Electrophoretic and electroosmotic flow through carbon nanotube membranes as chemical pumps

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Carbon nanotubes have three key attributes that make them of great interest for novel membrane applications 1) atomically flat graphite surface allows for ideal fluid slip boundary conditions and extremely fast flow rates 2) the cutting process to open CNTs inherently places functional chemistry at CNT core entrance for chemical selectivity and 3) CNT are electrically conductive allowing for electrochemical reactions and application of electric fields gradients at CNT tips. In general, the transport mechanisms through CNT membrane are a) ionic diffusion is near bulk expectation with no enhancement from CNT b) gas flow is enhanced by ~1-2 order of magnitude due to specular reflection off of flat graphitic surface c) and pressure driven flux of a variety of solvents (H2O, hexane, decane ethanol, methanol) are 4-5 orders of magnitude higher than conventional Newtonian flow [***1***] due to atomically flat graphite planes inducing nearly ideal slip conditions. Nearly all applications require chemical selectivity in what is allowed to pass across the membrane. However the act of placing selective functional chemistry at pore entrance or along the core of CNTs, dramatically/completely eliminates the enhanced flow effects by eliminating the near perfect slip boundary condition[***2***]. Needed is a mechanism to pump chemicals through the pore where selective chemistry is. This is routinely achieved in protein channels where permeates are accelerated through regions of precise functionality. The CNT membrane, with tips functionalized with charged molecules, is a nearly ideal platform to induce electro-osmotic flow with high charge density at pore entrance and a nearly frictionless surface for the propagation of plug flow. Through diazonium electrochemical modification we have successfully bound anionic surface charge to CNT tips and along CNT cores. High electro-osmotic flows of 0.16 cm/s-V at are seen by the pumping of neutral caffeine molecules. Improvements in electroosmotic power efficiency of 25-112 fold are seen in CNTs compared to conventional nanoporous materials with atomically rough interfaces [***3***]. Use of the electro-osmotic phenomenon for responsive/programmed transdermal drug delivery devices is discussed with the voltage gated delivery of clonidine and nicotine across CNT membrane at therapeutically useful fluxes [***4***]. In small diameter SWCNTs ion mobilities are seen to be ~6 fold enhanced due to induced electroosmotic flow. Electroosmotic flow enhancements of 10,000 fold are seen [***5***] and are consistent with pressure driven flow enhancements.

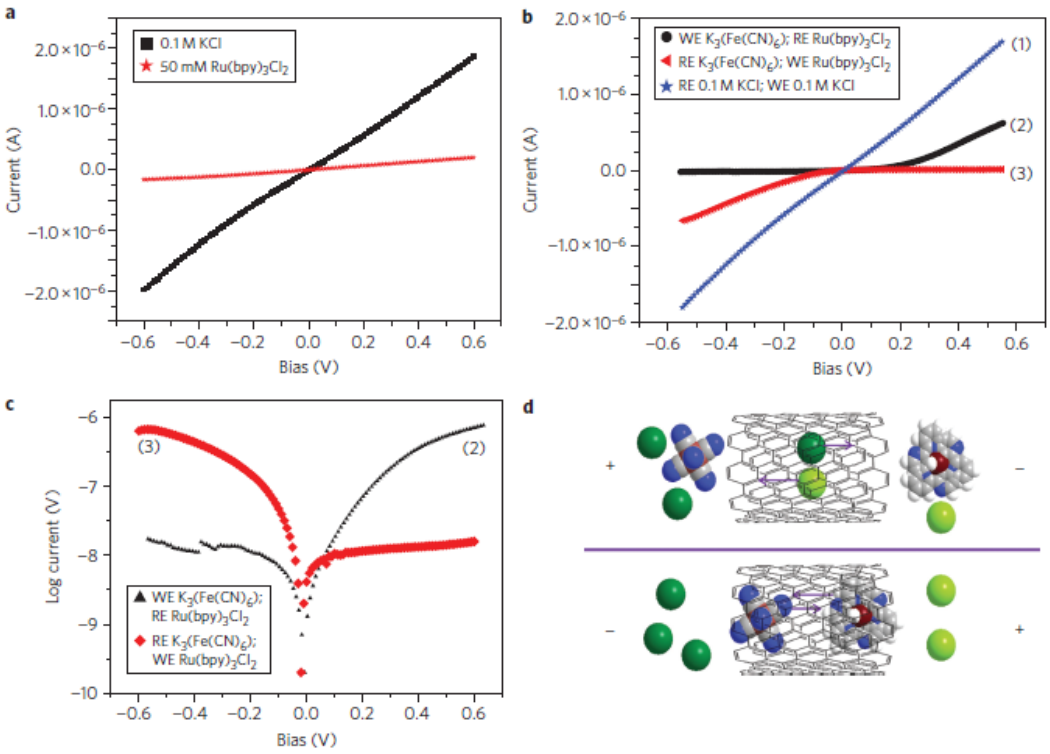

Figure 1. a, Ionic currents through SWCNT membranes rectification is seen when one side is filled with 25 mM K3(Fe(CN)6), and another side is filled with 50 mM Ru(bpy)3Cl2, and the control experiment with KCl. b, current shown on log scale. c, Data for experiments 2 and 3 plotted with current on a log scale.d, Schematic with space filling molecular models of ionic transport in SWCNT (10, 10) under electric field under opposite bias conditions (Dark green, K+; light green Cl-; grey, C; blue, N; dark brown, Ru2+; light brown, Fe3+; white, H). d, Schematic of electrochemical test cell. Pore area: 5.0×10-12 m2. Figure reproduced from *Nature Nanotech* DOI: 10.1038/NNANO.2011.240

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4 " Programmable transdermal drug delivery of nicotine using carbon nanotube membranes" J. Wu, K.S. Paudel, C.L. Strasinger, D. Hamell, Audra L. Stinchcomb*, B. J. Hinds* *Proc. Nat. Acad. Sci.* **2010** 107(26) 11698-11702.

5 "Electrophoretically Induced Aqueous Flow through sub-Nanometer Single Walled Carbon Nanotube Membranes" Ji Wu, Karen Gerstandt, Hongbo Zhang, Jie Liu, and Bruce. J. Hinds *Nature Nano* **2012** DOI: 10.1038/NNANO.2011.240