Nanoscience Seminar Series

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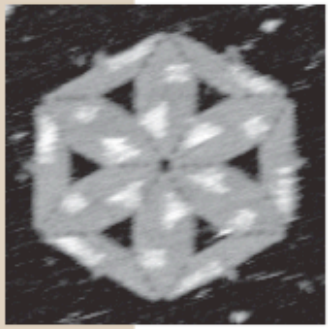
DNA Origami

Paul W.K. Rothemund

California Institute of Technology



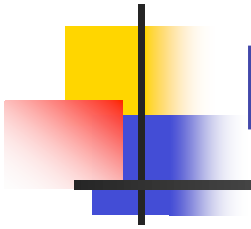
Abstract: A key goal for bottom-up nanofabrication has been to generate structures whose complexity matches that achieved by top-down methods. Towards this goal, DNA nanotechnology provides an attractive route. Here I describe a method for folding long single strands of DNA into arbitrary two dimensional 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 6 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 "nano-laboratory" 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 W.K. 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

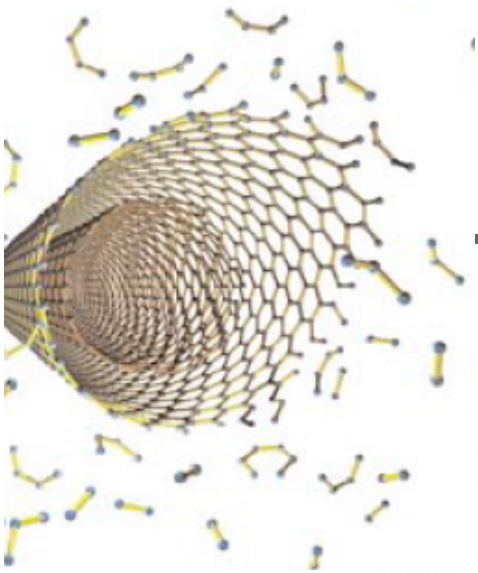
2:50 p.m.



NanoMaterials, introduction

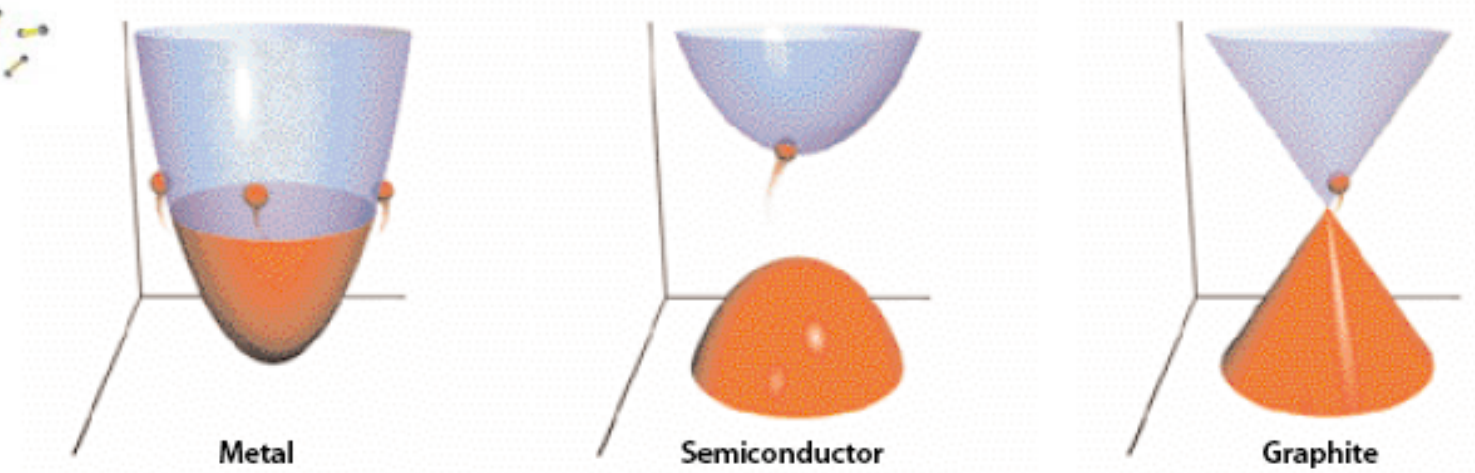
- Carbon nanotubes
  - MWCNT
  - SWCNT
- Nanoparticles
  - Material: Metal, Semiconductor
  - Size, shape, multi-layer
- Crystalline nanowires
  - Metal
  - Semiconductor
- Polymers

Carbon Nanotubes, electronics



Synthesis: arc, CVD, laser

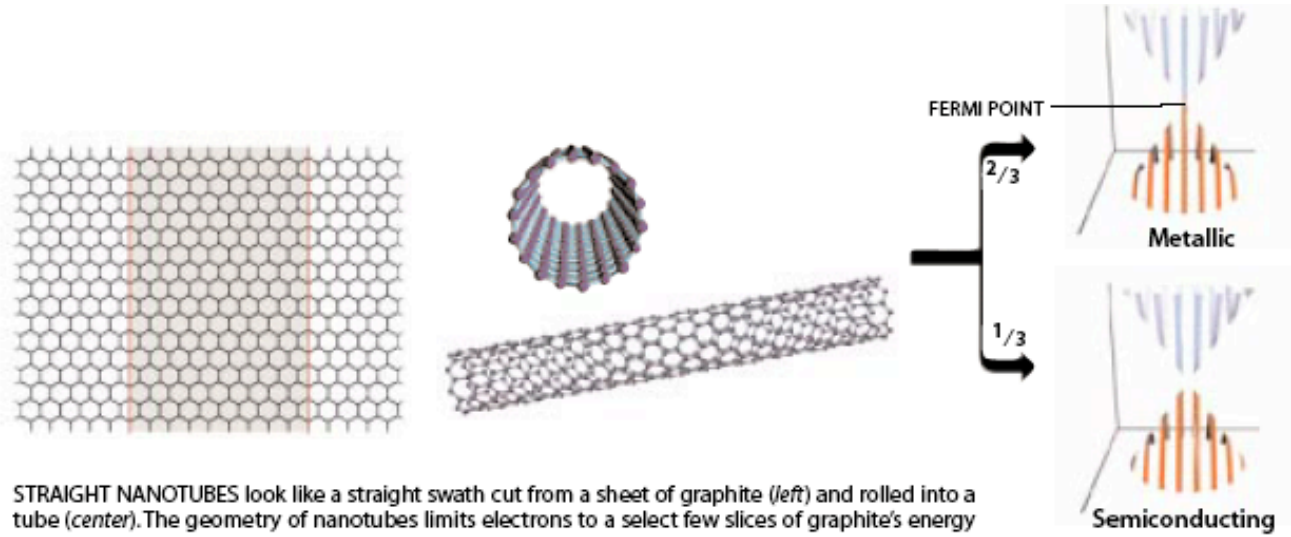
Philip G. Collins and Phaedon Avouris
SCIENTIFIC AMERICAN December 2000



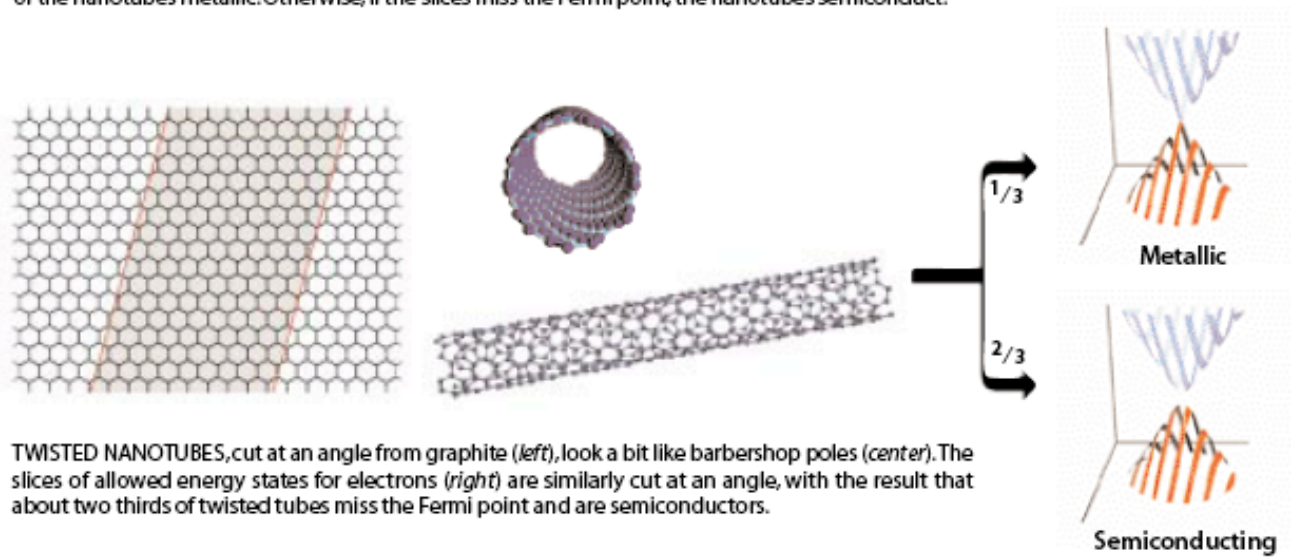
ELECTRICAL PROPERTIES of a material depend on the separation between the collection of energy states that are filled by electrons (*red*) and the additional "conduction" states that are empty and available for electrons to hop into (*light blue*). Metals conduct electricity easily because there are so 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

Philip G. Collins and Phaedon Avouris
SCIENTIFIC AMERICAN December 2000



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.

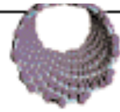
CNT

PROPERTY	SINGLE-WALLED NANOTUBES	BY COMPARISON
 Size	0.6 to 1.8 nanometer in diameter	Electron beam lithography can create lines 50 nm wide, a few nm thick
 Density	1.33 to 1.40 grams per cubic centimeter	Aluminum has a density of 2.7 g/cm³
 Tensile Strength	45 billion pascals	High-strength steel alloys break at about 2 billion Pa
 Resilience	Can be bent at large angles and restraightened without damage	Metals and carbon fibers fracture at grain boundaries
 Current Carrying Capacity	Estimated at 1 billion amps per square centimeter	Copper wires burn out at about 1 million A/cm²
 Field Emission	Can activate phosphors at 1 to 3 volts if electrodes are spaced 1 micron apart	Molybdenum tips require fields of 50 to 100 V/μm and have very limited lifetimes
 Heat Transmission	Predicted to be as high as 6,000 watts per meter per kelvin at room temperature	Nearly pure diamond transmits 3,320 W/m·K
 Temperature Stability	Stable up to 2,800 degrees Celsius in vacuum, 750 degrees C in air	Metal wires in microchips melt at 600 to 1,000 degrees C
 Cost	$1,500 per gram from Bucky USA in Houston	Gold was selling for about $10/g in October

LAURIE GRACE

Philip G. Collins and Phaedon Avouris
SCIENTIFIC AMERICAN December 2000

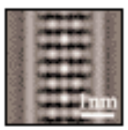
CNT



Other Uses for Nanotubes

Beyond Electronics

Feasibility Ratings
0 = Science Fiction
2 = Demonstrated
4 = Ready for Market

		THE IDEA	OBSTACLES	FEASIBILITY
	**Chemical and Genetic Probes** Tagged strand of DNA	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.	3
	**Mechanical Memory** Nonvolatile RAM	A screen of nanotubes laid on support blocks has been tested as a binary memory device, with voltages forcing some tubes to contact (the "on" state) and others to separate (the "off" 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.	2
	**Nanotweezers** Pincers five microns long	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.	2
	**Supersensitive Sensors** Oxygen sticks to tubes	Semiconducting nanotubes change their electrical resistance dramatically when exposed to alkalis, 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.	3
	**Hydrogen and Ion Storage** Atoms in hollow core	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.	1
	**Sharper Scanning Microscope** Individual IgM antibodies	Attached to the tip of a scanning probe microscope, nanotubes can boost the instruments' lateral resolution by a factor of 10 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.	4
	**Superstrong Materials** Nanotube stress test	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.	0

Compiled by W. Wayt Gibbs, staff writer

Nanoparticles

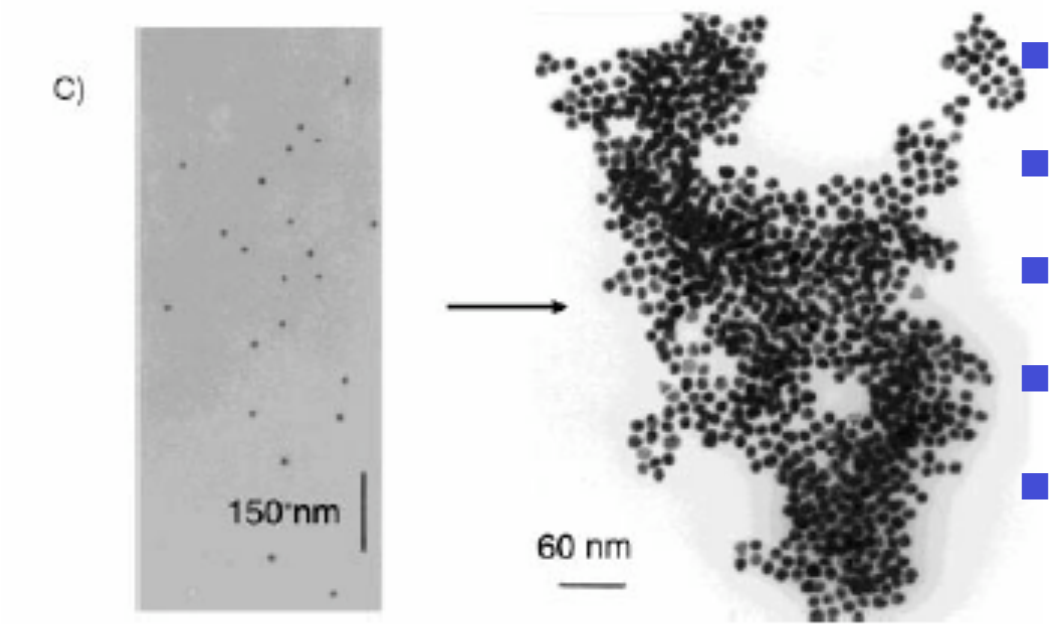


Figure 6. Cross-linking of Ag and Au nanoparticles functionalized with IgG molecules. Bivalent linkers with two terminal hapten groups, either monospecific 8 or bispecific 9, allow the directed assembly of homo-oligomeric (A) or heterodimeric (B) aggregates, respectively. The TEM images (C) were obtained from colloidal Au/antibody aggregates before (left) and after (right) the addition of linker 8. (Reproduced, with permission, from ref. [34].)

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

Nanoparticles

A. P. Alivisatos
SCIENCE • VOL. 271 • 16 FEBRUARY 1996

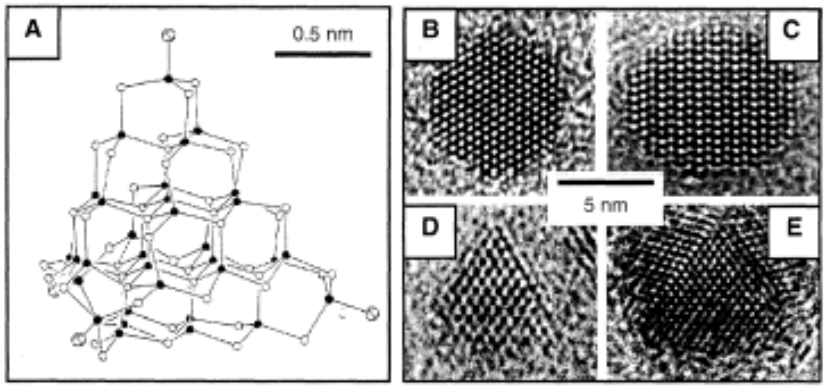


Fig. 2. Gallery of quantum dot structures. (**A**) Positions of Cd and S atoms in the molecular cluster $Cd_{32}S_{55}$, as determined by single-crystal x-ray diffraction. This cluster is a small fragment of the bulk CdS zinc blende lattice. The organic ligands on the surface are omitted for clarity. [Reprinted from (29) with permission] (**B** and **C**) Transmission electron micrographs of CdSe nanocrystals with hexagonal struc-

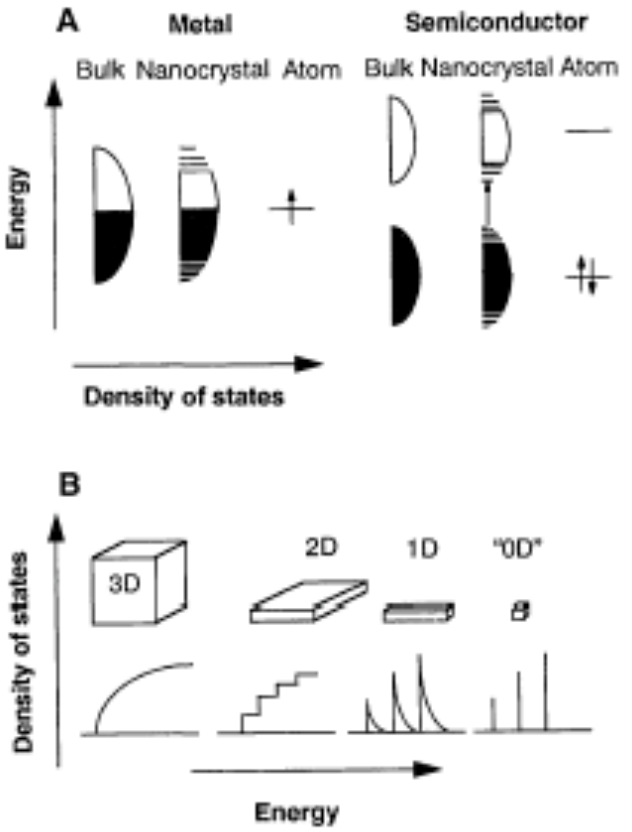


Fig. 1. (**A**) Schematic illustration of the density of states in metal and semiconductor clusters. (**B**) Density of states in one band of a semiconductor as a function of dimension.

Nanoparticles, metal replacement

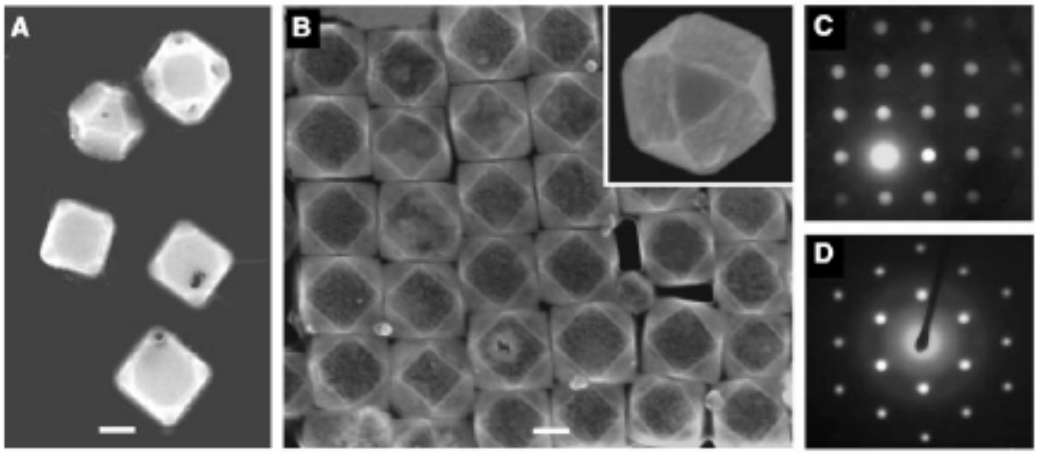


Fig. 3. SEM images of silver nanocubes (Fig. 1) after they had reacted with (A) 0.3 ml and (B) 1.5 ml of aqueous $HAuCl_4$ solution (1 mM). As indicated by the black spots in (A), the {111} facets of gold nanoboxes were incompletely closed in the early stages of this replacement reaction, when $HAuCl_4$ was in deficiency (as calculated from the stoichiometric equation). If excess $HAuCl_4$ solution was added [as in (B)], the area of {111} facets could increase up to a maximum value at the expense of {100} and {110} facets. (C and D) Electron diffraction patterns of two gold nanoboxes with their square and triangular facets oriented perpendicular to the electron beam, respectively. Scale bars, 100 nm.

Shape-Controlled Synthesis of Gold and Silver Nanoparticles, Yugang Sun and Younan Xia, 13 DECEMBER 2002 VOL **298** *SCIENCE* pp 2176

- Geometric crystals
- Metal replacement
- Solvothermal, etc.

Onset of Catalytic Activity of Gold Clusters on Titania with the Appearance of Nonmetallic Properties

M. Valden,* X. Lai, D. W. Goodman†

SCIENCE VOL 281 11 SEPTEMBER 1998

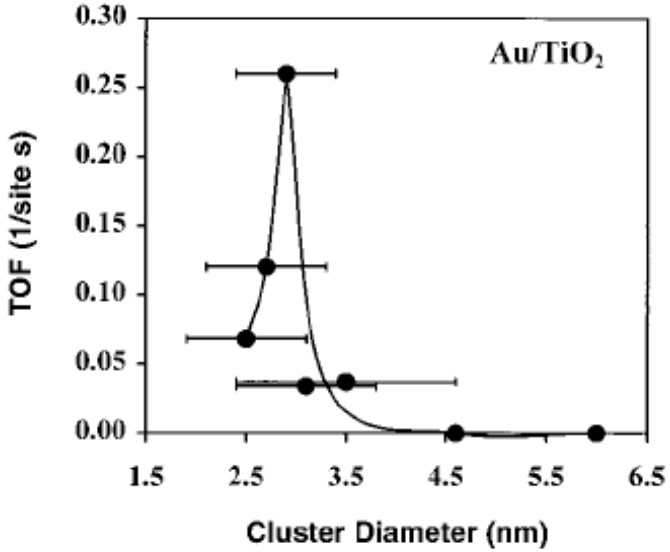
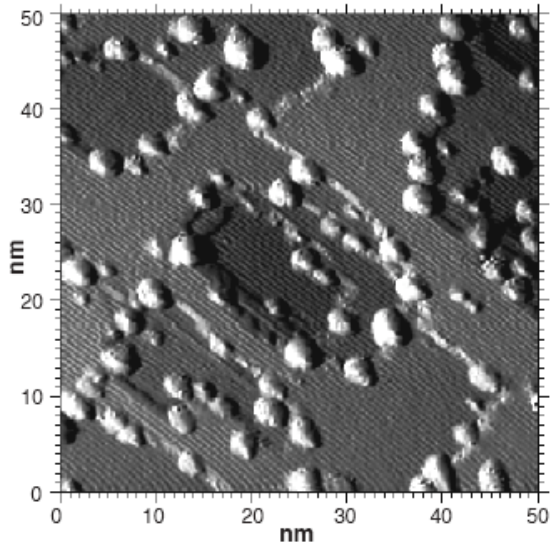
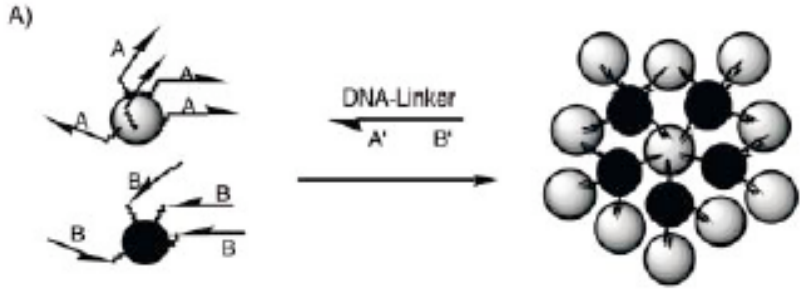


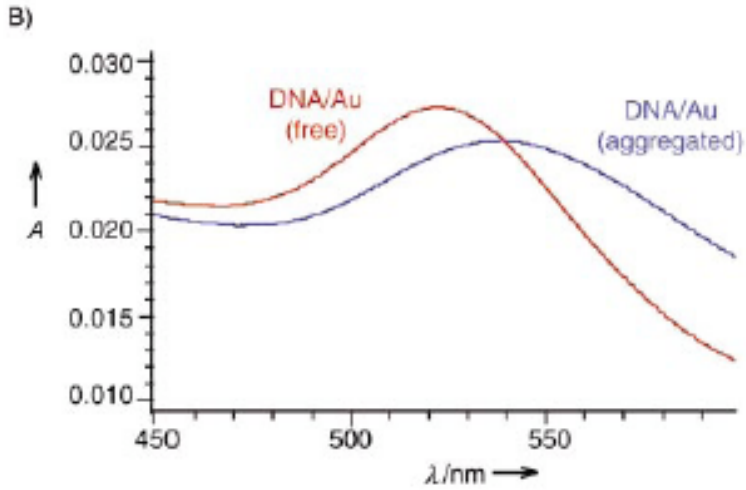
Fig. 1. CO oxidation turnover frequencies (TOFs) at 300 K as a function of the average size of the Au clusters supported on a high surface area TiO_2 support (7). The Au/TiO_2 catalysts were prepared by deposition-precipitation method, and the average cluster diameters were measured by TEM. The solid line serves merely to guide the eye.

- "Noble" metal catalyst.
- Nano size changes properties.



Nanoparticles and DNA





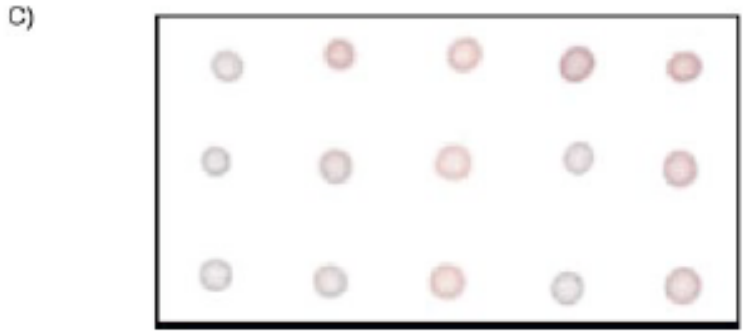
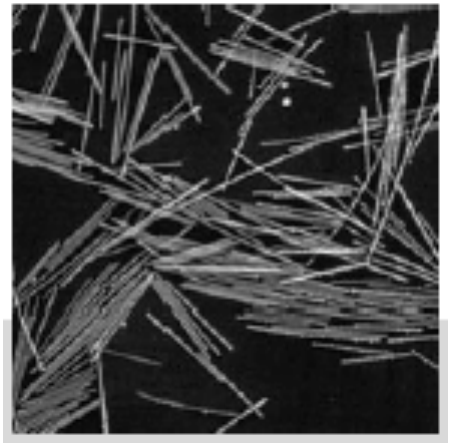


Figure 9. Assembly of gold colloids by using DNA hybridization. A) Two batches of gold particles are derivatized with noncomplementary oligonucleotides, either through 5′- or 3′-thiol groups. The nanoparticles are oligomerized by using a single-stranded nucleic acid linker molecule. Network formation leads to a characteristic change in the plasmon absorption (B). The color change can be used to macroscopically detect DNA hybridization by using an assay in which DNA/Au conjugates and a sample with potential target DNA is spotted on a hydrophobic membrane (C). Red spots indicate the absence of fully matched DNA, whereas blue spots are indicative of complementary target DNA. (Data in C are reproduced, with permission, from ref. [89]. Copyright 1999 American Chemical Society.)

J. Storhoff, C. A. Mirkin, *Chem. Rev.* 1999, **99**, 1849 - 1862.

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

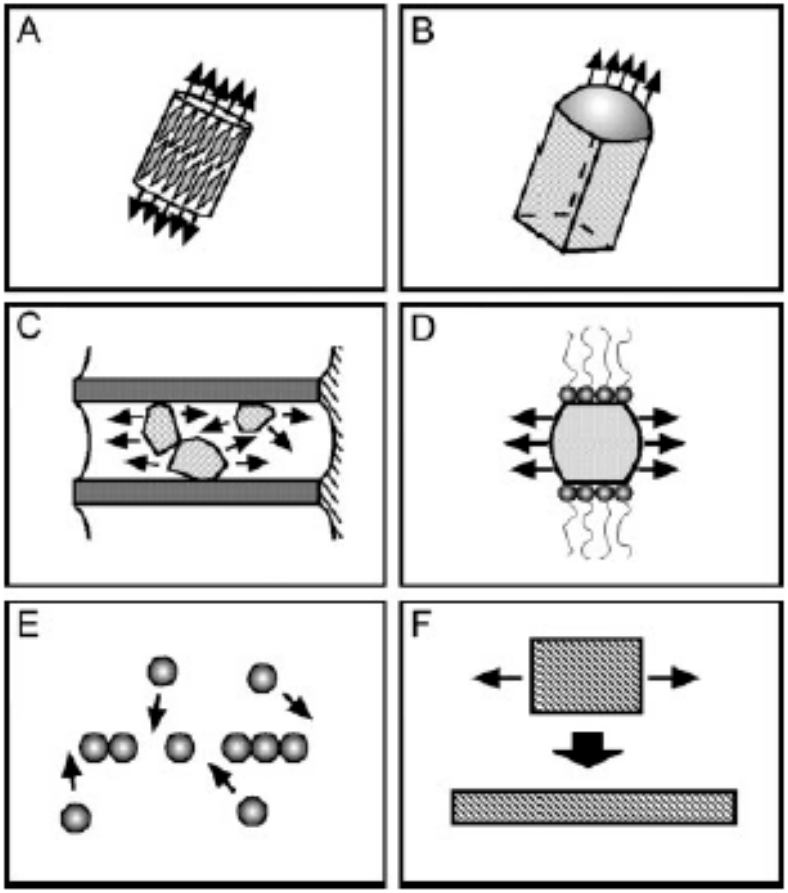


Fig. 1. Schematic illustrations of six different strategies that have been demonstrated for achieving 1D growth: a) dictation by the anisotropic crystallographic structure of a solid; B) confinement by a liquid droplet as in the vapor–liquid–solid process; C) direction through the use of a template;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

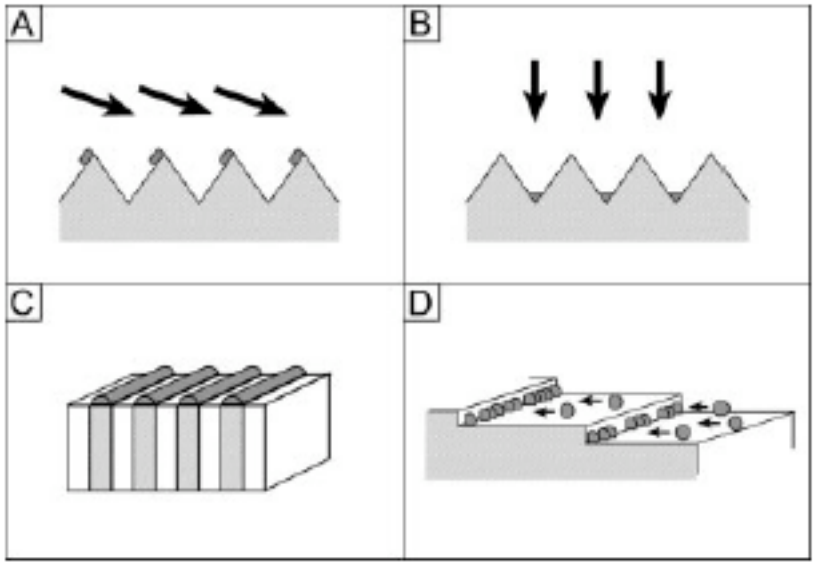


Fig. 6. Schematic illustrations of procedures that generated 1D nanostructures by A) shadow evaporation [58]; B) reconstruction at the bottom of V-grooves [60]; C) cleaved-edge overgrowth on the cross-section of a multilayer film [64]; and D) templating against step edges on the surface of a solid substrate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

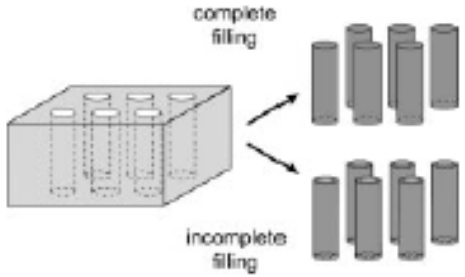


Fig. 7. Schematic drawings illustrating the formation of nanowires and nanotubes by filling and partial filling the pores within a porous membrane with the desired material or a precursor to this material [70,79].

Nanowires, crystal lattice

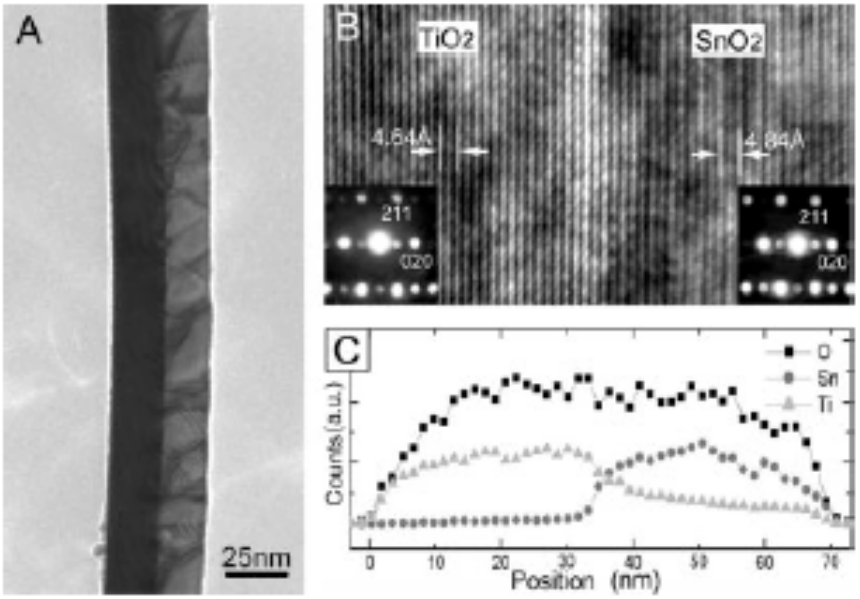


Fig. 10. A) TEM image of a TiO_2/SnO_2 nanotape obtained through epitaxial growth of TiO_2 on a single-crystalline SnO_2 nanobelt. B) A high-resolution TEM image of the atomically sharp TiO_2/SnO_2 interface. The fringe spacings of 4.64 and 4.84 Å correspond to the interplanar distances between the (010) 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 [$\bar{1}$02]. 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

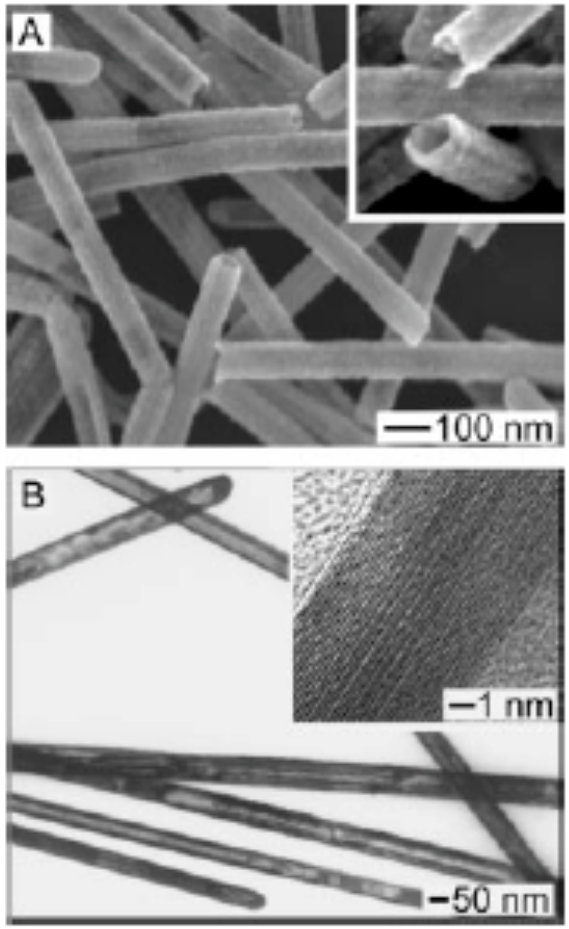


Fig. 11. A) SEM images of Pd nanotubes generated by reacting silver nanowires with an aqueous $Pd(NO_3)_2$ solution. The nanotubes were broken via sonication for a few minutes to expose their cross-sections. B) A TEM image of Au nanotubes prepared by reacting silver nanowires with an aqueous $HAuCl_4$ 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].