the swelling significantly increased the size of the interlayer channels and decreased the ordering of the GO laminar layers. This swelling effect is commonly encountered in pristine GO membranes. The resulting interlayer height of 0.65 nm for the wet GO membrane is much larger than the kinetic diameter of ethanol, which accounts for the low water/ethanol selectivity observed in the pristine GO membrane (Figure 3). In contrast, the peak shape and position (2θ = 11.48°) in the XRD pattern of the wet CS/GO membrane showed little change, suggesting a well-preserved membrane structure with highly ordered GO nanosheet stacking. Evidently, the swelling of the GO membrane was remarkably suppressed due to the electrostatic attraction between the CS and GO nanosheets. The constant interlayer height of 0.43 nm is highly desirable because it is much larger than the kinetic diameter of water (0.29 nm) but is not larger than those of important C2–C4 alcohols (ethanol: 0.43 nm, isopropanol: 0.47 nm, and n-butanol: 0.51 nm).2 Thus, the fast diffusion of water and strict size sieving effect for water over alcohol can be simultaneously achieved as the water–alcohol mixtures enter the interlayer channels of the GO laminate. Consequently, excellent separation performance (permeation flux and water/ethanol selectivity and stability) for the pervaporation dehydration of water/alcohol mixtures can be expected in the CS/GO membrane.

3.3 | Membrane transport properties

Conventional technologies, such as distillation, for separating C2–C4 alcohol/water mixtures consume a significant amount of energy because of the formation of an azeotrope between the alcohols and water. Fortunately, the pervaporation dehydration of alcohol/water mixtures can lower the energy consumption; however, its large-scale implementation is limited by the general trade-off between
permeability and selectivity of polymeric membrane. In addition to the hydrophilic nature of GO-based membranes, the CS/GO membrane has been shown to have suitable sieving channels for the selective diffusion of water molecules over C$_2$–C$_4$ alcohol molecules. Therefore, we applied the CS/GO membrane for the pervaporation dehydration of 90 wt% ethanol/water, isopropanol/water, and n-butanol/water mixtures.

Temperature control is commonly used to control industrial process efficiency because the temperature affects the membrane microstructure, driving force, and permeation activation energy. Figure 7 shows the effect of the feed temperature on the total flux and water/alcohol separation factor of the CS/GO membrane. Generally, with increase in the feed temperature, both the total flux and separation factor increased significantly. The observed temperature-enhanced flux was expected because the driving force (vapor pressure) of the pervaporation process increases with increase in feed temperature. Notably, higher separation factors were achieved at higher temperatures, which would not be expected for conventional polymeric membranes because the accelerated membrane swelling at high temperatures often decreases the size discrimination effect and, thus, the selectivity of the membrane. It’s known that inorganic membranes with molecular sieving mechanism will also show decreased selectivity at high temperature, since larger molecules have higher activation energy if the process is controlled by diffusion. It seems that the effect of higher temperature on weakening the molecular sorption plays a dominant role in this work. With the increase of temperature, the sorption of ethanol might be depressed more compared with water, leading to the increase of water/ethanol sorption selectivity and thus the separation factor. It is interesting to compare the separation performances of the CS/GO membrane for the dehydration of different alcohols (C$_2$–C$_4$). The order of total flux was butanol/water > isopropanol/water > ethanol/water, whereas the order of separation factors was water/isopropanol > water/butanol > water/ethanol.

To understand the temperature and alcohol-type dependent transport behavior further, the driving-force-normalized pervaporation performance indices, namely permeance and selectivity, were calculated to reflect the intrinsic transport properties of the CS/GO membrane. As shown in Figure 8a–c, the water and alcohol permeances gradually decreased with increase in temperature, showing the opposite trend to that observed in the temperature–flux curves (Figure 6). This confirms that the temperature-enhanced flux resulted from the increase in the driving force provided by the higher vapor pressure at higher temperatures. According to the solution-diffusion model, permeability (or permeance) is determined by solubility and diffusivity. Increasing the temperature would enhance the diffusivity while reducing the solubility. Thus, it is reasonable to conclude that the reduction in the water and alcohol permeance with increase in temperature is due to the reduced sorption of water and alcohol in the CS/GO membrane. Again, the increase in water/ethanol perm-selectivity suggest that the swelling of the GO laminate was inhibited by the electrostatic interactions with CS, and the selective diffusion of water molecules in the size-sieving interlayer channels was promoted at higher temperatures.

Ignoring the effect of the driving force on the separation performance, the CS/GO membrane still exhibited a distinct trend in water
permeance during the dehydration of the C2–C4 alcohol/water mix- 
tures, that is, the same order observed in the flux (Figure 7): butanol/ water > isopropanol/water > ethanol/water. This can be attributed to 
the water–alcohol coupling effect.36 Alcohol molecules interact with 
water molecules to form molecular clusters, thereby occupying the 
interaction sites of water molecules and inhibiting the preferential 
adsorption and diffusion of water molecules in the CS/GO mem-
brane.37 Because the alcohols only have a single hydroxyl group, the 
coupling effect of alcohol with water decreases with increase in car-
bon number. Namely, the order of the coupling effect is: butanol–water < isopropanol–water < ethanol–water. It well explains the 
orders of water permeance and water/alcohol perm-selectivity for the 
C2–C4 alcohol/water mixtures because of the following reasons. First, 
the lowest coupling effect in the butanol–water system results in the 
largest amount of “free” water molecules to be adsorbed in the mem-
brane and diffuse through the membrane. Second, butanol with larg-
est molecular size is the most difficult to diffuse through the 
membrane, allowing the most interlayer channels to be used for water 
diffusion. In addition, the affinity and molecular sieving effect both 
contributed to the highest perm-selectivity in the butanol–water sys-
tem. In addition, it should be noted that the driving force (i.e., vapor 
pressure) of the C2–C4 alcohol/water mixtures was different, as 
shown in Table S1. The highest activity and, thus, the highest vapor 
pressure of water also contributed to the largest flux obtained in the 
butanol/water mixtures.

Moreover, the effect of temperature on the transport properties 
can be understood by using the Arrhenius equation. By approximating 
the slope of the linear relationship between the log of the permeance 
versus the reciprocal temperature shown in Figure 8d–f, the

activation energies of permeation ($E_p$) of water in ethanol/water, iso-
propanol/water, and butanol/water were found to be $-11.81$, $-23.07$, and $-26.67$ kJ/mol, respectively. Likewise, the $E_p$ of ethanol, isopropanol, and butanol were calculated to be $-28.78$, $-46.62$, and $-67.86$ kJ/mol, respectively. $E_p$ comprises the activation energy of diffusion ($E_D$) and the enthalpy of sorption ($\Delta H$).31,38 Because $E_D$ is positive, the negative $E_p$ was dominated by the negative sorption, $\Delta H$. Again, the increase in flux can be attributed to the fact that the effect of temperature on the vapor pressure is significant. The difference in $E_p$ between the different C2–C4 alcohol/water mixtures reflects the variable sensitivities of the permeation components (water and alco-
hol) to changes in temperature. Owing to the coupling effect, among the C2–C4 alcohol/water mixtures, water and ethanol are mostly 
likely to form molecular clusters and occupy active sites on the mem-
brane that hinders the sorption of water molecules in the membrane. 
Thus, compared with isopropanol/water and n-butanol/water, the 
negative effect of temperature on water sorption is less in the 
ethanol–water system, leading to the slower decline of water 
permeance with the increase of temperature (Figure 8a–c). In addition, 
the negative activation energy of alcohol permeation is much larger than 
that of water is because of the larger molecular size of alcohol than water. 
Namely, molecule with larger molecular size generally exhibits larger acti-
vation energy of permeation: n-butanol > isopropanol > ethanol > water. 
Overall, the simultaneous increase in the total flux and separation factor 
on increasing the feed temperature is favorable for enhancing the separa-
tion performance of the CS/GO membrane for industrial dehydration.39

The pervaporation dehydration performance of the alcohol/water 
mixtures is also determined by the water concentration in the feed, 
which is often variable in actual separation systems.2 To test this, the

FIGURE 8  Effect of feed temperature on the permeance and selectivity of the CS/GO membrane for the pervaporation dehydration of 90 wt 
% (a) ethanol/water, (b) isopropanol/water, and (c) n-butanol/water mixtures. Arrhenius plots of the temperature-dependent permeance of water and alcohol through CS/GO membranes for the pervaporation dehydration of 90 wt% (d) ethanol/water, (e) isopropanol/water, and (f) n-butanol/ 
water mixtures. CS, chitosan; GO, graphene oxide [Color figure can be viewed at wileyonlinelibrary.com]
CS/GO membrane was applied for the pervaporation dehydration of ethanol/water mixtures with water concentrations varying from 0.5 to 20 wt%. As shown in Figure 9a, the total flux increased significantly with increase in water concentration. The increased swelling, together with the larger driving force, provided by the higher water concentration in the feed contributed to the much higher flux. The swelling would also decrease the size-sieving properties of the membrane, and thus, the selectivity. It was further confirmed by the calculated permeance and selectivity in Figure S4a. The permeance of ethanol and water both increase with increasing the water content in feed, while the selectivity shows an opposite trend. Nevertheless, even on feeding with the highest water concentration of 20 wt%, the separation performance was well preserved in the CS/GO membrane, achieving a total flux of 6.83 kg/(m² hr) and water content in the permeate of 99.6 wt%.

In addition, it is noticed that with the water concentration in feed less than 3 wt%, the permeate water content (86.37–89.93 wt%) and separation factor (433–1,261) are relatively low, reflecting that the dehydration of ultra-low water content in alcohol remains challenge for such CS/GO membrane. Pervaporation membrane technology is considered as a promising separation technology for dehydration of alcohol/water mixtures, which is particularly energy efficient for dehydration of alcohol/water azeotropes (e.g., 95 wt% ethanol/water at 78.2 °C; 87.9 wt% isopropanol/water at 80.4 °C; 88.2 wt% butanol/water at 79.9 °C). Likewise, the CS/GO pervaporation membrane developed in this work is also more suitable for dehydration of alcohol whose composition is around the azeotrope composition. Indeed, in some case the product needs to be pure than 99.9% alcohol, which would require combination of pervaporation with other separation technologies such as adsorption.

Operating stability is an important index of membrane separation performance with respect to practical implementation. The water stability of GO membranes is of particular concern because the oxygen-containing groups of GO can result in the GO laminate being redispersed in water, thus decreasing the separation performance, or even destroying the membrane. We evaluated the pervaporation performance of the CS/GO membrane for the continuous dehydration of approximately 90 wt% ethanol/water mixtures at 70 °C for 120 hr. As shown in Figure 9b, water content in permeate decrease from 99.6 to 98.5 wt%, but the total flux has been maintained at about 2.50 kg/(m² hr). To further understand the membrane stability, we calculated the permeance and selectivity over operating time. As show in Figure S4b, the water permeance is maintained at around 7,700 GPU. The ethanol permeance increases initially and then stabilized at ~9.9 GPU, leading to the stabilization of selectivity. This might be due to the structural relaxation of the CS/GO membrane. Nevertheless, no continuous upswing of permeance was observed, indicating the CS/GO membrane well maintained its structural integrity during the continuous PV process. The stability of the CS/GO membrane can be attributed to the robust electrostatic interactions between CS and GO that fixed the interlayer spacing and suppressed the swelling of the GO laminates.

In summary, for the separation of 90 wt% C₂–C₄ alcohol/water mixtures at 70 °C, the CS/GO membrane exhibited total fluxes for ethanol/water, isopropanol/water, and butanol/water of 2.35, 2.98, and 4.69 kg/(m² hr), respectively, and separation factors of 3,390, 5,790, and 4,680, respectively. This separation performance is excellent compared to those of state-of-the-art polymeric membranes and GO-based membranes for the pervaporation dehydration of alcohol/water mixtures (Figure 10, Tables S2–4). The comparison with permeance versus selectivity trade-offs in Figure S5 agrees well with the total flux versus separation factor in Figure 10. The low performance of pervaporation membranes (e.g., conventional PVA membrane) would require very large membrane area and high energy consumption to reach the industrial dehydration target. The high cost in investment and operation for these membranes made them less competitive than
current distillation technology. Having high permeation fluxes and water/alcohol separation factors, the CS/GO membranes showed performance well beyond those of the state-of-the-art pervaporation membranes. The fast and selective water permeation can be attributed to the highly ordered interlayer channels and the sharp size sieving effect of the GO laminates enhanced by the electrostatic interaction with the CS in the interlayer.

4 | CONCLUSIONS

In this study, a new type of CS/GO membrane was developed for the pervaporation dehydration of C<sub>2</sub>–C<sub>4</sub> alcohol/water mixtures. The electrostatic attraction created by the introduction of positively charged CS into the interlayer of negatively charged GO laminates successfully induced GO nanosheet assembly into ordered interlayer channels with molecular sieving and swelling resistant properties. A high permeation flux and an excellent water/alcohol selectivity were achieved in the CS/GO membrane during the pervaporation dehydration process, both of which increased with an increase in the operating temperature. Specifically, in the separation of 90 wt% alcohol/water mixtures at 70 °C, the membrane exhibited total fluxes for ethanol/water, isopropanol/water, and n-butanol/water of 2.35, 2.98, and 4.69 kg/(m<sup>2</sup> hr), respectively, and separation factors of 3,390, 5,790, and 4,680, respectively. Considering that this separation performance outperforms those of state-of-the-art polymeric membranes and GO-based membranes, our electrostatically enhanced GO membrane is a promising candidate for the highly efficient dehydration of C<sub>2</sub>–C<sub>4</sub> alcohols. This work also provides fundamental insights into the transport behavior of water and volatile organic compounds through 2D-material membranes.

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AUTHOR CONTRIBUTIONS

Song Liu: Investigation; methodology; writing-review and editing. Guanyu Zhou: Investigation; methodology; writing-original draft. Kecheng Guan: Investigation; methodology; writing-review and editing. Xi Chen: Investigation; methodology. Zhenyu Chu: Formal analysis. Gongping Liu: Conceptualization; formal analysis; resources; supervision; writing-review and editing. Wanqin Jin: Supervision; writing-review and editing.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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SUPPORTING INFORMATION
Additional supporting information may be found online in the Supporting Information section at the end of this article.

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