Article | Published: 09 November 2020

Two-dimensional adaptive membranes with programmable water and ionic channels

Daria V. Andreeva, Maxim Trushin, Anna Nikitina, Mariana C. F. Costa, Pavel V. Cherepanov, Matthew Holwill, Siyu Chen, Kou Yang, See Wee Chee, Utkur Mirsaidov, Antonio H. Castro Neto & Kostya S. Novoselov ⊠

Paper presentation

5th Group meeting

30-01-2021

Ankit Nagar

Background



Zhu, Z. et al. Journal of the American Chemical Society, 141(22), 2019

Relevance:

Desalination, Selective ion sensing, energy generation

Introduction

- Modern membranes: Flow determined by porous structure and osmotic pressure
- Protein channels: steric exclusion and electrostatic repulsion
- Adaptive and programmable membranes: changing permeability or selectivity depending on the environment
- Applications: Li⁺ extraction for Li-ion batteries, Cs⁺ removal from radioactive waste
- In this article:
 - Van der walls composite membrane
 - Permeability controlled by protonation state and presence of specific ions
 - Self-assembly of polyamine macromolecules (PA) and graphene oxide (GO) result in ionic channels

Characterization: XRD, AFM



Fig. 1. Structure of GO–PA membranes. **a**, Photograph of a 1-µm-thick free-standing GO–PA 25 kDa membrane. **b**, Schematic illustration of the sandwiched architecture of our membranes. The bottom half of the panel shows the magnified structure, with the chains and hexagonal planes representing PA molecules and GO layers, respectively. **c**,**d**, AFM height (**c**) and phase (**d**) images of the GO flakes assembled with PA at pH 2. **e**, Height profile taken along the yellow dashed line in **c**. **f**, X-ray reflection spectra for the GO–PA membranes prepared at pH 2 (top) and at pH 10.2 (middle), and the GO without PA (bottom) with extracted interlayer distances. **g**, Schematic illustrations for the membranes' structure depending on pH of the solution during assembly based on the X-ray diffraction data shown in **f**. GO and PA are represented in the same way as in **b**. **h**,**i**, AFM height (**h**) and phase (**i**) images of the GO flakes assembled with PA at pH 10.2. **j**, Height profile taken along the yellow dashed line in **h**. Scale for **c**,**d**,**h** and **i** is given by the scale bar in **c**, which is 0.5 µm. *Z* scale for **c** and **h** (height) from black to white is 0 to 20 nm. *Z* scale for **d** and **i** (phase) from black to white is 0 to 60 degrees.

Characterization: TEM, TGA, DSC



Figure S2. TEM image and the cross section of 250-nm thick membrane on an anodisc filter and TGA and DSC curves of GO, PEI and GO-PEI membrane that shows 1:1 ratio of GO and PA in the membrane.

• DSC proves that PA forms monomolecular layers confined in the rigid van der Walls structure

Water flux measurements



Fig. 2. Selective permeability of GO-PA membranes. a, Water flux as a function of pH for two of our GO-PA membranes. Black triangles show water flux for bare GO membranes demonstrating very weak dependence on pH. b, Dependence of surface charge density on pH for pristine GO flakes (black triangles) and others. The measurements are fitted by the Henderson–Hasselbalch equation with a = 4.5and $\sigma_0 = 0.2 \text{ Cm}^{-2}$ for GO; a = 4 and $\sigma_0 = 0.175 \text{ Cm}^{-2}$ for GO–PA (25 kDa); and a = 5.5 and $\sigma_0 = 0.4 \text{ Cm}^{-2}$ for GO–PA (750 kDa). c, Water permeability through GO (black triangles) and GO-PA (red squares for membrane assembled at pH 2 and orange diamonds for membrane assembled at pH 10.2). Each point was measured for 24 h. The membranes were tested under osmosis conditions against 2.5 M sucrose solution. d, Mass change of GO-PA membrane in acidic (pH 2, magenta curve) and basic (pH 11, green curve) media. The same membrane was used for both measurements. e, Photograph of a dual-cell for osmosis measurements. Right volume is filled by vellow sucrose solution for better visibility. f-h, Schematic illustrations of the permeability of the membranes for water regulated by proton gradients. Proton concentration is represented by the intensity of the blue colour.

$$\sigma_{\rm GO-PA/GO} = \pm \sigma_0 / \left(1 + 10^{(\pm pH \mp pK_a)/a}\right)$$

Water flux dependency on conformation of PA inside of the membrane



Figure S6. Surface hydrophobicity (contact angle measurements) of the membranes prepared at different pH and using 25kDa and 750 kDa PA.

Higher permeability of membranes prepared at pH=2:

Hopping paths for ions along the interfaces formed by coiled (pH 10.2) and uncoiled (pH 2) polymer chains;
the increased hydrophobic nature of weakly charged PA coils compared to more strongly charged stretched chains

Water permeability mechanism



Fig. 3. The inner and outer counterion concentrations creating osmotic water flow, as shown by green and red arrows at pH 1, pH 2, pH 4 and pH 7. We use a model structure for our composite membrane with two GO layers being placed at x=0 and x=2 nm and PA occupying the space in between. The water solution occupies the semi-volume at x<0, and the permeation chamber with sucrose occupies the semi-volume x>2 nm (not shown). The Debye length determines the outer concentration dependence according to the Poisson–Boltzmann equation with the GO surface charge density as an input parameter.

In-situ TEM observations



Figure S9. Transmission electron microscopy images recorded using liquid cell with water flow shows unfolding of wrinkled GO flakes upon water treatment. The folds are highlighted by arrows. The membrane prepared at pH 7 is unfolded within 30s. The membrane prepared at pH 4 shows less folds after 1h of water flow.

Ionic permeability

Ion permeability through GO-PA 750 kDa membranes:



Figure S10. Ionic permeability vs. the hydrated radii of ions for the 0.1 M mixture of ions adjusted to pH 2 and pH 6 (left) and ionic permeability of GO-PA membranes as a function of pH measured separately for K⁺ and Na⁺ (right) for the membrane prepared with 750 kDa PA.

Probable reasons:

- Large positive charge density of PA
- Longer hopping paths along long chains

Ionic permeability

lon permeability through GO-PA 25 kDa membranes:



Fig. 4. The pH-regulated ion permeability through the GO-PA 25 kDa membrane. **a**, lonic permeability of GO-PA membranes vs pH measured separately for K⁺, Na⁺, Cs⁺ and Li⁺ from 0.1 M aqueous solutions of corresponding salts. **b**, lonic permeability vs the hydrated radii of ions under osmosis conditions against 2.5 M sucrose solution for the 0.1 M mixture of ions adjusted to pH 2 and pH 5.5. **c**, lonic permeability of GO-PA membranes for Cs⁺ only for 12 h; after 12 h, K⁺ ions were added **d**,**e**, Potentiometric titration curves for suspensions of GO and GO-PA by 0.1 M base (NaOH, CsOH and LiOH). Titrations started from acidic solutions prepared by adding 0.1 M HCl; **f**, Attenuated total reflectance Fourier transform infrared spectra of the GO, PA and GO-PA membranes prepared at pH 10.2.

Conclusions

- No transport in normal state: strong repulsion between cations and PA
- Chains of carbonyl groups at the GO-PA interface act as selective ionic channels
- Large K⁺ replace protons at interfaces -> reduction in overall charge -> opening channels for hydrated ions of any species
- K⁺ acts as a gate in an ionic transistor
- Sensitivity of transistor can be regulated by charge state of PA through external pH