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Graphene Oxide-Carbon Nanotube Hybrid Membranes for High-Pressure and High-Flux Nanofiltration

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Graphene oxide (GO) membranes are promising candidates to revolutionize nanofiltration, due to their atomic thickness and ultrafast water transport. Yet their practical use is hindered by structural damage under high pressure. Conventional strategies like thickening membranes, reducing interlayer spacing, or cross-linking nanosheets improve pressure resistance but significantly reduce water permeability to impractical levels (e.g., 0.15 L m⁻² h^{-1} bar⁻¹ at 60 bar). Here, this dilemma is addressed by designing ultrathin GO/carbon nanotube (CNT) hybrid membranes. The CNT network reinforces the stacked GO nanosheets by reducing their free-standing diameter while increasing membrane thickness and Young's modulus. The pressure resistance is achieved up to 60 bar, triple that of the pristine GO membranes. A maximum water flux of 966 \pm 96 L m⁻² h⁻¹ is achieved by a 68 nm thick GO/CNT membrane with optimal GO nanosheet size and CNT loading amount, facilitating 1-3 orders of magnitude higher water flux per unit membrane thickness than all available membranes. This breakthrough resolves the critical trade-offs among pressure resistance, flux, and membrane thickness, marking a transformative leap in GO-based nanofiltration efficiency. The innovation holds immediate potential for applications in sustainable water remediation, pharmaceuticals, energy storage, and electronics.

membrane development. Graphene oxide (GO) membranes have exhibited the potential to revolutionize nanofiltration for their atomic-scale thickness^[5] and ultra-smooth interlayer confined space to maximize permeance,^[6] narrow interlayer spacing,^[7] and oxygen-containing functional groups for efficient separation.^[8] For instance, shear-aligned GO liquid crystal membranes achieved a water permeance of 71 L m⁻² h⁻¹ bar⁻¹, almost ninefold higher than the conventional NF270 membrane, while exhibiting comparable rejection (>90%) to dye molecules.^[9]

Nevertheless, GO membranes are restricted to the laboratory and lack industrial utilization, mostly due to their delamination under practical high pressure and tangential liquid flows.^[10–12] This is because the GO membranes are assembled by stacking isolated GO nanosheets, which are easily collapsed.^[13] Over the past decade, strategies like partial reduction,^[14,15] increasing thickness,^[16,17] covalent cross-linking,^[8,18] and ion/molecule intercalation^[19,20] significantly improved pressure resistance but often sacrificed water flux. For example, CO (*r*CO) membrane showed a caluant page

1. Introduction

The demand for clean water production across wide areas of sustainable water remediation,^[1] pharmaceuticals,^[2] energy storage,^[3] and electronics^[4] continues to drive nanofiltration

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Can be found under https://doi.org/10.1002/adfm.202503432

DOI: 10.1002/adfm.202503432

a thermally reduced GO (rGO) membrane showed a solvent permeance of only 0.15 L $m^{-2}~h^{-1}~bar^{-1}$ at 60 bar. $^{[21]}$

Carbon nanotubes (CNTs) have been integrated with GO to improve pressure resistance.^[22-29] The maximum filtering pressure record was 30 bar using a 3200 nm thick GO/CNT

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Figure 1. Pressure resistance of the GO and GO/CNT membranes. a, b) Schematic illustrating the structures of (a) the GO membrane and (b) the GO/CNT membrane during high-pressure filtering. c) Photograph (left) and SEM image (right) showing the damage on the GO membrane after high-pressure filtering. d) Photograph (left) and SEM image (right) showing the maintenance of the GO/CNT membrane after high-pressure filtering. e) Relationship between filtering pressure (P) and water flux of the GO membrane (gray lines) and the GO/CNT membrane (blue lines). Flux, denotes the maximum water flux. P_m denotes the maximum filtering pressure to keep the membrane from getting damaged.

membrane, yielding a relatively low water flux of 467 L m⁻² h⁻¹ (Table S1, Supporting Information).^[22] For practical industrial applications, membranes should maintain stability at pressure up to 41 bar, with greater pressure resistance being preferable.^[30] Consequently, there is an urgent demand to develop a strategy that can strike a balance between high-pressure resistance and large liquid permeance to maximize GO nanofiltration flux.

In this work, we conquer the above challenge via two innovations: a specially designed layer-by-layer wet-laid strategy, and optimization of GO nanosheet size and CNT loading amount. The hybrid GO/CNT membrane features a robust CNT network with significant π - π interaction with the supported GO layer, physically separating the GO layer into "islands" while serving as a microscopic supporting framework (Figure 1b; Figure S1, Supporting Information).^[31,32] During high-pressure filtering, such a structure can maintain the membrane's integrity (Figure 1d; Videos S1 and S2, Supporting Information), while the pristine GO membrane would sustain damage and fail in nanofiltration (Figure 1a,c; Videos S3 and S4, Supporting Information). Although CNT incorporation slightly reduces intrinsic permeability (slope in Figure 1e), the considerable rise in pressure resistance (P_m) significantly boosts maximum flux (Flux_m) due to the positive flux-pressure relationship (Figure 1e). Moreover, the strategy enables the production of GO/CNT membranes with 10 nmlevel thickness, which is 1-2 orders of magnitude thinner than those reported in the literature (Table S1, Supporting Information), therefore substantially reducing fabrication costs and promoting the transition of nanomaterials from laboratory to industrial applications.

2. Results and Discussion

2.1. Fabrication of GO/CNT Membranes

GO/CNT membranes were fabricated using the wet-laid method. 0-10 mg m⁻² CNT were first deposited onto a polyethersulfone

(PES) membrane substrate, marked as C0-C10 (Figure S2, Supporting Information). Subsequently, 25 mg m⁻² GO nanosheets with average diameters of 0.81, 4.6, and 29 µm (named SG, MG, and LG, as seen in Figure S3, Supporting Information) were deposited onto the CNT membrane, and the GO/CNT membranes were obtained after drying. Figure 2a illustrates a GO membrane without CNT loading. The GO layer exhibited a thickness of ≈ 20 nm (Figure S4a, Supporting Information) and was supported on a PES membrane substrate with an average freestanding diameter of 310 nm (Figure S5a, Supporting Information). When loaded with 2.5 mg m⁻² CNT, the pores on the PES substrate were separated into 110 nm (Figure 2b; Figure \$5b, Supporting Information). The CNT layer served as a microscopic framework to support and protect the GO layer, and a thin (≈45 nm) GO/CNT membrane was obtained (Figure 2c; Figure S4c, Supporting Information). The cross-sectional morphologies of membranes fabricated with varying sizes of GO nanosheets and CNT loading amounts are shown in Figure S4 (Supporting Information).

For both GO and GO/CNT membranes, the critical sieve size is determined by the interlayer spacing between GO nanosheets, which can be characterized by X-ray diffraction (XRD) patterns.^[33] XRD analysis revealed that the characteristic peaks for GO nanosheets appeared at $2\theta = 10.65^{\circ}-11.07^{\circ}$ (Figure 2d), indicating the interlayer spacings remained at $\delta = 0.80-0.83$ nm, which allows for water molecule penetration while rejecting larger-sized dye molecules.[33,34] The peak intensities in D and G bands (I_D and I_G) observed in Raman spectroscopy were associated with the defect/disordered sp³ and original sp² networks.^[35] SG and MG nanosheets showed a higher I_D/I_G ratio than LG nanosheets (Figure S6a, Supporting Information), suggesting a more disordered structure for their larger interlayer spacings.^[36] By peak-differentiating and imitating, the C 1 s XPS spectra could be fitted by typical peaks of C-H/C-C/C=C (284.8 eV), C-OH/C-O-C (286.9 eV), and C=O/COOH (288.4 eV) (Figure S6b-d, Supporting Information).





Figure 2. Physical property characterizations of GO and GO/CNT membranes. a–c) Surface SEM images and photos (inset) of (a) the GO membrane, (b) the CNT membrane, and (c) the GO/CNT membrane. SG and C2.5 indicate that the membrane is fabricated using small-sized (average size diameter: 0.81 µm) GO nanosheets and 2.5 mg m⁻² CNT. d) XRD spectra of pristine GO nanosheets in the dry state. The corresponding interlayer spacing values (δ) were marked in the plot, which was calculated by Bragg's Law. e) The average surface pore diameter (d_{ave}) of PES substrate and CNT membranes, and the corresponding images of pore size distributions are shown in Figures S2 and S5 (Supporting Information). f) Schematic illustrating the method for obtaining force-displacement curves. F_m and D_m indicate the maximum force and displacement before the membrane gets damaged. g) F_m of the free-standing GO/CNT (upper red points) and GO (bottom gray points) membranes without PES substrate. SG, MG, and LG indicate the membranes were fabricated using small (average size diameter: 0.81 µm), medium (4.6 µm), and large (29 µm) GO nanosheets. The size distribution of GO nanosheets is shown in Figure S3 (Supporting Information).

In accordance with the oxidation degree, the peak areas of oxygen-containing groups in the C 1s profiles of the MG nanosheets had the highest C–OH/C–O–C/C=O/COOH content of 56.2%, suggesting relatively larger interlayer spacings.^[37]

2.2. Mechanical Characterization of GO/CNT Membranes

The incorporation of CNT reduced the pore size of the supporting membrane from 10^2 to 10^0 nm scale (Figure 2e), therefore reducing the free-standing area of the GO membrane and enhancing its mechanical strength. A sensing device was built to evaluate the mechanical strength of membranes (Figure 2f; Figure S7a, Supporting Information). GO and GO/CNT membranes without the PES substrate were prepared and transferred onto a stainlesssteel ring with a 5 mm inner diameter (Figure S7b, Supporting Information). The ring was then held on a hollow base, allowing a force-sensing probe to press on the free-standing membrane until it got damaged (Figure S7c, Supporting Information). The obtained force-displacement curves are shown in Figure S8 (Supporting Information), in which the maximum allowable force was defined as F_m , and the corresponding displacement as D_m . After integrating 25 mg m⁻² CNT to 250 mg m⁻² GO membranes, $F_{\rm m}$ increased from 8.8, 10.9, and 12.3 to 20.1, 24.1, and 27.0 mN for SG, MG, and LG membranes (Figure 2g). The results demonstrated a 120%–130% improvement in $F_{\rm m}$, indicating a

superior mechanical strength of GO/CNT membranes, which is favorable for high-pressure filtration.

2.3. Nanofiltration Performance of GO/CNT Membranes

To assess the nanofiltration performance of the membrane under conditions that mimic industrial applications, pressure-driven cross-flow measurements were performed (Figure 3a). The feed solutions containing different dyes and tea polyphenol (TP) were pumped with P toward the membrane sample located in the filtering chamber. Smaller water molecules penetrated the membrane and were collected as permeate. Larger molecules were rejected by the membrane and returned to the feeding beaker. *P* was elevated from 0 to 62 bar throughout the filtration test. The maximum pressure to prevent membrane damage is designated as P_m . When the membrane got damaged, water permeance would suddenly rise while the rejection rate would significantly decline. We used Rose Bengal (RB, molecular weight: 1018 Da) dye to evaluate the $P_{\rm m}$ of GO and GO/CNT membranes. For GO membranes, the $P_{\rm m}$ for SG, MG, and LG was 20, 24, and 24 bar (Figure 3b), suggesting that GO membranes get damaged at relatively low pressures. Upon incorporation of 2.5 mg m⁻² CNT, the GO/CNT membranes showed elevated $P_{\rm m}$ of 24, 28, and 30 bar, respectively (Figure 3c). According to scanning electron microscopy (SEM) images, when subjected to high water

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Figure 3. Nanofiltration performance of GO and GO/CNT membranes. a) Schematic illustrating the principle of the cross-flow filtration for performance test. b,c) Water permeance and rejection to RB across (b) GO membranes and (c) GO/CNT membranes. A sudden increase in permeance accompanied by a sudden decrease in rejection means the membrane gets damaged. The maximum filtering pressure to keep the membrane from getting damaged is defined as pressure resistance, P_m . d) Values and optical microscopy images of water contact angle on different GO/CNT membranes. e,f) Water flux and rejection to (e) dyes and (f) TP in different liquids across the GO/CNT membrane (SG/C2.5) at 20 bar filtering pressure. MLB: methylene blue, CV: crystal violet, CR: Congo red, MB: methyl blue. All error bars show the standard deviation of three measurements.

pressure, the GO/CNT membranes collapsed together, and the breakage occurred in the weaker GO layer (Figure S9, Supporting Information). Besides, the SG/C2.5 membrane demonstrated superior permeance compared to the MG/C2.5 and LG/C2.5 membranes. The phenomenon is likely attributed to the assembly of smaller GO nanosheets, introducing more interlayer channels that promote permeability while compromising structural stability.^[38,39] Furthermore, the SG/C2.5 membrane exhibited increased hydrophilicity (Figure 3d), contributing to a higher water permeance.

As high temperature improves the water diffusion, the water flux increases with an increase in operation temperature (T).^[40] As shown in Figure S10a (Supporting Information), when T grew from room temperature 25-70 °C, the flux of the SG/C2.5 membrane at 20 bar increased from 376 ± 10 to 566 ± 14 L m⁻² h⁻¹. As RB is an anionic dye, its rejection rate would decrease in alkaline solution (pH = 11) because of the electrostatic repulsion (Figure S10b, Supporting Information).^[41] The flux for organic solvents was much lower than that for deionized (DI) water (Figure S10c, Supporting Information). This is because water transfers faster in GO layers than organic solvents owing to the unique combination of low interfacial friction and structured water formations within nanochannels between GO nanosheets.^[42] As methanol shows a smaller molecular size and viscosity than ethanol, it results in a larger permeance and flux.^[14] Besides, the RB rejection rates are also lower in organic solvents than in DI water. This may be due to the higher affinity of the organic solvent for the dye molecules, which reduces the interactions between dyes and membrane surfaces, thus reducing the rejection rate.^[43,44]

For smaller dye molecules, the SG/C2.5 membranes demonstrated high water flux (181 \pm 11–418 \pm 21 L m $^{-2}$ $h^{-1})$ and

effective rejection rates of 78.6 \pm 0.2% for methylene blue (MLB, 319.9 Da), 98.8 ± 0.3% for crystal violet (CV, 407.9 Da) and Congo red (CR, 696.7 Da), and $98.7 \pm 0.5\%$ for methyl blue (MB, 799.8 Da) at 20 bar (Figure 3e). The lower rejection rate for MLB might be attributed to two factors: 1) The numerous negatively charged carboxyl functional groups in the GO layers reject the negatively charged MLB molecules.^[45] 2) The minimum permeable molecular diameter (Pd^*) of MLB (0.48 nm) is smaller than the GO interlayer spacings (0.80–0.83 nm).^[45] Pd^{*} for other dye molecules are listed in Table S2 (Supporting Information). Considering that several essential components in drinks, including TP (458.4 Da), fall within the 10^2-10^3 Da range, GO/CNT membranes also have potential applications in beverage processing. TP in black tea, oolong tea, jasmine tea, and DI water could be efficiently rejected (90.4 \pm 0.2%–93.9 \pm 0.5%) while maintaining a high-water flux (439 \pm 17–569 \pm 21 L m⁻² h⁻¹) at 20 bar (Figure 3f).

For long-term performance, the SG/C2.5 membrane demonstrated good stability over 72 h at 20 bar (Figure S11a, Supporting Information). The rejection rate to RB exceeded 99.4% without damage or swelling. The stability of GO layers during operation may be attributed to the unavoidable introduction of divalent and multivalent cations during GO membrane preparation and performance testing (Figure S12, Supporting Information), which bind GO nanosheets and limit redispersion.^[46] Besides, the air-drying process before the nanofiltration test would remove water in the GO membranes, enabling the GO nanosheets to be tightly bound together through interlayer interactions, thus also enhancing stability.^[47] Moreover, abundant carboxyl groups on GO surfaces reduced the adhesion of hydrophobic contaminants, making the GO/CNT membrane of good antifouling

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Figure 4. Influence of CNT loading amount on nanofiltration performance. a–c) (a) P_m , (b) water permeance at P_m , and (c) Flux_m of GO/CNT membranes with different CNT loading amounts (Flux_m = water permeance at $P_m \times P_m$). Hollow points imply predicted values, as the test equipment has a maximum withstand pressure of 62 bar. The error bars show the standard deviation of three measurements. d) Mechanical simulation results of the influence of CNT loading amount on maximum σ_{vM} suffered by the GO layer. d_{ave} means the average surface pore size of the substrate, which is also the free-standing diameter of the corresponding GO layer; *n* means surface pore density; *h* means the thickness; *E* means Young's modulus. Detailed models and results are shown in Figure S13 and Table S3 (Supporting Information). e) Water flux per unit membrane thickness versus operating pressure plot of various GO-based membranes for dye nanofiltration. See details in Table S1 (Supporting Information). f) Comparison of water flux and rejection to RB across a commercial nanofiltration membrane (NF270) and the GO/CNT membrane (SG/C7.5) in this study.

performance (Figure S11b, Supporting Information).^[48] In a standard antifouling cycle test, the water flux at 20 bar recovered to 86% and 80% after the first and second cycles, respectively, after artificial fouling by bovine serum protein (BSA) and fouling removal by NaClO.^[49]

2.4. Influence of CNT Loading Amount on Nanofiltration Performance

Previous studies have shown that strong $\pi - \pi$ stacking, hydrogen bonding between GO nanosheets and CNTs, and their similar feature sizes make GO/CNT membranes show improved mechanical properties.^[50] Here, COMSOL mechanical simulations were applied to clarify the mechanism of CNT in enhancing the pressure resistance of GO membranes (Figure \$13, Supporting Information). By introducing CNT networks which are similar to stringer and frame in aircraft shell (Figure S14, Supporting Information), the von Mises stress (σ_{vM}) experienced by the GO layer is reduced (Figure 4d), resulting in an increased P_m (Figure 4a). It is worth clarifying that the enhancement in P_m is not only due to the reduced free-standing diameter of the GO layer (d_{ave}), but also includes the combined effect of increased surface pore density (n), membrane thickness (h), and Young's modulus (E). As shown in Figure 4d, when only considering the effect of reduction in d_{ave} , the simulated maximum σ_{vM} hardly decreased when loading more than 5 mg m $^{-2}$ CNT, which did not match the elevated $P_{\rm m}$ trend (Figure 4a).

As for the influence on permeance, the presence of CNT facilitates water transport in the transverse direction (gutter effect), while simultaneously increasing hydraulic resistance in the normal direction (blocking effect).^[51] The blocking effect can be demonstrated by Figure S15 (Supporting Information), which shows that the water permeance decreases from 1150 \pm 71 to 68.9 \pm 2.8 L m⁻² h⁻¹ bar⁻¹ when only loading 2.5–10 mg m⁻² CNT on PES membranes. The gutter effect has been demonstrated by previous similar studies, that the CNT layer would shorten the transport distance between the low-permeable GO layer and the high-permeable PES pores, thus facilitating the water permeance (Figure S16, Supporting Information).^[51,52] The two effects lead to optimal CNT loading amounts for the highest permeance of GO/CNT membranes (Figure 4b).

In summary, the integration of CNT to the GO membrane enhances the pressure resistance of the membranes, while slightly influencing the permeance. The most important water flux is determined by the product of water permeance and filtering pressure, making it essential to examine the optimal CNT loading amounts. Take GO/CNT membranes fabricated by 25 mg m⁻² small-sized GO nanosheets for example, as the CNT loading amount increased from 0 to 7.5 mg m⁻², the P_m was elevated by 200% from 20 to 60 bar, while the permeance at P_m decreased from 24.5 ± 3.0 to 16.1 ± 1.6 L m⁻² h⁻¹ bar⁻¹. When loaded with 10 mg m⁻² CNT, the membrane remained undamaged at 62 bar, which was the upper limit of the test equipment (Figure S17a, Supporting Information). Considering the observed trend of P_m increase, it is estimated that P_m could reach 85 bar

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(hollow point in Figure 4a) with the permeance at $P_{\rm m}$ approximating that at 62 bar (12.1 L m⁻² h⁻¹ bar⁻¹, hollow point in Figure 4b). When multiplying the permeance at $P_{\rm m}$ and $P_{\rm m}$, Flux_m was obtained (Figure 4c). As the CNT loading amount increased from 0 to 7.5 mg m⁻², the Flux_m was elevated by 97.1% from 490 ± 54 to 966 ± 96 L m⁻² h⁻¹. When the CNT loading amount increased to 10 mg m⁻², the Flux_m was estimated to be elevated by 110% to 1029 L m⁻² h⁻¹ (hollow point in Figure 4c). Using larger GO nanosheets in GO/CNT membranes demonstrated a similar pattern in $P_{\rm m}$, permeance at $P_{\rm m}$, and Flux_m (Figure S17b,c, Supporting Information).

Compared with other GO-based membranes reported in the literature, the GO/CNT membranes in this work showed higher pressure resistance and higher water flux with a thinner thickness, enabling 1-3 orders of magnitude improvement in water flux per unit membrane thickness (Figure 4e; Table S1, Supporting Information). Compared with a commercially obtained nanofiltration membrane NF270 (DuPont de Nemours, Inc., USA) with a 300 Da molecular weight cutoff, the SG/C7.5 membrane demonstrated a higher water flux while demonstrating comparable and better retention to RB (both >99%) over 4-60 bar filtering pressure (Figure 4f). Specifically at 60 bar, the SG/C7.5 membrane showed 45% higher water flux than the commercially obtained NF270 membrane, which indicated the same increase in clean water production, bringing significant environmental and economic benefits. The notable performance improvement will substantially enhance the cost-effectiveness ratio of GO nanofiltration membranes and advance them toward applications.

3. Conclusion

We designed ultrathin (45-68 nm) GO/CNT hybrid membranes using layer-by-layer wet-laid fabrication for highly efficient water purification. The mechanically robust CNT networks supported underneath the GO nanosheets enhance structural stability by reducing their free-standing diameter while increasing membrane thickness and Young's modulus. This structural reinforcement ensures a high-pressure resistance of up to 60 bar, which is triple that of the pristine GO membrane. The optimized GO/CNT membranes (SG/C7.5) demonstrate exceptional performance with a water flux of 966 \pm 96 L m⁻² h⁻¹ and an RB rejection rate of 99.6 \pm 0.1%. Notably, their water flux per unit membrane thickness exceeds previous reports by 1-3 orders of magnitude. Combining high-pressure resistance, ultrathin thickness, and superior water flux, the GO/CNT membranes hold promise for efficient nanofiltration applications in wide areas of sustainable water remediation, pharmaceuticals, energy storage, and electronics.

4. Experimental Section

Preparation of GO Membranes: Monolayer GO nanosheet dispersions (10 mg g⁻¹) were obtained from Hangzhou Gaoxi Technology Co., Ltd, and were first filtered to eliminate contaminants. DI water was then used to dilute the dispersion to 0.8 mg L⁻¹. The GO dispersion was subjected to ultrasound treatment (30 °C, 50 W) for 2 h, and 1 L dispersion was filtered across a PES substrate membrane (Nantong Longjin Membrane Technology Co., Ltd., diameter: 240 mm, nominal pore size: 0.1 µm, poros-

ity: 75%) via wet-laid method using a sheet former (Figure S18a, Supporting Information) (200GS-T, Guangdong Fiber Technology Research Co., Ltd., China). Subsequently, the GO nanosheets were deposited on the PES substrate and dried in an oven (40 $^\circ$ C) for 24 h.

Preparation of GO/CNT Membranes: Single-walled CNT dispersions (0.5%) were obtained from Nanchang Xinsu Nano Materials Co., Ltd. The dispersion was first diluted to 0.08 mg L⁻¹ by DI water, followed by the same procedures as GO membrane preparation, including ultrasound treatment, wet-laid, and drying. To achieve varying CNT loadings (2.5, 5, 7.5, and 10 mg m⁻²) on the PES substrate, corresponding volumes of dispersion (1, 2, 3, and 4 L) were used. Subsequently, the GO nanosheets were deposited on the obtained CNT membrane following the same procedures as GO membrane preparation, and the GO/CNT membrane was obtained.

Preparation of Free-Standing Membranes for Mechanical Test: For the free-standing GO membrane preparation, GO dispersion (5.6 L, 0.8 mg L⁻¹) was filtrated across a mixed cellulose esters (MCE) substrate membrane (Shanghai Xinya Purification Equipment Co., Ltd., diameter: 150 mm). Subsequently, the membrane was dried in an oven (25 °C) for 24 h, and was cut into 50 mm diameter. The MCE substrate was then removed by immersing the membrane in an ethyl acetate solution for 30 min.^[53] The GO membrane, floating on the solution surface, was then transferred to a stainless-steel ring with a 5 mm inner diameter and gradually rinsed with acetone to remove the MCE residue. Finally, the free-standing GO/CNT and CNT membrane preparation, the only difference was the prior loading of CNT before GO loading (if needed). Specifically, CNT dispersion (5.6 L, 0.08 mg L⁻¹) was filtrated across the MCE substrate, and then dried at 40 °C for 24 h.

Physical Property Characterization: SEM images were obtained using a scanning electron microscope (ThermoFisher Verios 5UC, USA). Pore and nanosheet size distributions were statistically analyzed based on their SEM images using MIPAR and ImageJ software, respectively. The forcedisplacement curves were obtained using a non-standard, custom-built device (model D-NI100TBP, refer to Figure S7a, Supporting Information), the working principle of which was shown in Figure 2f. The force-sensing probe contacting the membrane is a stainless-steel hemisphere with a diameter of 2 mm. The Young's modulus of the freestanding GO and CNT membranes was evaluated using the air-leak test (Figure S19a, Supporting Information). The freestanding membranes were mounted on a custombuilt chamber, and the pressure difference across the membranes was measured using a differential pressure gauge (DP-Cals 58, TSI, USA). The air pump created a negative pressure inside the chamber, resulting in the deformation of the freestanding membrane. The air valve was then sealed to allow the system to gradually release air, enabling the deformation to recover gradually, which was quantified using a confocal laser displacement sensor (LK-G5000, Keyence, Japan). The Young's modulus could be extracted by fitting the pressure-deformation relation (Figure S19b,c, Supporting Information). The XRD patterns of the GO nanosheets were obtained in the air (22-27 °C, <70% RH) using an X-ray diffractometer (EMPYREAN SERIES 3, PANalytical Empyrean, Netherlands). The water contact angle on the membranes was obtained using a contact angle measuring instrument (SDC-200SE, Dongguan SINDIN Precision Instrument Co., Ltd., China).

Nanofiltration Performance Test: Pressure-driven nanofiltration was performed using a cross-flow filtering device (Figure S18c, Supporting Information) (FlowMem0021-HP-C, Xiamen FMT Technology Co., Ltd., China). The membrane cell was 106 mm long and 58 mm wide, with the membrane samples supported on a perforated stainless-steel plate. Therefore, smaller membranes with dimensions of 132 mm in length and 74 mm in width (Figure S18d, Supporting Information) were obtained via laser cutting from the prepared circular membrane (Figure S18b, Supporting Information). Before each test, the membranes were pre-loaded with DI water at 5 bar (GO membrane) or 10 bar (GO/CNT membrane) for 30 min to achieve steady filtration. The feed solutions were pumped to the membrane with pressure in the range of 0–62 bar. The permeate was collected in a centrifuge tube, with the first 10 mL discarded. The flow rate was obtained by quantifying the rise in permeate volume over time. The

water permeance J (L m⁻² h⁻¹ bar⁻¹) was calculated by normalizing the volumetric permeate amount per hour V (L h⁻¹) by the membrane area $A = 6148 \text{ mm}^2$ and pressure gradient P (bar). To demonstrate the rejection rates (R) to small molecules, dyes (20 mg L⁻¹), tea polyphenol (TP, 20 mg L⁻¹) in DI water, and tea drinks were used as the feed solution. Dyes and TP were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. The tea drinks were purchased from Nongfu Spring Co., Ltd.'s Oriental Leaf series. R can be calculated according to:[⁵⁴]

$$R = (1 - A_2 \cdot A_1^{-1}) \times 100\%$$
⁽¹⁾

where A_1 and A_2 are the ultraviolet (UV) absorption of the feed and permeate solution, measured by a UV-vis spectrophotometer (L8, INESA, China). All experiments were repeated at least 3 times to minimize random error.

Mechanical Simulations: The COMSOL Multiphysics solid mechanics module was used to describe the stress in the GO layer.^[55] The membrane module was emulated as a cylinder domain with a diameter of 450 nm, in which the GO layer, CNT layer (if needed), and rigid hole layer were inserted in order (Figure S13a,b, Supporting Information). The pressure on the GO layer is 30 bar, and the other end was fixed. Other parameters required in the simulation and their references are shown in Table S3 (Supporting Information).

Statistical Analysis: All experiments were repeated at least three times to ensure reliability and accuracy. The statistical calculations of the raw data were performed using Excel in Microsoft Office LTSC 2021 and Origin 2021 software. The experimental data were expressed as mean \pm standard deviation (Mean \pm SD).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

X.Z., E.T., and Z.L. contributed equally to this work. This work was supported by the Guangdong Major Project of Basic and Applied Basic Research (2021B0301030002 (E.W., K.L. and K.L.)), the National Natural Science Foundation of China (52025023 (K.L.), 12427806 (K.L.), 52408122 (E.T.), T2188101 (K.L.), and U24A20285 (E.T.)), the Guangdong Basic and Applied Basic Research Foundation (2022A1515110897 (E.T.)), the New Cornerstone Science Foundation through the XPLORER PRIZE (K.L.), and the Hangzhou Tsientang Education Foundation (K.L.). The authors gratefully acknowledge Dr. Chuang Han and Mr. Fangyou Yang for their invaluable assistance with mechanical simulation modeling.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords

carbon nanotubes, graphene oxide, mechanical strength, water treatment, wet-laid

Received: February 6, 2025 Revised: April 29, 2025 Published online:

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