

## Supporting Information

# Organic Fouling of Graphene Oxide Membranes and Its Implications for Membrane Fouling Control in Engineered Osmosis

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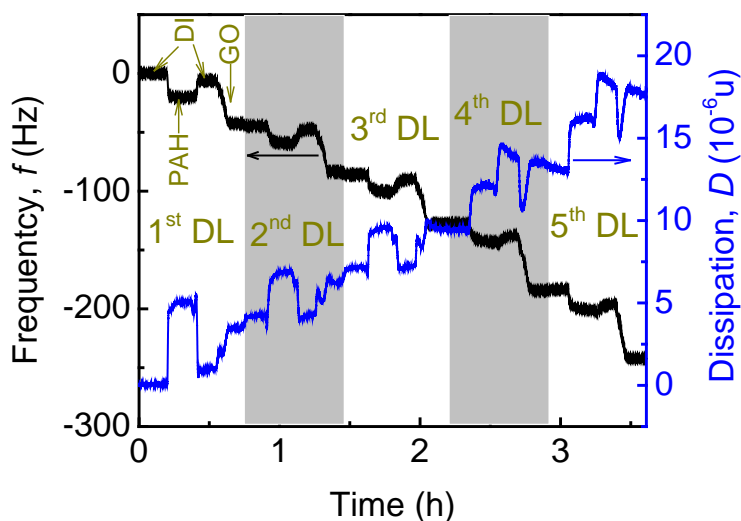
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## **Preparation of PA membranes**

The PA membrane was prepared by interfacial polymerization.<sup>1, 2</sup> First, a PSf membrane support was made by casting a 125- $\mu$ m thick PSf film (12 wt% dissolved in NMP) onto a polyester nonwoven fabric (PET, grade 3249, Ahlstrom, Helsinki, Finland), which was then immediately transferred into a 3 wt% NMP/DI coagulation bath and submerged for 10 min to allow complete phase separation. The PSf support was stored in DI water for several days with frequent replacement of DI water to remove any residual NMP in the support. To form a PA layer on the support, the PSf support was mounted in a 6-inch (15 cm) frame with the front side forming a reservoir to hold 15 mL MPD solution (3.4 wt% in DI) for 2 min; then the support was dried with a filter paper and 15 mL TMC solution (0.15 wt% in Isopar-G) was poured onto the membrane to allow interfacial polymerization; after 1 min of reaction, the frame was held vertically for 2 min to drain the TMC solution; and finally the membrane was released from the frame and post-treated in sequence by being soaked in 95 °C water for 2 min, 200 ppm NaOCl aqueous solution for 2 min, 1000 ppm NaHSO<sub>3</sub> aqueous solution for 0.5 min, and eventually 95 °C water for 2 min. The synthesized PA membranes were thoroughly rinsed with DI water and stored in a 4 °C fridge.

## **Monitoring of GO membrane synthesis by QCM-D**

The layer-by-layer (LbL) assembly of GO membrane was monitored using quartz crystal microbalance with dissipation (QCM-D) (E-4, Biolin Scientific, Linthicum Heights, MD), as described in our previous study.<sup>3</sup> A clean gold sensor was mounted in a flow chamber and exposed to PAH (1 g/L, pH 4) and then GO (1 g/L, pH 4) solutions. Each exposure step was followed by a DI water rinsing. The exposure-rinsing cycle was repeated for another four times (Figure S1). Analyzing the frequency and dissipation results showed that the 5-DL GO membrane is ~80 nm thick.



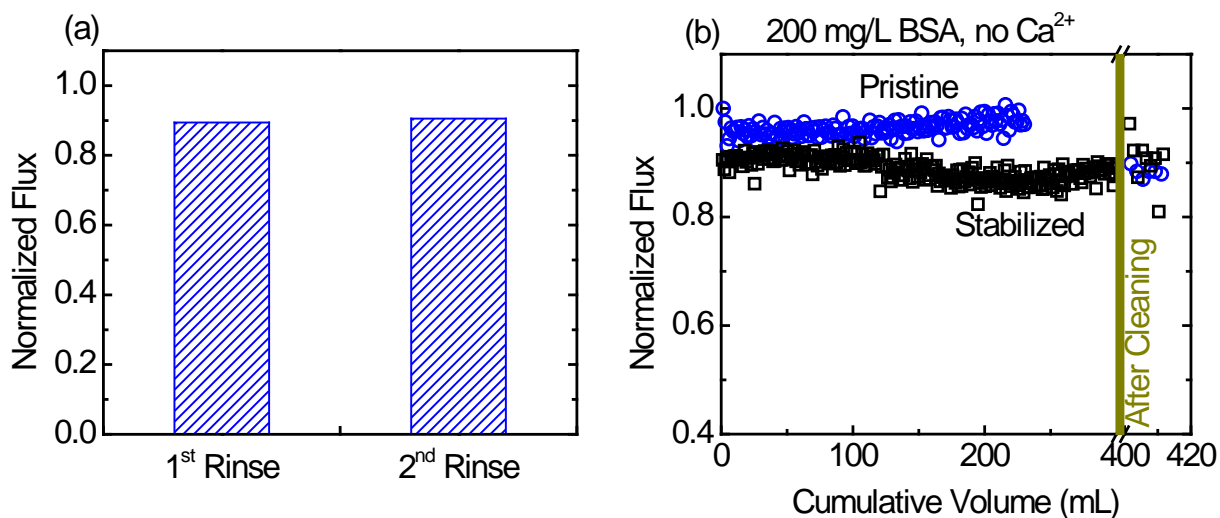
**Figure S1.** Frequency and dissipation plot for the LbL assembly of GO-PAH double layers (DL) at the 3<sup>rd</sup> overtone ( $n = 3$ ) in QCM-D.

### Impact of physical cleaning on GO membrane water flux

As a strange irreversible flux drop ( $\sim 10\%$ ) was observed after the cleaning of the GO membrane, we suspect that physical cleaning at higher crossflow rate actually causes the membrane structure change, which is responsible for the flux drop. To ensure that the 10% flux drop is not due to fouling, we tested the GO membrane with the same fouling and cleaning protocol as described in the main text except for not adding any foulant into the feed solution during the fouling experiment. Therefore, the GO membrane in this control experiment experiences the same hydrodynamic conditions without being fouled.

To run the control experiment, the GO membrane was first tested using the fouling protocol without adding any foulant in the feed solution with an initial pure water flux of  $\sim 4 \mu\text{m/s}$ . Both the feed and draw solutions were then replaced with DI water, and the system was flushed for 15 min at a cross-flow velocity of 21 cm/s (denoted as 1<sup>st</sup> rinse in Figure S2). The pure water flux was determined using 1 M sucrose as the draw solution and DI water as the feed solution, and

normalized by the initial PURE WATER FLUX. As shown in Figure S2(a), the normalized final pure water flux was ~90% of the initial pure water flux, indicating the 10% flux drop is indeed caused by the hydrodynamic condition change induced by the cleaning procedure.

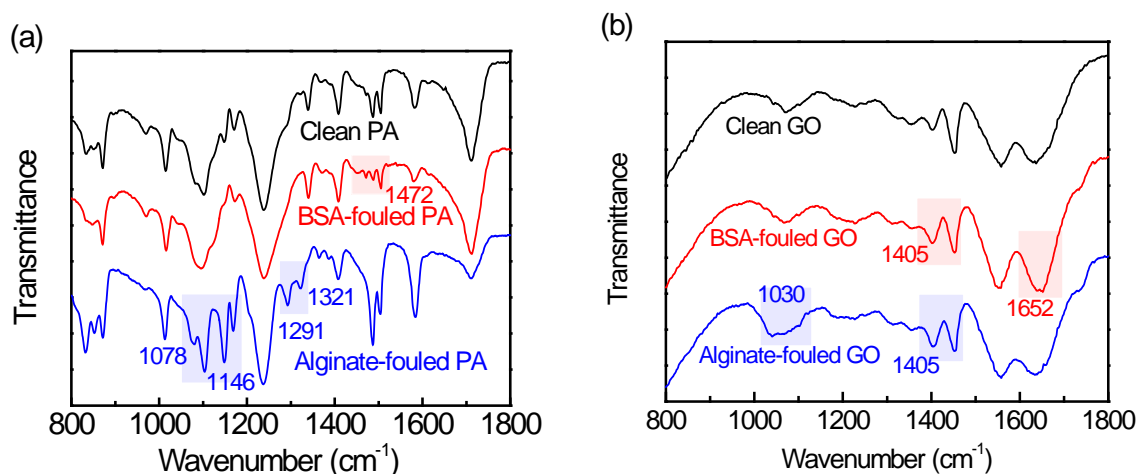


**Figure S2.** (a) GO membrane flux after the 1<sup>st</sup> rinse (physical cleaning by flushing the FO system with DI for 15 min after obtaining a baseline) and the 2<sup>nd</sup> rinse (physical cleaning by flushing the FO system with DI after BSA fouling), and (b) the fouling and cleaning behavior of stabilized (i.e., pre-flushed prior to fouling) and pristine GO membranes in FO mode.

After the control experiment, the same GO membrane was subsequently tested in a real fouling experiment with BSA dosed in the feed solution (in the absence of Ca<sup>2+</sup>) and cleaned using the same cleaning procedure. As compared in Figure S2(b), both pristine and stabilized GO membranes showed similar fouling profiles. The pure water flux of the cleaned GO membrane was determined again and normalized by the initial pure water flux. The normalized water flux (denoted as second rinse in Figure S2(a)) after this fouling and rinsing cycle was still ~90%, the same as that after the first rinse. It thus suggests that the GO membrane structure stabilizes after the first rinsing cycle and repeated rinsing cycle does not cause any further change to the membrane.

## Characterization of clean and fouled membranes by FTIR

To help verify the different locations of foulant deposition in PA and GO membranes in PRO fouling, the FTIR spectra of the support layers of both membranes were recorded (Figure S3). Compared to a clean membrane, the support layers of the corresponding fouled membranes show additional peaks indicative of the foulants used in the experiments. For the BSA-fouled PA membrane (Figure S3(a)), the spectral changes at  $1712\text{ cm}^{-1}$  and  $1580\text{ cm}^{-1}$  are likely caused by the amide I band ( $\sim 1652\text{ cm}^{-1}$ ) introduced by BSA.<sup>4,5</sup> For the alginate-fouled PA membrane, new peaks are observed in three different locations, identified as shaded areas in Figure S3(a). For the GO membrane, additional peaks due to foulant deposition are also observed on the support layer side, such as BSA-intensified peak at  $1652\text{ cm}^{-1}$  and alginate-introduced a new peak at  $1030\text{ cm}^{-1}$ .<sup>1,6,7</sup> Therefore, such evidence of foulant presence for both GO and PA membranes proves that foulant accumulation does occur on the support layer side of both membranes, however, the GO membrane is capable of maintaining the foulants only on the outside surface of the support layer.



**Figure S3.** FTIR spectra of the support layers of clean and fouled (a) PA and (b) GO membranes, all tested in PRO mode.

## References

1. Yu, H. Y.; Kang, Y.; Liu, Y. L.; Mi, B., Grafting polyzwitterions onto polyamide by click chemistry and nucleophilic substitution on nitrogen: A novel approach to enhance membrane fouling resistance. *Journal of Membrane Science* **2014**, *449*, 50-57.
2. Tiraferri, A.; Yip, N. Y.; Phillip, W. A.; Schiffman, J. D.; Elimelech, M., Relating performance of thin-film composite forward osmosis membranes to support layer formation and structure. *Journal of Membrane Science* **2011**, *367*, (1-2), 340-352.
3. Hu, M.; Mi, B., Layer-by-layer assembly of graphene oxide membranes via electrostatic interaction. *Journal of Membrane Science* **2014**, *469*, (0), 80-87.
4. Murayama, K.; Tomida, M., Heat-induced secondary structure and conformation change of bovine serum albumin investigated by fourier transform infrared spectroscopy. *Biochemistry-U.S.* **2004**, *43*, (36), 11526-11532.
5. Militello, V.; Casarino, C.; Emanuele, A.; Giostra, A.; Pullara, F.; Leone, M., Aggregation kinetics of bovine serum albumin studied by ftir spectroscopy and light scattering. *Biophys Chem* **2004**, *107*, (2), 175-187.
6. Sartori, C.; Finch, D. S.; Ralph, B.; Gilding, K., Determination of the cation content of alginate thin films by ftir spectroscopy. *Polymer* **1997**, *38*, (1), 43-51.
7. Lawrie, G.; Keen, I.; Drew, B.; Chandler-Temple, A.; Rintoul, L.; Fredericks, P.; Grondahl, L., Interactions between alginate and chitosan biopolymers characterized using ftir and xps. *Biomacromolecules* **2007**, *8*, (8), 2533-2541.