Zinc Oxide and Metal Dyes: The Energy Plants of the Future?

by John Emsley

If a significant proportion of the world's demand for electricity is to be met in sustainable ways, it will have to include better photovoltaic solar cells. Most solar cells today are made of ultra-pure silicon, which is not ideal because it is expensive and its surface decays at 1% per year. The search for alternatives is coming up with some remarkable materials, including organic polymers, but ones that are exciting particular interest are based on dye molecules that, like nature's own energy converter, chlorophyll, can capture a photon of light and kick an electron into action. Such cells are known as dye-sensitized cells (DSCs).

Michael Grätzel at the Swiss Federal Technology Institute of Lausanne made the first DSC in 1991. It relied on a ruthenium complex to activate electrons which were passed to a thin layer of titanium dioxide nanoparticles and thence to an electrode. In theory, DSCs are potentially

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Rank	Paper	Citations This Period (Mar-Apr 07)	Rank Last Period (Jan-Feb 07)
1	M. Law, *et al.*, **"Nanowire dye-sensitized solar cells,"** *Nature Materials*, 4 (6): 455-9, June 2005. [U. Calif., Berkeley; Lawrence Berkeley Natl. Lab., CA] *931RL	25	5
2	B.L. Chen, *et al.*, **"High H_2 adsorption in a microporous metal-organic framework with open metal sites,"** *Angew. Chem.-Int. Ed.*, 44 (30): 4745-9, 25 July 2005. [U Texas-Pan American, Edinburg; U. Michigan, Ann Arbor] *951HX	22	†
3	Z.L. Wang, J. Song, **"Piezoelectric nanogenerators based on zinc oxide nanowire arrays,"** *Science*, 312 (5771): 242-6, 14 April 2006. [Georgia Inst. Tech., Atlanta; Peking U., Beijing, China] *032HK	19	8

very versatile because, like the leaves of plants, they can absorb light coming from all directions and so don't need to be in direct sunlight. Unlike leaves, however, DSCs tend to be inefficient when it comes to utilizing the electrons they activate.

Paper #1 is a major step forward in solving this problem. The DSC it reports has the dye absorbed onto a close-packed array of zinc oxide nanowires, which gets over this problem of "lost" electrons. The report comes from the group headed by Peidong Yang and based in the Department of Chemistry at the University of California, Berkeley, and the Lawrence Berkeley National Laboratory. This is not the first time that Yang has graced the pages of *Science Watch.* Two summers ago we reported on his noteworthy work with gallium nitride nanotubes (16[3]: 7, May/June 2005), and a couple years before that we reported on his research into zinc oxide (ZnO) nanolasers (13[6]: 7, November/December 2002).

Now Yang has turned his attention to another aspect of ZnO in the form of nanowires. These are used to create direct electrical pathways which ensure the rapid collection of the electrons and holes that are generated by the dye molecules, and thereby achieve an efficiency

4	P.X. Gao, *et al.*, **"Conversion of zinc oxide nanobelts into superlattice-structured nanohelices,"** *Science*, 309 (5741): 1700-4, 9 September 2005. [Georgia Inst. Tech., Atlanta; Peking U., China; Natl. Ctr. Nanosci. & Nanotech., Beijing, China] *963WK	17	10
5	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	17	†
6	G. Ferey, *et al.*, **"A chromium terephthalate-based solid with unusually large pore volumes and surface area,"** *Science*, 309(5743): 2040-2, 23 September 2005. (U. Versailles, France; Inst. U. de France, Paris; Royal Inst., London, U.K.; European Radiat. Synchrotron Facility, Grenoble, France] *968SF	16	†
7	X. Huang, *et al.*, *et al.*, **"Cancer cell imaging and photothermal therapy in the near-infrared region by using gold nanorods,"** *J. Am. Chem. Soc.*, 128(6): 2115-20, 15 February 2006. [Georgia Inst. Tech., Atlanta; U. Calif., San Francisco] *014AX	16	†
8	M. Dinca, J.R. Long, **"Strong H_2 binding and selective gas adsorption within the microporous coordination solid $Mg_3(O_2C\text{-}C_{10}H_6\text{-}CO_2)_3$,"** *J. Am. Chem. Soc.*, 127(26): 9376-7, 6 July 2005. [U. Calif., Berkeley] *941NG	14	†

9	X.D. Shi, *et al.*, **"Synthesis of 2-cyclopentenones by gold(I)-catalyzed Rautenstrauch rearrangement,"** *J. Am. Chem. Soc.*, 127(16): 5802-3, 27 April 2005. [U. Calif., Berkeley] *919FB	13	†
10	M.J. Earle, *et al.*, **"The distillation and volatility of ionic liquids,"** *Nature*, 439(7078): 831-4, 16 February 2006. [Queen's U. Belfast, U.K.; U. Nova de Lisboa, Portugal; NIST, Boulder, CO] *012JA	13	†

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of 1.5% when exposed to the equivalent of direct sunlight.

The nanowire arrays were grown from a film of ZnO quantum dots deposited on a substrate of fluorine tin oxide glass (FTO) and then immersed in a hot (92 degrees C) aqueous solution of zinc nitrate, hexamethylenetetramine, and polyethylenimine for 2.5 hours. This produces an array of 35 billion wires per square cm, and these are 16 µm in diameter and 130-200 nm long. They are then baked in air at 400 degrees C for 30 minutes. The dye molecules are a complex of ruthenium and 2,2'-bipyridine-4,4'-dicarboxylic acid, and this is deposited on the nanowires by means of an ethanol solution of this ligand.

The DSC arrays are then sandwiched between platinized FTO electrodes and the internal space of the cell filled with a liquid electrolyte. This consists of lithium iodide, iodine, and 4-terbutylpyridine dissolved in 3-methoxypropionitrile as the solvent. (A fuller account of the work has been published in M. Law, *et al.*, *J. Phys. Chem. B*, 110[45]: 22652-63, 2006.) Yang is now working on a nanowire-based cell in which the liquid electrolyte is replaced with a solid one which has either a polymer or an inorganic electron absorber.

The commercial potential of DSC cells is enormous. Those that are currently being manufactured are based on titanium dioxide, but this has many drawbacks, not least of which is its disordered topography. So what of the future? Yang has no doubt that nanowire DSCs are the key to success: "By optimizing the light absorption, charge separation, as well as charge transport, the nanowire-based solar cell represents an ideal design for a low-cost solar cell with better efficiency."

Clearly the next step is to raise the efficiency of such cells by increasing the surface area of the nanowires, the better to absorb a higher concentration of dye molecules. There is a long way to go yet, but paper #1 shines a powerful beam showing the way to the future.■

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