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WHAT'S HOT IN... CHEMISTRY, May/June 2010

Carbon and Silicon Behave Unexpectedly

by John Emsley

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The current Hot Ten is again replete with papers on graphene, of which there are five. Of these, #8 and #9 are new to the list and both report graphene nanoribbons which were produced by unzipping carbon nanotubes. The two methods produce materials of very different behavior, and they might open up new uses for graphene as electronic components, sensors, and even body implants. Depending on their width, graphene nanoribbons display either metallic conductivity or semiconductivity. Those less than 10 nanometers wide behave as semiconductors.

These papers appeared in the same issue of *Nature*, one report being from the group headed by Liying Jiao and Xinran Wang at Stanford University (#8) and the other from Dmitry Kosynkin and colleagues at Rice University, Houston, Texas (#9). The former group unzipped their nanotubes by means of plasma etching and then flattened them out to give tapes, while the latter group used chemical methods to make them, which involved treating the nanotubes with concentrated sulfuric acid followed by potassium permanganate.

What Kosynkin's paper delivers are nanoribbons several layers thick—they are produced from multi-walled nanotubes—and surprisingly they are soluble in both organic solvents and water. At the edge of these nanotubes are oxygen atoms, and it appears to be these which disrupt the flow of charge along the ribbon. When they were removed by chemical reduction, for example by heating in an atmosphere of hydrogen, the resulting ribbons behaved like metallic conductors, as might be expected for graphene.

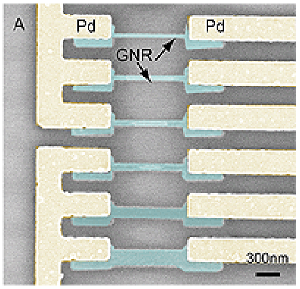
Jiao and Wang's method of opening up nanotubes was more like delicate surgery. They embedded them in a polymer film and then sliced them with an argon plasma, after which they were removed from the polymer and heated at 300oC. These nanoribbons could be as thin as a single layer and were consequently much narrower than Kosynkin's nanoribbons—and they were definitely not conductors but semiconductors.

Also in the current Hot Ten is paper #7 on a long-established semiconductor: silicon. This reports a way of making this versatile element behave as a thermoelectric material, in other words of having the ability to convert heat to electricity.

Generating electricity by conventional means results in a lot of energy being wasted; more than half ends up being lost to the environment as heat. If that energy could be tapped into, enormous benefits could accrue. Not that silicon has ever seemed a likely route to this because silicon is a good conductor of heat and so very unlikely to produce the necessary temperature gradient which thermoelectric devices must have.

And so it appeared until Allon Hochbaum and Renkun Chen of the University of California, Berkeley, showed that silicon could, in fact, display exactly this kind of behavior.

The researchers took silicon nanowires that were round and, by modifying them, observed thermoelectric efficiencies comparable to that of the best currently available: bismuth tellurium (Bi_2Te_3) and its alloys with antimony and selenium.



This figure of graphene nanoribbons is from an interview with Zhihong Chen, a scientist featured in the *ScienceWatch.com* Special Topic of Graphene.

Related: view a Research Front Map titled " Graphene Nanoribbons."

The silicon ones were made by inserting wafer-scale arrays of silicon nanowires into a bath of silver nitrate and hydrofluoric acid (HF). There the silver ions were reduced to silver atoms at the silicon surface, a process which creates a "hole" in the lattice, and this then acted as a site which the HF could attack and which produced a roughened surface. The residual silver atoms, which clustered as nanoparticles on the wires, were washed off by immersion in a bath of nitric acid.

The resulting "rough" silicon nanowires were 20 to 300 nanometers in diameter, and against all expectations they behave as thermoelectric materials. The thermal conductivity of this form of silicon was a hundred times less than conventional silicon for reasons yet unexplained.

A related paper from Hochbaum and Chen (*Physical Review Letters,* 101: no. 105501, 2008) reports their observations of thin silicon wires at low temperatures. They graphically describe the range of conductance behavior as varying from "the nearly ballistic to the completely diffusive."

Clearly there are still things to be learned about the two elements which come at the head of group 14 of the periodic table.

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

Chemistry Top 10 Papers

Rank	Paper	Citations This Period (Nov-Dec 09)	Rank Last Period (Sep-Oct 09)
1	Y. Kamihara, *et al.*, **"Iron-based layered superconductor La[$O_{1-x}F_x$]FeAs (x = 0.05-0.12) with T_c = 26 K,"** *J. Am. Chem. Soc.*, 130(11): 3296-7, 19 March 2008. [Tokyo Inst. Technol., Yokohama, Japan] *273SL	102	1
2	X.L. Li, *et al.*, **"Chemically derived, ultrasmooth graphene nanoribbon semiconductors,"** *Science*, 319(5867): 1229-32, 29 February 2008. [Stanford U., CA] *267SX	44	3
3	C. de la Cruz, *et al.*, **"Magnetic order close to superconductivity in the iron-based layered $LaO_{1-x}F_x$ FeAs systems,"** *Nature*, 453(7197): 899-902, 12 June 2008. [6 U.S. and China institutions] *311WV	40	2
4	D.C. Elias, *et al.*, **"Control of graphene's properties by reversible hydrogenation: Evidence for graphane,"** *Science*, 323 (5914): 610-3, 30 January 2009. [U. Manchester, U.K.; Inst. Microelectronics Tech., Chernogolovka, Russia; Cambridge U., U.K.; U. Nijmegen, Netherlands] *400JB	32	6
5	C. Lee, *et al.*, **"Measurement of the elastic properties and intrinsic strength of monolayer graphene,"** *Science*, 321(5887): 385-8, 18 July 2008. [Columbia U., New York, NY] *327FB	31	4
6	H. Takahashi, *et al.*, **"Superconductivity at 43 K in an iron-based layered compound $LaO_{1-x}F_x$ FeAs,"** *Nature*, 453(7193): 376-8, 15 May 2008. [Nihon U., Tokyo, Japan; Tokyo Inst. Technol., Japan] *301AI	29	5
7	A.I. Hochbaum, *et al.*, **"Enhanced thermoelectric performance of rough silicon nanowires,"** *Nature*, 451(7175): 163-7, 10 January 2008. [U. Calif., Berkeley; Lawrence Berkeley Natl. Lab., CA] *249GA	28	†
8	L.Y. Jiao, *et al.*, **"Narrow graphene nanoribbons from carbon nanotubes,"** *Nature*, 458(7240): 877-80, 16 April 2009. [Stanford U., CA] *433CS	24	†
9	D.V. Kosynkin, *et al.*, **"Longitudinal unzipping of carbon nanotubes to form graphene nanoribbons,"** *Nature*, 458(7240): 872-6, 16 April 2009. [Rice U., Houston, TX] *433CS	24	†
10	R. Banerjee, *et al.*, **"High-throughput synthesis of zeolitic imidazolate frameworks and application to CO_2 capture,"** *Science,* 319(5865): 939-43, 15 February 2008. [U. Calif., Los Angeles; Arizona St. U., Tempe] *262RM	22	†

SOURCE: Thomson Reuters Hot Papers Database. Read the Legend.

KEYWORDS: Graphene, graphene nanoribbons, carbon nanotubes, Dmitry Kosynkin, Liying Jiao, Xinran Wang, silicon nanowires, Allon Hochbaum, Renkun Chen.

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