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Nanocarbon Materials for Active Electronics and Bio-Nanotechnology

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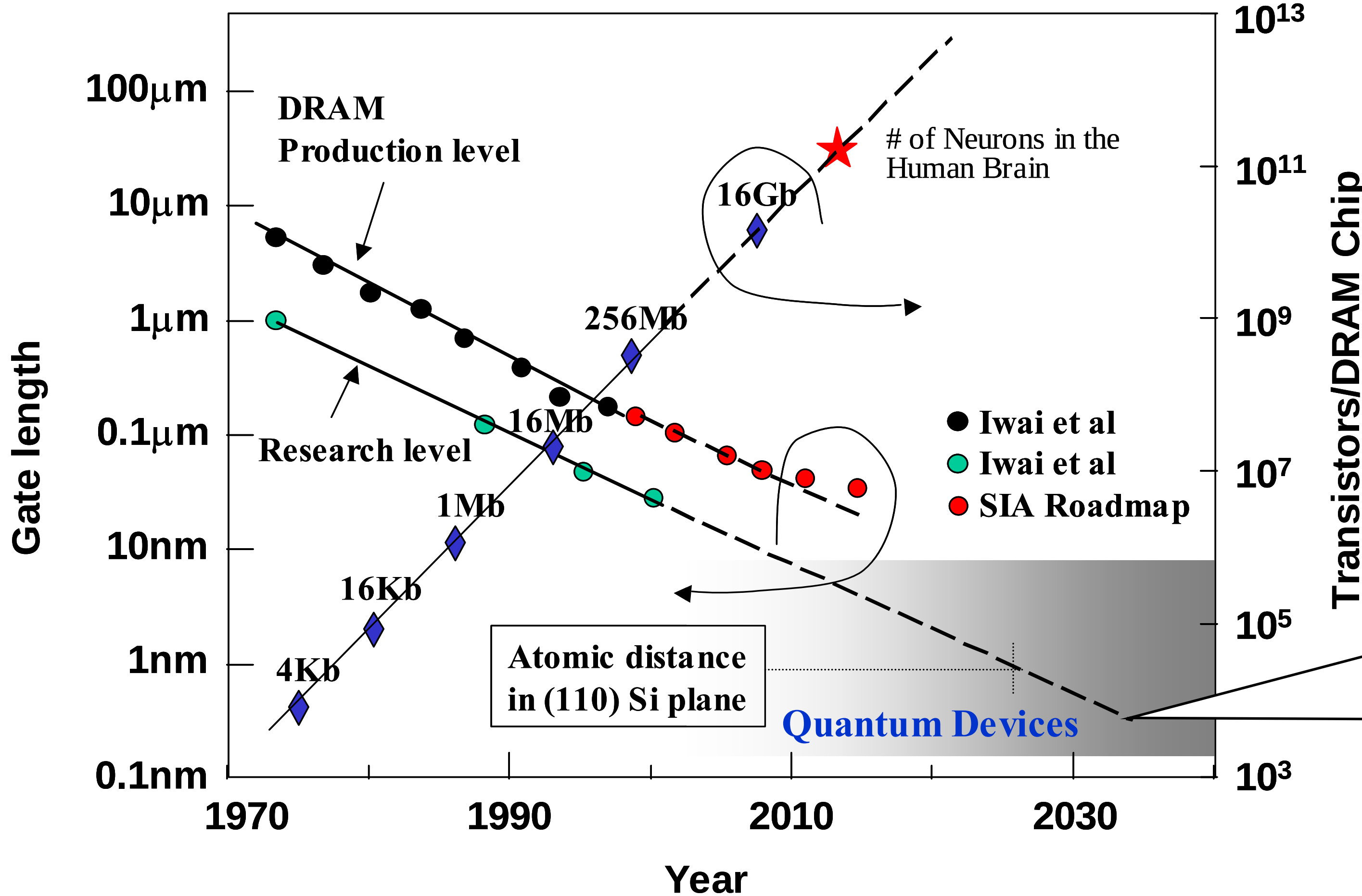
Scaling Trend – Story of Si



Limits in CMOS ?

Fab Cost Many $$

There's Plenty of Room at the Bottom (Feynman,1959)

Moore's law: Functionality per cost goes up 2x every 18 months
In 25 years: we will approach the inter-atomic distance
One has to pay for it: Moore's second Law: Every two generations, Fab cost goes up 2x
Challenge ?: Reaching the physical limit; the excessive cost (what is the future of computing?)
Opportunity: maneuvering and building things bottom-up

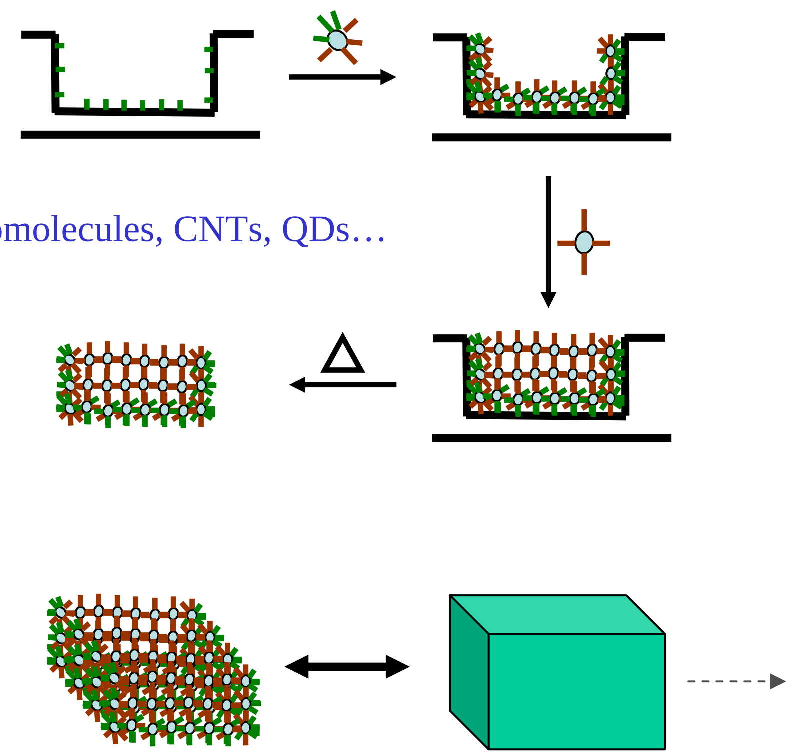
Applications of Nano Assembled Systems

- **Nanoeletronics** (LCDs, FETs, LEDs etc.)
- **Physicochemical techniques** (Bio mapping, refinement of SERS)
- **Therapeutic applications** (Drug & gene delivery, paramagnetic nanoparticles for cancer treatment)
- **Bio Labeling** (TEM & SEM analysis of protein or nucleic acid coated particles)
- **Nanoparticles as model systems** (Modeling of DNA-protein interactions, bio mineralization)

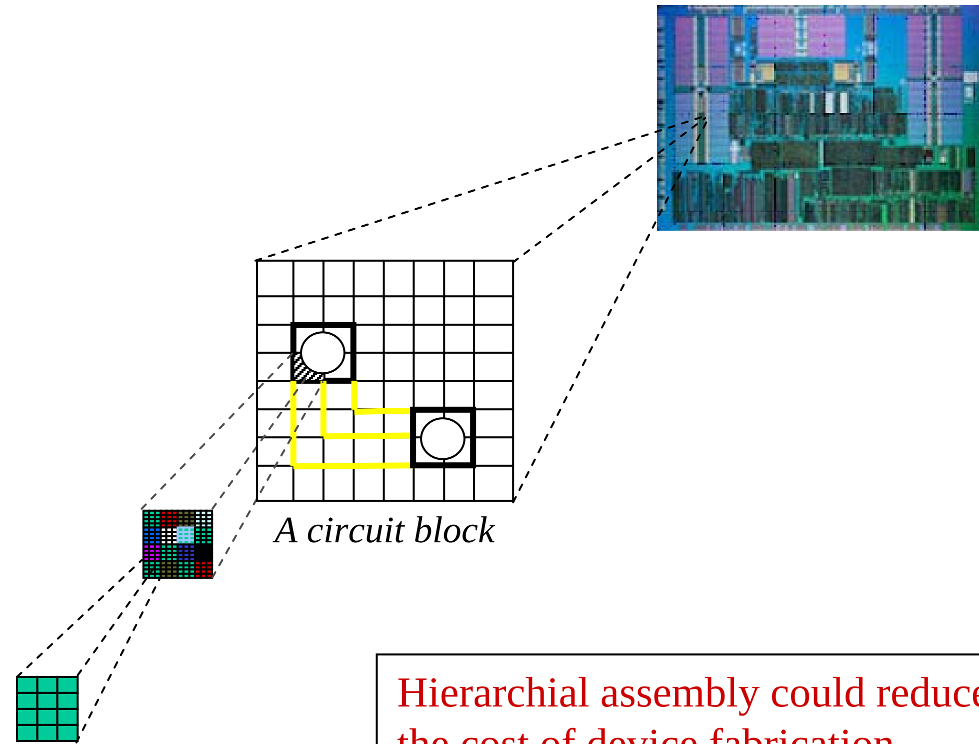
Self Assembly of Nano/Micro Devices and Circuits

Templated/Directed Self Assembly

Nanoscale building blocks



Hierarchial Self Assembly



- **Formation of 3-D nano- and micro- structures using nano building blocks.**
- **Dimensional restrictions imposed by 3-D patterned templates to manipulate the 2-D or 3-D shape.**

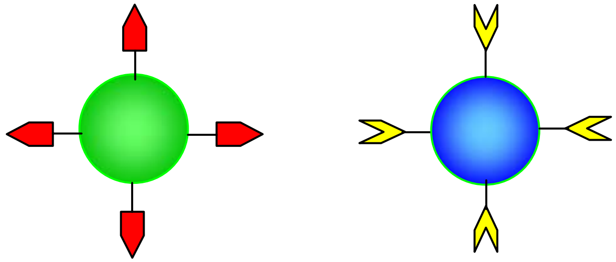
Hierarchial assembly could reduce the cost of device fabrication

Does not suffer from limitations imposed by top-down approaches

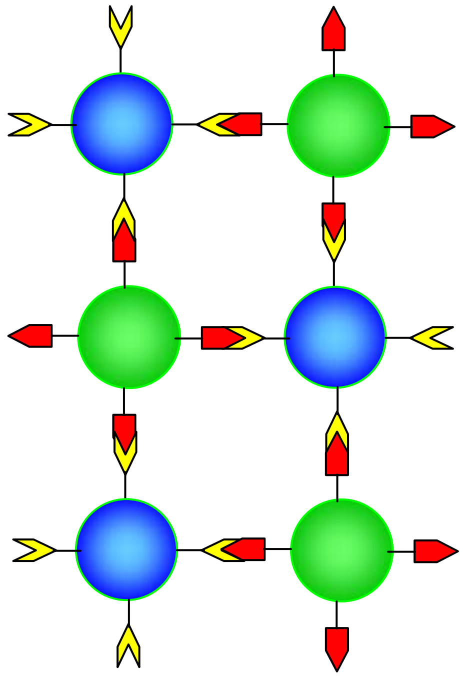
Most likely for the near future:
Drop-in technologies (HISA)

Assembly of Organic and Inorganic Nano Entities (*bottom-up* approach)

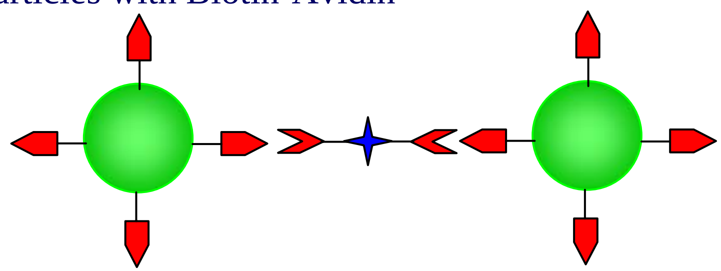
(A)



Two individual nano particles with recognition groups complimentary to each other.
Example nano particles with Biotin-Avidin

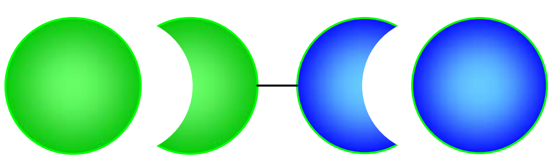


(B)



Two nano particles with non complimentary recognition groups, which can be bridged using bispecific linker molecules.
Example: nano particles with amine groups bridged by dialdehydes

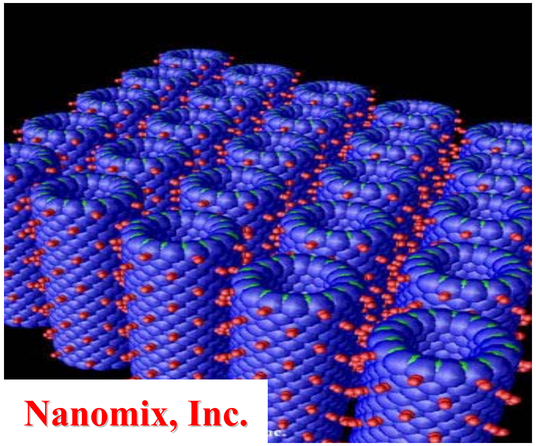
(C)

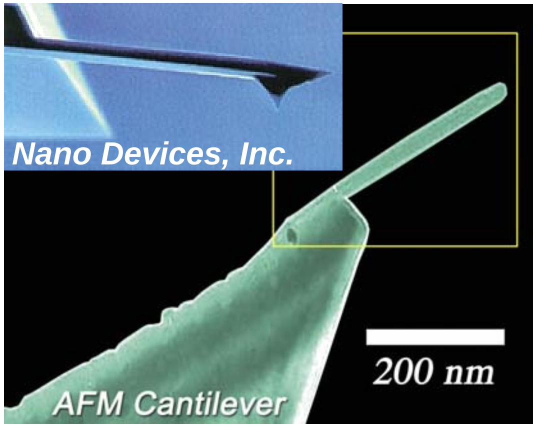


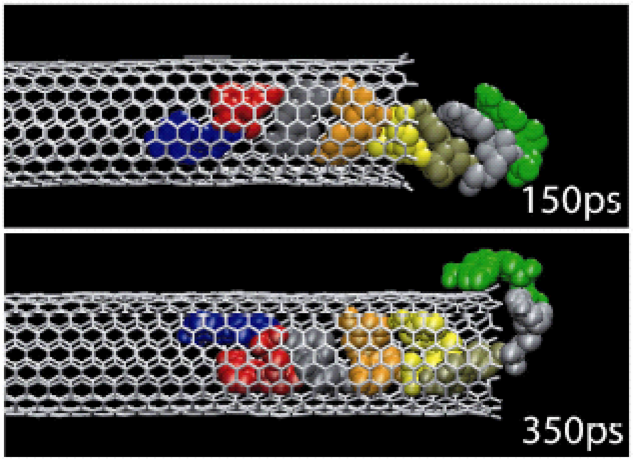
Bivalent linker that directly recognizes the surface of nano particles.
Example: Nano gold assembly with disulfide groups

Carbon Nanotubes

- Strongest and most flexible molecular material due to C-C covalent bonding and seamless hexagonal network architecture
- Young's modulus > 1 TPa (vs 70 GPa for Al)
- Strength to Weight ratio: 300 times > for Ti
- Thermal conductivity ~ 3000 W/mK in the axial direction with smaller values in the radial direction
- Can be metallic or semiconducting depending on chirality
- 'Tunable' bandgap via mechanical deformation and external magnetic field
- Multiwalled nanotubes – several coaxial cylinders - via CVD or laser vaporization of graphite (Iijima et al, NEC, 1991)
- Single walled Nanotubes – requires catalyst species (Fe, Co, Ni) (Iijima et al, 1993 and Bethune et al, IBM, 1993)







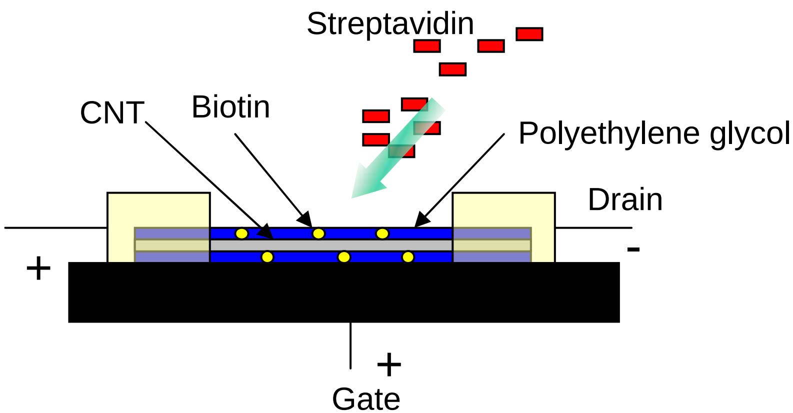
Functional Nanocarbon Materials

Nanosystems
- Bottom-up assembly
- Bio-Nano systems
- NEMS (such as Afm tips)

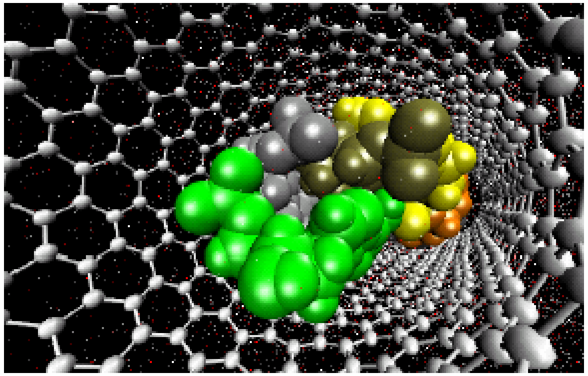
Nanoelectronics
- Molecular electronics
- Nanophotonics
- Spintronics

Sensors and Medicine
- Biological sensing
- Chemical sensing
- Gene delivery
- Drug delivery

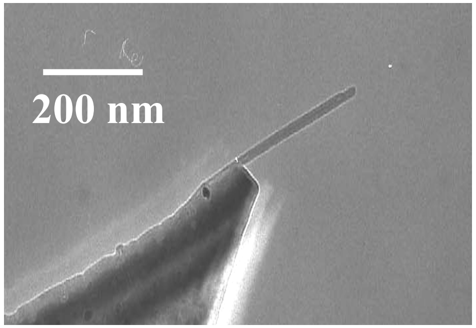
Structural Materials
- Composites
- Multifunctional materials



CNT Based Chemical Sensor

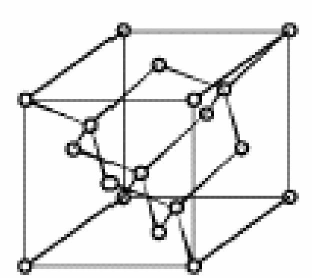


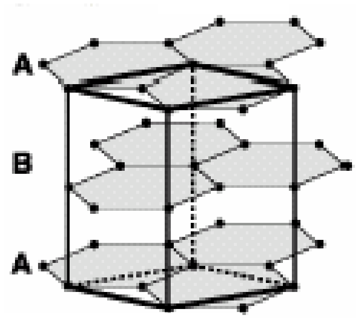
Gene Delivery Vehicle

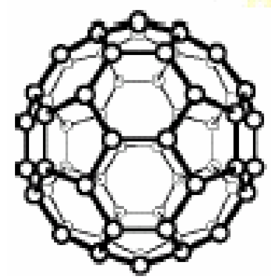


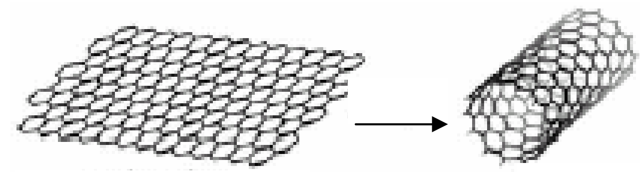
Ultrasharp AFM Tip

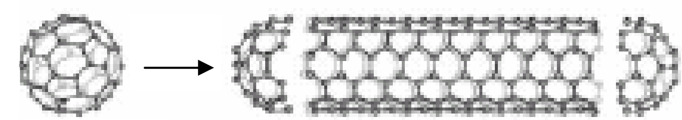
Structure of Carbon Nanotubes (CNT)







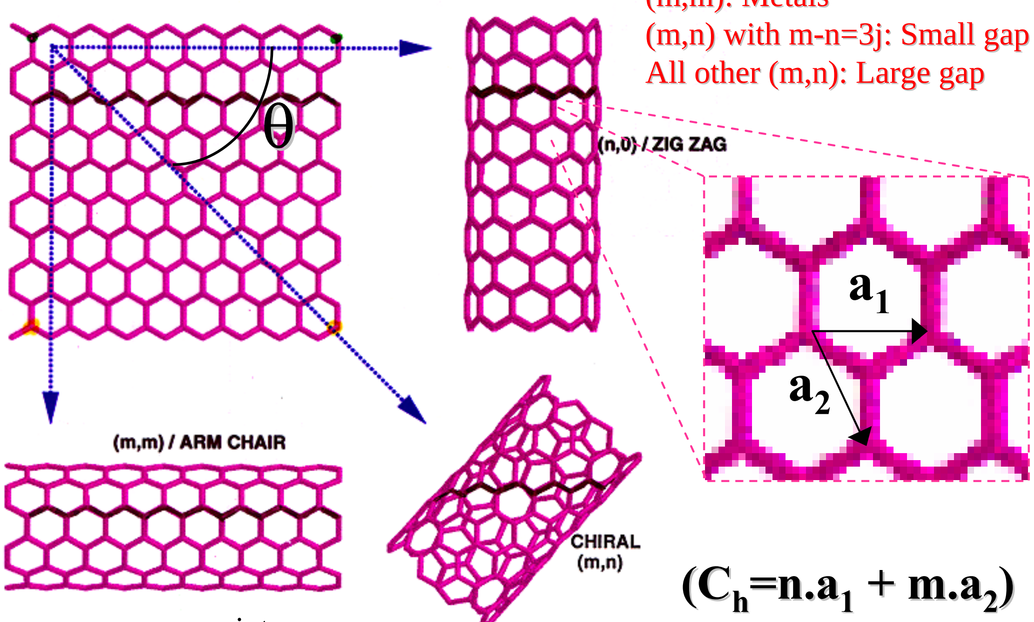




CNT : configurationally equivalent to a two dimensional graphene sheet rolled into a tube *Diameter: 0.7-1.4 nm Length: few nm to microns*

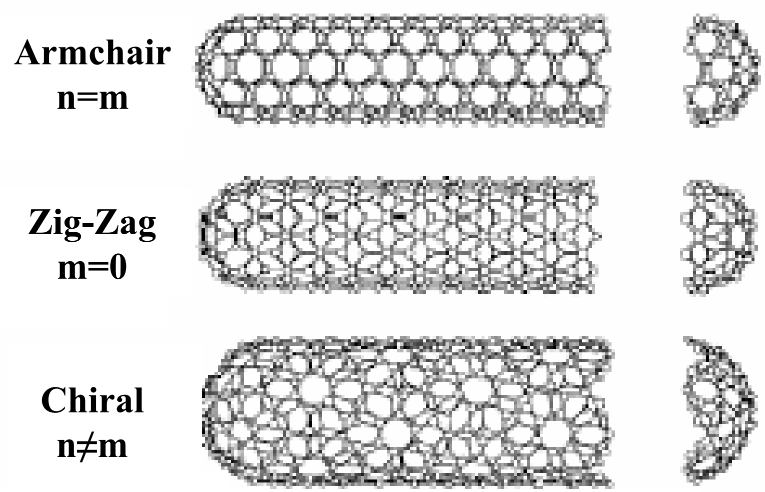
- STRIP OF A GRAPHENE SHEET ROLLED INTO A TUBE

(m,m): Metals
(m,n) with m-n=3j: Small gap
All other (m,n): Large gap



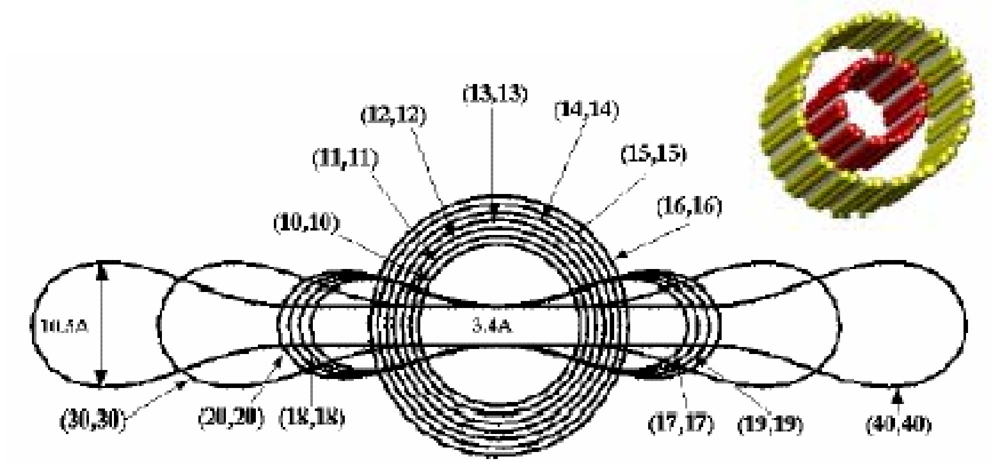
$$(C_h = n.a_1 + m.a_2)$$

www.ipt.arc.nasa.gov

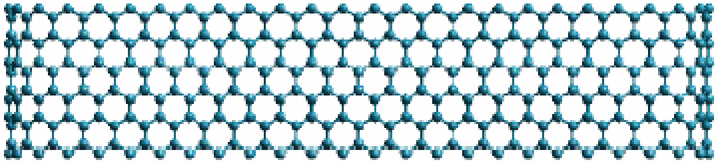


Carbon Nanotubes, by M.S. Dresselhaus, G. Dresselhaus and P. Avouris, Springer (2001)

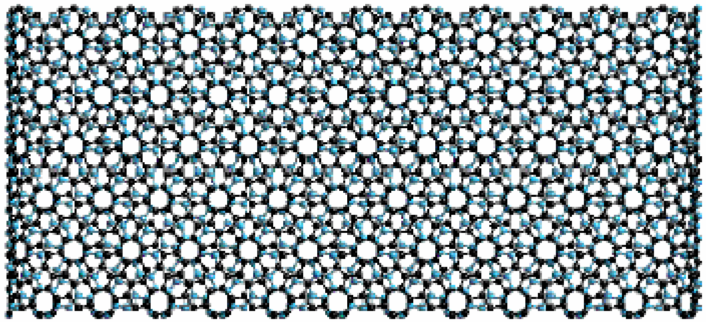
Multiwalled Carbon Nanotubes



Collapsed cross-section for larger radius in multi-walled carbon nanotubes

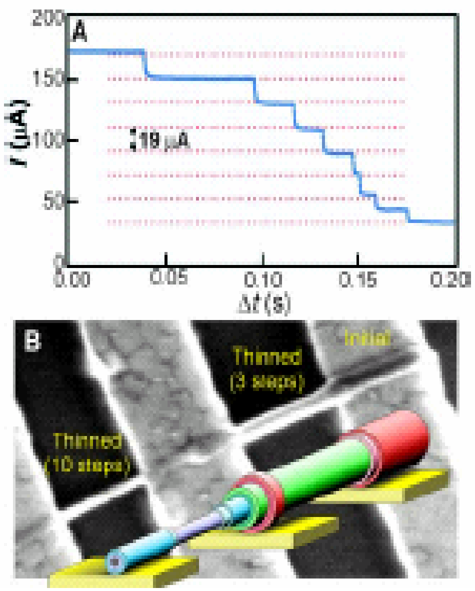


(50,0) Nanotube

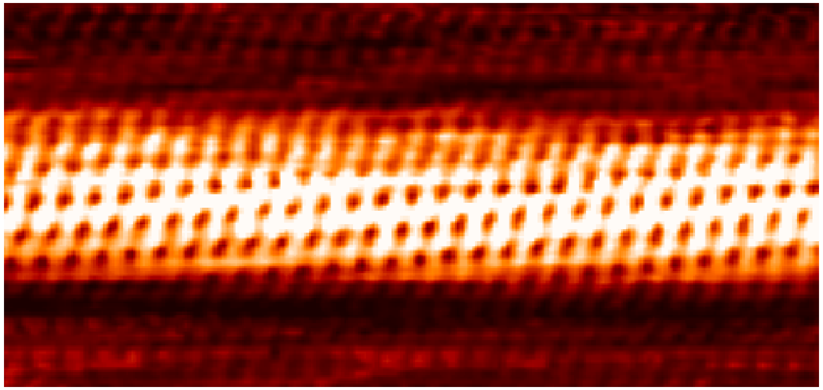


(50,25) Nanotube

Nanomix, Inc.



Collins et al, Science, 292, 706 (2001)



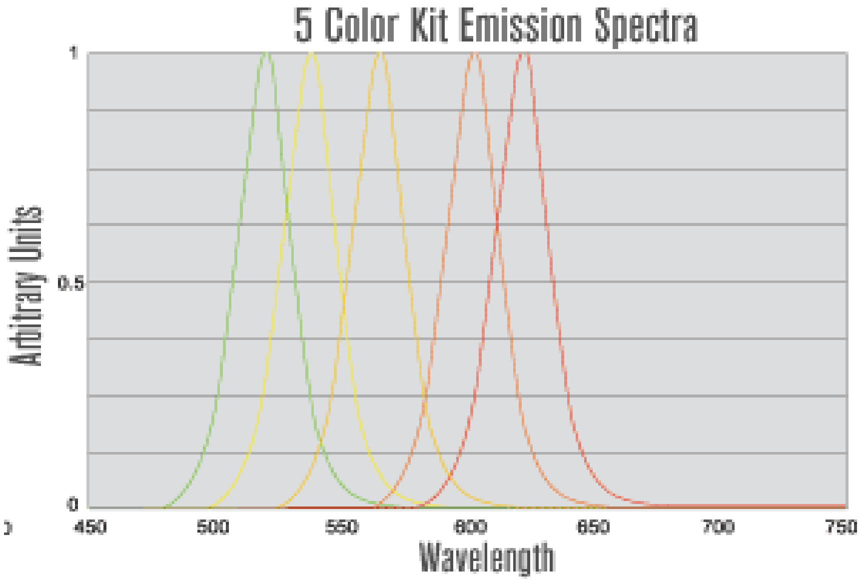
Scanning tunneling microscopy image of a MWCNT (Wildoer et al, Nature 1998)

Quantum Dots

- Optically active Semi-conducting Nanoparticles
- Example: CdSe Core with a passivating ZnS monolayer

Possible Applications

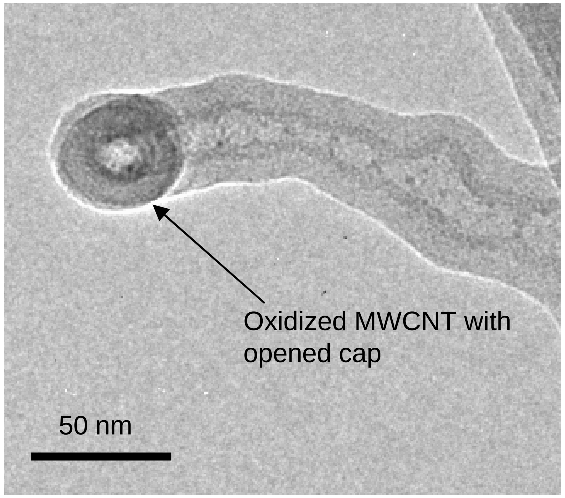
- Light Emitting Diodes
- Laptop Screens and Lighting
- Detection of Bio-agents
- Bio-Imaging



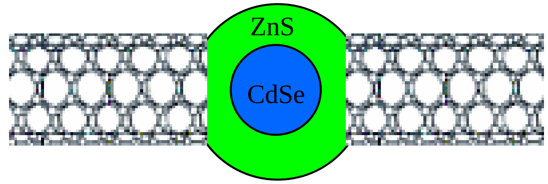
Advantages for Bio-Imaging

- Non – Isotopic
- Brighter than Conventional Organic Dyes
- Resistant to Photobleaching
- Narrow Emission Spectra
- Single Excitation Source
- Consistent Conjugation Procedure

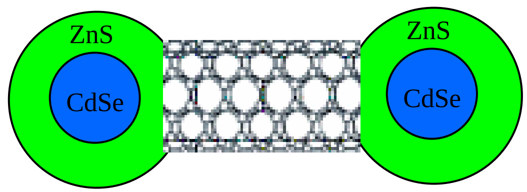
Carbon Nanotubes and Quantum Dots for NANO-ASSEMBLY



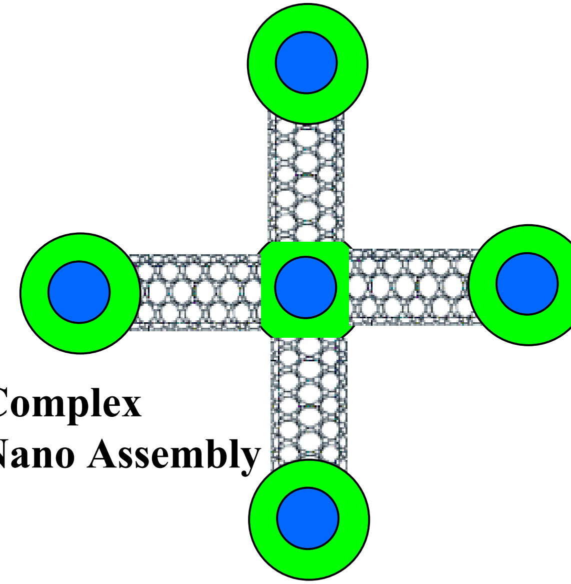
Ravindran et al, Nano Letters, 3, 4, 447 (2003)



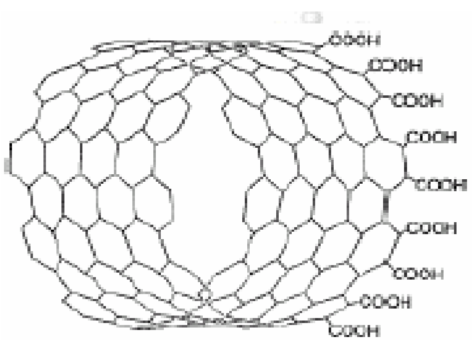
CNT-QD-CNT



QD-CNT-QD



Complex Nano Assembly



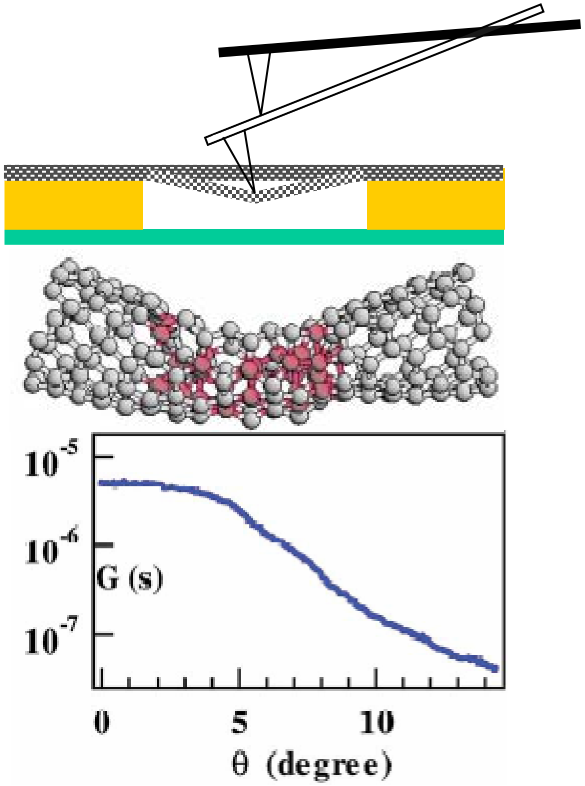
Purification and shortening of nanotubes is achieved via strong acid axidation

Liu et al, Science, 280, 1253 (1998)
Rinzler et al, Appl. Phys. A, 67, 29 (1998)
Rao et al, Phys. Rev. Lett., 86, 3895 (2001)

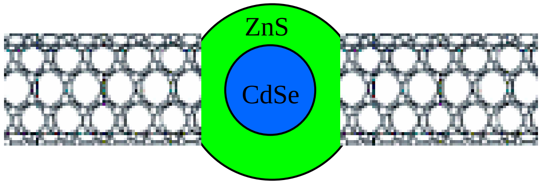
Ends of carbon nanotubes can be functionalized with a variety of groups, -COOH, $-NH_2$, etc. which provides flexibility for their utilization in assembly with other organic and inorganic materials.

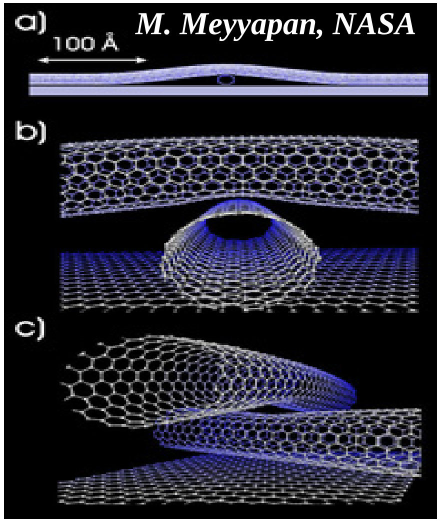
Electromechanical Coupling in CNT's and Motivation for CNT-QD Heterostructures

Carbon nanotube devices for memory and junction transistors rely on the overlapping of Carbon nanotubes…



Dai et al, Nature, 405, 769 (2000)

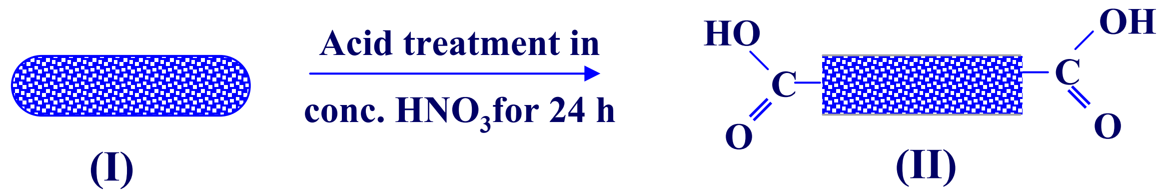




1. Such structural distortion <u>leads to energy barriers to electron transport</u> and is mainly responsible for the <u>reduced electrical conductance</u> of the nanotube system.
2. Alternatively, heterojunctions overcome this problem of energy barrier formation due to distortion.
3. CNT-QD structures are promising device structures
4. CNT-QD structures enable visualization of CNTs if its applied for mass transport applications in biosystems
5. 3-D complex assemblies for novel material sysnthesis (photonic crystals)

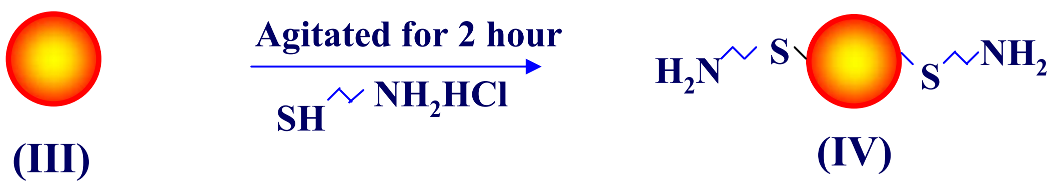
Scheme for CNT-QD Heterostructure Synthesis

(A)



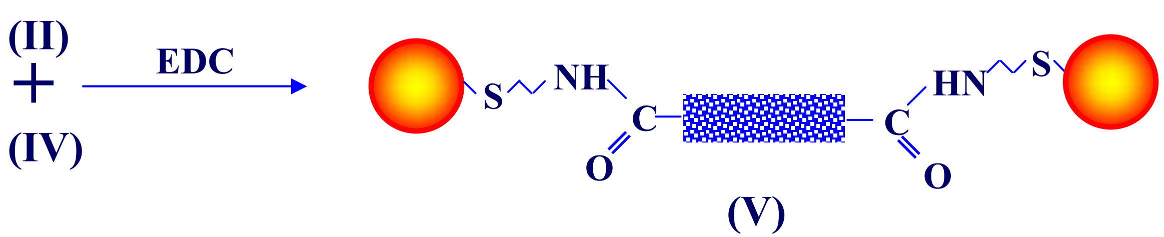
Introduction of carboxyl-terminal groups via acid treatment (Oxidation)

(B)



Water stabilization of CdSe/ZnS QDs via aminoethane thiol treatment

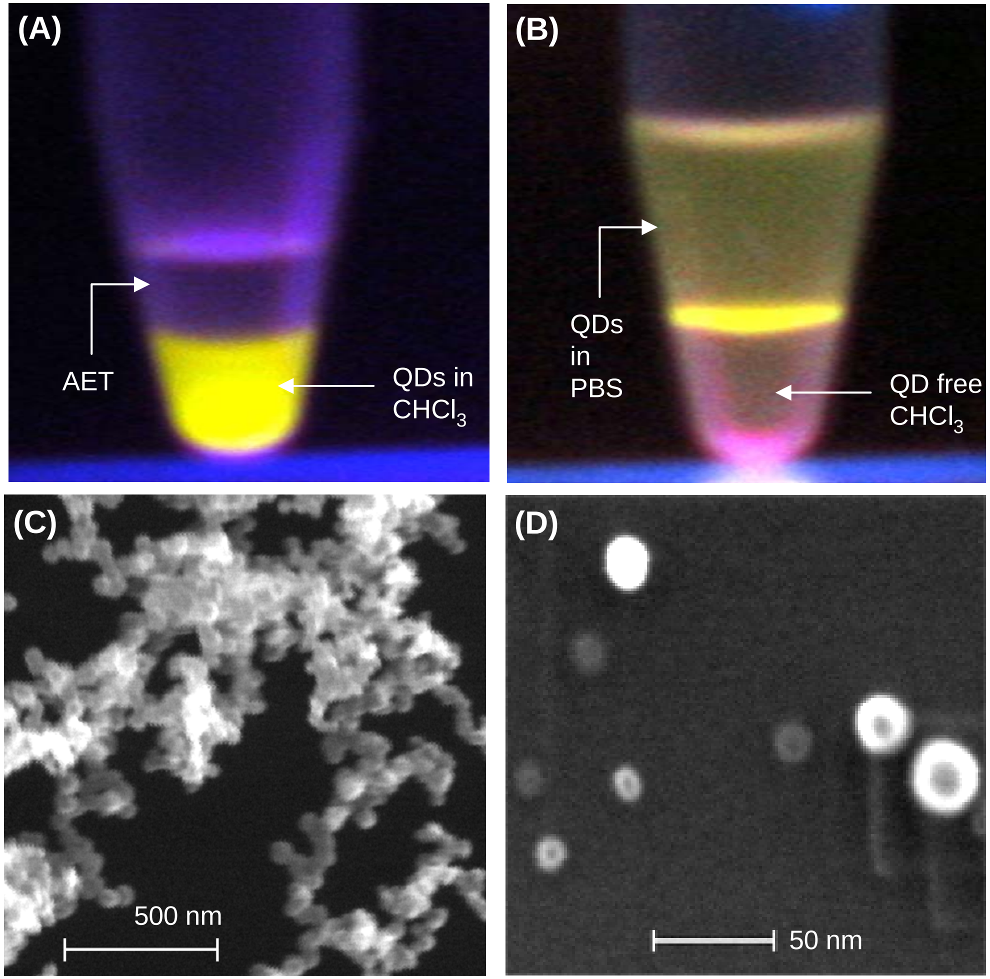
(C)



Heterojunction formation via Ethylene carbodiimide reaction

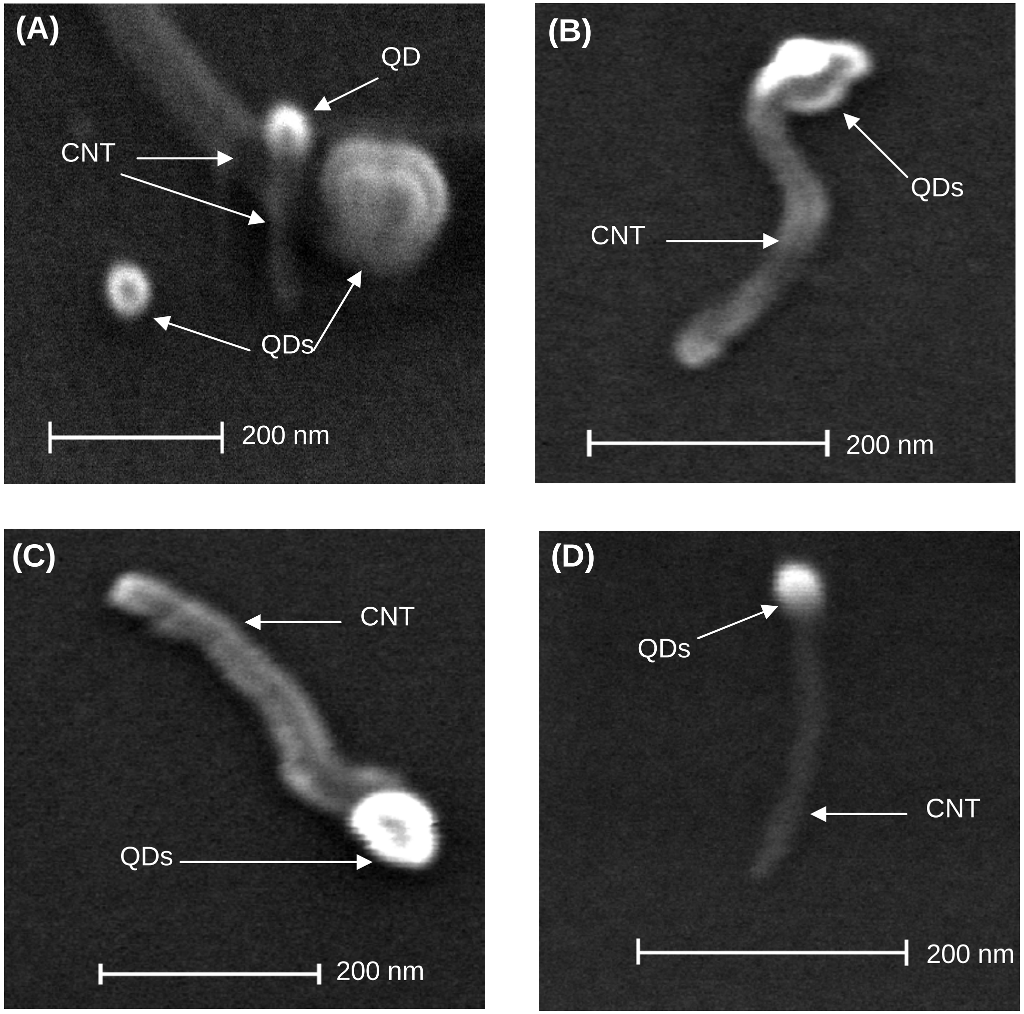
Water Stabilized QDOTs

Aqueous AET forms an immiscible layer over the organic QDOT-chloroform suspension



(A) CdSe/ZnS QDOTs are in the organic phase (chloroform).
(B) CdSe/ZnS QDs are treated with aminoethane thiol to introduce NH_2 groups at their surfaces and make them water soluble. (they go into the lighter aqueous phase)
(C) and (D) SEM image of water soluble Quantum dots ($QD\text{-}NH_2$)

CNT-QDOT Heterostructures



SEM images of MWCNTs tip conjugated to QDs by the EDC coupling procedure

SEM sample was prepared by putting a drop of the solution on a silicon substrate followed by vacuum drying

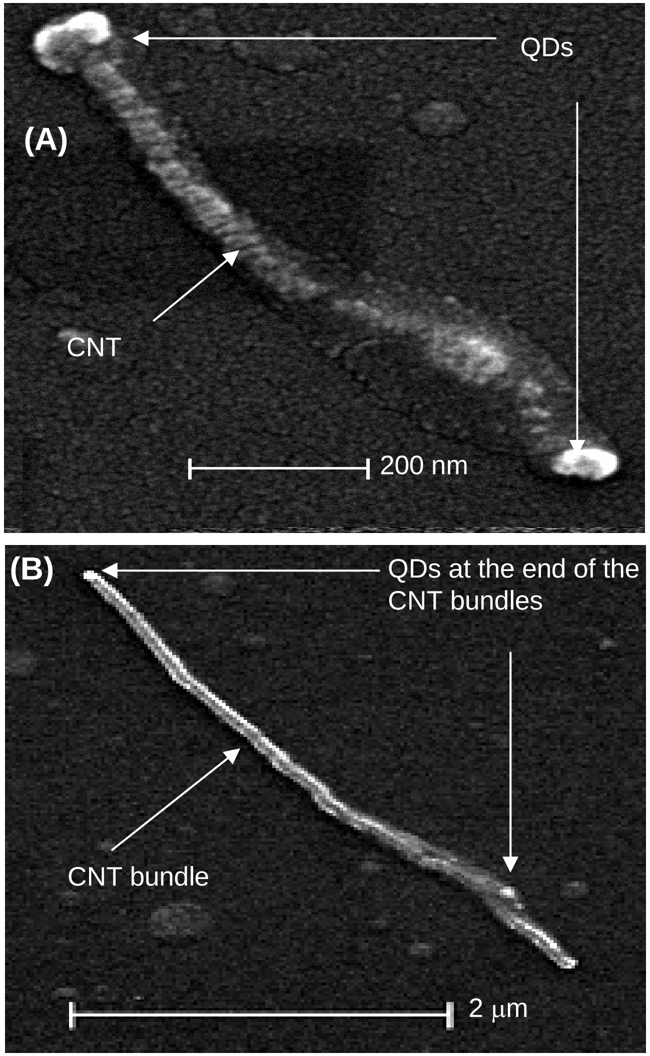
CNTs look dimmer due to smaller secondary electron density emitted

Clusters of quantum dots (20-40 nm) due to complex charge redistribution

No sidewall functionalization is observed, the conjugation process is very specific to take place at the ends of the nanotubes

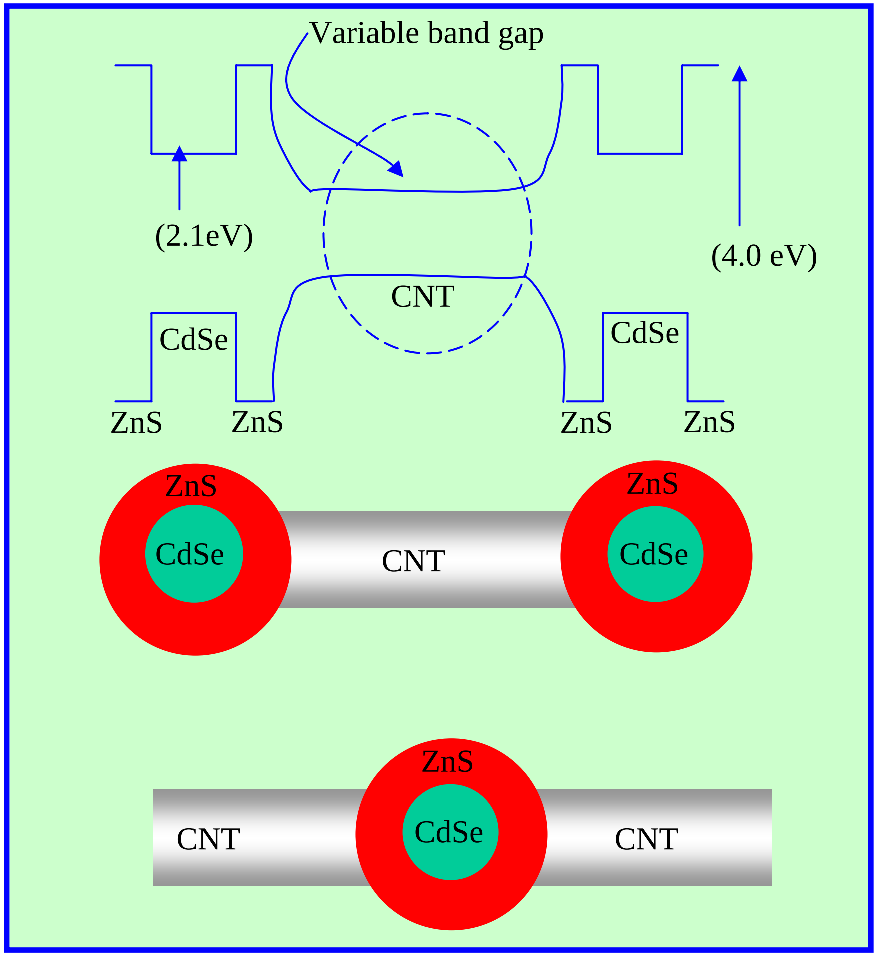
Nano Letters, 3 (4): 447-453 (2003)

QD end-conjugation for short and long CNTs



(A) CNT ~500 nm in length with QD conjugation at both the ends. (B) QD conjugation only at CNT ends for overall length larger than 4µm

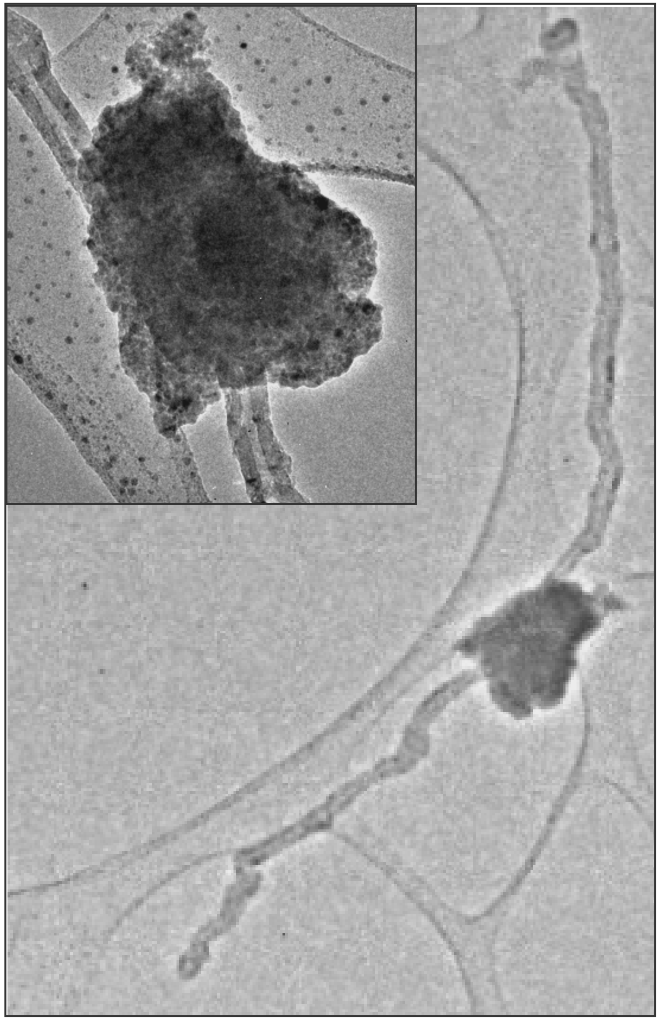
Energy-Band diagram of a QD-CNT-QD heterostructure

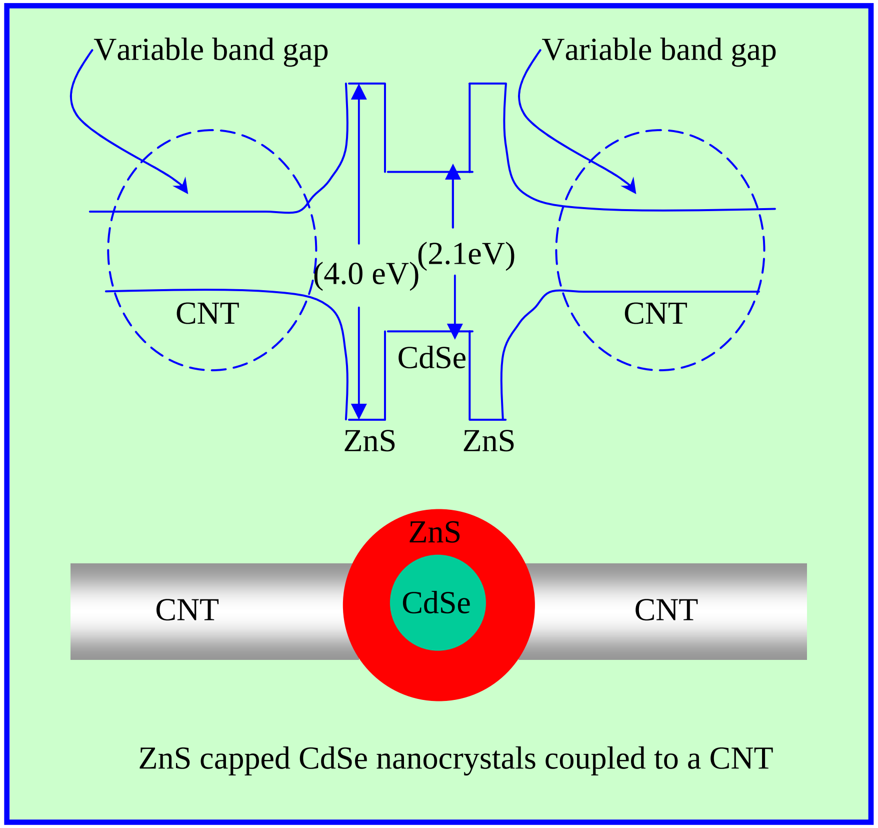


- Applications in Nanoscale electronic and spintronic devices

Nano Letters, 3 (4): 447-453 (2003)

QDs Sandwiched Between Two CNTs

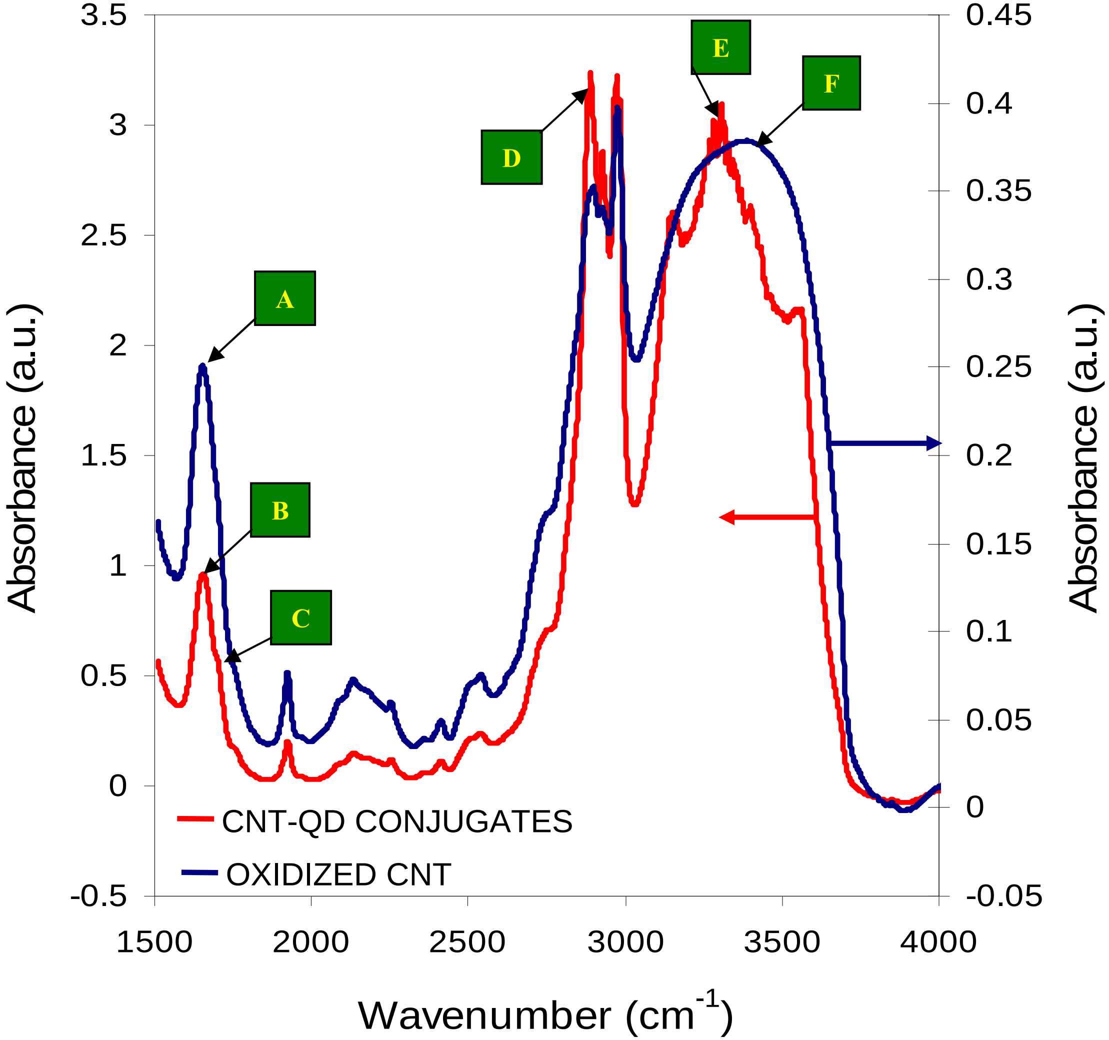




Band diagram of a CNT-QD-CNT heterostructure

(Submitted, 2003)

Fourier Transform Infrared Spectroscopy of CNT-QD Structures



A Peak @ 1644 cm^{-1}; C=O stretching in the ***carboxylate*** groups

B 1653 cm^{-1}; C=O stretching in the ***amide*** groups

C 1704 cm^{-1}; C=O stretching in the ***carboxylic*** groups

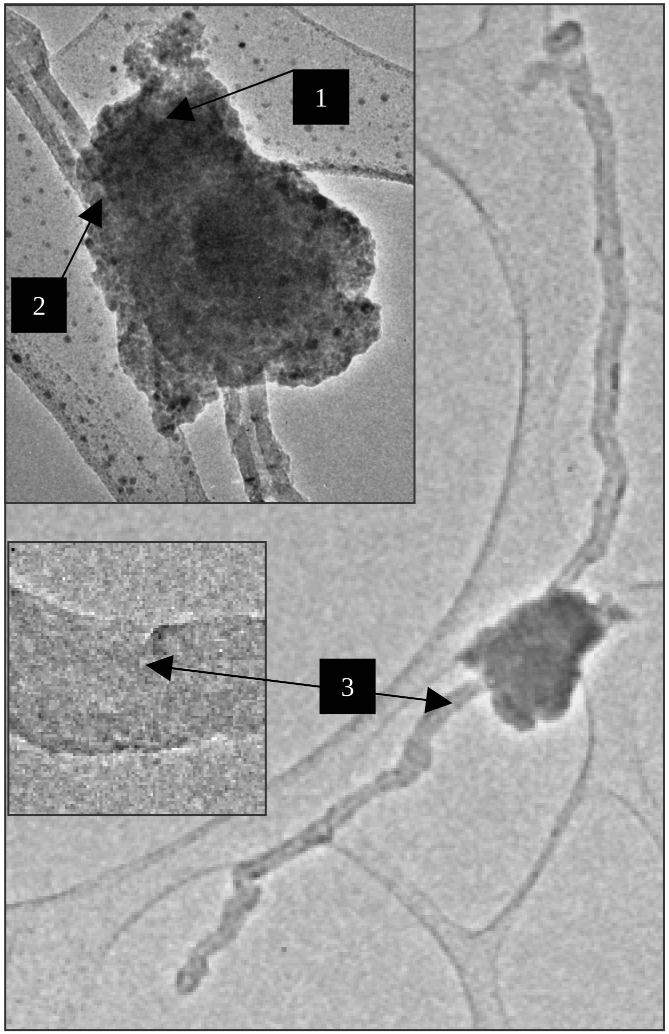
D 2977 cm^{-1}; C-H stretching

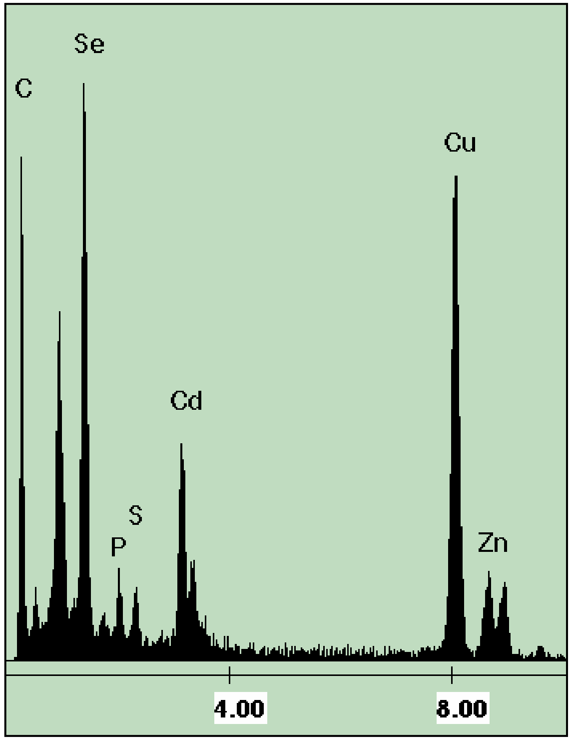
E 3314 cm^{-1}; N-H stretching

F 3403 cm^{-1}; O-H stretching in the ***phenolic*** groups

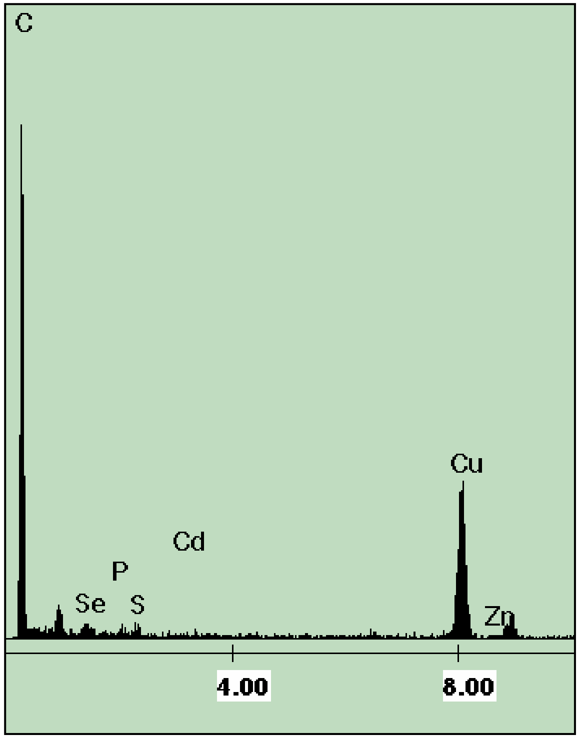
Reduction in the C=O stretching peak from COO^- and COOH and the appearance of the N-H stretching peak corresponding to amide bonds suggests that the acid groups have been utilized for the conjugation via amide bond formation.

Materials Characterization via Energy Dispersive Spectroscopy (EDS)





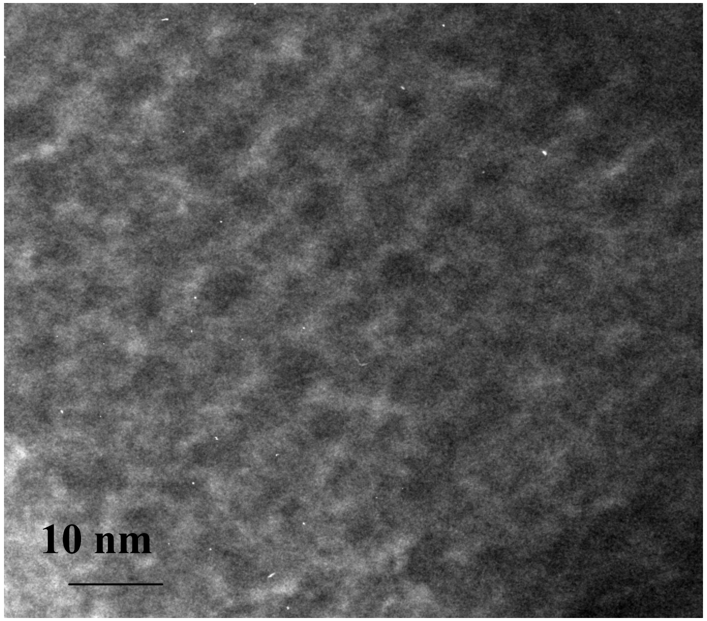
EDS data at the junction of the CNT and the QD cluster (position ‘2’) indicating signals from CdSe/ZnS (QDs) and C from CNT (Probe size: 5.6 nm)

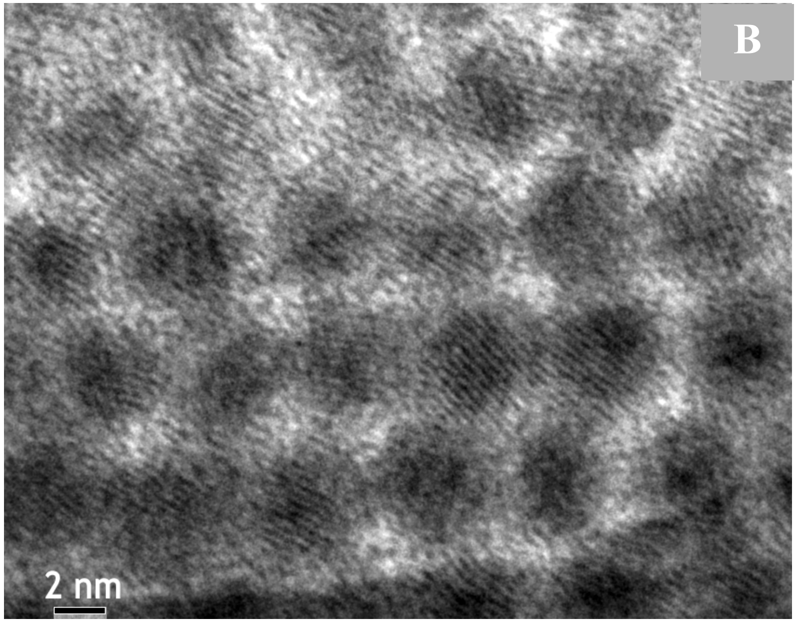


EDS data on the CNT alone (position ‘3’) indicating a C signal from the tube alone

(Submitted, 2003)

Ordered Quantum Dot Clusters at MWCNT Ends

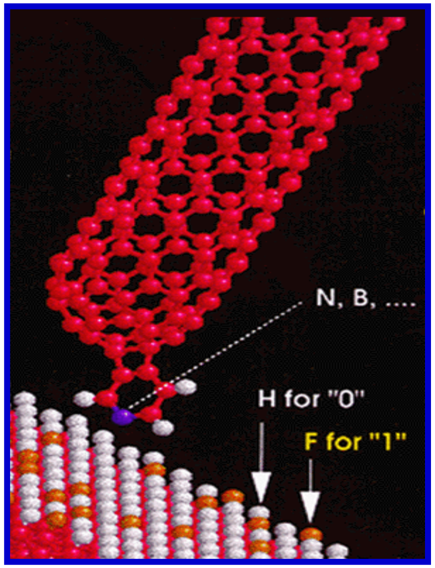




QD clusters (size distribution agrees with the as received size of the nanocrystals)

2-D Hexagonal Ordering of QDs with different orientation of lattice planes

(Carbon, in press, 2004)



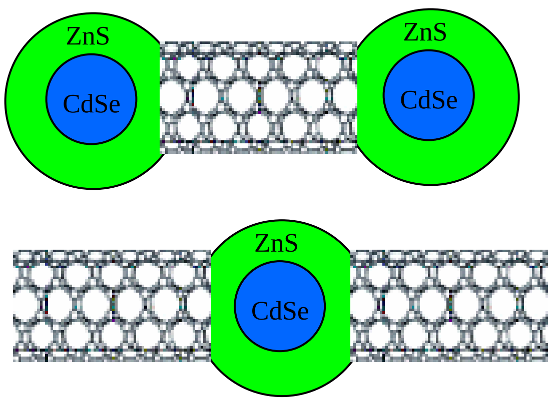
- **Novel data storage, (orders of magnitude denser)**
- **Novel self assembly of Nanostructures**

Quantum dots, nanopillars

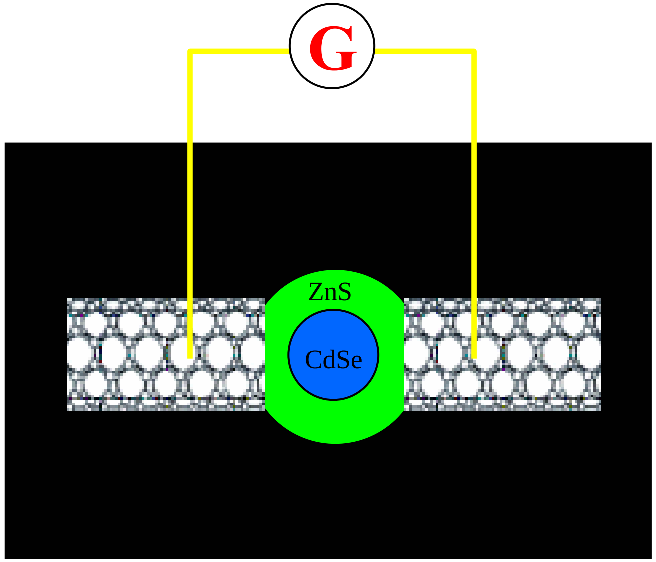
Patterned Nanotube-Quantum Dot Structures for Devices and Biosensing

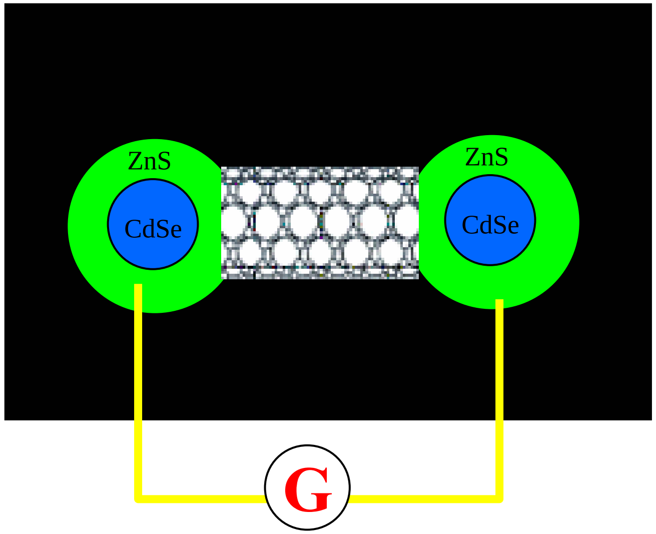
•CNT structures positioned over prepatterned electrodes

• Electron beam lithography patterning for CNT structures and devices

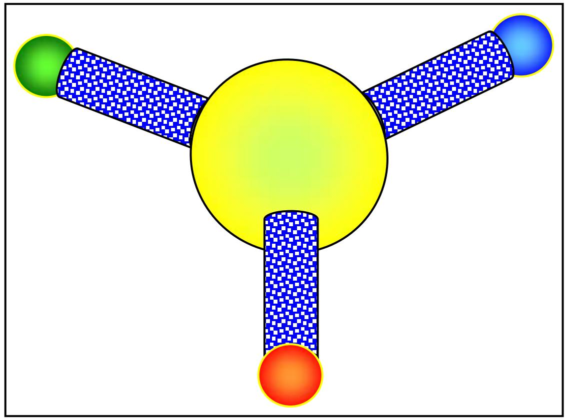


Applications
•Novel electronic and spintronic devices
•Nanoscale devices for biowarfare sensing

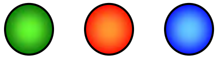




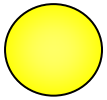
Nanoscale Building Blocks for 3-D Nanoassembly

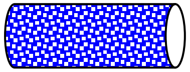


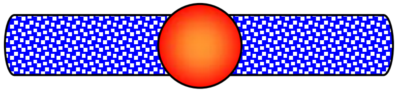
A nanoscale building block with multiple nano-components


= CdSe/ZnS QDOTs

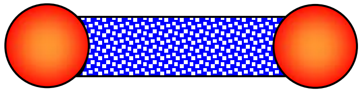
ZnS capping improves the quantum yield by passivating the surface dangling bonds and also eliminates the toxicity of the CdSe core for biological applications


= Nanoparticles such as colloids


= Carbon nanotubes



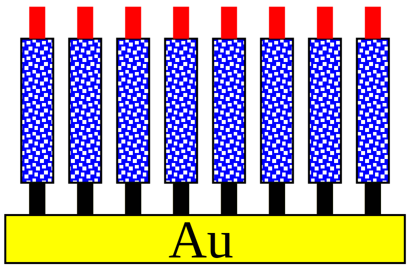
CNT-QD-CNT



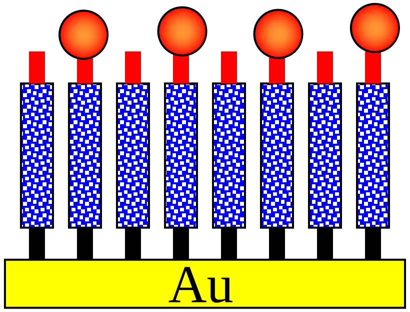
QD-CNT-QD

- Model system: CNT-QDOT conjugates
- Synthesize spatially co-ordinated nanoscale building blocks using solution chemistry

Multiple Functionalization of CNT's

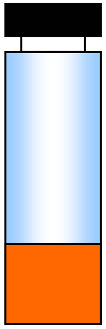


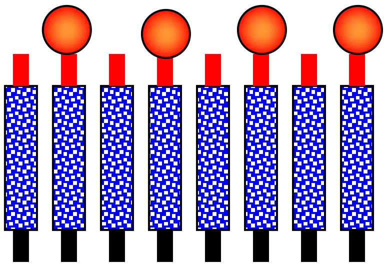
EDC reaction with amino thiol stabilized QDOTs



Oxidized CNTs are self assembled over an amine terminating thiol monolayer by the ethylene carbodiimide reaction (EDC) via amide bond formation

Ultrasonication





Sample A: the other end of CNT is a thiol held to the CNT by an amide bond.

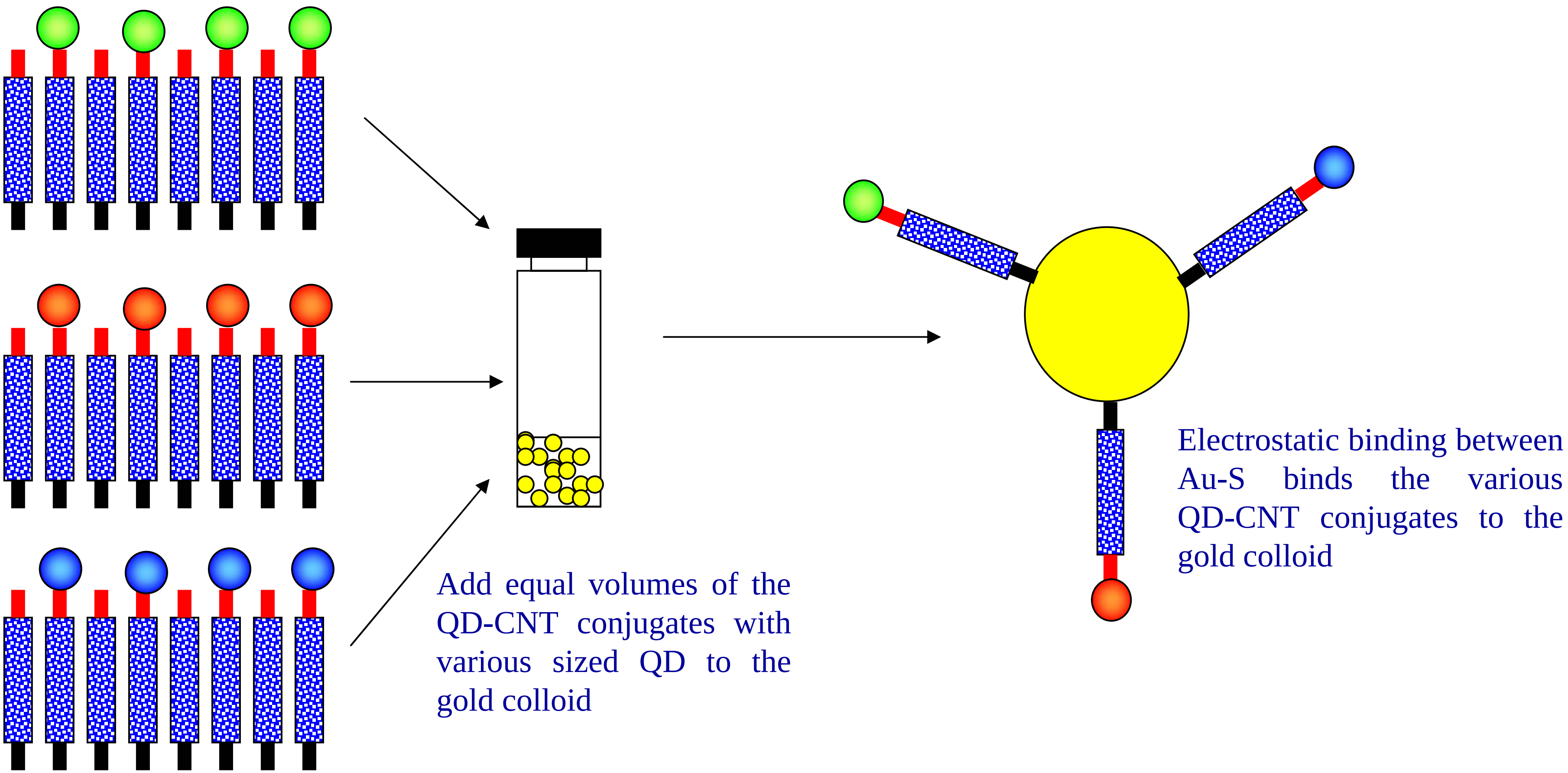
= -COOH

= -S-(CH2)2-NHCO-

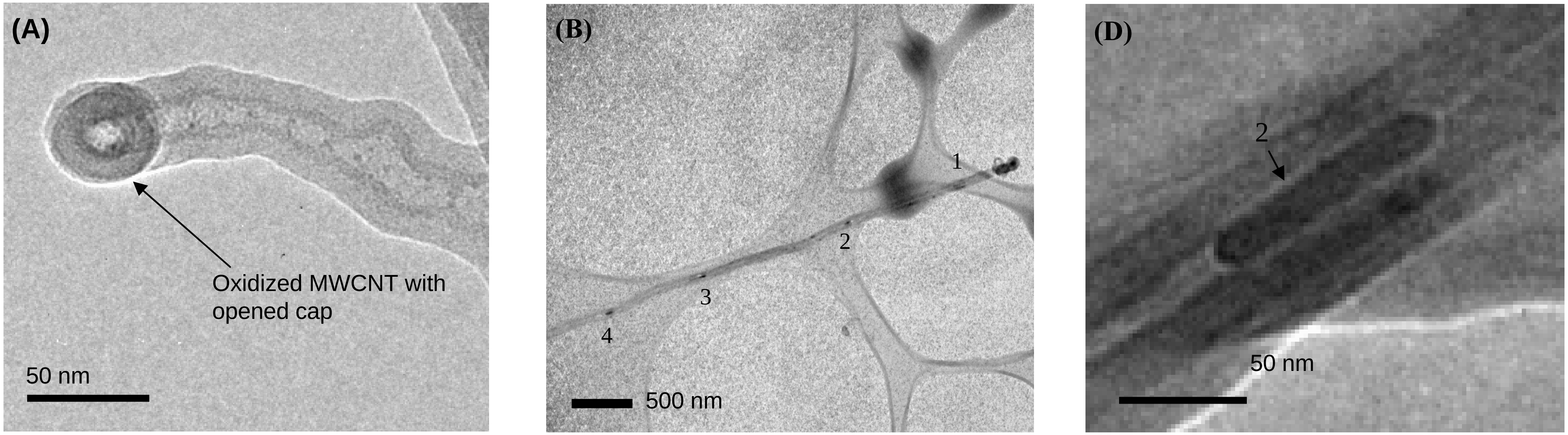
Ultrasonication frees the CNTs from the gold surface and the result is a suspension of CNTs with QDOTs conjugated on one side only and the other end has a free thiol

3D Nanoscale Building Blocks

Several suspensions containing CNTs conjugated at only one end with QDs of various sizes or types. All suspensions are characterized by CNTs with QDs at one end and free thiol group on the other end.



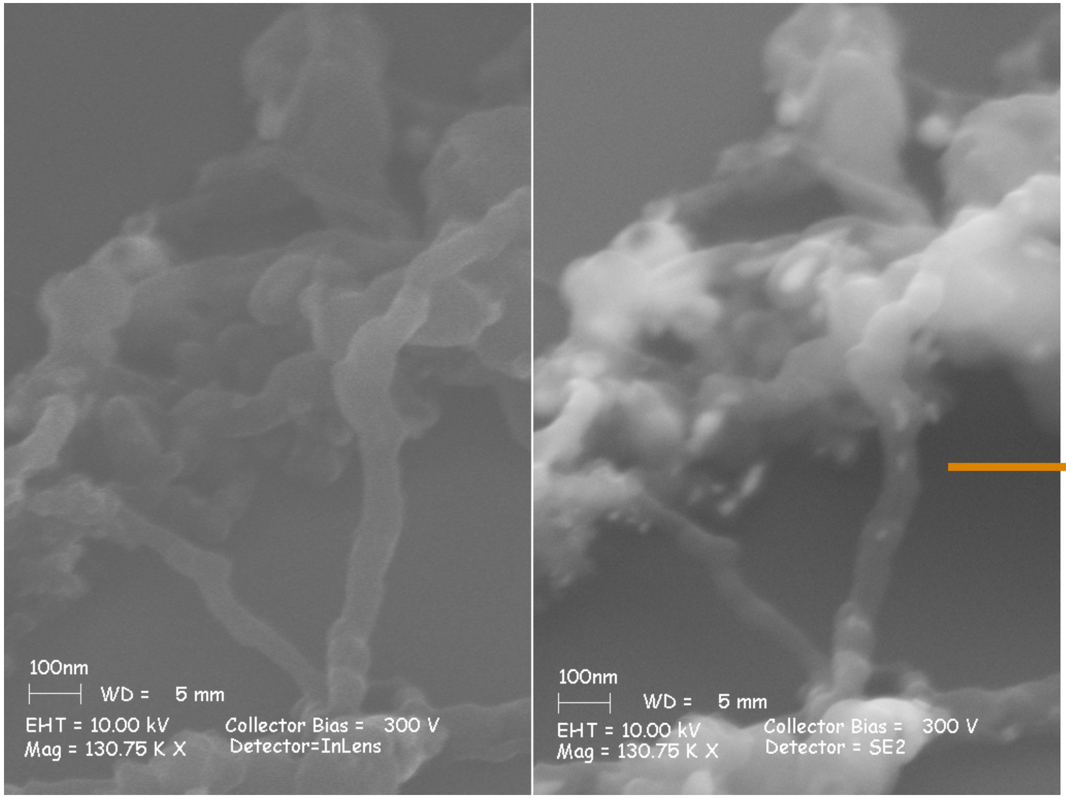
Encapsulation of Nanomaterials in CNTs



(A) An oxidized CNT with the cap removed (B) TEM image of a sample of CNTs stirred with QDs for 48 h at 50°C. Regions 1, 2, 3, and 4 indicated encapsulation (C) and (D) Region 2 in figure (B) is shown at higher magnification

Nano Letters, 3 (4): 447-453 (2003)

Encapsulation of Materials in Nanotubes

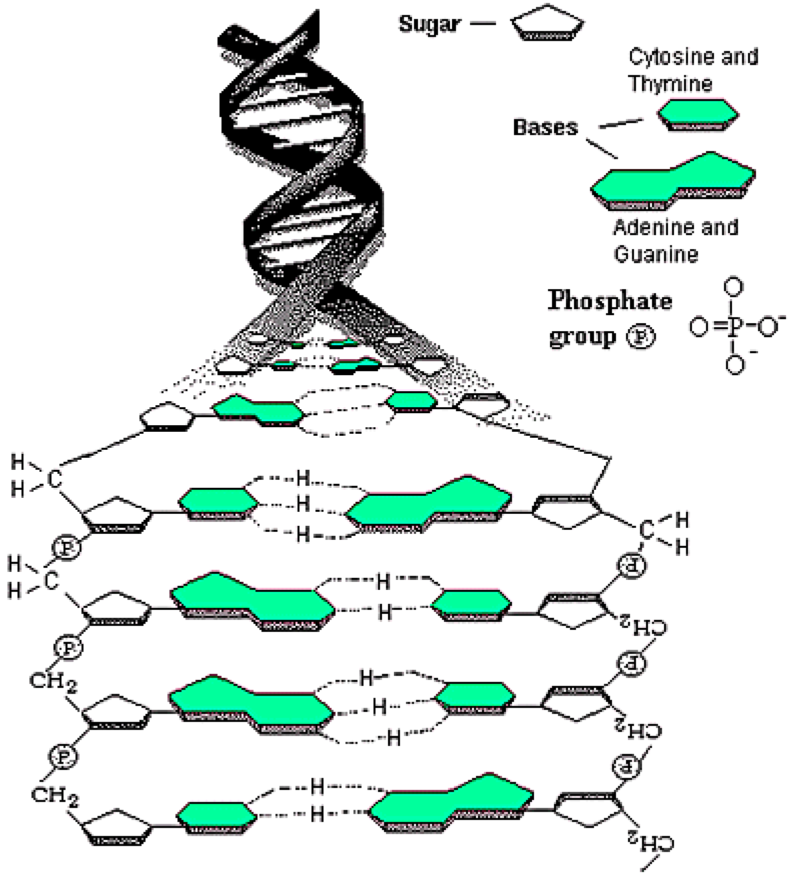


Fe catalyst particles remain encapsulated inside nanotubes from growth

So far, encaspulation of water molecules, gases, fullerenes have been demonstrated.

What about biomaterials such as proteins, drugs or DNA?

Structure and Properties of DNA



(National Health Museum)

•DNA is a double stranded molecule twisted into a helix

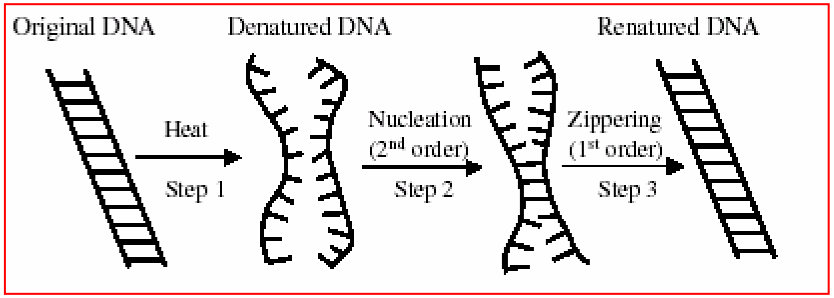
•Each spiraling strand contains of a sugar-phosphate backbone and attaching bases

•Complimentary strands are connected by non-covalent hydrogen bonding between base pairs

A-T: are connected by two hydrogen bonds

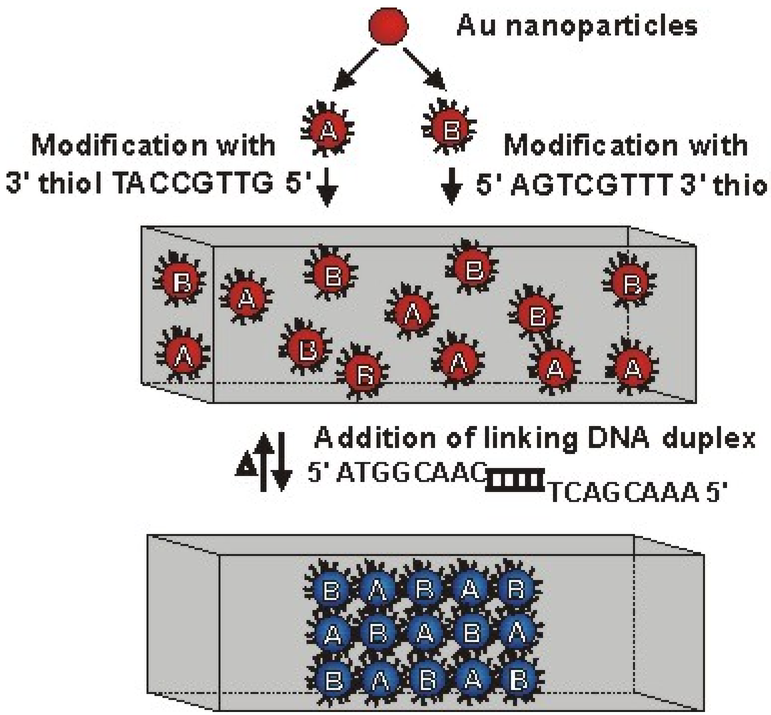
G-C: are connected by three hydrogen bonds

•DNA can be denatured by heating (80 C)



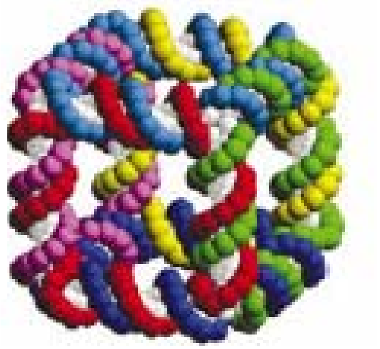
Role of DNA in Nanotechnology

•DNA in junctions (functionalized ends for binding)
•C. Keating, Penn-State; S. Esener, UCSD; C. Mirkin, NWU

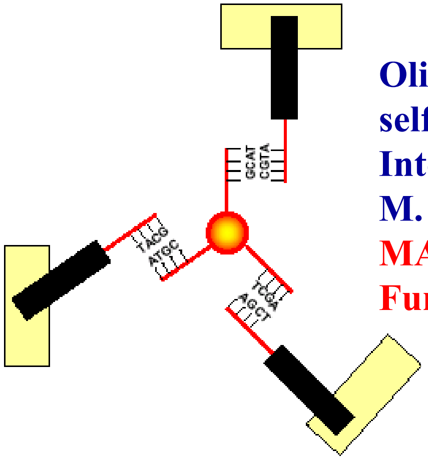


Assembly of Gold Nanoparticles
C. Mirkin, NWU

•DNA molecules as building blocks (complex polyhedra and topological constructs

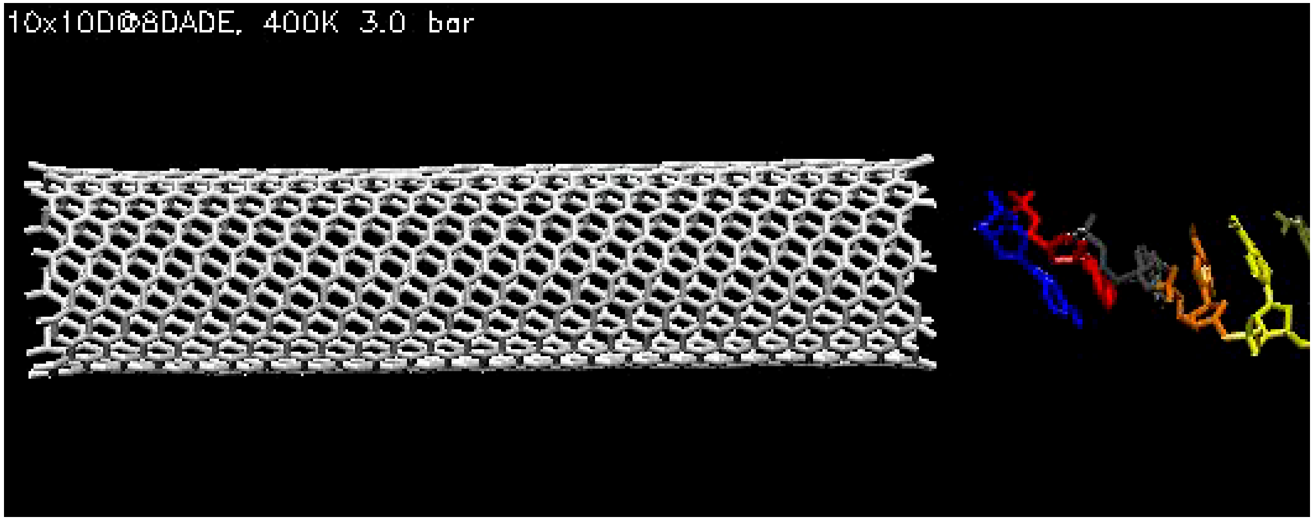


"DNA Cube" for NEMS
N.C. Seeman, New York University



Oligo functionalized CNTs and QD for self-synthesis of devices, contacts, and Interconnects (C. Ozkan, Jianlin Liu, M. Ozkan, R. Lake, A. Balandin, UCR; MARCO Center on Functional Engineered Nano Architectonics)

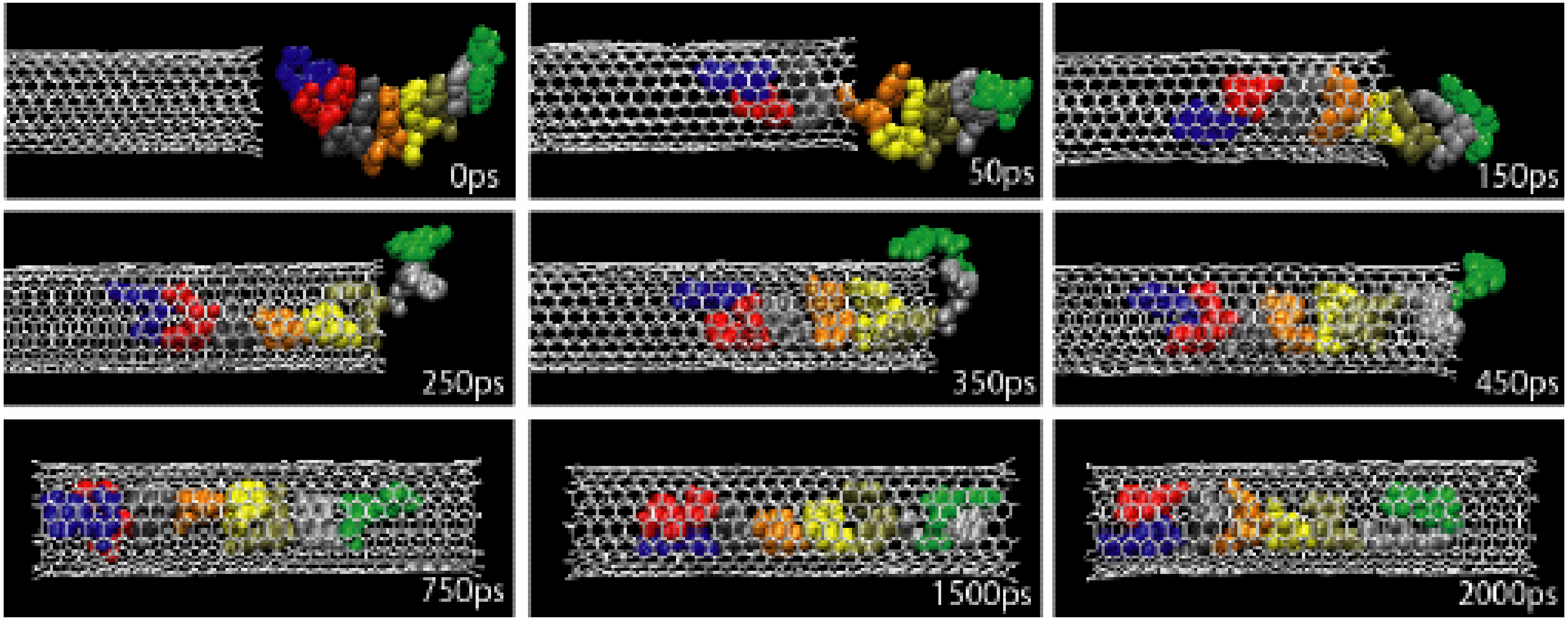
Molecular Dynamics Simulations of a DNA Oligonucleotide Interacting with a CNT



- Single strand DNA oligonucleotide with 8 Adenine bases
- Uncapped carbon nanotube (2.95 nm long, 1.36 nm diameter)
- Initially, DNA and CNT 0.6 nm apart and coaxially aligned
- Gromacs force field used for computations
- CNT-DNA complex desolvated (water molecules not shown)
- Dynamics simulated for t= 2 ns, P= 3 Bars and 1 fs steps
- Van der Waals and Hydrophobic Interaction Forces

Nano Letters, 3 (4): 471-473 (2003)

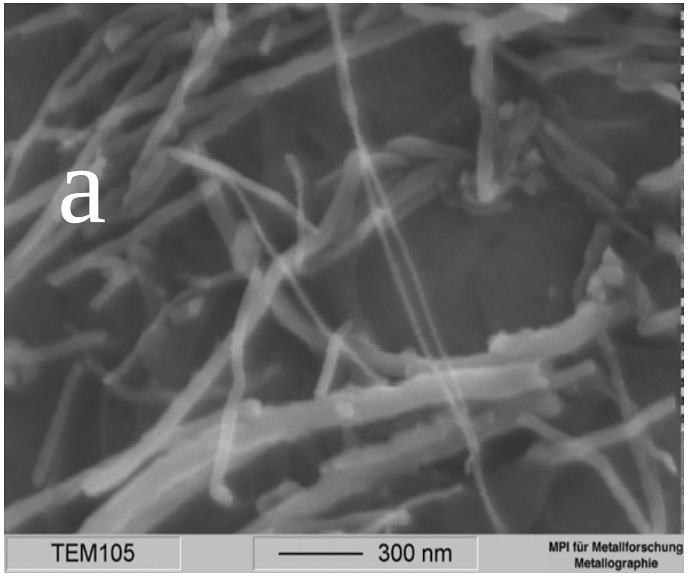
Molecular Dynamics Simulations of a DNA Oligonucleotide Interacting with a CNT

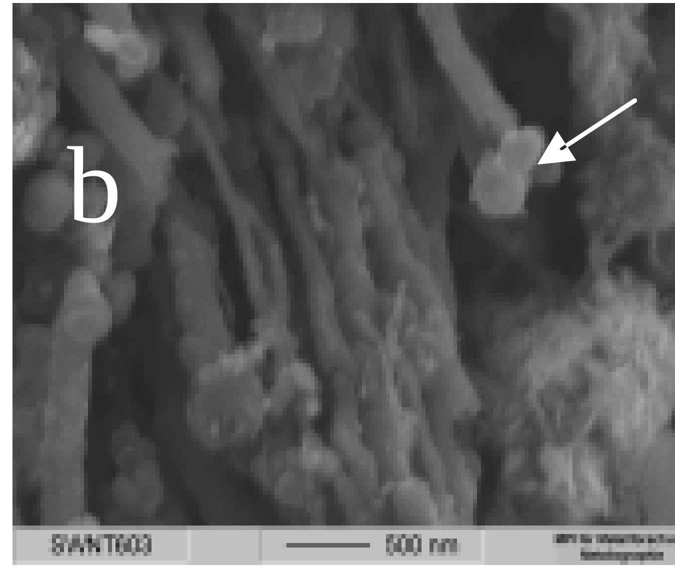


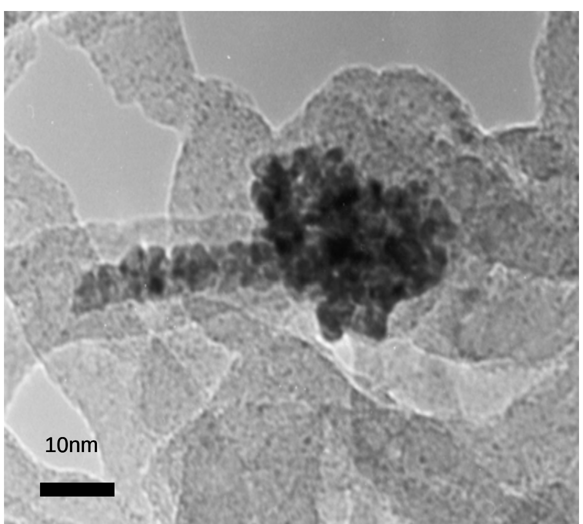
- At 50 ps : First couple bases of the DNA enter the CNT
- At 250 ps: Six bases are inside the CNT
- At 750 ps: All bases are inside the CNT

Nano Letters, 3 (4): 471-473 (2003)

Metallized DNA-Oligo Encapsulation in MWNTs







SEM images: 60bp DNA-oligos mixed with nanotubes at a mass ratio of 10:1and incubated for 20 minutes under the conditions of 400K and 3bar. (a) CNTs without DNA and (b) CNT with a partially inserted DNA fragment marked by arrow.

TEM image of a Pt-labeled 60 bp-DNA fragment partially entering a multiwalled carbon nanotube. The part of DNA outside the nanotube remains in a folded conformation. Image was obtained at the accelerating voltage of 200 KV.

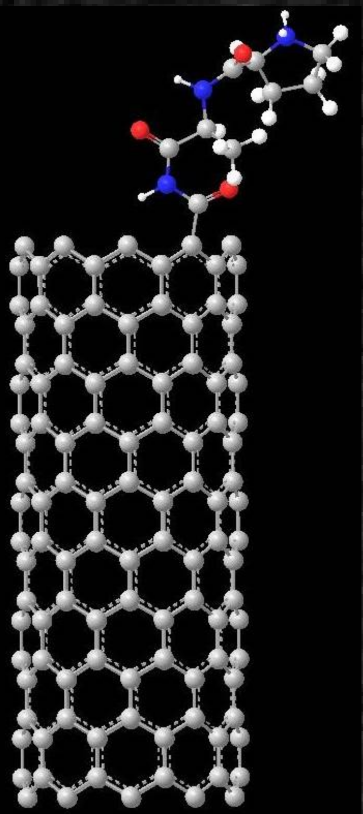
(Submitted, 2003)

A new Paradigm: Chemical and Biological Self-Synthesis of Integrated Circuits

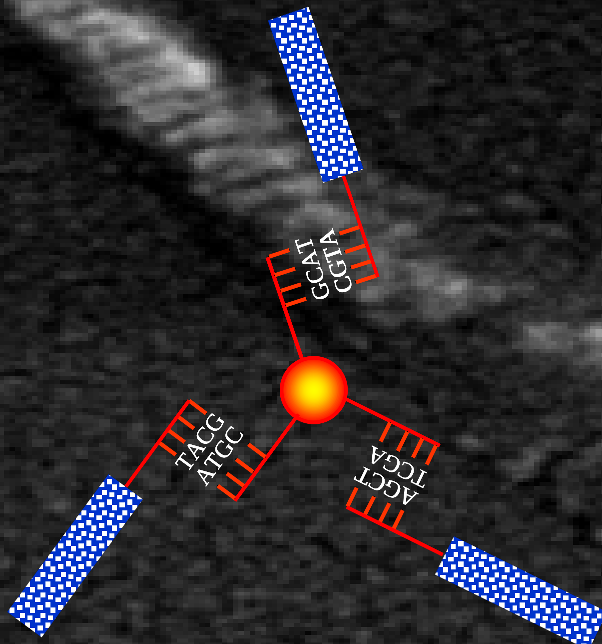
Hierarchical Bottom-up assembly of Devices

Nanocrystals, carbon nanotubes, nanocolloids

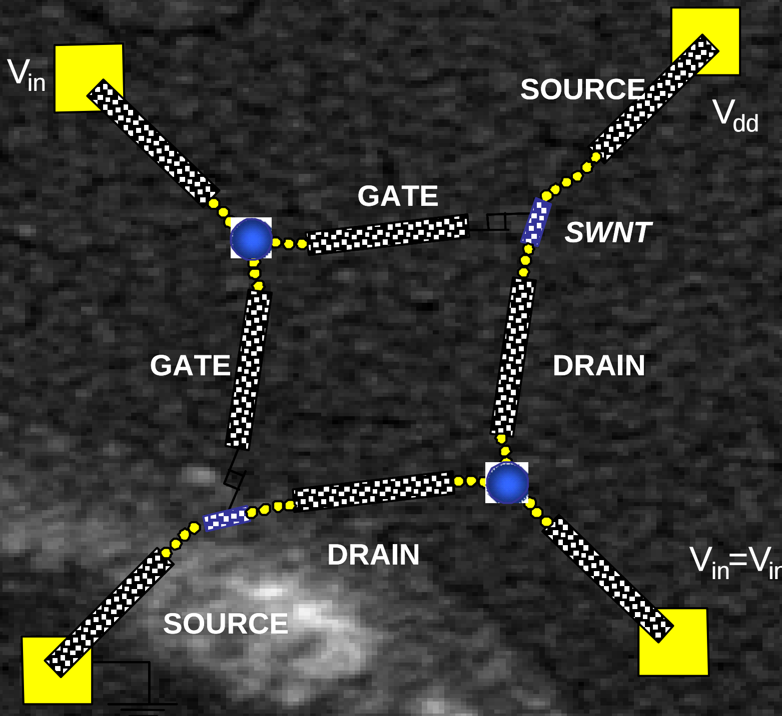
Linkers: Peptides, DNA, PNA, Viruses (In progress)



CNT-Peptide Complex

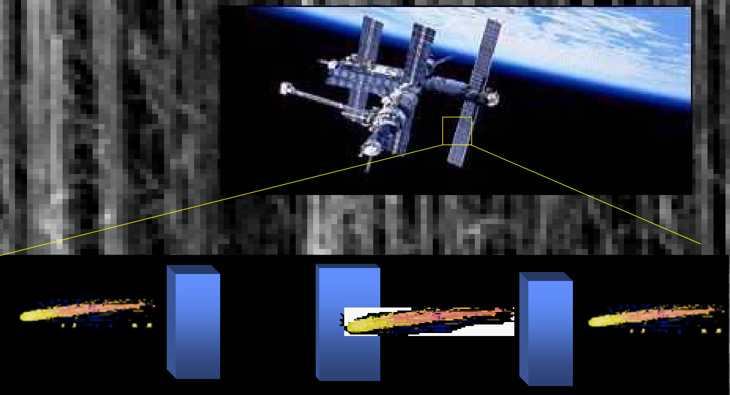


3-terminal device

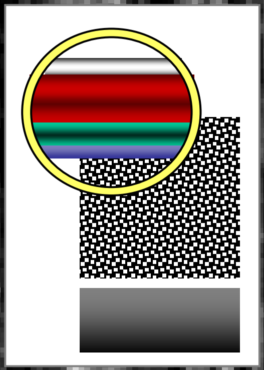


Synthesized inverter structure

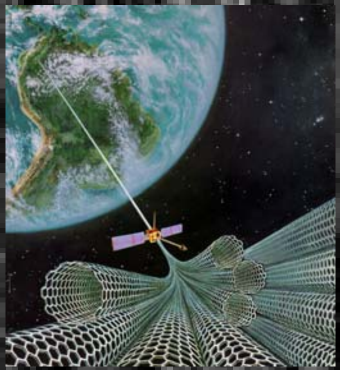
Current and Future Prospects of Bio-Nanosystems



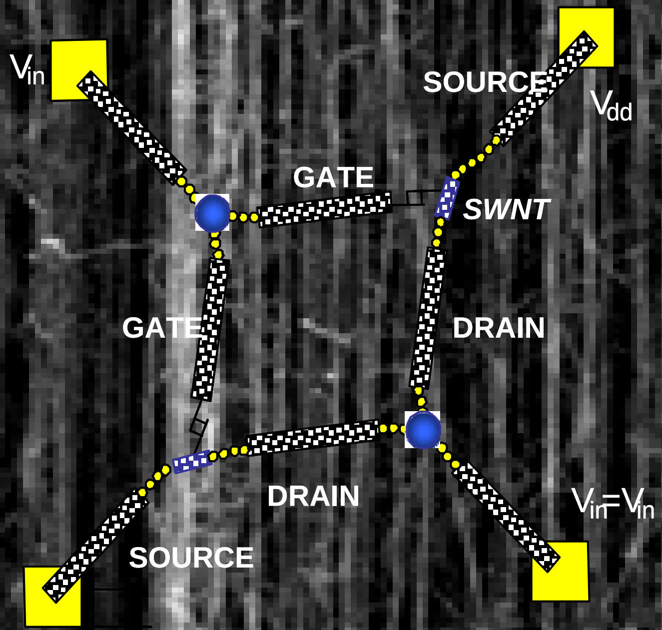
Self healing Materials



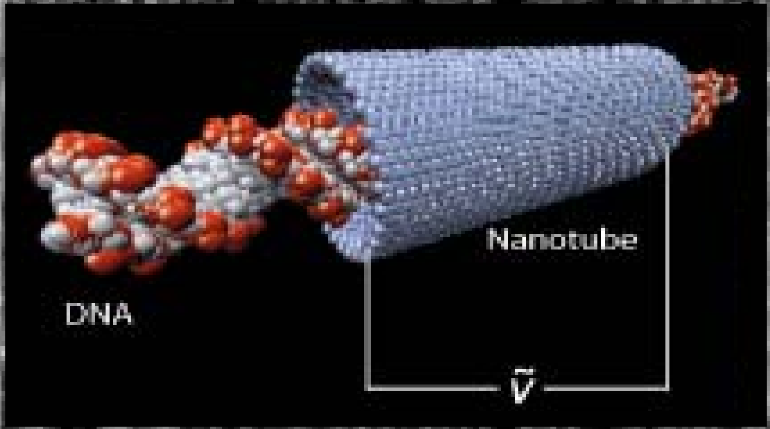
Multifunctional Nano-Composites



Tethering/Transport Systems



Novel Devices and Circuits



Bio-Sensing and Gene Delivery

And there is more room for your imagination…

Acknowledgements

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