Incorporating Graphene Oxide into Alginate Polymer with a Cationic Intermediate To Strengthen Membrane Dehydration Performance

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ABSTRACT: Two-dimensional graphene oxide (GO) in hybrid membranes provides fast water transfer across its surface due to the abundant oxygenated functional groups to afford water sorption and the hydrophobic basal plane to create fast transporting pathways. To establish more compatible and efficient interactions for GO and sodium alginate (SA) polymer chains, cations sourced from lignin are employed to decorate GO (labeled as cation-functionalized GO (CG)) nanosheets. A two-dimensional oxygenated functional group network of GO is employed to impart high dehydration capability. In a hybrid GO-SA membrane, the GO-cation interaction is presented to improve dehydration performance, whereas SA's hydrophilicity and flexibility provide fast water transfer across the membrane.

KEYWORDS: graphene oxides, cations, ionic cross-linking, hybrid membrane, solvent dehydration

1. INTRODUCTION

Graphene oxide (GO) comprising hydrophobic aromatic rings and hydrophilic oxygenated groups enables preferential molecular transport pathways inside its stacked laminates. Recurring this distinct property and with subsequent facile tailoring, GO nanosheets have become almost versatile building blocks for playing a role in membranes for gas separation, selective ion penetration, water purification, and solvent dehydration or recovery. With the aid of particular affinity to water molecules, GO-based materials were widely researched with configuration of either bulk phase (GO lamimates) or filler (GO-polymer hybrids) to construct membranes for water-related separation processes. For hybrid membranes, enhancing the interactions between fillers and polymer matrix is important to avoid or reduce unfavorable defects. Accordingly, properly introducing interactive species into the membrane structure is essential to acquire higher structural stability and separation performance.

Hydrogen bond and van der Waals force, in most cases, exhibit in stacked GO lamimates and GO-polymer environment attributed to the abundant polar oxygenated groups from GO, which are benign for the ordered GO arrangement in the lamimates or the good distribution in the polymer matrix. Still, both interactions are comparatively weak and are limited to strengthen the internal membrane structure and molecular separation process. Hence, functionalization of GO through interactions like covalent or noncovalent bonding appears to be efficacious for the desired property. A legion of active sites (e.g., aromatic ring, several kinds of oxygenated groups) within GO afford different routes (e.g., aromatic interaction, ring-opening reaction, and electrostatic interaction) to tailor the functionality. Recent researches have found that cations have valid interactions with GO through cation–π and coordination interactions. Through such functionality, GO membranes can acquire excellent mechanical and separating properties. With respect to a polymeric membrane, swelling in solvents is a common phenomenon caused by the sorption affinity of a polymer to a specific solvent. By affording larger free volume in a polymer matrix through swelling, permeation flux of the membrane is enhanced, whereas the molecular selectivity is correspondingly weakened for the sake of loose transport channels. To prevent the polymeric membrane from excessive solvation, methods have been developed to cross-link polymer chains rendered by a myriad of mechanisms, including physical entanglement, chemical cross-linking, and ionic interactions.

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example, are facile to cross-link by introducing divalent cations (e.g., Ca\(^{2+}\)) with the form of pairs of helical chains pack and surround ions that are locked in between. With this ionic interaction cross-linking mechanism, SA membrane sustains under aqueous environment to efficiently separate water from organic solvent. In addition, incorporating inorganic fillers (e.g., GO nanosheets) into SA matrix to fabricate hybrid membranes was widely researched\(^{27-29}\) to achieve better separation performance, breaking the “trade-off” effect of polymeric membranes.

Inspired by the cationic interactions with GO and cross-linking effect with SA matrix, calcium lignosulfonate (CaLS) was employed as a cationic intermediate to optimize both GO laminates and SA matrix to construct hybrid membranes for pervaporation dehydration from aqueous alcohol solution (Figure 1). As fillers in the polymer matrix, the cation-functionalized GO (labeled as CG) nanosheets provide more interactive sites to be combined in SA matrix with better compatibility. Meanwhile, cations from CG also partially cross-link the polymer chains inside SA matrix, conferring integrated structural stability and integration of hybrid membrane, the link the polymer chains inside SA matrix, conferring integrated compatibility. Meanwhile, cations from CG also partially cross-link the polymer chains inside SA matrix, conferring integrated structural stability and integration of hybrid membrane, the link the polymer chains inside SA matrix, conferring integrated compatibility.

![Figure 1. Illustration of CG-doped SA hybrid membrane structure and cationic interactions with GO and alginate chains.](image)

2. EXPERIMENTAL SECTION

2.1. Preparation of Cation-Decorated GO Nanosheets. GO was prepared by the modified Hummers method. GO suspension (1 mg mL\(^{-1}\)) was obtained through dispersing GO flakes into deionized water with the aid of sonication. Then, CaLS powder (weight ratio to GO is 1:1) was added into the suspension. The above suspension was sonicated again for several minutes to acquire homogeneous cation-decorated GO suspension.

2.2. Fabrication of Hybrid Membranes. Polyacrylonitrile (PAN) ultrafiltration membrane with average pore size of 20 nm was employed as the substrate of the composite membrane. Membrane casting solution was prepared by adding SA powder (2 wt % in solution) into CG aqueous suspension and was subsequently stirred at 30 °C for 2 h. The casting solution was placed still for another 1 h to remove air bubbles inside the solution. Afterward, the casting solution was spin-coated on the PAN substrate with the rotational velocity of 1000 rpm. After the membrane was dried in a desiccator at room temperature, it was immersed into 0.1 M CaLS aqueous solution for 10 min to cross-link the membrane; then, the membrane was rinsed several times by water to remove excessive CaLS on the surface of the membrane. Finally, the processed membrane was dried again in a desiccator at room temperature. Varying contents of CG in the hybrid membrane could be realized by changing the concentration of CG suspension. The corresponding fabricated hybrid membrane was denoted as SA−CG-X membrane, where the X represents the weight ratio (from 0 to 1.5 wt %) of GO to SA.

SA and GO−SA hybrid membranes were fabricated by not adding or adding alternative fillers, respectively. CaCl\(_2\)-decorated GO nanosheets were prepared through mixing equimolar Ca\(^{2+}\) amount with GO suspension, and the corresponding hybrid membrane using these fillers was fabricated similar to the SA−CG hybrid membranes (SA membranes with GO or CaCl\(_2\) decorated GO doped are denoted as SA−GO and SA−CaCl\(_2\)−GO, respectively). Notably, mixing CaCl\(_2\) with GO will instantly lead to flocculation of GO nanosheets in suspension due to strong electrostatic interaction. Therefore, the CaCl\(_2\)−GO suspension is kept under vigorous stirring before doping into SA matrix.

2.3. Measurement of Separation Performance. Pervaporation dehydration of water/ethanol solution was operated to analyze the separation performance of the membrane. A typical evaluation procedure can be found in a previous work.\(^{30}\) The compositions of the feed and the collected permeate were analyzed by gas chromatography. Permeation flux (\(J\)) and separation factor (\(\alpha\)) are two key parameters to reflect the separation performance of the membrane sample. They are defined as follows

\[
J = \frac{M}{At}
\]

\[
\alpha = \frac{y_i}{x_i}
\]

where \(M\) is the mass of collected permeates, \(A\) is the effective area of the membrane, and \(t\) is the operation time. \(y\) and \(x\) represent the mass fraction of water from the permeate and feed, respectively; \(y_i\) and \(x_i\) represent the mass fraction of ethanol from the permeate and feed, respectively.

2.4. Calculations of Activation Energy by the Arrhenius Equation. The relationship between operation temperature and permeation flux is determined by the Arrhenius equation\(^{12}\)

\[
\ln(J) = \ln(J_0) - \frac{E_a}{8.314} \frac{1000}{T}
\]

where \(J\) (kg m\(^{-2}\) h\(^{-1}\)) is the permeation flux of component \(i\); \(J_0\) (kg m\(^{-2}\) h\(^{-1}\)) is the pre-exponential factor; \(E_a\) (kJ mol\(^{-1}\)), the permeation-process-associated activation energy; \(R\) (kJ mol\(^{-1}\) K\(^{-1}\)), the gas constant; and \(T\) (K), the temperature.

As \(R = 8.314 \times 10^{-3}\) kJ mol\(^{-1}\) K\(^{-1}\), and taking the log of both sides of eq 3

\[
\ln(J) = \ln(J_0) - \frac{E_a}{8.314} \frac{1000}{T}
\]

Therefore, the value of \(E_a\) is obtained by plotting \(\ln(J)\) vs 1000/T.

2.5. Calculations of Driving Force-Normalized Form of Permeation Flux and Selectivity. The permeance of the individual component (\(P/\gamma\)), (gas permeation unit (GPU), 1 GPU = 7.501 \times 10^{-12} m^3(STP) m^{-1} s^{-1} Pa^{-1}) and selectivity (\(\beta\)) were calculated by following equations\(^{31-33}\)

\[
(P/\gamma) = \frac{l}{P_0 - P_i} = \frac{l}{R\omega m^0 - P_i}
\]

\[
\beta = \frac{(P/\gamma)_w}{(P/\gamma)_e}
\]

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where $J_i$ (g m\(^{-2}\) h\(^{-1}\)) is the permeation flux of component $i$; $l$ (m) is the thickness of the membrane; $p_{i0}$, $p_i$ (Pa) are the partial pressure of component $i$ in the feed side and permeate side. $p_i$ can take the value of 0 for the high-vacuum situation in the permeate side. $\gamma_{i0}$ is the activity coefficient of component $i$ in the feed solution; $x_{i0}$ is the mole fraction of component $i$ in the feed solution; $p_i^{sat}$ (Pa) is the saturated vapor pressure of pure component $i$. The permeation flux of water and ethanol should be transformed into the volumes under standard temperature and pressure (STP).

2.6. Calculations of the Swelling Degree. The preweighed membrane sample (after drying in an oven, mass = $m_0$, g) was immersed into feed solution for 100 h to reach the sorption equilibrium under room temperature. The feed solution droplets on the sample surface were removed by wipers, and then the mass of swelled membrane sample was weighed (mass = $m_1$, g). The swelling degree of the sample can be calculated\(^4\) by the following equation: swelling degree = $(m_1 - m_0)/m_0$.

2.7. Characterizations. The morphology observation and energy dispersive spectroscopy (EDS) analysis of the membrane samples were operated by a field emission scanning electron microscope (FESEM, S4800, Hitachi, Japan). The roughness data of the membrane surface with the range of 5 × 5 μm\(^2\) and the height profiles of GO or CG nanosheets with the range of 10 × 10 μm\(^2\) were obtained from the atomic force microscope (AFM, Bruker Dimension Icon, Germany and XE-100, Park SYSTEMS, Korea) characterizations. Water contact angles were examined by a contact angle dropmeter (A100P; MAIST).
Vision Inspection & Measurement Co., Ltd.). X-ray diffraction (XRD, Bruker D8 Advance, Germany) was performed at room temperature in the range of $5^\circ \leq 2\theta \leq 40^\circ$, with the increment of 0.02° per s. X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250) was recorded to analyze the containing elements in samples. Raman spectroscopy (LabRAM HR, Horiba, France) was carried out with 514 nm wavelength incident laser light. Fourier transform infrared (FTIR, Nicolet8700, Nicolet) spectra were recorded in a spectrophotometer with a range of 400$^{-1}$–4000 $^{-1}$. The thermal property of membrane samples was characterized by thermogravimetric analysis (TGA, NETZSCH STA 449F3) from room temperature to 600°C with a rate of 10°C min$^{-1}$. Differential scanning calorimetry (DSC, Q2000, TA Instruments) measurements were operated from 30 to 200°C in N$_2$ atmosphere to obtain the glass transition temperature values.

3. RESULTS AND DISCUSSION

3.1. Cation-Decorated GO. CaLS was employed as a cation source to decorate GO nanosheets via cation–π and cation–sp$^3$ (coordination) interactions. Additionally, the lignosulfonate acid groups (LS$^{2-}$) from CaLS also lean to the basal plane of GO due to the aromatic ring affinity ($\pi$–$\pi$ interaction).$^{35}$ The existing LS$^{2-}$ groups on GO surface endow GO nanosheets with good dispersibility after cation decoration (Figure S1) and active sites for a compatible combination with other species. Compared with the pristine GO nanosheet (height of 1–2 nm), CG nanosheets reveal higher heights (4–6 nm), as analyzed by AFM images (Figure 2), indicating successful CaLS decoration of GO nanosheet. It is noted that because of the cationic interaction, CG nanosheets possibly lean to each other compared with pristine GO. Some CG nanosheets may be few-layered aided by such strong interaction. Therefore, obviously a higher height can be observed in AFM. Raman spectra (Figure 3a) of GO and CG confirm that cations and/or LS$^{2-}$ groups preserved the original structural state of GO nanosheets via noncovalent interaction and coordination. Consequently, the hydrophilicity of pristine GO is retained.

As revealed by XPS spectra (Figure 3b–d), Ca and S elements were newly introduced into GO by CaLS functionalization. Ca$^{2+}$ absorbed on GO nanosheet can exchange Na$^+$ from SA matrix to cross-link the internal polymeric chains of SA when CG is initially doped. Accordingly, the CG-doped SA matrix possesses a more stable structure. Meanwhile, other functional groups like sulfonate acid group brought by LS$^{2-}$ also favor the transport of water rather than organic matters. The water contact angle (Figure 3e,f) of CG was lower than that of GO, revealing improved...
hydrophilicity with CaLS functionalization. With the benign effects brought by cations and hydrophilic groups in CaLS, the CG is much propitious for the selective water transport process in the membrane layer.

3.2. Physiochemical Properties of Hybrid Membranes. SA−CG-1 membrane was taken as a typical example to compare the morphological change of SA membrane after CG doping. The surface of bare SA membrane is smooth and dense (Figure 4a), whereas the SA−CG-1 membrane exhibits a few wrinkles due to the existence of CG nanosheets (Figure 4b). Bulk element analysis of SA−CG-1 membrane was carried out to observe the element distribution (Figure S2). The Ca and S distribution amount tallies with XPS analysis. The effective membrane layer was less than 200 nm (Figure 4c), supported by PAN substrate with fingerlike pores (Figure 4d). The composite membrane structure endowed the active layer with enough mechanical strength as well as negligible transport resistance. AFM images of SA and SA−CG-1 membrane (Figure 5) turn out to be without significant difference both in morphology and surface roughness in the 5 × 5 μm² scanning area. CG nanosheets tend to arrange horizontally inside the SA matrix guided by the centrifugal force and shear force during spin-coating process. For this reason, as also revealed by SEM images (Figure 4b), the SA−CG membrane retains morphology similar to that of the bare SA membrane.

As Ca element content takes up ∼0.7 wt % in the CG membrane sample analyzed by XPS (Figure 3b), CaLS modification amount in CG can be calculated as 9.3 wt %. Hence, controlling SA−GO hybrid membrane with GO doping amount of 0.9 wt % is accordingly fabricated for comparison, labeled as SA−GO-0.9. Attenuated total reflection (ATR)-FTIR spectra (Figure 6a) of PAN-supported hybrid membranes with different doping amounts are similar, comprising typical adsorption peaks such as −C=O, C=C, and −C−O from CG nanosheet and/or SA matrix. Thermal properties of SA−CG-1 and SA−GO-0.9 homogeneous membranes and the bare SA membrane were tested by TGA analysis (Figure 6b). All three samples reveal similar thermal decomposing properties, and the differences in the weight loss rate can be attributed to the doping of fillers. XRD spectra of SA−CG membranes with different doping amounts are also similar to that of the bare SA membrane (Figure 6c). No GO characteristic peak is revealed in these spectra, indicating that CG nanosheets distribute homogeneously inside the SA matrix, which is identical to the literature report.²⁸

The chain mobility of the bare SA membrane and SA−CG membranes is revealed by glass transition temperature (Tg),³⁶−³⁸ as obtained from differential scanning calorimetry (DSC) measurement (Figure 6d). Almost all SA−CG
membranes possess higher $T_g$ value compared with bare SA membrane due to the nanosheets that restrict the chain mobility of SA polymer. With more CG nanosheets added, the $T_g$ first decreases and then increases. This change is ascribed to two effects: (i) benign interactions between CG fillers and SA matrix contributing to the chain mobility and (ii) agglomeration of CG nanosheets obstructing the chain mobility.

3.3. Dehydration Performance of Hybrid Membranes.

Bare SA polymer membrane and SA−CG hybrid membrane performances were evaluated by the pervaporation dehydration process with the feed of ∼90 wt % ethanol−water mixed solution. The experimental result in Figure 7a shows that both permeation flux and separation factor were improved through doping CG nanosheets in the SA polymer membrane. The optimal doping amount is 1 wt % (namely SA−CG-1 membrane) with permeation flux of ∼3200 g m$^{-2}$ h$^{-1}$ and separation factor approaching 5600. With doping amount less than 1 wt %, the permeation flux of the SA−CG membrane steadily rises with increased CG content in SA polymer matrix. The separation factor also gets improved following this trend. $T_g$ values (Figure 6d) reflect the polymer chain mobility situation that has impacts on the molecular permeation; although the addition of CG nanosheets restricts the mobility of the polymer chain, as revealed, the favorable hydrophilicity of CG nanosheets enables high sorption of water molecules, which brings extra permeation flux compared to that of the bare SA polymer membrane. However, as more and more CG nanosheets are doped into the SA matrix, both permeation flux and separation factor decline. Similar to other hybrid or mixed matrix membranes,39,40 excessive amount of fillers (e.g., CG nanosheets in this work) may lead to serious agglomeration inside the polymer matrix, resulting in a much higher $T_g$ value. Observed from SEM images in Figure 7b, the nanosheets oriented parallel to the membrane surface at low doping content (≤1 wt %), whereas agglomeration and curving of the nanosheets could be found with more fillers doped (>1 wt %). Under this circumstance, the advantages of CG nanosheets with a high aspect ratio cannot fully exert. In addition, polymer chain mobility will also be considerably hindered (represented by a higher $T_g$ value) and as elucidated in Section 3.2, no CG nanosheets were obviously exposed outside the polymer surface, which means these nanosheets tend to align parallel to the membrane surface.29 The basal plane (graphenelike area) of CG nanosheets can restrict the direct diffusion of molecules, whereas the water sorption effect of CG nanosheets brings contributive effects such as a higher molecular diffusion rate (Figure 7c). Consequently, there is a pair of contrary effects for CG nanosheets inside the SA matrix. Excessive CG nanosheets (>1 wt %) exhibited higher restricting effect than the contribution (the transport pathways for molecules are extended), resulting in the drop of permeation flux. Because the agglomerated CG nanosheets are also not able to give more

![Figure 6](https://example.com/figure6.png)

**Figure 6.** a) ATR-FTIR spectra, (b) TGA curves, (c) XRD spectra, and (d) DSC curves of different membrane samples.
facilitated transport for water molecules and may create unwanted interfacial defects with the polymer matrix, the separation factor is cut down.

The membrane performance is usually varied with the feed temperature. Bare SA and SA−CG-1 membranes were evaluated with the feed temperature range from 30 to 70 °C. Both permeation flux and separation factor increase under elevated feed temperature for SA (Figure S3) and SA−CG-1 membranes (Figure 8a). Accordingly, the water content in permeates grows from 95.0 to 98.1 and 99.2 to 99.8 wt % for SA and SA−CG-1 membranes, respectively. To acquire better understanding of the water or ethanol molecular transporting behavior through the membrane, the apparent activation energy ($E_a$) was calculated (Figure S4). $E_a$ values are all positive for water ($E_{water}$) and ethanol ($E_{ethanol}$) in SA and SA−CG-1 membranes, which means the transmembrane process is endothermic. Hence, the permeation flux increases with incremental driving force resulted from temperature growing. $E_{water}$ value of SA−CG-1 membrane is higher than that of the SA membrane, whereas $E_{ethanol}$ of SA−CG-1 membrane is lower than that of the SA membrane, leading to a higher separation factor due to the more temperature-sensitive permeation flux. SA−CG-1 membrane thus achieves better separation performance. Besides, the driving force-normalized form of permeation flux and selectivity under different operation temperatures were calculated to analyze the permeation behavior and the results are listed in Table S1. The permeance values of SA−CG-1 and SA membranes decreased at higher temperatures, which indicated that the driving force was the dominant parameter for the permeation flux. Moreover, it also revealed that the membrane structure was not swelled obviously at high temperatures to afford the increased permeance. The water selectivity over ethanol for SA−CG-1 kept increasing with elevated temperature, which means ethanol molecules encountered higher transport resistance under high temperatures.

With the purpose of exploring the contributive effects of CG nanosheet fillers, control membranes of SA, SA with 0.9 wt % pristine GO fillers (SA−GO-0.9), and SA with 1 wt % CaCl$_2$-decorated GO fillers (SA−CaCl$_2$−GO-1, this filler content was calculated on the basis of the same Ca$^{2+}$ decoration amount as that of CG, which is actually 0.98 wt % and herein is approximately 1 wt %) were fabricated to compare their dehydration performance with that of SA−CG-1 membrane (Figure 8b). Comparing SA−GO-0.9 and SA−CaCl$_2$−GO-1 membranes, the former reveals higher flux, whereas the latter shows a higher separation factor. This demonstrates that the introduction of Ca$^{2+}$ enables more effective microstructure for

Figure 7. a) Separation performance of SA membrane and SA−CG membranes with different CG contents under 70 °C; (b) SEM cross-sectional images of free-standing SA−CG membranes with different CG doping contents; (c) illustration of transport pathways inside CG membranes with different CG contents.
separating molecules, possibly resulted from better filler combination with polymer and partial cross-linking of polymer chains inside the polymer matrix (revealed by the drop of permeation flux compared with SA−GO-0.9 membrane). Besides, GO nanosheets offering fast selective water transport channels render high permeation flux and separation factor simultaneously compared to those of the bare SA membrane. With respect to SA−CG-1 membrane, except the benefits brought by Ca\(^{2+}\), the LS\(^{2-}\) groups also exert advantageous properties for the selective transport of water molecules (including more active sites for combination with polymer and hydrophilicity for water sorption). Effects of operation temperature on membrane performance for SA−GO-0.9 and SA−CaCl\(_2\)−GO-1 membranes can be found in Figure S5. In view of this, the performance of SA−CG-1 membrane is outstanding among these control membranes.

3.4. Membrane Stability. Generally, the SA precursor membrane is soaked in calcium chloride aqueous solution to complete the gelation or cross-linking process before being put into separation processes. The \(\alpha\)-guluronic acid blocks of alginate will rapidly gel with the presence of divalent cations such as Ca\(^{2+}\).\(^{39}\) Here, the CaLS was employed as a Ca\(^{2+}\) source to accomplish the cross-linking process of SA or CG membranes. To observe the stability of CaLS cross-linked membrane, the cross-linked membrane sample (SA−CG-1) along with the control membrane sample without cross-linking was soaked in feed solution (90 wt % ethanol−water). The control sample gradually dissolved in the feed solution in several hours due to the sorption of water, whereas the cross-linked one swelled to some extent but remained as a complete piece even after several months (Figure 9). For this reason, the CaLS is also valid for the cross-linking of SA-based membranes. In the meantime, the swelling degree of cross-linked SA−CG-1 and SA membrane were evaluated. After 100 h soaking in feed solution, the swelling degree of CG-1 membrane is 2.02%, whereas that of the SA membrane is 7.01%. As a few CaLS have been already introduced into the CG membrane when CG nanosheets are doped into the SA matrix ahead of the final cross-linking process (soaking in CaLS membrane), the CG membrane could possibly own a higher cross-linking degree compared to that of the SA membrane under same conditions. CG nanosheets may also rigidify the SA polymer chains to swell less in aqueous solution.

Additionally, SA−CG-1 membrane was also evaluated with water-rich feed solution (50 wt % ethanol−water, Figure S6). With higher water content in the feed, membranes usually swell by the sorption of water. Under this condition, the permeation flux of SA−CG-1 membrane reached almost 8000 g m\(^{-2}\) h\(^{-1}\), which is pretty high among polymeric membranes, and a compromised 95.8 wt % water content value in permeate was acquired. The water-rich feed solution lead to a swelled membrane structure, resulting in faster water transfer through the membrane, but the separation of water and ethanol molecules is less effective. Nevertheless, despite soaked in water-rich feed solution, our membrane still exhibited good separation performance with considerable permeation flux and proved the stability of the membrane structure as well.

Long-term operation of SA−CG-1 membrane was carried out to observe the performance change. With feed solution of 90 wt % ethanol−water, the SA−CG-1 membrane continuously worked during the pervaporation dehydration process for 100 h. The decline of permeation flux at first 50 h was attributed to the relaxation of SA polymer chains.\(^{38}\) Finally, the permeation flux stabilized with a value of \(\sim 2500\) g m\(^{-2}\) h\(^{-1}\) and the water content in the permeate was larger than 99.7 wt % (Figure 10a). More importantly, SA−CG membranes present impressive ethanol dehydration performance compared with recently reported SA-based and GO-based membranes (Figure 10b, see the detailed list in Table S2).


4. CONCLUSIONS

In conclusion, a new kind of GO-based filler (CG nanosheets) is prepared through cation decoration by CaLS. By incorporating CG nanosheets into SA polymer matrix, the ethanol dehydration performance is strengthened, with stable permeation flux of ~2500 g m⁻² h⁻¹ and water content in permeate >99.7 wt % (compared with 1560 g m⁻² h⁻¹ and 97.3 wt % of SA membrane). Cation-decorated GO nanosheets lead to proper combination with SA polymer chains as well as more stable internal structure of the SA matrix. Besides, the LS²− groups from CaLS also act as hydrophilic sites, contributing to the transport of water molecules. The content of CG fillers affect their arrangements in polymer matrix and polymer chain mobility, resulting in varied forms of transporting channels in the membrane layer and accordingly different membrane performances. Significantly, aided by the effective external cross-linking of SA−CG membranes through immersion in CaLS solution, combining internal Ca²⁺−GO fillers cross-linking, the SA−CG membrane reveals stable and excellent dehydration performance among literature reports. The cation-decorated GO fillers are also promising for application in other hybrid membranes to afford different assembling behaviors and performances.

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