Marcos Surmani

Seunghyun Hong[1], Charlotte Constans[1], Juan Carrio[1,2], Seow Yong Chin[1], Slaven Garaj[1,3,4]

1. National University of Singapore - Centre for Advanced 2D materials, Singapore.
2. Mackenzie Presbiterian University – Faculty of Engineering – Sao Paulo – Brazil.
3. National University of Singapore – Department of Physics – Singapore.
4. National University of Singapore – Department of Biomedical Engineering – Singapore.

e0010793@u.nus.edu

Graphene-based membranes for ionic sieving

The global demand for clean water has been continuously increased over the last years due to the rapid growth of word's population and industrial needs [1,2]. Among different materials that can be applied in systems for molecular sieving and water desalination, nanostructured graphene oxide (GO) membranes have attracted the attention in the last years as an excellent candidate for new filtration technologies [3]. The membrane comprises interlocked GO sheets in a laminated structure, where the functional chemical groups act as spacer between the sheets and define the percolative path of graphenic channels available for the water flow. It has been shown that water flows with little friction in the channels, leading to ultra-high water flux through such membranes [3].

Here we will present an extensive set of measurements of permeability for different ions, which allowed us to clearly pinpoint the physical mechanism governing the ionic rejection. We implemented the microscopic drift-diffusion technique, where we measure ionic currents through $\sim\mu m^2$ membranes driven by both the ionic concentration gradient and the voltage drop across the membranes. This allowed us to separately measure intrinsic permeability of both cations and anions (Figure 1a), over a small area of the membranes unimpeded by the microscopic defects.

The measurements of permeability of ions with different hydrated radius and charges (figure 1c) suggested that the most important mechanisms driving the ionic sieving of GO membranes are: (i) the steric impediment which acts as an energy barrier requiring the deformation of the ionic hydration shell within the membrane's nanochannels (ii) repulsion of co-ions due to the surface charge of the channels originated by charged oxygen-based functional groups and [4]. The later leads to high charge selectivity of GO based membranes, reaching values up to 96%. By chemically modifying the graphene membranes, we find that the role of different functional groups goes beyond providing interlayer spacing and the surface charge, they could also constrain the swelling of the membrane upon hydration. At the end, we will demonstrate that the careful engineering of the functional groups could lead to much improved performance of the membranes, in terms of the size cut-off and the salt rejection. We will demonstrate the feasibility of different membranes produced in our group as reverse-osmosis and electrodialysis membranes, and will directly compare them to the currently used commercial membranes.

References

[1] Loo, S.L., Fane, A.G., Krantz, W.B. and Lim, T.T., 2012. Water research, 46(10), pp.3125-3151;
[2] Li, H., Zou, L., Pan, L. and Sun, Z., 2010. Separation and Purification Technology, 75(1), pp.8-14.
[3] Nair, R.R., Wu, H.A., Jayaram, P.N., Grigorieva, I.V. and Geim, A.K., 2012. *Science*, *335*(6067), pp.442-444.

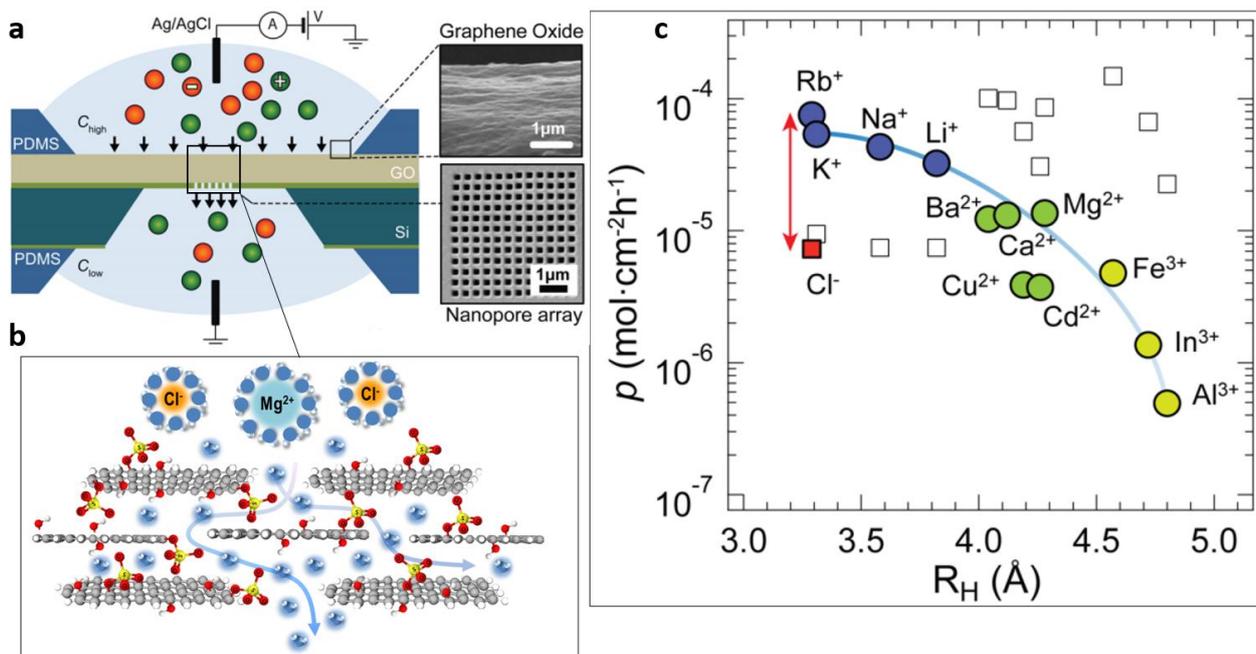[4] , J.A. and Garaj, S., 2017. Nano letters, 17(2), pp.728-732.

Figures

Figure 1: (a) Schematics of the experimental setup: the graphene oxide membrane was mounted on a freestanding SiNx membrane with an 12 × 12 array of square-shaped windows, separating two electrolyte-filled reservoirs; Ag/AgCl electrodes in each reservoir are used to apply an electric potential across the GO membrane and to measure the ionic currents flowing through the membrane. (b) Schematic of the ion rejection mechanism of the membrane containing different functional groups. (c) Permeation rates (p) obtained for a conventional GO membrane for different cations (circles) and corresponding chloride counter-ions (open and filled squares) as a function of hydrated radius (R_H) of the cations. The filled square represents the chloride permeability when in RbCl solution, where the hydration radii are very similar for both ions; the two-headed arrow shows the permeation difference resulting purely from the charge- rejection effects. The solid blue line is a guide to eye.