

## Electronic Supplementary Information

### **Ultrafast liquid water transport through graphene-based nanochannels measured by isotope labelling**

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## **Materials and Methods**

### ***1. Preparation of GO membranes***

Monolayer GO flakes were synthesized by the modified Hummers' method from natural graphite, which was treated with potassium permanganate, sodium nitrite and concentrated sulfuric acid subsequently.<sup>1</sup> Figure S1 exhibits the SEM and AFM images of the as-synthesized GO sheets, which reveals that the GO flakes are single-layered with a typical lateral dimension of  $\sim 1 \mu\text{m}$ . As-synthesized GO flakes were re-dispersed in deionized water by sonication to form the 0.1 mg/mL GO preparation solutions. After that, the micrometer-thick GO membranes were fabricated by vacuum-filtrating 25 mL (0.1 mg/mL) GO colloidal solutions using the commercial cellulose microfilters. The polymeric microfilters possess pores with diameters of  $\sim 0.22 \mu\text{m}$  and a porosity of  $\sim 80\%$ . After the vacuum-filtration process, the GO membranes with the microfilters underneath (named as "GOCM") were dried in air at  $55^\circ\text{C}$  for 24 h before use. This drying procedure is important because the GO membranes without drying are poorly adhered to the microfilters, further leading to the ease of exfoliation of GO membranes during the permeation tests in which the GOCM samples were immersed in water for at least 8 h. As a control experiment, the blank cellulose microfilters were also dried in air at  $55^\circ\text{C}$  for 24 h before use.

### ***2. Permeation test setup***

The isotope labelled water permeation tests were done with a self-made penetration apparatus, as shown in Figs. 1b and c. Briefly the source reservoir and drain reservoir were separated by a plastic plate with an aperture ( $\sim 5 \text{ mm}$  in diameter) in the center. A piece of

GOCM (or blank microfilter) was sealed with double-sided copper tape onto the aperture within the plastic plate. The double-sided copper tape possessed the same sized hole (~5 mm in diameter) in the center so that the GOCM (or blank microfilter) could directly connect the solutions in source and drain reservoirs with an effective diffusion area of ~19.6 mm<sup>2</sup>. The regions around the effective diffusion membranes were also sealed with copper tapes as a protection, as shown in Fig. 1b. It should be noted that the double-sided copper tapes could provide excellent seal for the membrane permeation processes, which was demonstrated by sealing the permeation hole completely without any percolated membranes, injecting 100 mL 0.1 M MgCl<sub>2</sub> solution and deionized water into the source and drain reservoirs respectively and measuring the conductivity variations of the drain solution. We found that the conductivity of the drain left nearly unchanged for tens of hours, which were far beyond the periods of trans-membrane permeation tests, thus demonstrating the excellent seal of double-sided copper tapes. In addition, we have demonstrated in our previous work<sup>2,3</sup> that the same experimental setup with GO membranes could afford selectivity towards various ions in source solutions. These facts all demonstrate that the double-sided copper tapes could provide adequate seal for our trans-membrane permeation experiments. Before and after the permeation experiments, the intactness and continuity of GO membranes were checked by optical microscopy to ensure that no cracks were formed on the GO membranes and the results obtained by isotope labelled water permeation reflected the true behavior of GO membranes.

During the water permeation experiments, 100 mL of D<sub>2</sub>O labelled water with various D<sub>2</sub>O mass concentrations and deionized water were injected into the source and drain reservoirs with the same speed. Mild magnetic stirrings were applied to both the source and drain solutions during the whole permeation process to avoid possible D<sub>2</sub>O concentration gradients near the membranes. During the permeation process, equivalent trace amount of solutions in sources and drains were taken out at regular intervals (typically 2 h) for characterization to avoid the external hydrostatic pressures across the membranes caused by the unequal liquid levels in sources and drains. The filtrates in drains were then examined by Fourier transform infrared (FTIR) spectroscopy to afford accurate concentrations of D<sub>2</sub>O tracers, based on which the permeation behavior of water through GO membranes could be studied.

### ***3. Characterizations***

As-synthesized GO flakes were characterized by scanning electron microscope (SEM, LEO 1530, 10kV) and atomic force microscopy (AFM, Agilent 5100). The thickness of as-prepared GO membranes was determined by white light interferenc microscope (MicroXAM-1200) and stylus profilometry (Ambios XP-1). The thickness of cellulose microfilters was evaluated by optical microscope (ZEISS, Axio Scope.A1). The accurate concentrations of D<sub>2</sub>O were measured by Fourier transform infrared (FTIR) spectroscopy (Nicolet 6700FTIR). In terms of ions dissolving in source solutions, the concentrations of Mg<sup>2+</sup> cations were measured by atomic emission spectroscopy (IRIS Intrepid II).

### ***4. Model and Calculation***

### 1) *Water diffusion coefficients through GO, microfilter and GOCM membranes*

The diffusion coefficients of D<sub>2</sub>O through GO, GOCM and blank microfilter membranes were calculated by Fick's first law based on the fact that the increase of the amount of D<sub>2</sub>O in drains was less than 5% compared to the source concentration after such a long 8 h of permeation, as shown in Figs. 2c and S4.

As illustrated in the inset of Fig. 2d, the flux of D<sub>2</sub>O through GOCM (1) can be expressed as the following equation:

$$J_1 = D_G \frac{c_0 - c_1}{l_G} = D_M \frac{c_1 - c_2}{l_M} \approx D_M \frac{c_1}{l_M} = D_{total} \frac{c_0 - c_2}{l_G + l_M} \approx D_{total} \frac{c_0}{l_G + l_M} \quad (1)$$

where  $J_1$  is the flux of D<sub>2</sub>O through GOCM membrane,  $D$  is the diffusion coefficient,  $c_0$ ,  $c_1$  and  $c_2$  are concentrations of D<sub>2</sub>O in source, at the interface between GO and microfilter and in drain, respectively.  $l$  is the thickness of the membranes. The subscripts "G", "M" and "total" represent GO, microfilter and GOCM, respectively. The value of  $c_2$  is much smaller than those of  $c_0$  and  $c_1$ , so it can be neglected. On the other hand, the flux of D<sub>2</sub>O through microfilter (2) can be expressed as follows:

$$J_2 = D_M \frac{c_0 - c_3}{l_M} \approx D_M \frac{c_0}{l_M} \quad (2)$$

where  $J_2$  is the flux of D<sub>2</sub>O through microfilter and  $c_3$  is concentration of D<sub>2</sub>O in drain in the case of water permeation through microfilter. The value of  $c_3$  is much smaller than that of  $c_0$ , so it can be neglected. Combining Eqs. (1) and (2), one can calculate the diffusion coefficients of D<sub>2</sub>O through GO, microfilter and GOCM membranes, respectively, as shown in Fig. 2e.

## 2) Evaluation of the water diffusion coefficients through GO and microfilter channels

Considering the microstructures of GO membranes and microfilters, the water diffusion coefficients through the channels within GO membranes and microfilters can be evaluated according to the previous method used by Nair, et al.<sup>4</sup> and Joshi, *et al.*<sup>5</sup>, which has been proved to provide sufficient matches with the experimental results and molecular dynamics calculations. As discussed in the main text, a graphitic nanocapillary network can be formed by connecting the  $sp^2$  clusters across all the stacking layers, which is mainly responsible for the transport of water molecules, as illustrated in the inset of Fig. 2f. The lateral dimensions of GO flakes ( $b$ ) within the membranes can be evaluated as  $\sim 1 \mu\text{m}$  according to the SEM and AFM characterizations in Fig. S1, while the interlayer distances between GO flakes ( $d$ ) can be evaluated as  $\sim 1 \text{ nm}$  according to the previous XRD analyses.<sup>2-7</sup> The thickness of our GO membrane samples ( $l$ ) is  $\sim 4 \mu\text{m}$ , as shown in Figs. 1d and S2. Therefore, the effective length of graphene nanochannels can be evaluated as  $l_{\text{eff}} = bl/d = 4 \text{ mm}$ , while the effective diffusion area can be evaluated as  $A_{\text{eff}} = Adb/b^2 = Ad/b = 0.1\%A$ , which occupies only a tiny fraction of the total GO membrane area. Based on these parameters, the water diffusion coefficient through the nanochannels within GO membranes can be calculated based on the following equation:

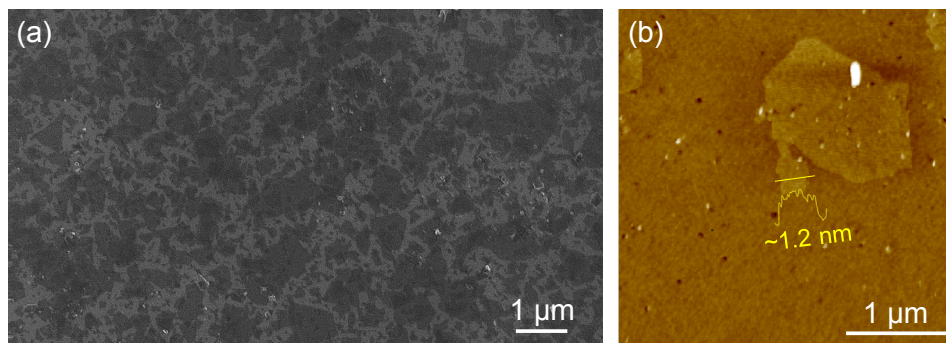
$$D \frac{A}{l} = D_{\text{channel}} \frac{A_{\text{eff}}}{l_{\text{eff}}} \quad (3)$$

According to Eq. (3),  $D_{\text{channel}}$  can be calculated as  $10^6 D_G$ . Note that the evaluated  $D_{\text{channel}}$  for GO membranes here is a lower bound because the functionalized C-O regions suppress

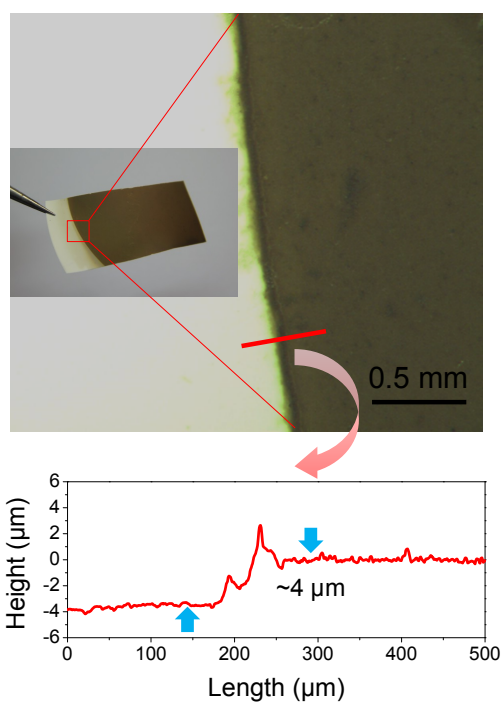
the through-permeation of water seriously, according to the recent simulation studies.<sup>8,9</sup> In addition, the cellulose microfilters used for vacuum filtration possess a rough surface topography. During the filtration of GO solutions, the bottom GO flakes are likely to insert into the pores within cellulose microfilters, further leading to the disordered and random arrangement of the GO flakes underneath, which would break the parallel order of the bottom GO layers and thicken the whole GO membranes<sup>10,11</sup> (beyond the well-stacked thickness of  $\sim 4 \mu\text{m}$ , as demonstrated by white light interference microscope and stylus profilometry characterizations in Figs. 1d and S2 respectively).

Similarly, for the case of cellulose microfilters used here, the pore size is  $\sim 0.22 \mu\text{m}$  and the porosity is  $\sim 80\%$ . The effective diffusion area  $A_{\text{eff}}$  can be calculated as  $80\%A$  while the effective length of diffusion channels  $l_{\text{eff}}$  is equivalent to the thickness of microfilters ( $\sim 115 \mu\text{m}$ , as shown in Fig. 1e). According to Eq. (3), the water diffusion coefficient through microfilter channels can be calculated as  $1.25 D_M$ , which is comparable to the bulk case. The results for water diffusion coefficients through the channels within GO membranes and microfilters are plotted in Fig. 2f, revealing that the diffusion coefficients of water through graphene-based nanochannels are 4~5 orders of magnitude greater than the bulk diffusion case.

## Supplementary figures

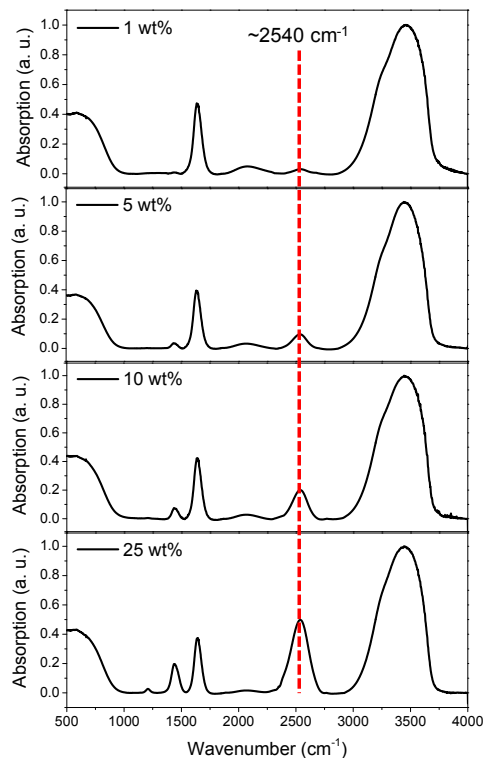


**Fig. S1.** SEM (a) and AFM (b) characterizations of as-synthesized GO flakes. The inset in (b) shows the height profile for the corresponding yellow line.

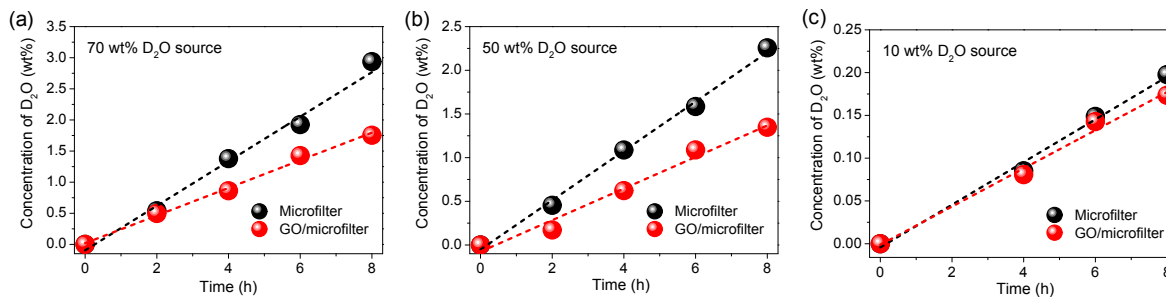


**Fig. S2.** Measuring the thickness of the GO membrane by stylus profilometry. The photograph inset is an example of the as-fabricated GO membrane with the cellulose microfilter underneath. The red line in the optical image shows the measured region.

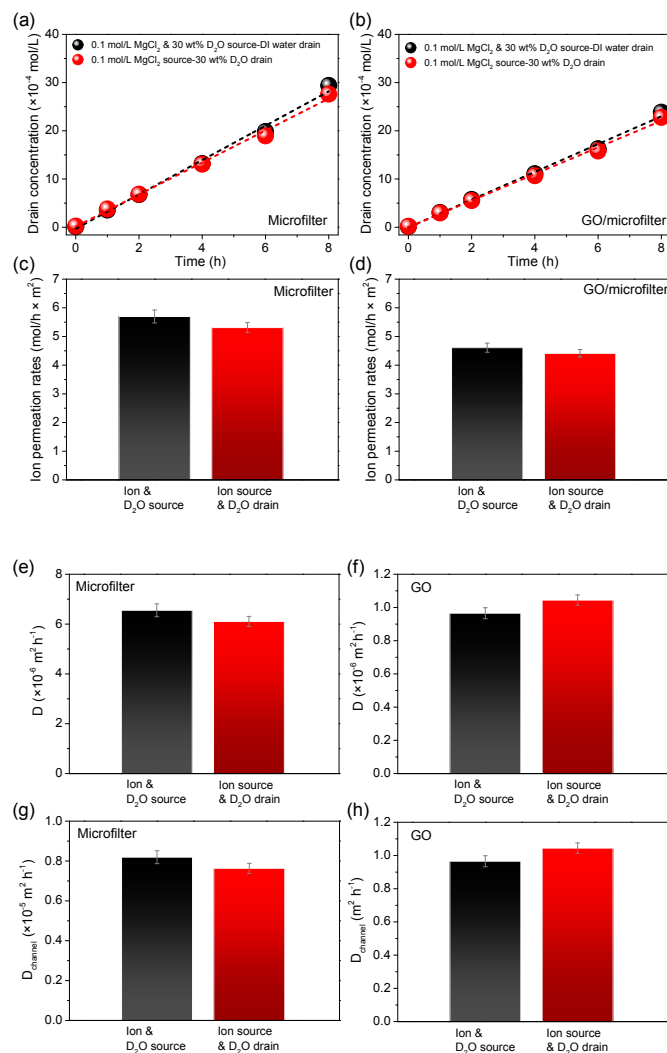




**Fig. S3.** FTIR spectra of the D<sub>2</sub>O solutions with fixed mass concentrations: 1 wt%, 5 wt%, 10 wt% and 25 wt%, respectively.



**Fig. S4.** D<sub>2</sub>O labelled water trans-membrane permeation through GOCM and microfilter membranes with various D<sub>2</sub>O source concentrations. (a) 70 wt%, (b) 50 wt%, and (c) 10 wt%.



**Fig. S5. Ion permeations through microfilter and GOCM membranes.**  $Mg^{2+}$  ion permeations through microfilters (a) and GOCMs (b) in the presence of 30 wt%  $D_2O$  in sources and drains, respectively.  $Mg^{2+}$  ion permeation rates through microfilters (c) and GOCMs (d) in the presence of 30 wt%  $D_2O$  in sources and drains, respectively.  $Mg^{2+}$  ion diffusion coefficients through the entire microfilters (e) and GO membranes (f) in the presence of 30 wt%  $D_2O$  in sources and drains, respectively.  $Mg^{2+}$  ion diffusion coefficients through the channels within microfilters (g) and GO membranes (h) in the presence of 30 wt%  $D_2O$  in sources and drains, respectively.

## References

- (1) W. S. Hummers, R. E. Offeman, *J. Am. Chem. Soc.* **1958**, *80*, 1339.
- (2) P. Sun, M. Zhu, K. Wang, M. Zhong, J. Wei, D. Wu, Z. Xu, H. Zhu, *ACS Nano* **2013**, *7*, 428–437.
- (3) P. Sun, F. Zheng, M. Zhu, Z. Song, K. Wang, M. Zhong, D. Wu, R. B. Little, Z. Xu, H. Zhu, *ACS Nano* **2014**, *8*, 850–859.
- (4) R. R. Nair, H. A. Wu, P. N. Jayaram, I. V. Grigorieva, A. K. Geim, *Science* **2012**, *335*, 442–444.
- (5) R. K. Joshi, P. Carbone, F. C. Wang, V. G. Kravets, Y. Su, I. V. Grigorieva, H. A. Wu, A. K. Geim, R. R. Nair, *Science* **2014**, *343*, 752–754.
- (6) M. J. McAllister *et al.*, Single sheet functionalized graphene by oxidation and thermal expansion of graphite. *Chem. Mater.* **2007**, *19*, 4396.
- (7) K. Raidongia, J. Huang, *J. Am. Chem. Soc.* **2012**, *134*, 16528–16531.
- (8) N. Wei, X. Peng, Z. Xu, *Phys. Rev. E* **2014**, *89*, 012113.
- (9) N. Wei, X. Peng, Z. Xu, *ACS Appl. Mater. Interfaces* **2014**, *6*, 5877–5883
- (10) T.-M. Yeh, Z. Wang, D. Mahajan, B. S. Hsiao, B. Chu, *J. Mater. Chem. A* **2013**, *1*, 12998–13003.
- (11) Y. Huang, H. Li, L. Wang, Y. Qiao, C. Tang, C. Jung, Y. Yoon, S. Li, M. Yu, *Adv. Mater. Interfaces* **2014**, 1400433.