NANOPORE

Ionic blockade

Classic ionic conduction through an inorganic monolayer nanopore shows analogies to the quantum-mechanical phenomenon of electronic Coulomb blockade.

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The transport of ions through nanochannels is a mesoscopic phenomenon lying squarely in the difficult and uncertain interface between classical and quantum physics. Perhaps this is why the transport mechanism — despite its importance to the ion channels of biological cells, and its increasing technological significance (for instance, in DNA sequencing) — has remained an enduring mystery. The observation by Jiandong Feng, Aleksandra Radenovic and colleagues of ionic Coulomb blockade[2,3] in a water-filled subnanometre-wide channel through a molybdenum disulphide (MoS_2) monolayer, reported in *Nature Materials*[1], is thus of particular interest: it shows that the ions are behaving in many respects like the electrons in a quantum dot (that is, they display quantum-mechanical features).

Single-electron quantum-mechanical phenomena play an important role in the fast-growing field of molecular electronics, which exploits the possibility of using individual molecules as electronic components[4]. Such measurements have been implemented in quantum dots, carbon nanotubes, C_{60} and DNA, and have not only contributed substantially to the understanding of fundamental quantum physics but are also paving the way to a diversity of quantum devices. The work of Feng and co-authors heralds comparable possibilities for single-ion phenomena and technologies.

The authors' experiments measured conduction between two bulk reservoirs of an aqueous ionic solution, separated by a MoS_2 membrane pierced by a single 0.6 nm nanopore[5] (Fig. 1a). The room temperature current–voltage (*I*–*V*) characteristics of ion transport through the nanopore exhibited strikingly nonlinear (non-Ohmic) effects. In particular, the current at low voltages was almost entirely suppressed, but rose abruptly when the voltage exceeded a threshold value of about 400 mV (Fig. 1b). This kind of behaviour typifies the presence of a gap separating the potential energies of the allowed states of a system. These nonlinear characteristics differed markedly from those of ion transport through larger nanopores. For diameters above 1 nm, the *I*–*V* curves were found to be Ohmic, thus eliminating the possibility that the nonlinearity seen in the smaller nano-channel originated from hydrophobic effects.

The existence of an energy gap is readily understandable by taking account of the fact that the tiny system has a correspondingly tiny capacitance, meaning that a charging energy must be exceeded before transport through the membrane channel can occur. As a result, there are discrete energy levels for the ion in the nanopore (Fig. 1c). In the absence of a bias voltage (Fig. 1c, left-hand diagram) it would require too much energy for the M^{2+} ion to enter the nanopore, so conduction is blocked. In the presence of a sufficient bias voltage however (Fig. 1c, right), it becomes energetically favourable for the ion to pass through.

Such behaviour represents a beautiful example of Coulomb blockade, a well-known electrostatic phenomenon (related to charge discreteness and energy quantization) controlling conduction in tunnel junctions and quantum dots. The main difference is that the conduction in a quantum dot involves electrons moving between discrete energy levels via quantum tunnelling whereas here current is carried by ions (which also undergo transitions between discrete levels) through classical electrodiffusive transport (that is, under the influence of thermal fluctuations).

Ionic Coulomb blockade had in fact been predicted for low-capacitance, water-filled, charged nanotubes — both for artificial nanopores[5] and for biological ion channels[3]. The quantum-like behaviour reported by Feng and co-workers now offers experimental support for these ideas, and shows that ionic Coulomb blockade effects — resulting from the quantization of charge and occupancy — are not only observable, but can even become dominant in sub-nanometre-wide water-filled nanopores. These features of nano-channels are interesting from both a theoretical and a practical point of view, and further research elucidating the origin of these phenomena in more detail will certainly be of importance. The observed similarity of single-ion and single-electron phenomena augers well for a new generation of electrochemical devices. On the basis of selective single-ion conduction through sub-nanometre-sized pores (both synthetic and natural), novel technology as well as new drugs targeting biological ion channels, can be anticipated.

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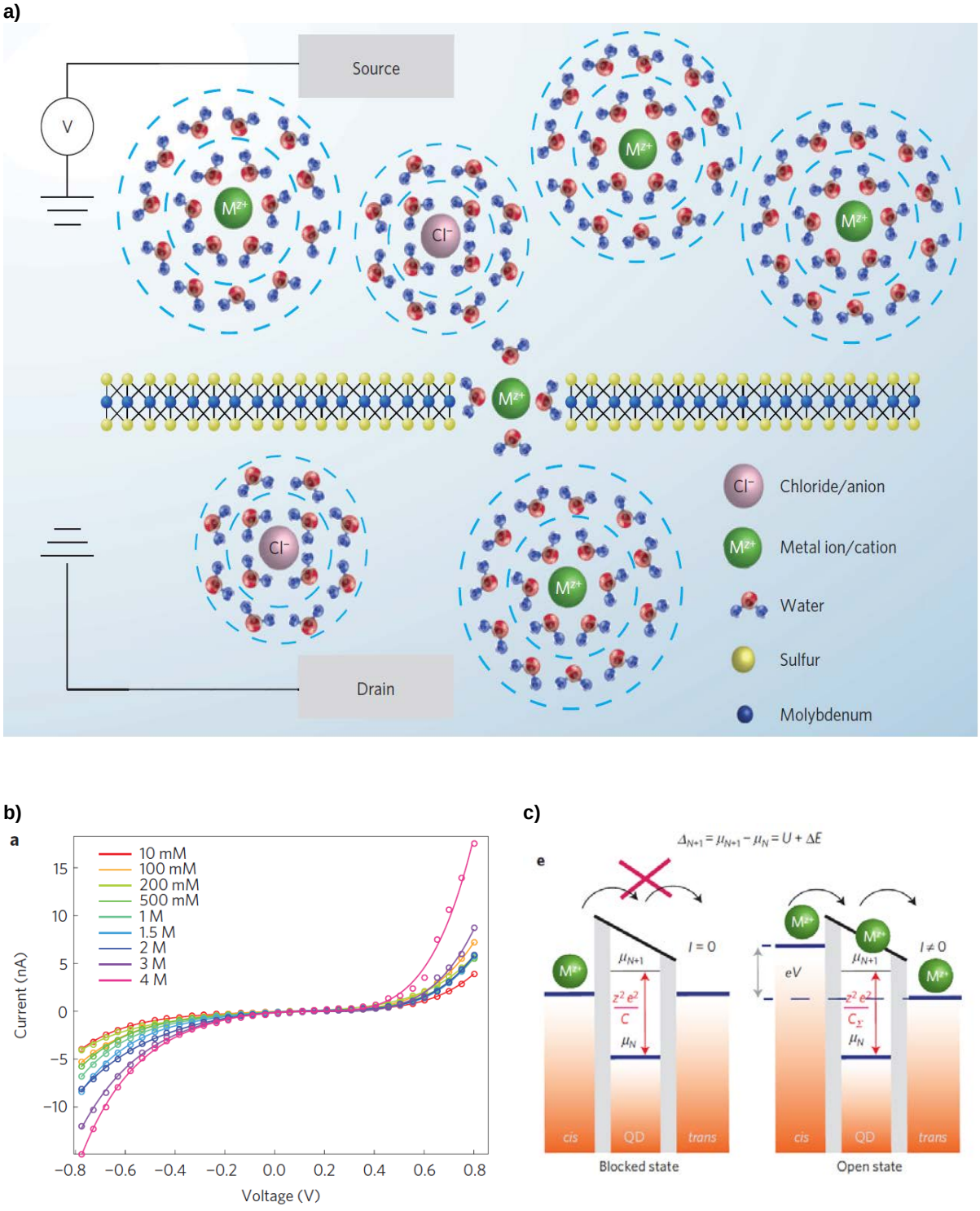

Figure 1 | Coulomb blockade in ionic transport through a membrane nanopore. a, Sketch of the experimental arrangement used by Feng, Radenovic and colleagues. With a sufficient potential difference V, the M^{2+} cations are found to pass through the 0.6-nm-diameter nanopore in the MoS_2 monolayer. **b**, Current–voltage (I–V) curves (for different ion concentrations) exhibit a non-Ohmic behaviour. **c**, Energy levels for an ion crossing the nanopore in the absence (left) and in the presence (right) of a bias voltage. In each case, the centre plot shows the charging energy for an ion inside the nanopore, compared to the ionic energies on both sides of the membrane. In the left panel, there is an energy barrier impeding the ion from entering the nanopore, thus leading to the blocked state. In the right panel, the bias voltage energy surmounts the charging energy, thereby creating an open state.