WHAT'S HOT IN... CHEMISTRY , September/October 2008

Water Flows Through Nanotubes at an Impossibly Rapid Rate

by John Emsley

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Paper #1 reports the discovery that gas and water flow through carbon nanotubes at much faster rates than theories predict. The research may be the basis for new separation techniques, and could have applications for the desalination of seawater, which might one day help to solve the global shortage of drinking water. The research has even wider implications because "nanofluidics" is the key to transfer of molecules across membranes.

Paper #1 comes from a group headed by physicist Olgica Bakajin and chemist Aleksandr Noy based at the Lawrence Livermore National Laboratory (LLNL) in California. The team developed membranes with carbon nanotube pores of diameter less than 2 nanometers. They used a catalytic chemical deposition process to grow double-walled nanotubes on the surface of a silicon chip and sealed the gaps between them with silicon nitride generated by low-pressure chemical vapor deposition. That the membranes really were free of gaps was proved by their impermeability to both liquids and gases. The ends of the tubes were then re-opened using argon ion etching to strip away the surface layers of silicon nitride.

The nanotubes were between 2 and 3 microns in length, and there were 250 billion of them per square centimeter. They had diameters of 1.3 to 2.0 nanometers (nm), the upper limit shown by their not allowing 2 nm gold particles to pass through. Transmission electron microscopy showed that the inner diameter of the tubes

Chemistry Top Ten Papers

Rank	Papers	Cites Mar-Apr 08	Rank Jan-Feb 08
1	J.K. Holt, *et al.*, "Fast mass transport through sub-2-nanometer carbon nanotubes," *Science*, 312(5776): 1034-7, 19 May 2006. [Lawrence Livermore Natl. Lab., Livermore, CA; U. Calif., Berkeley] *043UX	16	†
2	L. Venkataraman, *et al.*, "Dependence of single-molecule junction conductance on molecular conformation," *Nature*, 442(7105): 904-7, 24 August 2006. [Columbia U., New York, NY] *076LT	16	†
3	S. Stankovich, *et al.*, "Graphene-based composite materials," *Nature*, 442(7100): 282-6, 20 July 2006. [Northwestern U., Evanston, IL; Purdue U., West Lafayette, IN] *064WT	15	†
4	P. Jurecka, *et al.*, "Density functional theory augmented with an empirical dispersion term. Interaction energies and geometries of 80 noncovalent complexes compared with *ab initio* quantum mechanics calculations," *J. Comput. Chem.*, 28(2): 555-69, 30 January 2007. [U. Calgary, Canada; Acad. Sci. Czech Rep., Prague] *122PK	15	†

was about the width of six water molecules.

What was remarkable about the new membranes was the speed with which gas and water molecules could flow through them. This was more than 100 times faster than the Knudsen model for diffusion of gases, and more than 1,000 times faster than theory would predict for the hydrodynamic flow of water. However, the flow of water was in accord with molecular dynamic calculations, which predict a flow of 12 water molecules per nanosecond through a 1nm hole. The rapid flow of water is promoted by "wires" of hydrogen-bonded molecules pulling themselves down a tube with an almost frictionless surface. Bakajin and Noy report their nanofluidics research in more detail in *Nano Today* (see A. Noy, *et al.*, 2[6]: 22-9, 2008).

These researchers are in fact the first to provide unambiguous *experimental* evidence of the remarkable flow of gas and water through carbon nanotube pores. Their new devices might well be important in two key areas: as models for cell membranes, which by their very nature must permit only selected molecules to pass through them; and as a method for desalinating seawater.

In this latter respect the LLNL team has been working on the transport of ions through nanotubes and have reported on this in the online edition of *PNAS,* (10.1073/pnas.0710437105). They placed negatively charged groups around the openings of the nanotubes and report that these restrict access by common ions like sodium. Ion exclusion was as high as 98% for highly charged ions. This ion blocking might well be the key to future desalination plants, which currently work on the basis of reverse osmosis, a process requiring enormous water pressures to make it effective. Lower-pressure desalination would have worldwide benefits.

5	D. Enders, *et al.*, "Control of four stereocentres in a triple cascade organocatalytic reaction," *Nature*, 441(7095): 861-3, 15 June 2006. [Aachen U., Germany] *052SL	14	8
6	P. Schreiner, *et al.*, "Many density functional theory approaches fail to give reliable large hydrocarbon isomer energy differences," *Organic Lett.*, 8(17): 3635-8, 17 August 2006. [U. Giessen, Germany; Princeton U., NJ; U. Gottingen, Germany] *072EJ	14	†
7	N. Tian, *et al.*, "Synthesis of tetrahexahedral platinum nanocrystals with high-index facets and high electro-oxidation activity," *Science*, 316 (5825): 732-5, 4 May 2007. [Xiamen U., China; Georgia Inst. Tech., Atlanta] *163RR	14	†
8	S.Z. Luo, *et al.*, "Functionalized chiral ionic liquids as highly efficient asymmetric organocatalysts for Michael addition to nitroolefins," *Angew. Chem.-Int. Ed.*, 45(19): 3093-7, 5 May 2006. [Chinese Acad. Sci., Beijing; Nankai U., Tianjin, China] *042MY	13	†
9	M. Rueping, A.P. Antonchick, T. Theissmann, "A highly enantioselective Brønsted acid catalyzed cascade reaction: Organocatalytic transfer hydrogenation of quinolines and their application in the synthesis of alkaloids," *Angew. Chem. Int. Ed.*, 45(22): 3683-6, 26 May 2006. [U. Frankfurt, Germany] *050DP	13	†
10	J.E. Green, *et al.*, "A 160-kilobit molecular electronic memory patterned at 1011 bits per square centimetre," *Nature*, 445 (7126): 414-7, 25 January 2007. [Caltech, Pasadena; U. Calif., Los Angeles; Ohio St. U., Columbus] *128WD	13	9

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The other area in which their discovery might well have a role is cell membrane simulation, but if that is to be effective, the carbon nanotubes will have to operate in a fluid medium. However, suspending carbon nanotubes in a liquid phase has so far defeated researchers, but now Bakajin and Noy have breached this barrier. They coated the nanotubes with an inorganic shell which allowed them to be transferred to the liquid, where the coating could be removed. What is equally remarkable is that the nanotubes still display their original electronic properties in the new medium—see A. B. Artyukhin, *et al.*, *International Journal of Nanotechnology,* 5(4-5): 488-96, 2008. For earlier work in this area consult: A.B. Artyukhin, *et al.*, *Nano Letters,* 6(9): 2080-5, 2006; and S.C.J. Huang, *et al.*, *Nano Letters*, 7(11): 3355-9, 2007.

Bakajin and Noy are optimistic about the future: "We believe that we can utilize the enhanced transport

properties of carbon nanotube pores to create the world's best membranes for new generations of separation technologies." I believe they may well be right.

Dr. John Emsley is based at the Department of Chemistry, Cambridge University, U.K.

Keywords: carbon nanotubes, Olgica Bakajin, Aleksandr Noy, carbon nanotube pores, water desalination, fast mass transport.

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