## Supplementary Information for Environmental Science: Nano

## Scalable Graphene Oxide Membranes with Tunable Water Channels and Stability for Ions Rejections

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## Synthesis of graphene oxide (GO)

GO was synthesized from natural Graphite flake (325 mesh, 99.8%, Alfa Aesar) by modified Hummers method. Generally, the graphite powder (10 g) was added into concentrated  $H_2SO_4$  (40 mL) at 80 °C, containing K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (8.33 g) and P<sub>2</sub>O<sub>5</sub> (8.33 g), for 4.5 h. After that, the mixture was collected and rinsed with deionized water until the pH became neutral, dried in oven overnight at 60 °C, thus pre-oxidized graphite obtained. The pre-oxidized graphite powder (10 g) and NaNO<sub>3</sub> (5 g) were put into an ice bath (0 °C) concentrated H<sub>2</sub>SO<sub>4</sub> (230 mL), and KMnO<sub>4</sub> (30 g) was slowly added with continuous stirring to keep the temperature below 4 °C. Then the mixture was stirred at 35 °C for 2 h, after which deionized water (460 mL) was gradually added, producing much heat. The mixture was further stirred for 15 min at 98 °C to increase the oxidation level, following an addition of deionized water (460 mL) and 30% H<sub>2</sub>O<sub>2</sub> solution (25 mL) to terminate the reaction, so as to obtain graphite oxide. The resultant bright yellow mixture was rinsed by 10% HCl solution (3.6 L) to remove the residual  $SO_4^-$  (checked by 0.01 mol L<sup>-1</sup> BaCl<sub>2</sub>) and metal ions, followed by centrifugation at 8000 rpm. The solid phase was re-dispersed in deionized water and peeled off by ultra-sonication for 30 min at 250 W of power. The centrifugation and ultra-sonication was repeated 3 times, and the solution was subjected to dialysis to remove the acid and other impurities. Finally, GO was obtained as powder after vacuum drying at 60 °C.

## **Data analysis**

**Surface free energy:** On the basis of Young's equation, the contact angle can be given as follows.

$$\gamma_s = \gamma_{s1} + \gamma_1 \cos\theta \tag{2}$$

Where  $\gamma_s$ ,  $\gamma_1$  and  $\gamma_{s1}$  represent the solid surface free energy, liquid surface free energy and solid-liquid interfacial energy, respectively.  $\vartheta$  is the contact angle between the solid surface and liquid. Therefore, the work of adhesion between a solid surface and liquid can be described as:

$$W_{s1} = \gamma_s + \gamma_1 - \gamma_{s1} \tag{3}$$

Combining equating (2) and (3):

$$W_{s1} = \gamma_1 (1 + \cos \theta) \tag{4}$$

The Neumann's method was used to determine the surface free energy of membranes. On the basis of the equation of state theory, the contact angle between the solid and liquid is given as follows:

$$\cos\theta = -1 + 2\sqrt{\frac{\gamma_s}{\gamma_l}} e^{\beta(\gamma_s - \gamma_l)^2}$$
<sup>(5)</sup>

where  $\gamma_s$  and  $\gamma_l$  represent solid and liquid surface free energy, respectively.  $\beta$  is the constant coefficient related to a specific solid surface. Reorganization of equation 1 results in the following equation:

$$ln\left[\gamma\left(\frac{(1 + \cos\theta)}{2}\right)^2\right] = -2\beta(\gamma_s - \gamma_l)^2 + ln(\gamma_s)$$
(6)

	Water	Formamide	Diiodomethane	Ethylene glycol	Glycerol
GOM	$61.63 \pm 1.60$	$15.50 \pm 1.75$	$36.93 \pm 1.61$	$18.40 \pm 1.66$	$42.50 \pm 1.68$
GOM-Ca <sup>2+</sup>	$64.17 \pm 1.57$	$16.80 \pm 1.75$	$40.20 \pm 1.60$	$20.07 \pm 1.65$	$44.73 \pm 1.67$
GOM-Ca <sup>2+</sup> -R	93.73 ± 1.20	33.30 ± 1.69	$22.10 \pm 1.67$	$15.60 \pm 1.67$	$41.00 \pm 1.69$

Table S1. Average contact angle (deg) for different solvents at GOMs interface.

	Water	Formamide	Diiodomethane	Ethylene glycol	Glycerol
GOM	107.388	114.283	91.406	93.546	111.186
GOM-Ca <sup>2+</sup>	104.523	113.916	89.601	93.086	109.465
GOM-Ca <sup>2+</sup> -R	68.060	106.844	97.868	94.232	112.301

Table S2.	Work o	f adhesion	on GOMs	interface	(mJ r	n <sup>-2</sup> )



Figure S1. Optical photographs of GO dispersions at different concentrations.



Figure S2. SEM images of GOMs at 500 nm scale, (a) GOM, (b) GOM-Ca<sup>2+</sup> and (c) GOM-Ca<sup>2+</sup>-R.



Figure S3. XRD patterns of rGO and GOM-Ca<sup>2+</sup>-R.



**Figure S4.** Deconvolution of XPS spectra for C1s (a, b and c) and O1s (d, e and f). The letters a and d represent GOM, b and e represent GOM-Ca<sup>2+</sup>, e and f represent GOM-Ca<sup>2+</sup>-R respectively.



Figure S5. Derived thermogravimetric (DTG) thermograms of GOMs.



**Figure S6.** Optical photographs of GOM- $Ca^{2+}$  and GOM- $Ca^{2+}$ -R after sonication in acidic and alkaline solutions. No sedimentation or delamination of GOM- $Ca^{2+}$  and GOM- $Ca^{2+}$ -R was observed.



**Figure S7.** (a) Filtration curves of ions with rejection % through GOM-Ca<sup>2+</sup>-R. (b) Rejection % of Cu<sup>2+</sup>, Ni<sup>2+</sup>, and Pb<sup>2+</sup>, by GOMs.