

Fig. 1 | A combination of DNA phase-separation and hybridization yields new all-DNA colloids that could not be realized with each process in isolation. As with hybridization, the phase-separation process can be tailored based on, among other properties, DNA sequence, offering a new handle in programmable assembly.

assemblies or multi-particle structures, including all-DNA core–satellite structures or colloidal assemblies of gold nanoparticles and DNA colloids that can be ruptured using light.

This work bridges concepts of DNA programmable assembly, chemistry, materials science and polymer science, highlighting the overarching value of interdisciplinary science in driving new

discoveries. Interesting from both a fundamental and technological standpoint, the work by Walther and co-workers has elucidated new phase behaviour in a complex system and contributed a simple, versatile pathway to realize all-DNA structures in different physical states. These could be used as a new route for understanding chemical reactions in confined spaces. They also may be valuable from a biomedical standpoint, because they are made completely of biological or biocompatible components, and one could imagine using these kinds of all-DNA colloids in gene regulation, immune engineering or drug delivery once challenges concerning particle uniformity are mediated. In sum, Walther and co-workers offer an exciting addition to our materials synthesis toolbox, welcome news for the community. □

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ELECTROSTATIC MODULATION

Moving ions confined between graphene sheets

Permeation experiments and simulations show that the ion diffusion rate in confinement can be reversibly modulated and significantly enhanced with a potential of less than 0.5 V.

Yury Gogotsi

What is common in the function of cellular membranes, batteries and water desalination membranes? They all depend on the control of ion

transport in confined nanopores. Electric fields arising from either a surface charge or externally applied voltage can strongly affect diffusion of ions. State-of-the-art

technologies such as capacitive deionization, salinity gradient energy harvesting, electrochemical capacitors and field-effect transistors with gate dielectrics of ionic

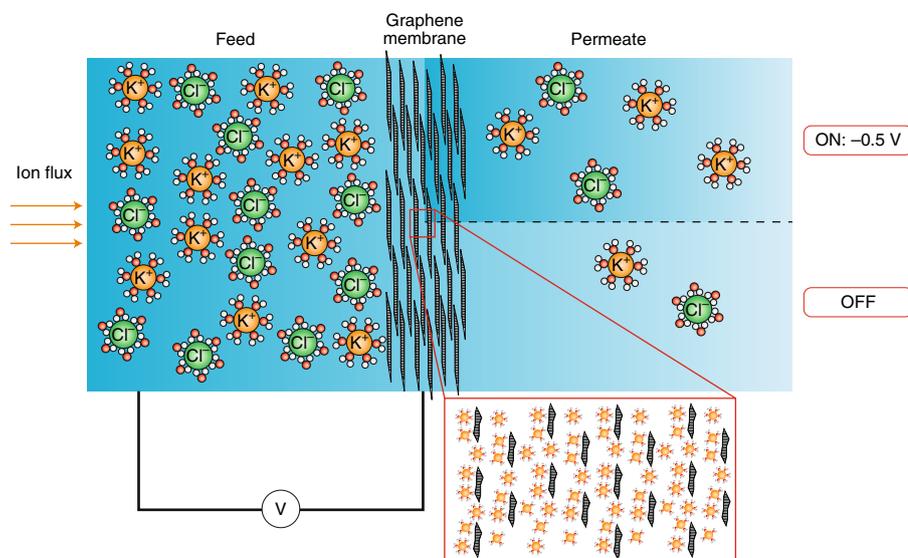


Fig. 1 | Schematic illustration of ion gating in a membrane built of conductive 2D nanosheets.

Illustration by Samantha Buczek.

liquids that rely on the flow of ions can be mediated by an applied electric potential. To understand and control ionic transport is of high importance fundamentally and for many applications such as those listed above. However, recent studies have demonstrated unusual phenomena that are inexplicable by conventional theory¹, such as ultra-dense packing of ions, drastic changes in diffusion coefficients (both increase and decrease were observed), and even partial breaking of Coulomb's law that may occur when ions are confined in nanometre-wide spaces. Now, writing in *Nature Nanotechnology*, Cheng et al. use graphene-based membranes to study transport of ions through two-dimensional (2D) channels using low-voltage electrostatic modulation². The researchers investigated tunable nanoconfinement of ions between graphene sheets to understand how ion diffusion responds to an applied potential.

When a material possessing a surface charge is placed into an electrolyte solution, ions with charge opposite to the surface are electrostatically attracted, while similarly charged ions are repelled from the surface. It is well established that surface charge can modulate transport of ions in minerals due to different co- and counter-ion sorption affinities, affecting ion diffusion both near and along mineral surfaces³. At a depth of 1–2 nm into the surface layer, the potential decays exponentially with a characteristic length, known as the Debye length, of the electrical double layer (EDL). Ionic transport can be controlled within the Debye length by either a surface charge, arising

from intrinsic chemistry of the material surface, or an externally applied electric field (provided that the material has sufficient electrical conductivity). In membranes with nanochannels small enough to enable overlapping of EDLs of the channel walls, electrostatic manipulation of ions in the nanochannel is possible⁴.

Voltage-gated rejection of ions and molecules by conductive membranes was introduced more than three decades ago by Burgmayer and Murray⁵. They showed that ion rejection can be electrically controlled using conducting polymer deposited on a gold grid. Other conducting materials, such as porous carbon⁴, have shown a gating effect under applied potential, increasing rejection of molecular species. The ability to control the electrostatic interaction between a porous membrane and relevant ions with a slight applied potential opens up opportunities to engineer electroactive membranes via gated rejection. This approach may be used to selectively reject anions or cations, as well as release adsorbed ions or charged molecules during membrane cleaning.

2D materials have been used as building blocks for separation membranes⁶, in which efficient rejection by way of steric effects is required, as well as electrochemical capacitors, in which enhancement of ion transport may be achieved in their slit-shaped 2D nanochannels. Electrically conducting 2D materials with a large EDL capacitance, such as graphene⁷ or MXenes (2D carbides and nitrides)⁸, only require a small change in surface potential to achieve

a significant change in the population of ions at the charged surface. 2D layers provide uniformly narrow slit pores of comparable size to the confined ions. Yet, there is little information on the electrical control of ion transport (acceleration or deceleration) in membranes fabricated from 2D nanomaterials. The availability of electrically conductive graphene-based membranes opens the door for building model systems for systematic experiments².

Cheng et al.² use a three-electrode cell set-up with a 10–80- μm -thin layered graphene-based nanoporous membrane electrode (reduced graphene oxide), a platinum mesh counter-electrode and a reference electrode (Ag/AgCl). Aligned as a result of vacuum-assisted filtration, graphene sheets form 2-nm-wide slits (micropores) covered by oxygen-containing functional groups and confining aqueous solution. The permeation of ions through the graphene membrane is measured when steady-state diffusion curves are generated under various potentials between -0.5 and 0.5 V. Chen et al. measure a change in normalized ion flux with respect to 0 V, showing that the diffusion rate can be reversibly modulated and enhanced by a low voltage (less than 0.5 V) by a factor of 4–7. However, the effect of the applied potential is dependent on the ion type. For example, the diffusion flux of K^+ is enhanced by more than 6 times, while little effect is seen for divalent Mg^{2+} . This asymmetry in diffusion enhancement also occurs between cations and anions (for example, K^+ and Cl^-), independent of their similar mobilities in solution (Fig. 1). These discrepancies can be explained by different solvation energies/water polarization for different ions, as well as dissimilar interactions of the ions with the graphene surface. Asymmetry of capacitive behaviour, resulting from this phenomenon, has been observed in related fields in the past, for example, in the investigation of electrolytes for supercapacitors⁹.

Cheng et al.² also use molecular dynamics simulations to reveal details of the EDL structure confined in graphene nanoslits and calculate the dielectric constant. Simulations show an increase in co-ion concentration with increasing surface potential under confinement, suggesting the existence of ion–ion correlations that can influence ion transport. This finding indicates that ion pairs can be selected to control the diffusion — stronger ion–ion correlations, such as in metal sulfates, lead to more significant modulation of diffusion. The magnitude of diffusion enhancement is predicted to increase with decreasing slit width. The dielectric constant is shown to decrease

in nanoconfinement. Furthermore, the increase of the relative flux with the applied potential was predicted to be greater for a lower solution concentration (50 mM) compared to a higher concentration (0.5 M), in agreement with experimental observations.

It is also noteworthy that reversible oxidation or reduction of the membrane material surface has been used to gate rejection of ions¹⁰. When a polypyrrole membrane, impermeable under no applied potential, is reduced under negative potential or oxidized under positive potential⁹, the charge balance of the membrane is compensated via the adsorption of ions from feed side or desorption of ions on the permeate side, creating an ion pump.

So, how can the control of ionic flux be useful in real-life technologies? For batteries and electrochemical capacitors, it can help us better understand the inner workings of the mechanisms of charge transfer and storage. Moreover, controlling the flow of ions in desalination membranes can lead to improved rejection, yielding potable water more efficiently. Membrane processes have become increasingly important, and energy-efficient water purification technologies

are needed to ensure water availability globally. Ideal desalination and water purification membranes should deliver high flux, higher stability, and resistance to chemicals and fouling. Membranes should be thin enough and mechanically stable to maximize water permeability and provide consistent salt rejection. Graphene-based 2D materials, such as graphene and graphene oxide, offer ultrahigh flux, selective molecular and ion sieving as well as strong resistance to biofouling⁷. Cheng et al. now demonstrate how the graphene-based separation membrane system benefits from the low-voltage electrostatic modulation of transport of ions². What about other systems? Conducting polymers and their hybrids with low-dimensional materials may potentially be used. MXenes are gaining heightened attention as materials for both supercapacitors and water purification membrane fabrication due to their high electronic conductivity, exceeding that of solution-processed graphene⁸. Their interlayer spacings act as ionic channels, making them suitable for voltage gating, too. Other 2D materials with similar properties should certainly be studied as well. Furthermore, the improved understanding of voltage-gated modulation of ion diffusion

achieved in Cheng's study² may also benefit other technologies using ionic currents such as field-effect transistors and diodes operating with ionic liquids¹¹, and controlled drug-release systems. □

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NANOTECHNOLOGY AND AGRICULTURE

Achieving food security through the very small

Nanotechnology could make agriculture more efficient and more sustainable, but more systematic understanding of the mechanisms involved is necessary to prove the potential of nano-enabled agrochemicals.

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With a projected global population of 9.7 billion by 2050, agricultural production will need to increase by up to 60%, making achieving and sustaining global food security among the most significant 'grand challenges' we face (Fig. 1)^{1,2,3}. Further confounding this effort is the fact that this growth in food production will have to occur in the face of a changing climate and on decreasing acreage of arable land. Ideally, the strategies driving this effort will also need to be sustainable, efficiently using water and energy resources while minimizing negative environmental impacts. One of the major shortcomings of current agricultural practices is the high inefficiency of agrochemical delivery and utilization, with losses averaging 10–75% presenting a prime target for

improvement. As such, there has been significant interest over the past decade in using nanotechnology to address these inefficiencies³. From areas of research such as materials synthesis, nanomedicine and electronics, it is known that substances at the nanoscale behave differently, including being more reactive and mobile, and potentially biocompatible. It is thus clear that many of the novel properties afforded to materials at the nanoscale may be of direct benefit for reducing the inefficiencies currently plaguing agricultural production. Now, writing in *Nature Nanotechnology*, Melanie Kah et al.⁴ provide a systematic effort to critically evaluate the current literature on nano-enabled pesticide and fertilizer efficacy (that is, nanopesticide and nanofertilizer), assessing the overall benefit

of these materials against conventional counterparts, including an investigation of fate/environmental impact. The authors conducted an in-depth analysis of 78 published papers and concluded that the median gain in efficiency with nanotechnology was approximately 20–30%.

In their detailed analysis, Kah et al. not only evaluated nanopesticides and nanofertilizers separately, but they also reported on a number of shortcomings in this rapidly developing yet somewhat limited dataset. This assessment of shortcomings will indeed be valuable to future efforts in this field, as much of these points can be taken as recommendations to produce more robust experimental design and resulting data. Among the most important shortcomings in the existing literature is the