

## Ion sieving in graphene oxide membranes via cationic control of interlayer spacing

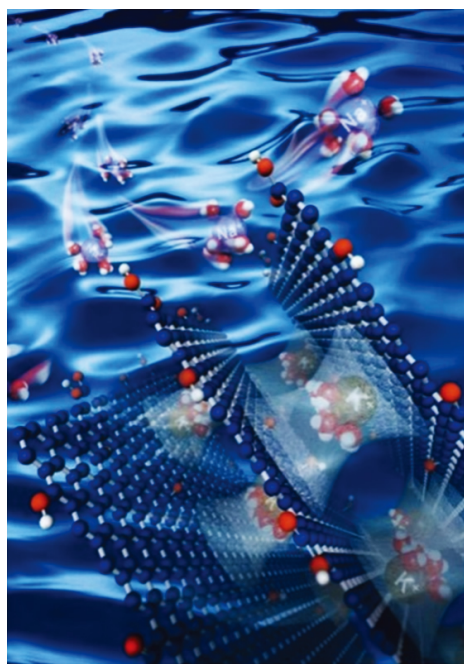
With the support by the National Natural Science Foundation of China, a collaborative study by the research groups led by Prof. Fang Haiping (方海平) from Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Prof. Wu Minghong (吴明红) from Shanghai Applied Radiation Institute, Shanghai University, Prof. Jin Wanqin (金万勤) from the State Key Laboratory of Materials-Oriented Chemical Engineering, Nanjing Tech University, and researchers from Zhejiang Provincial Key Laboratory of Chemical Utilization of Forestry Biomass, Zhejiang A&F University demonstrates that cationic control of the interlayer spacing of graphene oxide membranes with ångström precision and ion sieving with these membranes, which was published in *Nature* (2017, 550: 380).

Graphene oxide membranes—partially oxidized, stacked sheets of graphene—can provide ultrathin, high-flux and energy-efficient membranes for precise ionic and molecular sieving in aqueous solution. These materials have shown potential in a variety of applications, including water desalination and purification, gas and ion separation, biosensors, proton conductors, lithium-based batteries and super-capacitors.

Unlike the pores of carbon nanotube membranes, which have fixed sizes, the pores of graphene oxide membranes—that is, the interlayer spacing between graphene oxide sheets (a sheet is a single flake inside the membrane)—are of variable size. Furthermore, it is difficult to reduce the interlayer spacing sufficiently to exclude small ions and to maintain this spacing against the tendency of graphene oxide membranes to swell when immersed in aqueous solution. These challenges hinder the potential applications of graphene oxide membranes.

Here we experimentally demonstrate cationic control of the interlayer spacing of graphene oxide membranes with ångström precision using  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Li}^+$  or  $\text{Mg}^{2+}$  ions. Moreover, membrane spacings controlled by one type of cation can efficiently and selectively exclude other cations that have larger hydrated volumes. First-principles calculations and ultraviolet absorption spectroscopy reveal that the fixing of the interlayer distances was mainly due to the interaction between the hydrated cations and aromatic rings (cation- $\pi$  interactions) on the graphene oxide sheet, together with the interaction between the hydrated cations and the oxidized groups on the graphene oxide sheet. We note that although it was proposed 20 years ago that the cation- $\pi$  interaction was greatly reduced by the hydrated cations [Chem Rev, 1997, 97: 1303; Chem Rev, 2013, 13: 2100], which have been usually neglected before, their studies showed that this interaction is still strong enough to result in a strong adsorption of hydrated cation on graphitic surfaces (such as, graphene, graphite, graphene oxide, and carbon nanotube), due to the polycyclic aromatic rings structure which includes more  $\pi$  electrons, and thus the present work realized.

Previous density functional theory computations show that other cations ( $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cr}^{2+}$  and  $\text{Pb}^{2+}$ ) should have a much stronger cation- $\pi$  interaction with the graphene sheet than  $\text{Na}^+$  has, suggesting that other ions could be used to produce a wider range of interlayer spacings and a wide range of potential applications are expected.



**Figure** Interlayer spacings in freestanding cation-controlled GOMs