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ARTICLE OPEN Advanced hybrid nanosheet membranes with stable nanochannels for ultrafast molecular separation

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Lamellar graphene oxide (GO) membranes have gained substantial interest for molecular separation processes. However, GO membranes have shown inefficient separation performance levels due to their possession of sufficient functional groups that lead to swelling under applied hydraulic pressure. Herein, we demonstrate a highly stable and ultrafast filtrable graphene oxide-boron nitride (GOBN) hybrid membrane by incorporating boron nitride (BN) nanosheets into a GO membrane to restrict swelling and provide efficient hydraulic pressure separation characteristics. This new heterostructure retains the GOBN membrane microstructure and provides more nanochannels around the incorporation sites due to the small size of BN nanosheets; this phenomenon increases the permeance to $1310 \, \text{Lm}^{-2} h^{-1} \text{bar}^{-1}$, which is nearly six times higher than that of the pure GO membrane, with a high rejection reaching 99.2% for aqueous organic dyes. More importantly, the GOBN hybrid membrane shows an impressive permeance and dye molecule rejection performance characteristics are better than those for the GO membrane. Our GOBN membrane with a stable microstructure opens opportunities for developing a high-performance multiple solvent nanofiltration membrane that surpasses the permeability-selectivity trade-off.

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INTRODUCTION

The development of efficacious separation technologies to remove contaminants and purify organic substances is of paramount significance to ensure clean water resources and organic solvent processing^{1,2}. With the obvious benefits of modularity, scalability, compactness and high-energy efficiency, membrane separation nowadays is a universal technique that has been utilized in water, food, energy, biotechnology and chemical processing applications for more than half a century^{3,4}. Specifically, organic solvent nanofiltration (OSN) membranes function as new paradigm separation technologies in organic solvent operations for high-value-added products, motivated by the merits of using membranes for aqueous applications instead of conventional evaporation or distillation techniques³. However, the tradeoff between permeance and selectivity remains a challenge for the further application of the membrane to related separation efforts. Therefore, a new generation of nanofiltration membranes with high solvent permeance and good separation performance levels is needed to purify concentrate multicomponent from aqueous, and organic media^{5,6}.

Two-dimensional lamellar membranes, which are built from the imperfect stacking of nanosheets, are widely researched and implemented to address multifarious challenges in separation processes, such as issues regarding the permeance, selectivity, cost, thermal properties and antipollution characteristics⁷. Relative to conventional polymeric membranes, the two-dimensional lamellar membranes possess better broad chemical compatibilities, avoiding dissolution and swelling under harsh chemical environments and extreme operating conditions⁸. Hence, many two-dimensional (e.g., graphene oxide and its derivative^{9,10},

exfoliated dichalcogenides¹¹, layered metal oxides¹², zeolites¹³, metal-organic framework¹⁴, MXene¹⁵, and clay¹⁶) nanosheetbased membranes are being reassembled and investigated to obtain excellent solvent permeance and selectivity properties to meet the industrial demands for practical applications. Among these membranes, graphene oxide (GO) membranes have high potential for future separation applications because of their tunable molecular selectivity, attractive permeance, and controllable cost characteristics. Nevertheless, GO membranes lose their structural integrity due to their rich oxygen-containing groups; furthermore, they severely swell in aqueous solutions, reducing their separation performance^{17,18}. Therefore, the design of a GO membrane with a fixed nanochannel size to avoid swelling is desired for filtration applications.

To tackle the issue of GO membrane swelling, tremendous efforts have been made to improve the stabilities of GO membranes, such as partial reduction¹⁹, covalent cross-linking²⁰ intercalation with ions and molecules²¹, functional group doping²² or physical encapsulation¹⁰. Although some achievements have been made in controlling the intralayer of the GO membrane, the permeance decreases drastically^{22,23}. Hence, further improving the solvent permeance without sacrificing the separation efficiency is an ongoing dilemma. Impressively, intercalating GO membranes with nanomaterials is a good approach for sustaining the GO membrane with high selectivity and even for enhancing the permeance. For example, copper hydroxide nanostrands²⁴, graphite carbon nitride nanosheets^{25,26}, zeolitic imidazolate framework-8 nanocrystals²⁷ have been prepared in GO membranes to produce more nanochannel networks, giving enhanced permeance with similar rejection characteristics for molecule

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Fig. 1 Schematic illustration of hybrid GOBN and pure GO laminate membranes for molecular separation. a Transmission electron microscopy (TEM) image of the small BN nanosheets loaded on the GO nanosheets. The small BN nanosheet was uniformly scattered on the GO nanosheets. The scale bar is 1 μ m. **b** Cross-sectional scanning electron microscopy (SEM) image of the GOBN hybrid membrane. The thickness of the GOBN with a mass density of 69 mgm⁻² was approximately 50 nm. To measure the thickness of the GOBN membrane clearly, anodic aluminum oxide (AAO) substrate was selected to support the GOBN membrane. The scale bar is 2 μ m. **c** GO and BN nanosheet orderly stacking and stable laminate membranes for molecule separation. The enlarged inset shows that the BN nanosheets locked the structure in the solvent environment. GO nanosheets with carboxylic/hydroxy functional groups are displayed in black tablets, while BN nanosheets with possible molecular pathways through each membrane.

separation. While the above intercalated nanomaterials significantly improve the GO membrane with high separation performance in aqueous solutions, a competitive effective separation performance in organic solution remains unexplored for GO membranes. Therefore, new nanomaterials are needed to develop hybrid GO membranes with high molecular selectivity and improved permeance in organic and aqueous systems.

Boron nitride (BN), otherwise known as 'white graphene', is widely used for extreme thermal, acidic, alkaline and corrosive environments because of its distinctive physical and chemical properties^{28,29}. We have recently studied an amino functionalized BN nanosheet-assembled membrane for efficient molecule separation in aqueous and organic solutions³⁰. The small BN nanosheets account for the abundant nanochannels for high performance, and the stable intralayer distance is applicable for solute sieving. Furthermore, the BN nanosheet incorporated with nanofibers improves the nanocomposite membrane with ultramechanical performance, and supports the presence of more nanochannels for ions to pass through³¹. Therefore, BN nanosheets are promising platforms for creating GO hybrid membranes to investigate molecular flow in agueous and organic systems under extreme confinement; these nanosheets have the potential for a technological translation that generates useful membrane separation characteristics.

Herein, we have developed highly stable and ultra-permeable laminate GO and BN nanosheet hybrid membrane architectures (GOBN); the BN nanosheets confined in the micropores of GO nanosheets contribute to regenerated nanochannels and enable efficient and stable separation performance levels in aqueous and organic solutions under applied pressure. We have assessed the

stable multiple solvent compatibility characteristics of our membrane architectures and investigated the influences of BN nanosheet loading amounts on the solvent and solute transport mechanisms. The GOBN membrane shows an impressive permeance and molecule rejection from aqueous and organic solutions, with a high perm-selectivity of Eosin Y $(1140 \, \text{Lm}^{-2} \text{h}^{-1} \text{bar}^{-1})$ and 98.4% rejection), rose bengal $(1280 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1} \text{ and } 99.2\% \text{ rejection}), \text{ brilliant yellow}$ (1320 Lm⁻²h⁻¹bar⁻¹ and 98.8% rejection) and Evans blue $(1320 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1} \text{ and } 98.8\% \text{ rejection})$ from aqueous, acid fusion (900 $\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$ and 87% rejection) from methanol. Congo red (350 Lm⁻²h⁻¹bar⁻¹ and 89% rejection) from ethanol, brilliant Blue (200 Lm⁻²h⁻¹bar⁻¹ and 99% rejection) from isopropyl alcohol, respectively. The results of this study may improve the GO-based membranes for aqueous and organic solution separation, providing insights into the design of nextgeneration multiple solvent nanofiltration hybrid membranes.

RESULTS AND DISCUSSION

Preparation and characterization of the GOBN membranes

GOBN membranes with designed weight ratios and adjusted thicknesses were prepared by filtering GO and BN mixture dispersions on nylon membrane substrates with the aid of a vacuum assisted setup. The transmission electron microscopy (TEM) image showed that the BN nanosheets were well distributed on the GO nanosheets before membrane fabrication, ensuring the effective BN nanosheets incorporation into the GOBN membrane microstructure effectively (Fig. 1a). The resulting membrane was



Fig. 2 Preparation and characterization of the GOBN membrane. a UV-Vis spectra of the GO, BN and GOBN dispersions. The inset shows the optical images of the GO (0.3 mgmL^{-1}), BN (0.11 mgmL^{-1}) and GOBN (0.14 mgmL^{-1}) dispersions. To make the absorbance intensity comparable, the GO, BN and GOBN dispersions were diluted with deionized water (DI) water. **b** Fourier transform infrared (FTIR) spectra of the GO, BN and GOBN samples. **c** Raman spectra of GO, BN and GOBN. **d** Top view SEM image of the GO membrane with nylon substrate (69 mgm⁻²). The scale bar is 2 µm. **e** Top view SEM image of the GO₁BN₂ membrane with nylon substrate (69 mgm⁻²). The scale bar is 2 µm.

noted as GO_xBN_y ; x/y = 2/1, 1/1, and 1/2 correspond to the BN weight ratio in the GOBN membranes (Fig. 1b). This filtration process incorporated the BN nanosheets into the GO membrane and endowed the GOBN membranes with more stable nanochannels via the surface interactions of amine groups from BN nanosheets and carboxyl groups/hydroxyl groups from GO nanosheets, resulting in a locked microstructure with ultrafast solvent transport for molecule separation in aqueous and organic solutions (Fig. 1c).

The dispersion of BN nanosheets was prepared via a ball milling methodology according to our previous work³⁰, excepting centrifuging at 8000 rpm for 30 min to make the BN nanosheets with similar micromorphology. Scanning electron microscopy (SEM), and transmission electron microscopy (TEM) images showed BN nanosheets with diameters of 50~500 nm, which were collected for further measurement and membrane fabrication process (Supplementary Fig. 1). X-ray diffractometry (XRD) verified that exfoliated BN nanosheets were prepared via ball-milling (Supplementary Fig. 2). The commercial GO nanosheet (from XFNANO, approximately 5 μ m) dispersion was diluted and used to fabricate the GOBN membrane.

To fabricate uniform GOBN membranes, the BN nanosheet dispersion with the desired weight ratio was firstly blended with the GO nanosheet dispersion. The GO_1BN_2 sample was characterized to understand the hybrid microstructure. Ultraviolet-visible (UV-Vis) spectra demonstrated the mixed dispersion in water with characteristic absorbance peaks of 204 nm for BN nanosheets and 235 nm for GO nanosheets^{32,33} (Fig. 2a). To understand the uniform structures of the GO_1BN_2 membranes, the mixed dispersions were freeze-dried for Fourier transform infrared (FTIR) and Raman spectra measurements. As shown in Fig. 2b, the

 GO_1BN_2 mixture showed C = O, C-O, C = C, and C-OH in GO nanosheets and in BN nanosheets undergoing out-of-plane B-N-B bending vibration and in-plane B–N stretching vibration^{34,35}. In particular, the C-OH and B-N peaks overlapped and were enhanced due to the incorporation of BN nanosheets instead of GO nanosheets. Similarly, the Raman results demonstrated that the GOBN possessed an E_{2g} peak at 1380 cm⁻¹ from BN nanosheets and a D band³⁰, G band at cm⁻¹ and 2D band at cm⁻¹ from GO nanosheets³⁵. The elementary constitution of the GOBN membrane was analyzed via an X-ray photoelectron spectroscopy (XPS) experiment (Supplementary Fig. 3). The boron signal was detected in the XPS survey of the GOBN membrane. The main peak at 398.1 eV in the N 1 s spectrum corresponded to the N-B bond of BN, while the satellite peak at 400.3 eV corresponds to the N-C³⁶. These results confirmed that the amino groups on the BN nanosheets interacted well with the GO nanosheets, allowing the chemical adhesion of the GO nanosheets with BN nanosheet incorporation.

Top view SEM images of the membranes showed that the pure GO membrane had a smooth surface; the GOBN membrane had a rough surface because the BN nanosheets were smaller size than the GO nanosheets and they were incorporated into the membrane (Figs. 2d, e). The inset optical images from the insets solidly confirmed the even construction of the GO and BN nanosheets in the GOBN membrane. Atomic force microscopy (AFM) images revealed that the BN nanosheets wrinkled in the GOBN membranes, increasing the number of nanochannels in the GOBN membranes (Supplementary Fig. 4). In summary, the BN nanosheets were incorporated into the GO nanosheets randomly, giving the stabilized GOBN membrane potential for practical molecule separation applications.



Fig. 3 GOBN membranes for molecule separation in aqueous environment. a Water permeance characteristics of GOBN and GO membranes with various mass densities. Here error bars mean standard deviation. **b** Arrhenius plots of the water permeation rate (In P) versus inverse temperature (1000/T) for GOBN and GO membranes. **c** Solvent filtration ability versus the viscosities of different solvents through the GO membrane (blue triangle dot) and GOBN membrane (red hexagonal dot). The green dashed line shows the improved permeance of the GO₁BN₂ membrane. **d** UV-Vis absorption spectra of aqueous solutions of rose bengal (RB, concentration of 4.54 mgL⁻¹) before and after filtration through GO₁BN₂ membrane with a mass density of 69 mgm⁻²; the left inset photo shows the feed (F, left) and permeate (P, right) of the RB solution, the right inset shows the molecular structure of RB and the right. **e** Comparison of the separation performance of the GO₁BN₂ membranes (69 mgm⁻²) versus other reported membranes in aqueous media. The reported membranes for dye separation were summarized with balls in various colors, the dyes separated through the GO₁BN₂ membranes (69 mgm⁻²) were collected with five-pointed star by different colors. MB stands for Methylene blue (319.85 gmol⁻¹, concentration is 1.57 mgL⁻¹), R6G means Rhodamine 6G (479 gmol⁻¹, concentration is 1.92 mgL⁻¹), BY represents Brilliant yellow (624.55 gmol⁻¹, concentration is 4.54 mgL⁻¹). Esin Y (691.85 gmol⁻¹, concentration is 3.63 mgL⁻¹), RB denotes Rose Bengal (1017.6 gmol⁻¹, concentration is 4.54 mgL⁻¹).

GOBN membrane for solvent permeance and molecule separation

The permeance performance levels of the GOBN membranes were investigated by accumulating a volume of 40 mL of pure water through the membranes at room temperature under a pressure of 1 bar (Supplementary Fig. 5). A transparent increasing trend was found in the permeance values versus GOBN membranes with decreasing mass densities when tested with 97, 83, and 69 mgm⁻²

mass densities (Fig. 3a). All the collected data were averages of three parallel tests. For the pure GO membrane, the permeance value increased from 50 ± 15 to $240 \pm 60 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$ as the mass density decreased from 97 to 69 mgm^{-2} , showing a thickness (mass density) dependent relationship. However, with BN nanosheets incorporated into the GOBN membranes, the permeance increased to $1520 \pm 100 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$, which is nearly six times higher than the pure GO membrane with the

same mass density of 69 mgm⁻². Furthermore, the contents of BN nanosheets obviously affected the GOBN permeance. When maintaining the mass density and taking 97 mgm^{-2} as an showed example, GO₁BN₂ а permeance of $145 \pm 40 \,\mathrm{Lm^{-2}h^{-1}bar^{-1}}$, which was higher than the permeance GO_2BN_1 $(120 \pm 30 \, \text{Lm}^{-2} \text{h}^{-1} \text{bar}^{-1}),$ values of GO₁BN₁ $(105 \pm 20 \, \text{Lm}^{-2} \text{h}^{-1} \text{bar}^{-1}),$ membranes and pure GO $(50 \pm 15 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1})$. For a lower mass density of 69 mgm⁻², the incorporation of BN nanosheets into the membrane noticeably improve the permeance, by up to six times; the higher mass density of 97 mgm^{-2} increased the permeance by three times. This phenomenon occurred because of the lower mass density supporting shorter nanochannel lengths through the GOBN membrane: the BN nanosheets with small sizes created more nanochannels, allowing for water molecules to pass though. The Arrhenius activation energy for water filtration through the membranes was calculated by fitting the permeation rate (Fig. 3b; Supplementary Fig. 6). After fitting the speed versus the operating temperature curve, the Ea value of the GO₁BN₂ membrane was 16.46 kJmol^{-1} , indicating a higher thermal response for water permeance than that of the GO membrane $(Ea = 22.2 \text{ kJmol}^{-1}).$

The GO_1BN_2 membrane with a mass density of 69 mgm⁻² was further studied to understand the permeance levels of different solvents versus their viscosities (Fig. 3c). The GO_1BN_2 membrane showed a visible enhancement in permeance relative to the pure

GO membrane. Specifically, the GO_1BN_2 membrane had an extraordinarily high permeance of $1670 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$ for acetone because of the incorporated BN nanosheets and its low solvent viscosity (0.32 centipoise, cP). This value is approximate six times and six hundred times higher than the values for GO and commercial OSN membranes³, respectively. Nevertheless, for 2-propanol with a comparable molecular size to acetone, the permeance of the GO₁BN₂ membrane decreased to $180 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$ due to the high viscosity (2.37 cP), which was 30 times higher than that of the GO membrane. In general, both the molecule size and viscosity of the solvent accounted for the enhanced permeance through the GO₁BN₂ membrane, which was similar to the other OSN membranes^{3,37}.

The GO₁BN₂ membrane (69 mgm⁻²) for the frequent filtration of aqueous were operated to test the long-term performance (Supplementary Fig. 7). After 10 Dl water filtration cycles, the permeance raised with the operation time and then stabilized up to around $2600 \, \text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$, which was a nearly 120% improvement relative to the fresh GO₁BN₂ membrane. Even though the permeance of the GO membrane with the same mass density increased from 60 to $80 \, \text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$, the permeance of GO₁BN₂ membrane was 32 times higher than that of GO membrane. Hence, incorporating BN nanosheets into the GOBN membrane is a great candidate for improving the permeance, demonstrating the ability of the hybrid membrane to be work well after soaking in water for a long time (Supplementary Fig. 8).



Fig. 4 GOBN membranes for molecule separation in various organic solutions. a Organic solvent (methanol, ethanol, and isopropyl alcohol) permeance conditions of GOBN membranes with various mass densities. Here error bars mean standard deviation. **b** UV-Vis absorption spectra of a methanol solution of Evans blue (EB, concentration of 3.3 mgL^{-1}) before and after filtration through GOBN; the left inset is the molecular structure of Evans blue and the right inset photo shows the feed (F, left) and permeate (P, right) of the Evans blue solution. **c** UV-Vis absorption spectra of an ethanol solution of fast green FCF (concentration of 3.16 mgL^{-1}) before and after filtration through GOBN; the left inset is the molecular structure of Fast green FCF (concentration of 3.16 mgL^{-1}) before and after filtration through GOBN; the left inset is the molecular structure of Fast green FCF (concentration of 3.16 mgL^{-1}) before and after filtration through GOBN; the left inset is the molecular structure of Fast green FCF (concentration of 3.16 mgL^{-1}) before and after filtration through GOBN; the left inset is the molecular structure of Fast green FCF and the right inset photo shows the feed (F, left) and permeate (P, right) of the Fast green FCF solution. **d** Comparison of the separation performance of the GOBN membranes versus other reported membranes in organic media. AF means acid fuchsin (585.53 gmol⁻¹, concentration is 3.34 mgL^{-1}), CR stands for Congo red (696.7 gmol⁻¹, concentration is 2.27 mgL^{-1}), BB is Brilliant blue (792.9 gmol⁻¹, concentration is 5 mgL^{-1}). FG represents Fast Green FCF (808.9 gmol⁻¹, concentration is 3.36 mgL^{-1}). Triangle represents the dyes dissolved in methanol, circle denotes the dyes dissolved in ethanol, and the five-pointed star means the dyes dissolved in isopropyl alcohol. The present works were labelled in red.



Fig. 5 Mechanism of permeation enhancements. **a** MS simulation of how the water molecules flow through the GOBN nanochannels. The 001 crystal plane index of graphite is highlighted with an arrow. **b** Interlayer spacing change in the GOBN membrane when dry and wet status. **c** Schematic of various solvents, such as water, ethanol, methanol, and Isopropanol molecule passing through the GOBN membrane, respectively.

The membrane separation process showed large potential in the pursuit of high water permeance and ideal separation performance levels for practical application requirements. Usually, dye molecules with different structures, sizes and charges would be selected to discern the separation ability of a membrane because of their easily soluble and examine (Supplementary Fig. 9). The organic dyes were spiked in solvents and tested separately. The concentrations of different dyes at various stages, such as feed, permeate, and retentate were measured with UV-Vis spectroscopy. The hydrophilic GO₁BN₂ membrane completely rejected the rose Bengal molecules (1017.6 gmol⁻¹) from the water molecules (Fig. 3d). Impressively, the flux of the membrane was 1280 Lm⁻²h⁻¹bar⁻¹and the rejection rate reached 99.2%. The GO₁BN₂ membrane treated with ten cycles of water filtration was further examined for RB molecules in water solution, showing a stable rejection rate of 99.3% (Supplementary Fig. 10). Similarly, other dye molecules were further selected to investigate the performance of the GO1BN2 membrane, all increasing high the separation performance for MB (1310 Lm⁻²h⁻¹bar⁻¹ and rejection of 95.6%), R6G (1450 Lm⁻²h⁻¹bar⁻¹ and rejection of 89.4%), BY $(1320 \, \text{Lm}^{-2} \text{h}^{-1} \text{bar}^{-1})$ and rejection of 98.4%), Y Fosin (1140 Lm⁻²h⁻¹bar⁻¹ and rejection of 98.4%). FB (1610 $\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$ and rejection of 86%). The molecular weight, size and charge characteristics of the dyes all contributed to the aqueous flux and rejection rate³⁰. The incorporation of BN nanosheets into the GOBN membrane improved the separation rate (high flux) and the separation ability (high rejection) for dye separation applications.

Relative to other GO based membranes prepared via various procedures, such as an external particle incorporation, surface modification, and posttreatment, the BN nanosheet incorporated GOBN membrane prepared in this work exhibits excellent separation performance under similar experimental conditions^{19,24,27,38–42} (Fig. 3e). In some reports, although the GO based membranes showed good rejection rates, their water permeance levels decreased dramatically²². Similarly, some related works drastically increased the water permeance at the cost of rejection ability collapse. To consider the efficiency and interest for future practical applications, researchers sought techniques for increasing the permeance and rejection characteristics of GO membranes. Hence, the GOBN membrane exhibited much better dye molecule separation than the reported GO based membrane under the experimental conditions (Supplementary Table 1).

While the GOBN membrane showed exciting separation performance for dyes separation in DI water, we then used the real water from Chaohu Lake (31.5°N 117.5°E) to dissolve dyes for practical application. The GOBN membrane exhibited a notable decreasing trend for 10-cycle filtration tests for real water

compared to the results of DI water (Supplementary Fig. 7b). Micro bacterium, dissolved soil, dissolved rubbish, and dissolved micropollutants account for the decreasing permeance due to their accumulation on the interface of the GOBN membrane. However, the comparable dyes separation performance between DI water and real water further gives the potential of GOBN membrane for future application (Supplementary Fig. 11).

Since membrane-based organic solvent nanofiltration (OSN) could potentially reduce the energy consumption by 90% relative with now-dominant evaporation or distillation process for organic solvent recovery, the existing polymeric materials challenged the long-term stability and operation safety in solvents^{3,43}. The application of nanoporous GO based membranes for OSN has rarely been reported due to their low solvent permeance and weak rejection characteristics of dye molecules. Inspired by the above impressive solvent permeance (Fig. 3a), we explicitly measured how the mass density of the GO₁BN₂ membrane, such as 69, 55, and 41 mgm⁻² affected the filtration performance for organic solutions including methanol (0.55 cP), ethanol (1.07 cP) and isopropyl alcohol (2.37 cP), respectively (Fig. 4a). By taking methanol as an example, as the mass density of the GO₁BN₂ membrane decreased from 69 to 41 mgm⁻², the corresponding permeance improved from 900 \pm 20 to 1400 \pm 100 Lm⁻²h⁻¹bar⁻ Similarly, isopropyl alcohol showed an enhancement from 200 ± 15 to $780 \pm 70 \, \text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$ as the mass density decreased. The viscosity of the solvents and the mass densities of the membranes governed the permeance reverse, which was similar to that in an aqueous environment (Fig. 3c).

For the following dye separation processes from organic solvents, we selected a GO₁BN₂ membrane with a mass density of 69 mgm⁻². For methanol solutions, the GO₁BN₂ membrane showed high separation performance for Evans blue (780 $\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$, rejection rate of 99.1%) and acid fuchsin (880 $\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$, rejection rate of 87.5%) dye molecules (Fig. 4b and Supplementary Fig. 12). For ethanol solutions, the GO₁BN₂ membrane exhibited high separation performance for fast green FCF ($310 Lm^{-2}h^{-1}bar^{-1}$, rejection rate of 99.3%), Congo red $(350 Lm^{-2}h^{-1}bar^{-1}$, rejection rate of 89.6%), and acid fuchsin (290 Lm⁻²h⁻¹bar⁻¹, rejection rate of 89.2%) dye molecules (Fig. 4c and Supplementary Fig. 13). For isopropyl alcohol solutions, the GO₁BN₂ membrane displayed high separation performance for Brilliant blue (180 $\text{Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$, rejection rate of 99.5%) dye molecules (Supplementary Fig. 14). Then, GO₁BN₂ membranes were filtrated with methanol and ethanol solvents for 10 cycles to evaluate their stabilities. Although the GO₁BN₂ membrane showed a dramatic decrease in permeance to 100 and 170 Lm⁻²h⁻¹bar⁻¹ for the methanol and ethanol filtration tests (Supplementary Fig. 15). respectively, the separation performance remained

comparable to that of the reported GO based membrane in methanol and ethanol solutions (Supplementary Table 2). This result demonstrated that the organic solvent limited the swelling of GOBN nanosheets¹¹, reducing the permeance relative to that in aqueous solutions.

Comparisons with other membranes in the literature are shown in Fig. 4D and Supplementary Table $2^{37,43-48}$. Our GO₁BN₂ membranes clearly produced much higher permeance and selectivity charactertics than the state-of-the-art commercial and laboratory-scale membranes for dye separation from organic solutions. This phenomenon was attributed to the incorporation of BN nanosheets into the GOBN membranes, exposing more nanochannels and sustaining the nanochannel structure.

Mechanisms of permeation enhancements

We used materials studio (MS) simulations to understand how the water molecules flowed through the nanochannels of the GOBN membrane (Fig. 5a and Supplementary Fig. 16). The velocity distribution was symmetric along the 001 (hkl) plane, and the movement rate was faster near graphene oxide. This phenomenon occured because the hydroxyl and carboxyl groups were grafted on the surface of graphene oxide, having strong interactions with water molecules because of hydrogen bonding, and greatly strengthening the thermal motion of water molecules. When the BN layer was grafted with amino groups, the interaction between the BN layer and water was weaker. Accordingly, the thermal motion of water molecules did not change significantly. Then, the BN nanosheets replaced the GO in the GOBN membrane supported more nanochannels for solvents to pass through. As calculated in our previous work, the pure GO membrane showed an effective length two order of magnitudes longer than that of the pure BN membrane⁴⁹. Hence, with the incorporation of BN nanosheets, the effective length of the GOBN membrane decreased dramatically. The permeation enhancements for solvents depending on the BN content of the GOBN membrane verified this deduction. Moreover, even though the BN nanosheets showed higher friction coefficients than the GO nanosheets, amino functionalization further reduced the friction of the BN nanosheets⁵⁰, favoring the permeation value. The water contact angle on the GO membrane surface (55°) was lower than that on the GOBN membrane (59°) surface further indicating that BN is less hydrophilic than GO (Supplementary Fig. 17). The membranes used for separation contained numerous BN nanochannels and were hydrophilic, thus causing the solvents permeance levels of GOBN membranes to be several times higher than those of GO membranes.

For the stabilities of the membranes, the XRD patterns of the GO and GOBN membranes were measured under dry and wet conditions, respectively (Fig. 5b and Supplementary Fig. 18). A wider interlayer spacing change was collected for the GO membrane; the GOBN membranes showed decreasing spacing distances depending on the BN content of the hybrid membrane. Specifically, with increasing BN content in the GOBN membrane, the main peak of the interlayer spacing decreased from 8.7785 to 9.2337 Å. Correspondingly, the pure GO membrane showed widened interlayer spacing of 1.3055 Å due to the swelling of GO nanosheets in water; the GOBN membrane dramatically decreased to 0.1049 Å as the incorporation of BN nanosheets and their content ratio levels increased. The physical microstructure integrity of the GOBN membrane was enhanced and stabilized when dipped into water; the GO membrane evidently lost its microstructure integrity (Supplementary Fig. 8). The above discussion indicated that the incorporation of BN nanosheets produced more nanochannels and stabilized the nanosheets via the functional groups between GO and BN nanosheets; additionally, this process enhanced the separation performance relative to the pure GO membrane (Fig. 5c).

In summary, stable and efficient separation nanochannels have been successfully fabricated by incorporating BN nanosheets into a GO membrane to make a new hybrid membrane. The established nanochannels are less than 1 nm in width and sufficiently stable in aqueous and organic environments. Consequently, GOBN membranes achieve high rejection and improved flux characteristic toward dye molecule separation under external pressure; this phenomenon mainly relies on the size exclusion mechanism, differing from the sole GO membranes. The amino functional groups from BN nanosheets interact with carboxylic/ hydroxy groups from GO nanosheets, increasing the number of nanochannels and stabilizing the microstructure; GOBN membranes demonstrate impressive permeance and molecule rejection levels from aqueous and organic solutions, with a high permselectivity of Eosin Y (1140 Lm⁻²h⁻¹bar⁻¹ and 98.4% rejection) from aqueous, Evans blue (780 Lm⁻²h⁻¹bar⁻¹ and 99% rejection) from methanol, fast green FCF (310 Lm⁻²h⁻¹bar⁻¹ and 99% rejection) from ethanol, and Brilliant Blue (200 Lm⁻²h⁻¹bar⁻¹ and 99% rejection) from isopropyl alcohol. Therefore, the GOBN hybrid membrane with high separation performance designed in our work showed potential for the efficient separation and consistent purification resources.

METHODS

Materials

BN powder was purchased from Momentive Performance Materials Inc. and graphene oxide nanosheets dispersions were obtained from XFNANO. Urea, RhB, Eosin Y, R6G, methylene blue, brilliant yellow, Evans blue, acid fusion, fast green FCF, Congo red, and brilliant blue were obtained from Sigma-Aldrich. All chemicals were used as received. Nylon ultrafiltration membrane supports with 0.22 µm pores were obtained from Zhejiang Yibo Separator Company.

Synthesis of BN nanosheets

The BN nanosheet dispersion was prepared using commercial h-BN powder (from Momentive Performance Materials Inc.) and ball milling the powder with urea (from Sigma–Aldrich) as the functional agent³⁰. Typically, the bulk BN powder (0.5 g) was mixed with urea (10 g) in a ball milling machine (Miqi YXQM-0.4 L, Changsha). Then, the mixture was washed with DI water for ten days after balling milling at 400 rpm for 20 h at room temperature. After centrifuging the mixture for 30 min at 8000 rpm, we obtained FBN dispersions in water with a controllable concentration.

Fabrication of the GOBN membranes

The GOBN hybrid membranes were prepared via the vacuum filtration method. Typically, BN nanosheet dispersions and GO nanosheet dispersions with various content ratios were mixed well and then filtrated on a commercial substrate with the aid of a vacuum pump at a negative pressure of 1 bar. For the permeation test, the GOBN membrane varied in thickness (mass density) from 69 to 97 mgm⁻², while the GOBN membrane with a mass density of 69 mgm⁻² was selected for all the dye molecule separation measurement until further note. Herein, the nylon substrate was chosen because of its weak effect on the separation performance.

Characterization

XRD analysis was performed using a Bruker D8 Advance (CuKa radiation source, $\lambda = 1.5406$) with 20 ranging from 5 to 60° with intervals of 0.02°. The FTIR spectra were measured on a Thermo Fisher Nicolet IS50 infrared spectrometer (USA). The membrane morphologies were observed by using an S-4800 scanning

8

electron microscope (Hitachi, Japan) with an accelerating voltage of 2 kV. AFM images were collected on an Asylum research MFP3D microscope. TEM images were taken using a JEM-2100F microscope (JEOL, Japan) at an acceleration voltage of 80 kV. The UV-Vis absorption spectra were conducted by a UV-2550 spectrophotometer (Shimadzu, Japan). XPS spectra were obtained by using an ESCALAB 250XI photoelectron spectrometer (ThermoFisher Scientific, USA). Raman spectra were collected on a LabRAM HR Evolution confocal laser Raman spectrometer (Horiba Jobin Yvon, France). Contact angle tester (Jinzhitang, China).

Dye separation performance evaluation

Dye rejection performance of the membrane evaluated using a dead-end filtration device. As dead-end filtering may encounter the concentration polarization challenge, especially for separating dye molecules, half of the solutions were designed to pass through the membrane to control the polarization effect. The effective filtration area of the membrane is 7.5 cm². All the astested membranes were firstly filtrated with pure water until constant fluxes were attained. The applied transmembrane pressure is fixed at 1 bar. The dyes in aqueous and organic solvents were diluted depending on the absorbance of the detected dyes. The water from Chaohu Lake (31.5°N 117.5°E) was filtrated with Nylon membrane (200 nm) and then used for the real water metrics tests. The resulting concentrations of feed, permeate, and retentate solutions were determined by a UV/vis spectrophotometer.

The permeance J $(Lm^{-2}h^{-1}bar^{-1})$ and rejection (%) were collected and calculated according to the following equation:

$$J = \frac{V}{A \triangle t \triangle P}$$
(1)

$$R = \left(1 - \frac{C}{C_0}\right) \times 100\%$$
 (2)

Where V refers to the permeated volume of solvent with the unite of L, A is the effective filtration area of the membrane with the unite of m^2 , Δt is the filtration time with the unite of h, ΔP is the pressure given with a nitrogen cylinder with a fixed value of 1 bar, and C_o and C are the concentrations of dyes in the feed and permeate parts, respectively.

Materials studio simulation

The molecular dynamics process was calculated using the forcite module in Materials Studio. The original structures of BN and graphene were obtained from the database, and then the amino and carboxyl groups and hydroxyl groups were grafted to the surface using a self-compiled Perl script. The water molecules between the layers are pressed in by packing in THE amorphous cell module. The constructed system was geometrically optimized, and then the 500 ps relaxation structure was operated using NVT ensemble molecular dynamics, in which the temperature control method used Nose-hoover, and then the final configuration was subjected to 500 ps NVE ensemble molecular dynamics to collect the required data.

DATA AVAILABILITY

The data generated or analysed during this study are included in this published article and its supporting information files. Source data are provided in this paper. Source data are also available on Figshare at https://doi.org/10.6084/m9.figshare.22707604.v1.

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REFERENCES

- Werber, J. R., Osuji, C. O. & Elimelech, M. Materials for next-generation desalination and water purification membranes. *Nat. Rev. Mater.* 1, 16018 (2016).
- Lively, R. P. & Sholl, D. S. From water to organics in membrane separations. *Nat. Mater.* 16, 276–279 (2017).
- Marchetti, P., Jimenez Solomon, M. F., Szekely, G. & Livingston, A. G. Molecular separation with organic solvent nanofiltration: a critical review. *Chem. Rev.* 114, 10735–10806 (2014).
- Vandezande, P., Gevers, L. E. M. & Vankelecom, I. F. J. Solvent resistant nanofiltration: separating on a molecular level. *Chem. Soc. Rev.* 37, 365–405 (2008).
- Liang, B., He, X., Hou, J., Li, L. & Tang, Z. Membrane separation in organic liquid: technologies, achievements, and opportunities. *Adv. Mater.* 31, 1806090 (2019).
- McVerry, B. et al. Next-generation asymmetric membranes using thin-film liftoff. Nano Lett. 19, 5036–5043 (2019).
- Kim, S., Wang, H. & Lee, Y. M. 2D nanosheets and their composite membranes for water, gas, and ion separation. *Angew. Chem. Int. Ed.* 131, 17674–17689 (2019).
- Prozorovska, L. & Kidambi, P. R. State-of-the-art and future prospects for atomically thin membranes from 2D materials. *Adv. Mater.* 30, 1801179 (2018).
- Koenig, S. P., Wang, L., Pellegrino, J. & Bunch, J. S. Selective molecular sieving through porous graphene. *Nat. Nanotechnol.* 7, 728–732 (2012).
- Abraham, J. et al. Tunable sieving of ions using graphene oxide membranes. Nat. Nanotechnol. 12, 546–550 (2017).
- Ries, L. et al. Enhanced sieving from exfoliated MoS₂ membranes via covalent functionalization. *Nat. Mater.* 18, 1112–1117 (2019).
- Thormann, A., Teuscher, N., Pfannmöller, M., Rothe, U. & Heilmann, A. Nanoporous aluminum oxide membranes for filtration and biofunctionalization. *Small* 3, 1032–1040 (2007).
- Kumar, P. et al. One-dimensional intergrowths in two-dimensional zeolite nanosheets and their effect on ultra-selective transport. *Nat. Mater.* 19, 443–449 (2020).
- Qiu, S., Xue, M. & Zhu, G. Metal–organic framework membranes: from synthesis to separation application. *Chem. Soc. Rev.* 43, 6116–6140 (2014).
- Ding, L. et al. A two-dimensional lamellar membrane: MXene nanosheet stacks. Angew. Chem. Int. Ed. 56, 1825–1829 (2017).
- Huang, K. et al. Cation-controlled wetting properties of vermiculite membranes and its promise for fouling resistant oil-water separation. *Nat. Commun.* 11, 1097 (2020).
- Yeh, C.-N., Raidongia, K., Shao, J., Yang, Q.-H. & Huang, J. On the origin of the stability of graphene oxide membranes in water. *Nat. Chem.* 7, 166–170 (2015).
- Liu, G., Jin, W. & Xu, N. Graphene-based membranes. Chem. Soc. Rev. 44, 5016–5030 (2015).
- Han, Y., Xu, Z. & Gao, C. Ultrathin graphene nanofiltration membrane for water purification. *Adv. Funct. Mater.* 23, 3693–3700 (2013).
- Yang, J. et al. Self-assembly of thiourea-crosslinked graphene oxide framework membranes toward separation of small molecules. *Adv. Mater.* **30**, 1705775 (2018).
- Chen, L. et al. Ion sieving in graphene oxide membranes via cationic control of interlayer spacing. *Nature* 550, 380–383 (2017).
- Qian, Y. et al. Enhanced ion sieving of graphene oxide membranes via surface amine functionalization. J. Am. Chem. Soc. 143, 5080–5090 (2021).
- Liu, J. et al. Bioinspired graphene membrane with temperature tunable channels for water gating and molecular separation. *Nat. Commun.* 8, 1–9 (2017).
- Huang, H. et al. Ultrafast viscous water flow through nanostrand-channelled graphene oxide membranes. Nat. Commun. 4, 2979 (2013).
- Wu, Y. et al. 2D heterostructured nanofluidic channels for enhanced desalination performance of graphene oxide membranes. ACS NANO 15, 7586–7595 (2021).
- Wang, Y. et al. Water transport with lltralow friction through partially exfoliated g-C₃N₄ nanosheet membranes with self-supporting spacers. *Angew. Chem. Int. Ed.* 56, 8974–8980 (2017).
- Zhang, W.-H. et al. Graphene oxide membranes with stable porous structure for ultrafast water transport. *Nat. Nanotechnol.* 16, 337–343 (2021).
- Golberg, D. et al. Boron nitride nanotubes and nanosheets. ACS NANO 4, 2979–2993 (2010).
- Sharma, V., Kagdada, H. L., Jha, P. K., Śpiewak, P. & Kurzydłowski, K. J. Thermal transport properties of boron nitride based materials: a review. *Renew. Sust. Energ. Rev.* **120**, 109622 (2020).
- Chen, C. et al. Functionalized boron nitride membranes with ultrafast solvent transport performance for molecular separation. *Nat. Commun.* 9, 1902 (2018).
- Chen, C. et al. Bio-inspired nanocomposite membranes for osmotic energy harvesting. *Joule* 4, 247–261 (2020).

- 32. Kumbhakar, P. et al. Nonlinear optical properties and temperature-dependent uv-vis absorption and photoluminescence emission in 2d hexagonal boron nitride nanosheets. *Adv. Opt. Mater.* **3**, 828–835 (2015).
- Nguyen-Phan, T.-D. et al. The role of graphene oxide content on the adsorptionenhanced photocatalysis of titanium dioxide/graphene oxide composites. *Chem. Eng. J.* **170**, 226–232 (2011).
- Shi, Y. et al. Synthesis of few-layer hexagonal boron nitride thin film by chemical vapor deposition. *Nano Lett.* **10**, 4134–4139 (2010).
- Feng, H., Cheng, R., Zhao, X., Duan, X. & Li, J. A low-temperature method to produce highly reduced graphene oxide. *Nat. Commun.* 4, 1539 (2013).
- Tian, K. et al. Single-site pyrrolic-nitrogen-doped sp2-hybridized carbon materials and their pseudocapacitance. *Nat. Commun.* 11, 3884 (2020).
- 37. Huang, L. et al. Reduced graphene oxide membranes for ultrafast organic solvent nanofiltration. *Adv. Mater.* 28, 8669–8674 (2016).
- Kong, G. et al. Efficient dye nanofiltration of a graphene oxide membrane via combination with a covalent organic framework by hot pressing. J. Mater. Chem. A 7, 24301–24310 (2019).
- Kang, X., Cheng, Y., Wen, Y., Qi, J. & Li, X. Bio-inspired co-deposited preparation of GO composite loose nanofiltration membrane for dye contaminated wastewater sustainable treatment. J. Hazard. Mater. 400, 123121 (2020).
- Akbari, A. et al. Large-area graphene-based nanofiltration membranes by shear alignment of discotic nematic liquid crystals of graphene oxide. *Nat. Commun.* 7, 1–12 (2016).
- Ying, Y., He, P., Wei, M., Ding, G. & Peng, X. Robust GQDs modified thermally reduced graphene oxide membranes for ultrafast and long-term purification of dye-wasted water. *Adv. Mater. Interfaces* 4, 1700209 (2017).
- Gao, S. J., Qin, H., Liu, P. & Jin, J. SWCNT-intercalated GO ultrathin films for ultrafast separation of molecules. J. Mater. Chem. A 3, 6649–6654 (2015).
- Shen, L. et al. Highly porous nanofiber-supported monolayer graphene membranes for ultrafast organic solvent nanofiltration. *Sci. Adv.* 7, eabg6263 (2021).
- Zheng, S., Tu, Q., Wang, M., Urban, J. J. & Mi, B. Correlating interlayer spacing and separation capability of graphene oxide membranes in organic solvents. ACS NANO 14, 6013–6023 (2020).
- Yang, Q. et al. Ultrathin graphene-based membrane with precise molecular sieving and ultrafast solvent permeation. *Nat. Mater.* 16, 1198–1202 (2017).
- Nie, L. et al. Realizing small-flake graphene oxide membranes for ultrafast sizedependent organic solvent nanofiltration. Sci. Adv. 6, eaaz9184 (2020).
- Zhang, L., Zhang, M., Liu, G., Jin, W. & Li, X. Fungal cell wall-graphene oxide microcomposite membrane for organic solvent nanofiltration. *Adv. Funct. Mater.* 31, 2100110 (2021).
- Li, Y. et al. Graphene oxide (GO)-interlayered thin-film nanocomposite (TFN) membranes with high solvent resistance for organic solvent nanofiltration (OSN). J. Mater. Chem. A 7, 13315–13330 (2019).
- Chen, C. et al. Ultrafast, stable ionic and molecular sieving through functionalized boron nitride membranes. ACS Appl. Mater. Interfaces 11, 30430–30436 (2019).
- Saito, T. & Honda, F. Chemical contribution to friction behavior of sintered hexagonal boron nitride in water. Wear 237, 253–260 (2000).

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AUTHOR CONTRIBUTIONS

Q.G., M.X., Q.T., Y.L., W.Z., C.G.: conceptualization, writing-original draft, investigation, methodology. X.Z., Y.Z., S.Y., D.L., W.L., and C.C.: writing-review and editing, funding acquisition, project administration. All authors approved the manuscript.

COMPETING INTERESTS

The authors declare no competing interests.

ADDITIONAL INFORMATION

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