Nanoscience Seminar Series

DNA Origami

Paul W.K. Rothemund
California Institute of Technology

Abstract: A key goal for bottom-up nanofabrication has been to generate structures whose complexity matches that achieved by top-down methods. Towards this goal, DNA nanotechnology provides an attractive route. Here I describe a method for folding long single strands of DNA into arbitrary two dimensional target shapes using a raster fill technique. Self-assembled in a one-pot reaction from the 7 kilobase genome of phage M13mp18 and more than 200 synthetic oligodeoxynucleotides, the shapes are roughly 100 nm in diameter and nearly 5 megadaltons in mass. (For comparison the eukaryotic ribosome, one of nature’s most complex molecular machines, is 4.2 megadaltons in mass.) Experimental shapes approximate target shapes, such as a 5-pointed star, with a resolution of 3.5 to 5 nm and may be decorated by arbitrary patterns at 6 nm resolution to form words or images. Enabled by a program for laying out complicated designs and, utilizing inexpensive unpurified oligodeoxynucleotides, this method helps move DNA nanotechnology from the realm of research towards that of engineering. The ability to create arbitrary shapes provides a new route to the bottom-up nanofabrication of complex nano-scale devices and instruments. Physicists and materials scientists should be able to use DNA origami to arrange optical, electronic, and mechanical components into novel materials or even an integrated “nanolaboratory” of their choosing. Biologists may be able to use these structures to position proteins and other biomolecules in precise arrangements to study their coupling. Indeed these structures may be thought of as a versatile “nanobreadboard”, a simple platform for creating arbitrary nanostructures.

Bio: Paul WK. Rothemund is a graduate of Caltech, where he dual majored in biology and computer science. His undergraduate project in information theory was one of the first designs for a DNA computer, and became one of the first patents for DNA computation. Dr. Rothemund works as a research fellow in Caltech’s Center for the Physics of Information.

Tuesday, February 21, 2006
CIEMAS Auditorium B
2:50 p.m.
NanoMaterials, introduction

- Carbon nanotubes
  - MWCNT
  - SWCNT

- Nanoparticles
  - Material: Metal, Semiconductor
  - Size, shape, multi-layer

- Crystalline nanowires
  - Metal
  - Semiconductor

- Polymers
Carbon Nanotubes, electronics

Synthesis: arc, CVD, laser

ELECTRICAL PROPERTIES of a material depend on the separation between the collection of energy states that are filled by electrons (red) and the additional “conduction” states that are empty and available for electrons to hop into (light blue). Metals conduct electricity easily because there are so many electrons with easy access to adjacent conduction states. In semiconductors, electrons need an energy boost from light or an electrical field to jump the gap to the first available conduction state. The form of carbon known as graphite is a semimetal that just barely conducts, because without these external boosts, only a few electrons can access the narrow path to a conduction state.
CNT, electronics

STRAIGHT NANOTUBES look like a straight swath cut from a sheet of graphite (left) and rolled into a tube (center). The geometry of nanotubes limits electrons to a select few slices of graphite's energy states (right). Depending on the diameter of the tube, one of these slices can include the narrow path that joins electrons with conduction states. This special point, called the Fermi point, makes two thirds of the nanotubes metallic. Otherwise, if the slices miss the Fermi point, the nanotubes semiconduct.

TWISTED NANOTUBES, cut at an angle from graphite (left), look a bit like barbershop poles (center). The slices of allowed energy states for electrons (right) are similarly cut at an angle, with the result that about two thirds of twisted tubes miss the Fermi point and are semiconductors.
<table>
<thead>
<tr>
<th>PROPERTY</th>
<th>SINGLE-WALLED NANOTUBES</th>
<th>BY COMPARISON</th>
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<tbody>
<tr>
<td>Size</td>
<td>0.6 to 1.8 nanometer in diameter</td>
<td>Electron beam lithography can create lines 50 nm wide, a few nm thick</td>
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<td>Density</td>
<td>1.33 to 1.40 grams per cubic centimeter</td>
<td>Aluminum has a density of 2.7 g/cm³</td>
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<td>Tensile Strength</td>
<td>45 billion pascals</td>
<td>High-strength steel alloys break at about 2 billion Pa</td>
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<td>Resilience</td>
<td>Can be bent at large angles and restraightened without damage</td>
<td>Metals and carbon fibers fracture at grain boundaries</td>
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<tr>
<td>Current Carrying Capacity</td>
<td>Estimated at 1 billion amps per square centimeter</td>
<td>Copper wires burn out at about 1 million A/cm²</td>
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<td>Field Emission</td>
<td>Can activate phosphors at 1 to 3 volts if electrodes are spaced 1 micron apart</td>
<td>Molybdenum tips require fields of 50 to 100 V/µm and have very limited lifetimes</td>
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<td>Heat Transmission</td>
<td>Predicted to be as high as 6,000 watts per meter per kelvin at room temperature</td>
<td>Nearly pure diamond transmits 3,320 W/m-K</td>
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<td>Temperature Stability</td>
<td>Stable up to 2,800 degrees Celsius in vacuum, 750 degrees C in air</td>
<td>Metal wires in microchips melt at 600 to 1,000 degrees C</td>
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<td>Cost</td>
<td>$1,500 per gram from Bucky USA in Houston</td>
<td>Gold was selling for about $10/g in October</td>
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# Other Uses for Nanotubes

## Beyond Electronics

<table>
<thead>
<tr>
<th>THE IDEA</th>
<th>OBSTACLES</th>
<th>FEASIBILITY</th>
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<td><strong>Chemical and Genetic Probes</strong></td>
<td>A nanotube-tipped atomic force microscope can trace a strand of DNA and identify chemical markers that reveal which of several possible variants of a gene is present in the strand. This is the only method yet invented for imaging the chemistry of a surface, but it is not yet used widely. So far it has been used only on relatively short pieces of DNA.</td>
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<td><strong>Mechanical Memory</strong></td>
<td>A screen of nanotubes laid on support blocks has been tested as a binary memory device, with voltages forcing some tubes to connect (the &quot;on&quot; state) and others to separate (the &quot;off&quot; state). The switching speed of the device was not measured, but the speed limit for a mechanical memory is probably around one megahertz, which is much slower than conventional memory chips.</td>
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<td><strong>Nanotweezers</strong></td>
<td>Two nanotubes, attached to electrodes on a glass rod, can be opened and closed by changing voltage. Such tweezers have been used to pick up and move objects that are 500 nanometers in size. Although the tweezers can pick up objects that are large compared with their width, nanotubes are so sticky that most objects can't be released. And there are simpler ways to move such tiny objects.</td>
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<td><strong>Supersensitive Sensors</strong></td>
<td>Semiconducting nanotubes change their electrical resistance dramatically when exposed to alkaloids, halogens and other gases at room temperature, raising hopes for better chemical sensors. Nanotubes are exquisitely sensitive to so many things (including oxygen and water) that they may not be able to distinguish one chemical or gas from another.</td>
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<td><strong>Hydrogen and Ion Storage</strong></td>
<td>Nanotubes might store hydrogen in their hollow centers and release it gradually in efficient and inexpensive fuel cells. They can also hold lithium ions, which could lead to longer-lived batteries. So far the best reports indicate 6.5 percent hydrogen uptake, which is not quite dense enough to make fuel cells economical. The work with lithium ions is still preliminary.</td>
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<td><strong>Sharper Scanning Microscope</strong></td>
<td>Attached to the tip of a scanning probe microscope, nanotubes can boost the instruments' lateral resolution by a factor of 50 or more, allowing clearer views of proteins and other large molecules. Although commercially available, each tip is still made individually. The nanotube tips don't improve vertical resolution, but they do allow imaging deep pits in nanostructures that were previously hidden.</td>
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<td><strong>Superstrong Materials</strong></td>
<td>Embedded into a composite, nanotubes have enormous resilience and tensile strength and could be used to make cars that bounce in a wreck or buildings that sway rather than crack in an earthquake. Nanotubes still cost 10 to 1,000 times more than the carbon fibers currently used in composites. And nanotubes are so smooth that they slip out of the matrix, allowing it to fracture easily.</td>
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Nanoparticles

- "0D nanostructures"
- Nanocrystals
- Nanospheres
- Quantum dots
- Core-shell nanoparticles
Nanoparticles

Fig. 2. Gallery of quantum dot structures. (A) Positions of Cd and S atoms in the molecular cluster Cd$_{32}$S$_{26}$, as determined by single-crystal x-ray diffraction. This cluster is a small fragment of the bulk CdS zinc blende lattice. The organic ligands on the surface are omitted for clarity. [Reprinted from (29) with permission] (B and C) Transmission electron micrographs of CdSe nanocrystals with hexagonal structure.

Fig. 1. (A) Schematic illustration of the density of states in metal and semiconductor clusters. (B) Density of states in one band of a semiconductor as a function of dimension.
Nanoparticles, metal replacement

- Geometric crystals
- Metal replacement
- Solvothermal, etc.

Shape-Controlled Synthesis of Gold and Silver Nanoparticles, Yugang Sun and Younan Xia,
13 DECEMBER 2002 VOL 298 SCIENCE pp 2176
Onset of Catalytic Activity of Gold Clusters on Titania with the Appearance of Nonmetallic Properties

M. Valden,* X. Lai, D. W. Goodman†

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2/28/06 LaBean COMPSCI 296.5

- “Noble” metal catalyst.
- Nano size changes properties.

Fig. 1. CO oxidation turnover frequencies (TOFs) at 300 K as a function of the average size of the Au clusters supported on a high surface area TiO₂ support (7). The Au/TiO₂ catalysts were prepared by deposition-precipitation method, and the average cluster diameters were measured by TEM. The solid line serves merely to guide the eye.
Nanoparticles and DNA

Nanowires

- “1D nanostructures”
- Advantages of miniaturization
  - Lower cost, higher speed, lower power consumption, lower heat generation
- New phenomena
  - Ballistic conductance, size-dependent excitation or emission, Coulomb blockade (SET), metal insulator transition
- In situ fabrication (e-beam, FIB, X-ray or EUV litho.) vs chemical synthesis and assembly
NW, synthesis

Fig. 1. Schematic illustrations of six different strategies that have been demonstrated for achieving 1D growth: a) dictation by the anisotropic crystallographic structure of a solid; B) confinement by a liquid droplet as in the vapor-liquid-solid process; C) direction through the use of a template; D) kinetic control provided by a capping reagent; E) self-assembly of 0D nanostructures; and F) size reduction of a 1D microstructure.

Fig. 6. Schematic illustrations of procedures that generated 1D nanostructures by A) shadow evaporation [58]; B) reconstruction at the bottom of V-grooves [60]; C) cleaved-edge overgrowth on the cross-section of a multilayer film [64]; and D) templating against step edges on the surface of a solid substrate [68].

Fig. 7. Schematic drawings illustrating the formation of nanowires and nanotubes by filling and partial filling the pores within a porous membrane with the desired material or a precursor to this material [70, 79].
Nanowires, crystal lattice

Fig. 10. A) TEM image of a TiO$_2$/SnO$_2$ nanotape obtained through epitaxial growth of TiO$_2$ on a single-crystalline SnO$_2$ nanobelt. B) A high-resolution TEM image of the atomically sharp TiO$_2$/SnO$_2$ interface. The fringe spacings of 4.64 and 4.84 Å correspond to the interplanar distances between the (010) planes of TiO$_2$ and SnO$_2$ (in the rutile structure), respectively. The insets show electron diffraction patterns taken from each side of the interface along the same zone axes of [101]. C) Compositional line profile across the TiO$_2$/SnO$_2$ interface in the direction perpendicular to the long axis of the nanotape [104].
Nanowires, metal replacement

Fig. 11. A) SEM images of Pd nanotubes generated by reacting silver nanowires with an aqueous Pd(NO₃)₂ solution. The nanotubes were broken via sonication for a few minutes to expose their cross-sections. B) A TEM image of Au nanotubes prepared by reacting silver nanowires with an aqueous HAuCl₄ solution. The inset shows a high-resolution TEM image of the edge of an individual gold nanotube, indicating its highly crystalline structure and uniformity in wall thickness [112].