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# Fluidics Meets Electronics: Carbon Nanotubes as Nanopores**

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Single-walled carbon nanotubes are molecular-scale hollow cylinders with atomically thin walls, and many of their properties are a direct consequence of this geometry. Most famously, quantization of electronic wavefunctions around the circumference of the cylinder causes nanotubes with only minute differences in diameter or chirality to be either metallic or semiconducting. Perhaps more prosaically, their hollow structure also signifies that nanotubes may represent a near-ideal form of piping for nanofluidic systems. As recently shown by Liu et al.[1] in experiments on individual nanotubes, the combination of an approximate inner diameter of only 1 nm, a high aspect ratio, and atomically perfect $sp^2$-hybridzed carbon sidewalls leads to surprising observations that challenge our understanding of the transport of salt ions and polyelectrolytes at the nanoscale.

Interest in nanometer-scale orifices—or nanopores—that separate liquid-filled reservoirs has grown tremendously over the last two decades. This growth occurred because this seemingly benign system allows the extraction of information about a molecular-sized object (e.g., the presence or absence of a molecule inside the orifice) using an electrical signal (the flow of ions through the orifice, which is influenced by the size and charge of the obstructing molecule). Studies of nanopores have yielded important insights into the transport of ions and biomolecules,[2] and efforts are underway to develop nanopore-based technologies, in particular for DNA sequencing.[3] Knowledge of (or, even better, control over) the size, shape, and charge distribution of the pore at or near the molecular scale is key in turning a nanopore into a useful tool for biomolecular science and technology. The first nanopores to be studied extensively at the single-pore level were biomolecular pores;[4] the enormous advantages of these systems are knowledge of the exact structure and charge distribution of the pore, reproducibility of their behavior, and the ability to alter the pore by biochemical engineering. More recently, techniques have also been developed for preparing so-called solid-state nanopores in thin membranes of insulating materials.[5] Although they do not provide quite the same atomic-level precision as biological nanopores, these devices are stable, robust, and more flexible for integration in complex systems.

Single-walled carbon nanotubes combine several of the advantages of these two approaches. The nanotubes, which have inner diameters comparable to the diameter of DNA, are an essentially defect-free atomic structure (except near the ends), and offer opportunities for targeted functionalization. Yet carbon nanotubes are also sufficiently robust to survive the rigors of microfabrication, and can be electrically contacted to external wiring for added functionality. Insulating membranes with multiple imbedded nanotubes,[6] in which each molecule provides a parallel channel that connects the two sides of the membrane, have previously been reported. In their recent work, Liu et al. extended this concept by studying the ionic transport properties of individual nanotubes. Because large variations were observed between nanotubes, this approach provides much more complete information than earlier ensemble measurements. The construction of such devices is however not trivial. It is particularly critical to ensure that the solution is being transported in the inside bore of the tube, rather than through defects in the surrounding insulator caused by the presence of the nanotube. This transport was achieved by taking advantage of the fact that as-grown nanotubes have closed ends; the ends could be opened in selected devices by etching, and transport occurred only in devices with ends that had been explicitly opened.

Direct measurement of the water flow through a nanotube would be extremely challenging because of the tiny volumes involved. Instead, Liu et al. measured the electrical current that arises from the response of the solvated ions to a voltage applied across the two reservoirs. The ion conduction in some devices was much higher than one would expect from simple geometry and Ohm's law, consistent with measurements on membranes containing large numbers of double-walled carbon nanotubes.[6] More surprisingly, and difficult to deduce from ensemble measurements, all nanotubes that exhibited this anomalously high conductance were metallic nanotubes, while semiconducting nanotubes systematically exhibited a lower conductance. Such a direct influence of the electronic properties of the "pipe" down which the ions are being transported is an unexpected finding.

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Having demonstrated the feasibility of addressing individual nanotubes, Liu et al. proceeded to show that short oligomers of single-stranded DNA, which are thin enough to fit within the bore of a nanotube, could also be transported in this manner. The translocation of DNA was elegantly confirmed by polymerase chain reaction (PCR). Remarkably, translocation only occurred through the "anomalous", high-ionic-conductance metallic nanotubes. The transport of DNA was also marked by transient signatures in the ionic current. Firstly, a slow, continuous increase in the background current was observed. Secondly, a large spike of current occurred at random time intervals, and each such spike was immediately followed by a steplike decrease of the background current. Comparison of the PCR and transport data indicates that each spike corresponds to the transport of a few tens of DNA molecules, thus suggesting that DNA is somehow stored in the nanotube for extended periods of time.

These results differ markedly from observations in conventional nanopores, where passage of a DNA molecule through the pore occurs swiftly because the electric field that drives the ionic current also pulls at the DNA. Under suitable conditions, translocation in conventional nanopores is also accompanied by a "spike" in the current. Perhaps counterintuitively, this current is not primarily due the negative charge of the DNA, but rather, the DNA carries with it an atmosphere of compensating, positively charged ions. As shown in Figure 1a, transport of these ions along the DNA provides an additional path for current when the DNA is in the pore. In the experiments carried out by Liu et al., the DNA oligomers are instead much shorter than the length of the nanotube, thus precluding a single DNA molecule from "short-circuiting" the whole channel. The observed slow rise of the background current could instead be the more gentle contribution to the ionic conductance from a larger number of DNA molecules that slowly build up inside the nanotube (Figure 1b), only to be released simultaneously in "spike" events.

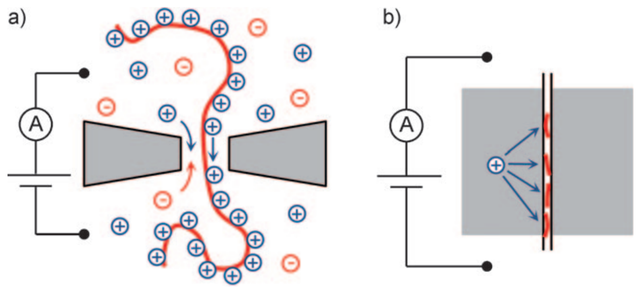

***Figure 1.*** a) Sketch of DNA translocation through a solid-state nanopore. Positively charged counterions migrating along the DNA can increase the ionic current. b) Probable situation in a carbon nanotube. Short DNA oligomers cannot bridge the two ends of the nanotube but instead accumulate inside, therefore leading to counterion enrichment.

The latter observation leads to the question of why the DNA does not quickly flow down the nanotube as it does in a conventional nanopore experiment. Several elements are likely to play a role in this effect. Firstly, single-stranded DNA is known to bind to (the outside of) carbon nanotubes,[7] which could lead to the inside of the nanotube to be coated with DNA. This effect alone does not explain the cataclysmic "spike" events, however. Secondly, passing an ionic current through a nanochannel whose walls are discontinuously charged causes extensive, nonlocal redistribution of ions, with regions of enrichment or depletion of both cations and anions.[8] As DNA itself is highly charged, similar focusing might contribute to its accumulation inside the nanotube. An indication of such ionic redistributions is rectification of the ionic current. Current rectification was indeed observed in the experiments reported by Liu et al., thus rendering this conjecture plausible. Thirdly, transport may be influenced by the fact that the nanotubes themselves are highly conducting. Electrons inside the nanotube can rearrange so as to screen out an externally applied electric field, thus reducing the electric force on both ions and DNA inside the nanotube. The extent of the screening depends in part on the relation between the electrons' chemical potential and net charge density. As this relation differs for metallic and semiconducting nanotubes, screening might contribute to giving metallic nanotubes their unique properties for ionic transport.

An understanding of the interplay between specific interactions, screening, and the electronic properties of carbon nanotubes represents a new opportunity to test our knowledge of ion and polyelectrolyte transport on the nanoscale. In terms of new functionality, the unforeseen dependence of ion and DNA transport on electronic properties is intriguing. As it is possible to electrostatically dope semiconducting nanotubes to essentially turn them into metals, one can envision devices in which an electrostatic potential is used to switch DNA translocation on or off.

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