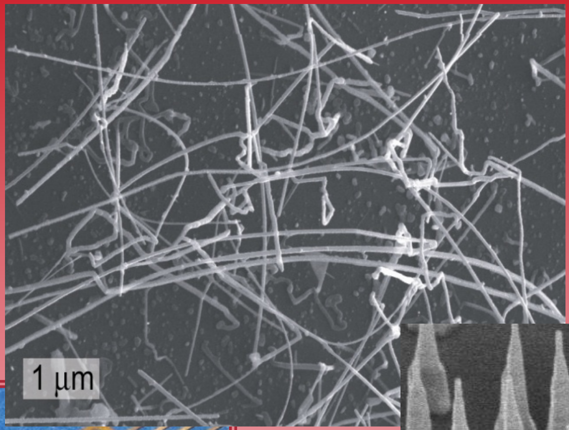
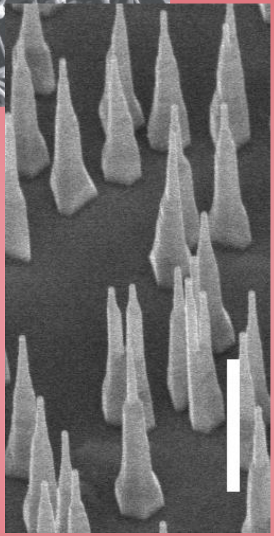
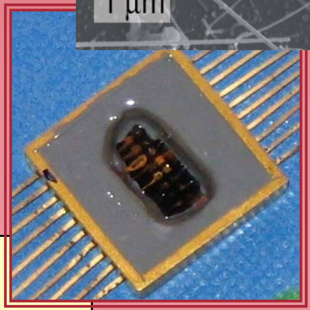
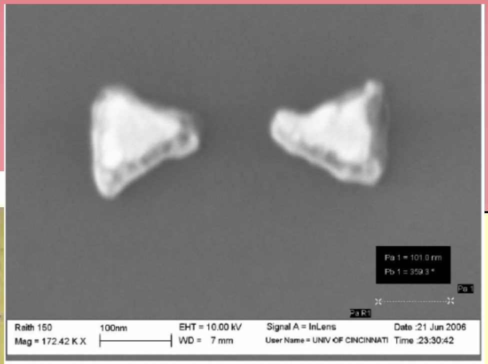
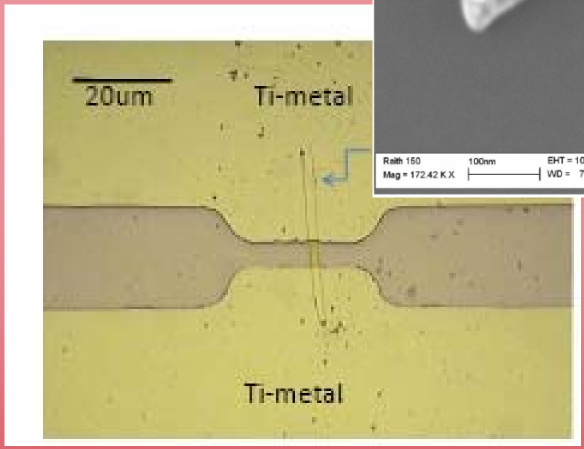
Nanotechnology:
Here, There, Everywhere !

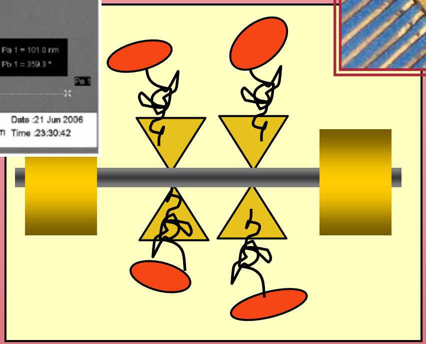












But,
What of These Nanowires?

Jan Yarrison-Rice, Physics, Miami University

What is Nano anyway?

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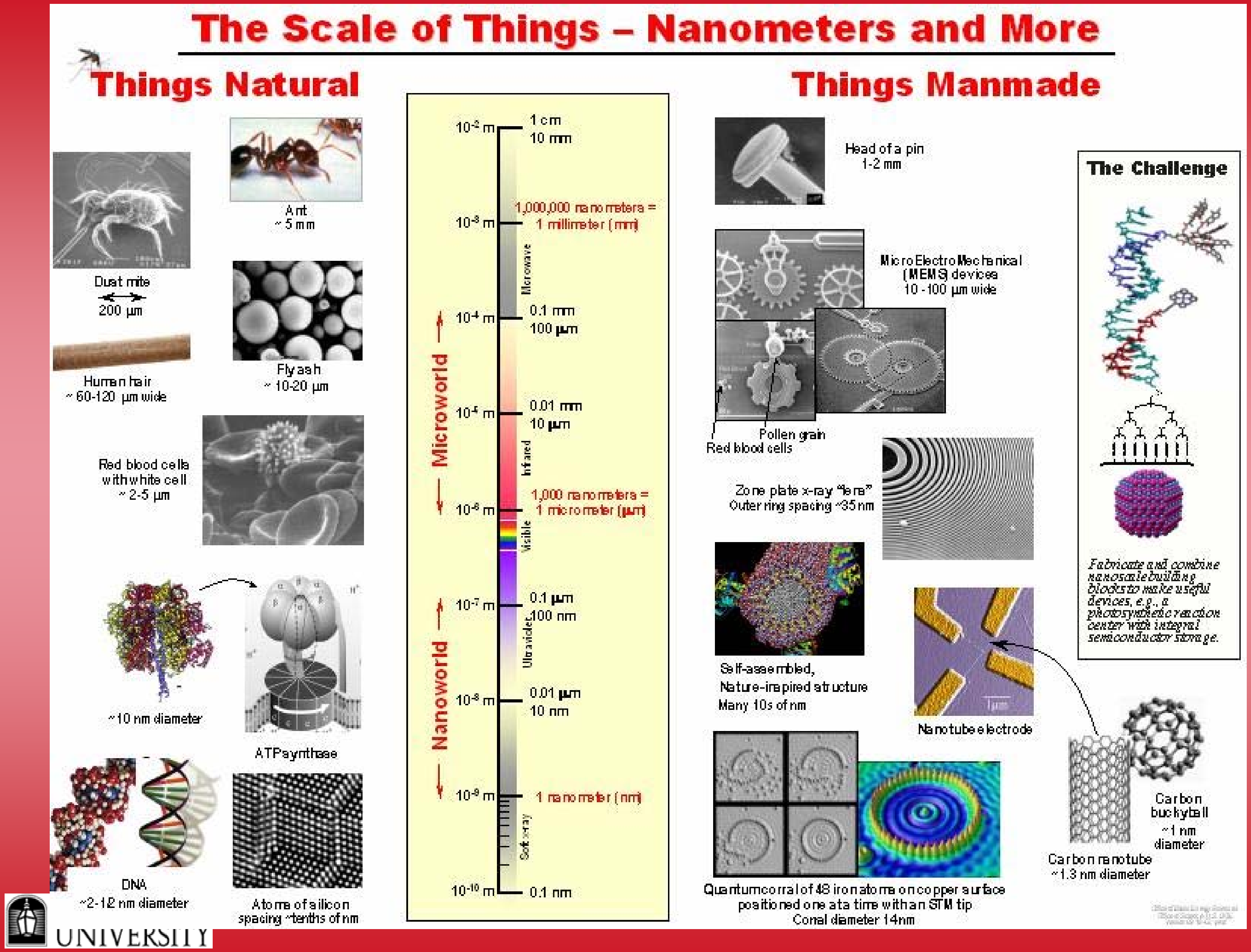
The Scale of Things – Nanometers and More
Things Natural
Things Manmade
Dust mite
200 µm
Ant
~ 5 mm
Fly ash
~ 10-20 µm
Human hair
~ 60-120 µm wide
Red blood cells
with white cell
~ 2-5 µm
~10 nm diameter
ATP synthase
DNA
~2-1/2 nm diameter
Atoms of silicon
spacing ~tenths of nm
10-2 m
1 cm
10 mm
10-3 m
1,000,000 nanometers =
1 millimeter (mm)
Microwave
10-4 m
0.1 mm
100 µm
10-5 m
0.01 mm
10 µm
Infrared
Microworld
10-6 m
1,000 nanometers =
1 micrometer (µm)
Visible
10-7 m
0.1 µm
100 nm
Ultraviolet
Nanoworld
10-8 m
0.01 µm
10 nm
10-9 m
1 nanometer (nm)
Soft x-ray
10-10 m
0.1 nm
Head of a pin
1-2 mm
MicroElectroMechanical
(MEMS) devices
10 -100 µm wide
Pollen grain
Red blood cells
Zone plate x-ray "lens"
Outer ring spacing ~35 nm
Self-assembled,
Nature-inspired structure
Many 10s of nm
Nanotube electrode
Quantum corral of 48 iron atoms on copper surface
positioned one at a time with an STM tip
Corral diameter 14nm
Carbon nanotube
~1.3 nm diameter
Carbon
buckyball
~1 nm
diameter
The Challenge
Fabricate and combine nanoscale building blocks to make useful devices, e.g., a photosynthetic reaction center with integral semiconductor storage.
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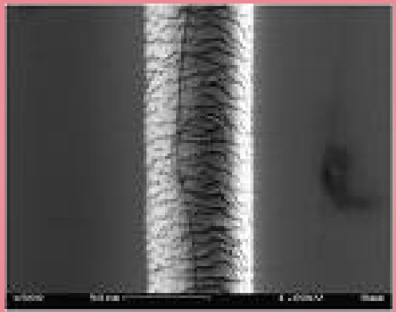
The scale of things…

Q.

If your hair were 1 km wide (and recall that is ~100 μm), then how large would 1 nanometer (nm) be?



www.nsf.gov

To help with your estimate:

1 Km is about the distance from Rte. 65 to River Falls Golf Course – or From Main to 6th St.

A. 1 cm !

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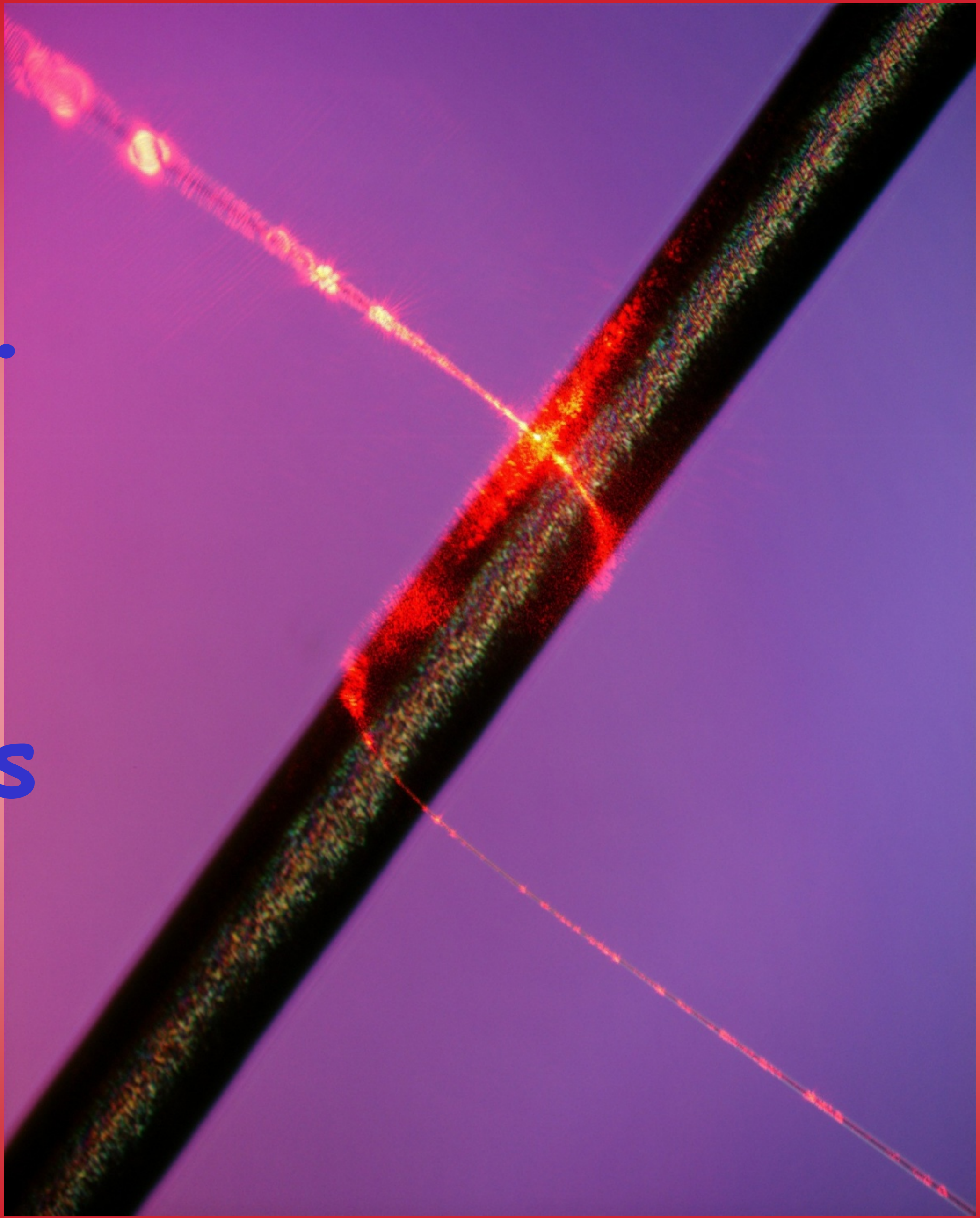
A Silica NW
~50 nm Diam.

The Hair
50-100 microns



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www.hno.harvard.edu

"Nanotechnology has given us the tools...to play with the ultimate toy box of nature -- atoms and molecules. Everything is made from it...The possibilities to create new things appear limitless..."

Horst Stormer, Nobel Laureate
Columbia University
Lucent Technologies

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Building Nanostructures

- Top Down Construction: making large things smaller
- Bottom Up Construction: building things from atoms and molecules

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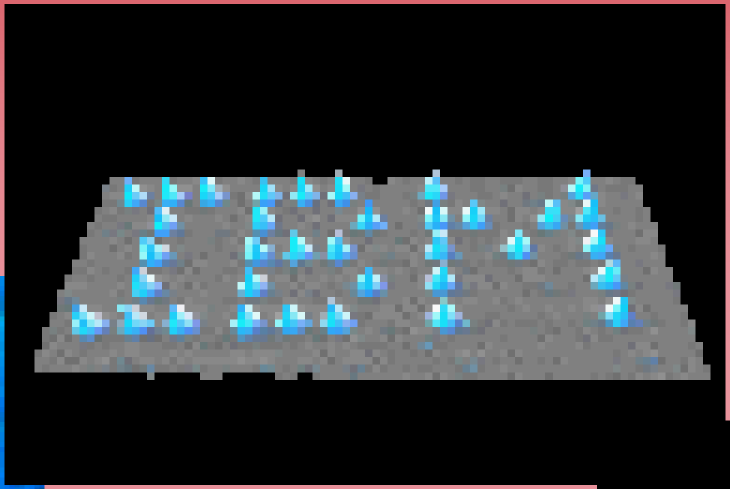
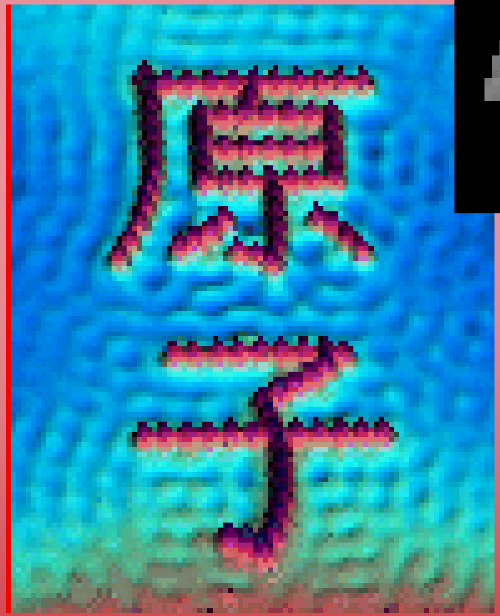
Using Atoms and Molecules to Build -- STM Images from Almaden

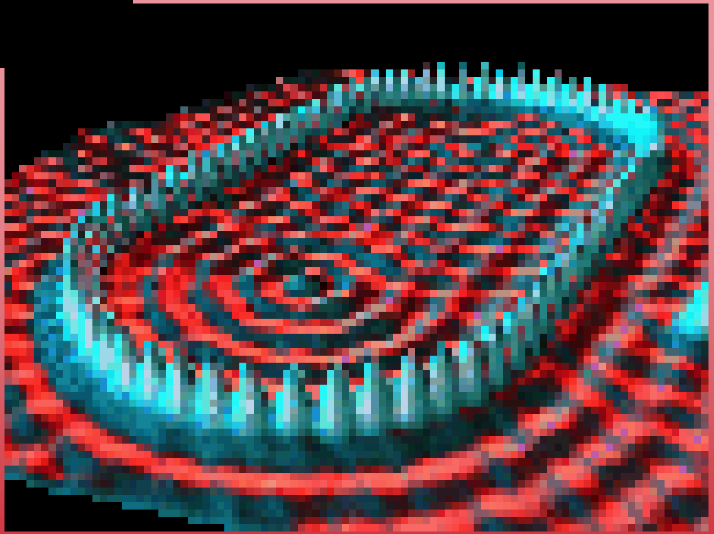


Xenon on Nickel



Iron on Copper

Iron on Copper



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http://www.almaden.ibm.com/vis/stm/corral.html

Common Nanostructures… our building blocks!

- Chemically Synthesized Quantum Dots
- Self-assembled Quantum Dots
- Carbon Nanotubes
- Semiconducting Nanowires & Nanosheets
- Other self-assembled molecules

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Mighty Small Dots

. . . nanoscience and nanotechnology will change the nature of almost every human-made object in the next century.

—The Interagency Working Group on Nanotechnology, January 1999

Howard Lee and his colleagues have synthesized silicon and germanium quantum dots ranging in size from 1 to 6 nanometers. The larger dots emit in the red end of the spectrum; the smallest dots emit blue or ultraviolet.

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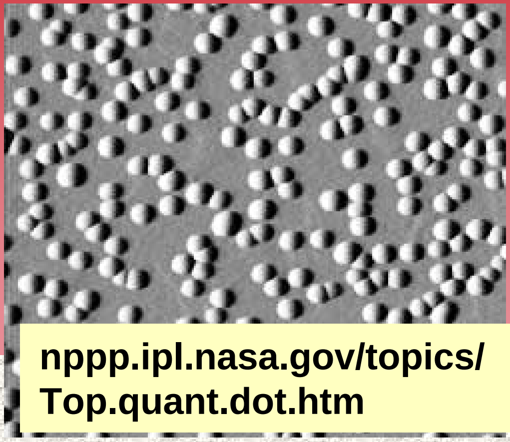
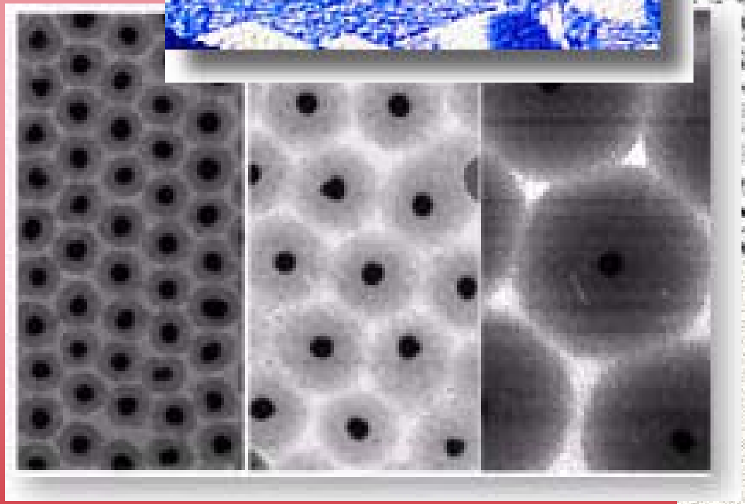
Lawrence Livermore Lab

Quantum Dots – all shapes and sizes

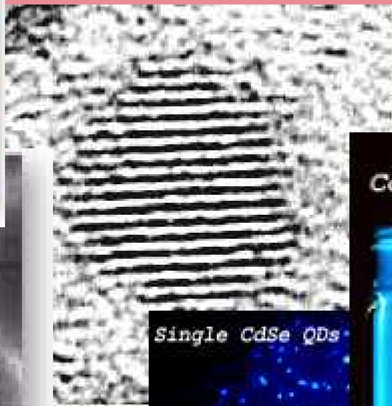
www.scifi.com/sfw/issue203/
drexler3.jpg

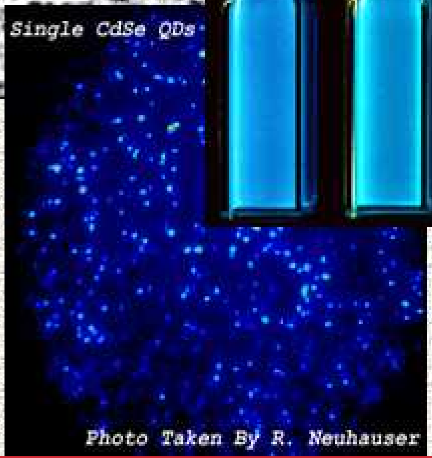


nppp.ipl.nasa.gov/topics/
Top.quant.dot.htm



The University of Melbourne





Bawendi, MIT

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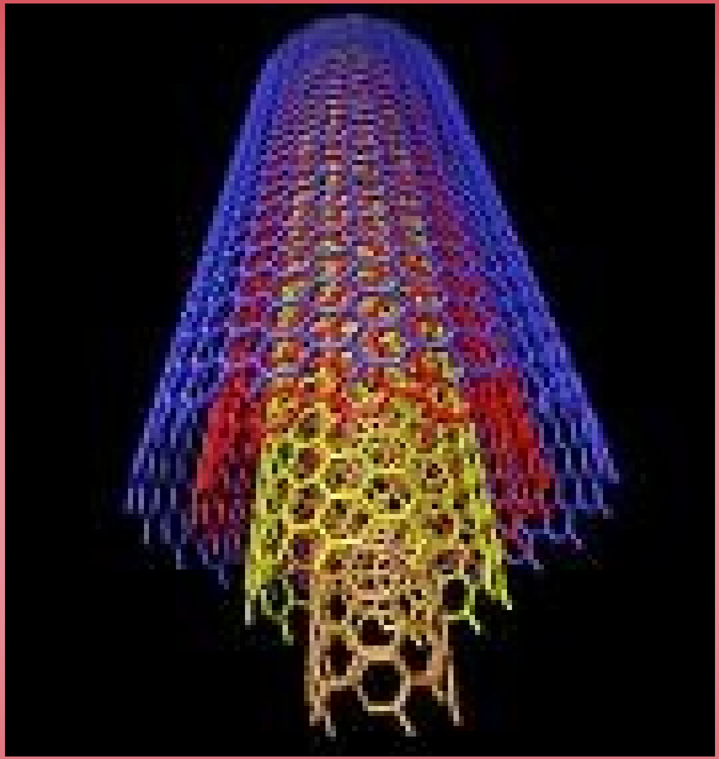
Carbon Nanotubes



www.rdg.ac.uk

CNT Geometry

CNTs: SEM Images

www.me.mtu.edu

www.lanl.gov

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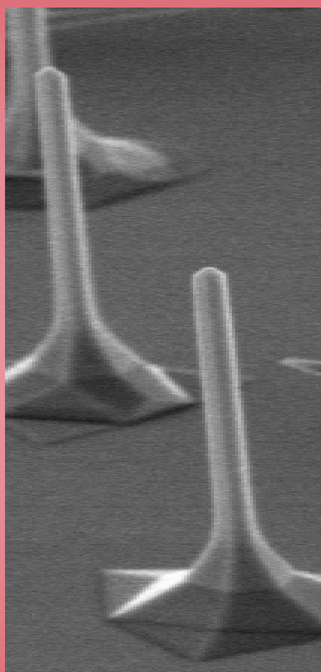
And the ever famous:



Nanowires

&

Nanosheets !

All pictures of NWs are from ANU and all Nanosheets from KIST

Nanotechnology Begins to Take Its Place

"The National Nanotechnology Initiative (NNI) is an extraordinarily important investment in the future strength of America's economy, industrial base, and scientific leadership. Recent scientific and technical advances have made it possible to assemble materials and components atom by atom, or molecule by molecule. We are just beginning to understand how to use nanotechnology to build devices and machines that imitate the elegance and economy of nature."

Charles M. Vest
President
Massachusetts Institute of Technology

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Nanotechnology is indeed here, there, and everywhere:

- In the clothes you wear
- In the makeup you use
- In the car you drive

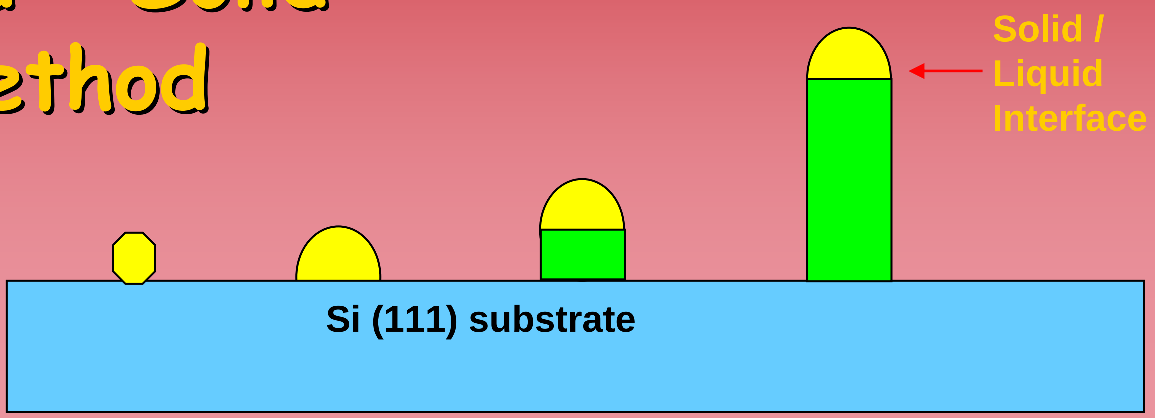
- And, coming soon to medicines and medical procedures that help to cure you

My particular interest is in:

- Understanding the physics of NWs
- Applying this knowledge to make NW-based sensors and devices

Nanowire Growth

Vapor – Liquid – Solid Or VLS Method



- Begin with Gold Nanosphere
- Melt Gold
- Melted Gold Droplet's Diameter → NW Diameter
- Introduce NW material
- NW material enters Gold & forms eutectic
- NW grows below Gold as solid forms beneath

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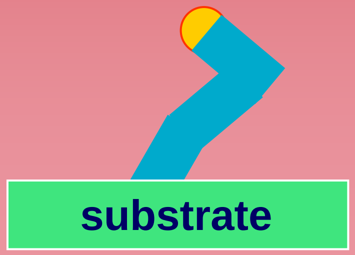
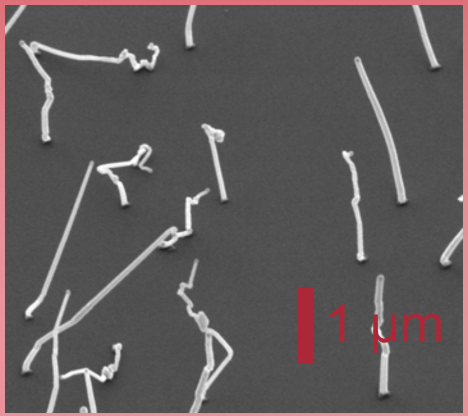
Different Growth Conditions are responsible for different NW structures:

GaAs (111)B substrate

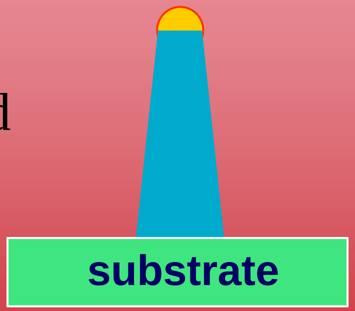
- $T_g < 390$ °C
  - Irregular orientation
  - Kinked

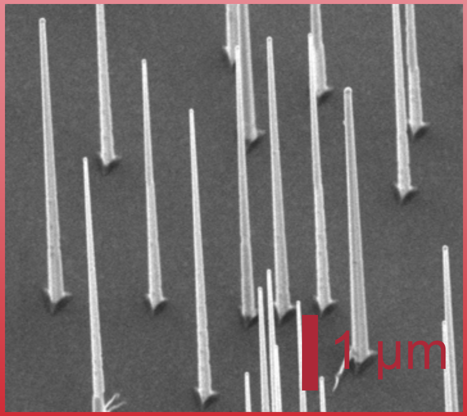




390 °C

- $T_g > 410$ °C
  - Straight, [111]B aligned
  - Tapered





450 °C

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TEM pictures of GaAs NW internal structure

Original procedure

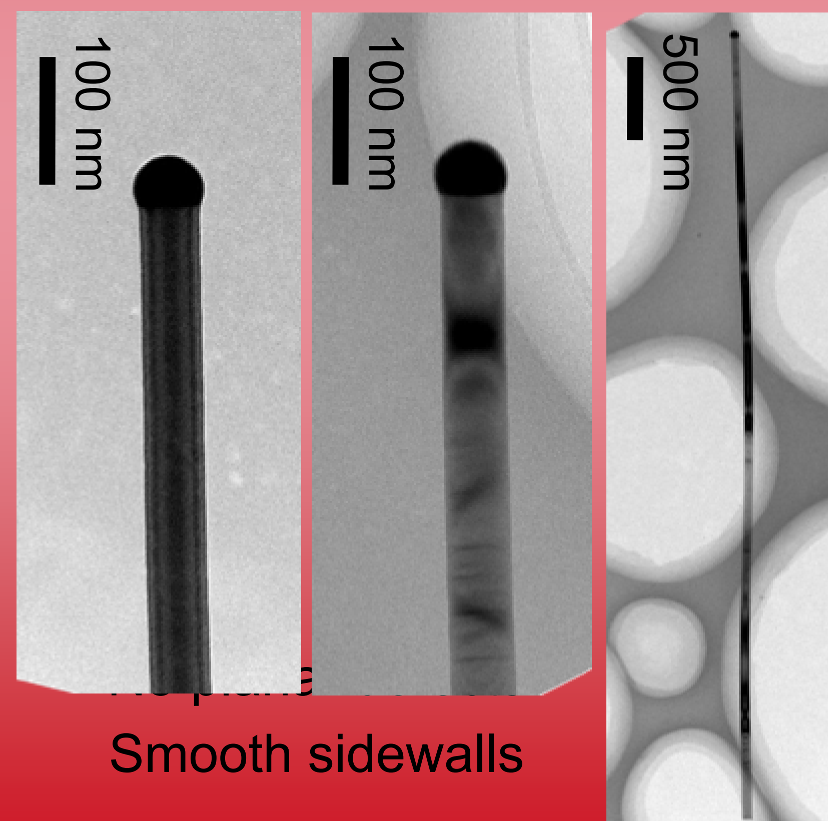
450 °C

Twin defects

Facetted sidewalls

Two-temperature procedure

T_n = 450 °C, T_g = 390 °C



Smooth sidewalls

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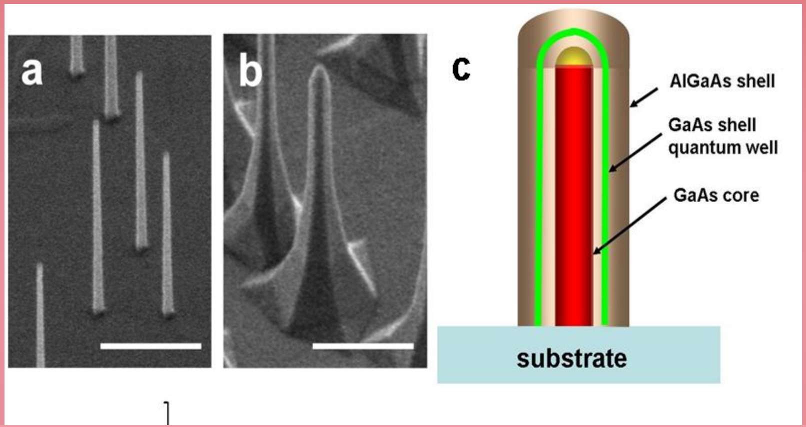
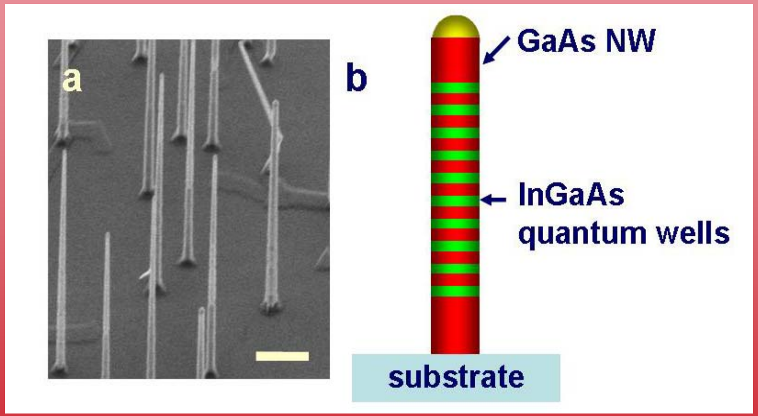
NWs can also be grown into interesting nanostructures.



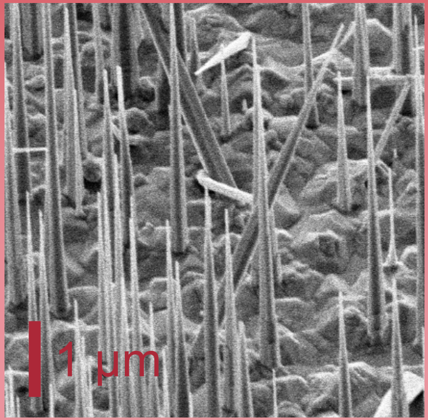
Core-shell Structure – NanoTUBE !

Axial Differential Growth – Quantum Well in NW !

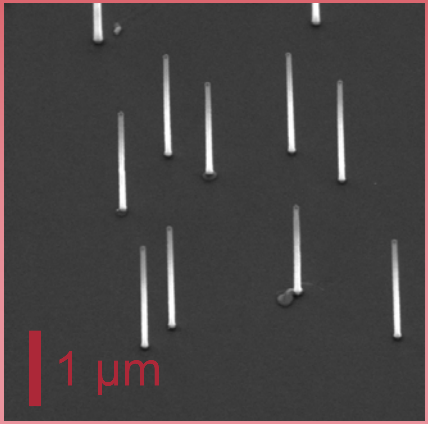


III-V Nanowires

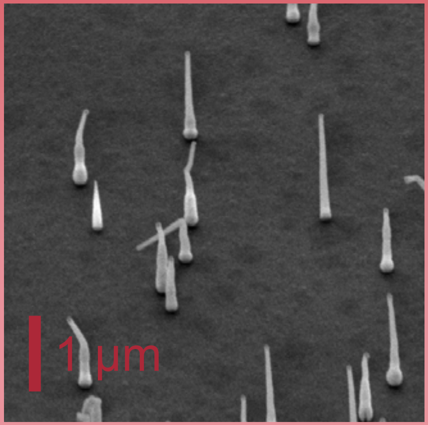
SEM images



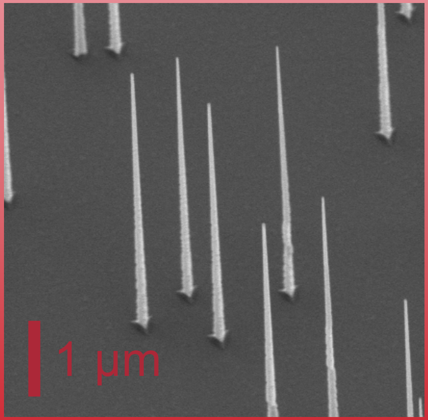
InAs NWs



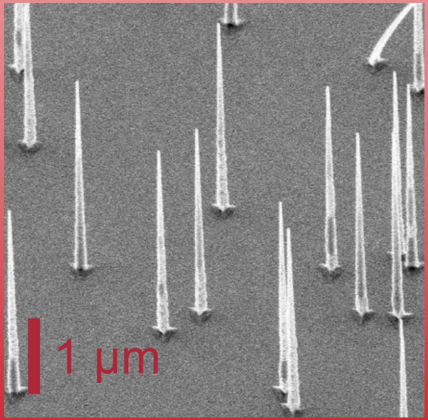
GaP NWs



AlAs NWs



GaAs NWs



AlGaAs NWs

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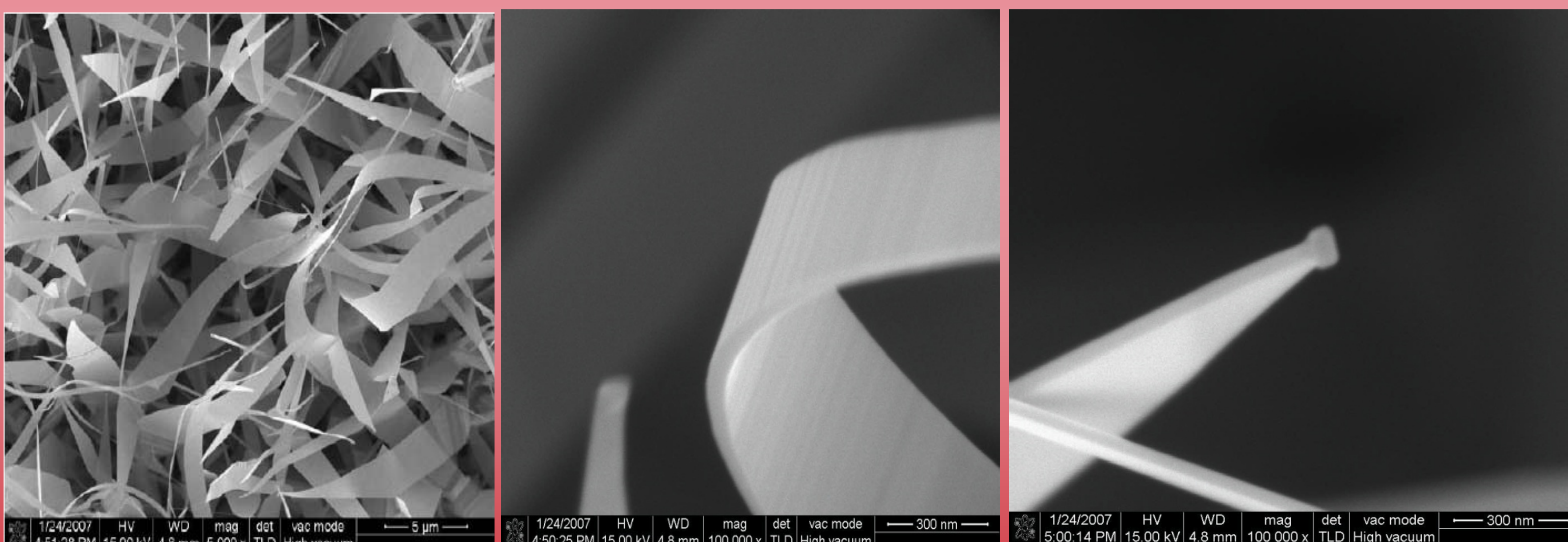
II-VI CdS Nanosheets

- Grown by pulsed laser deposition using vapor-phase transport method with gold catalysts (800^{o}C; 20min)
- Dimensions: ~50 *nm* thick; ~ 4 *μm* wide & 30-100 *μm* long



SEM images of ensemble and single nanosheets

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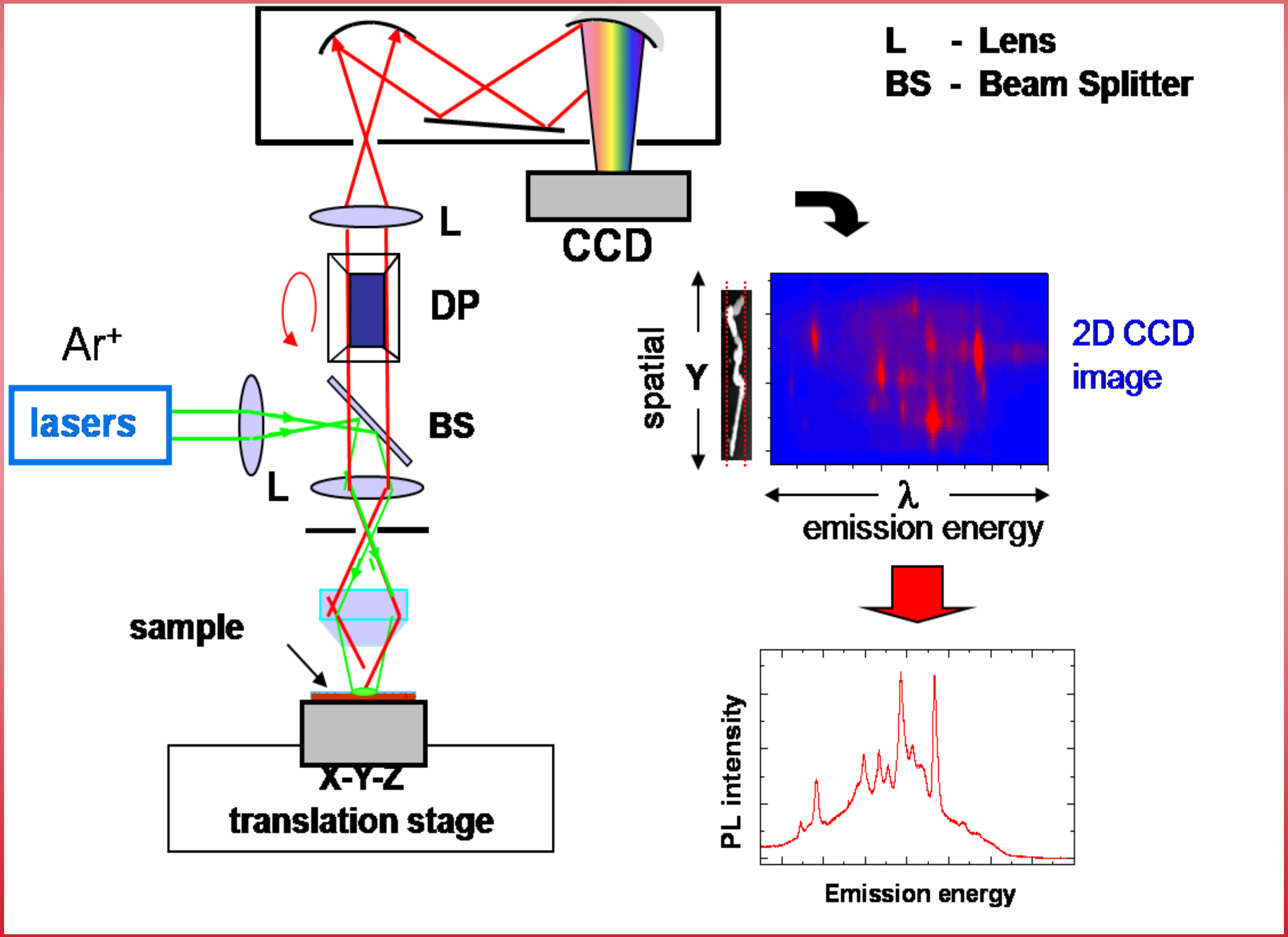
NW Characterization (some physics !)

Slit confocal spectroscopy



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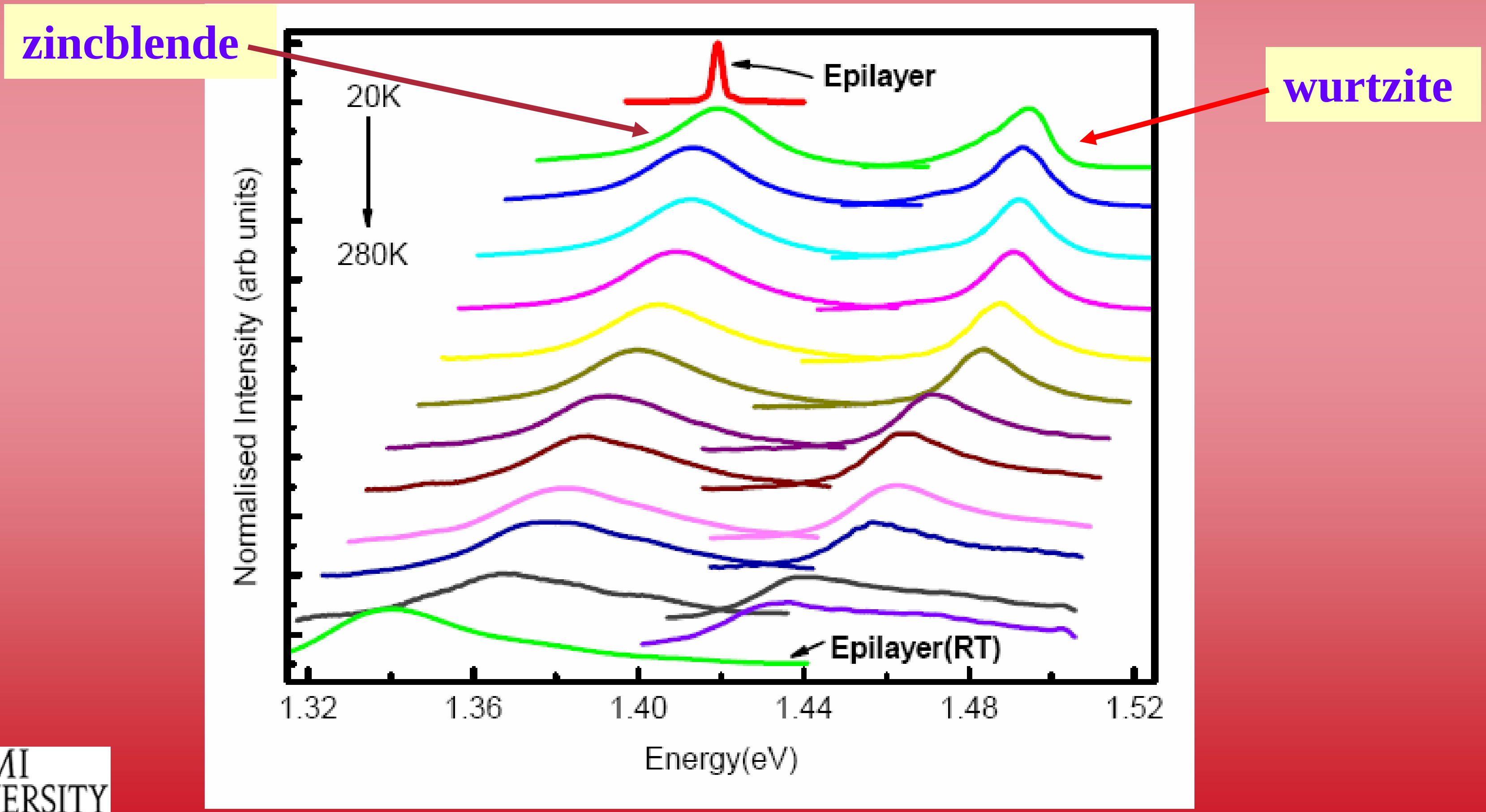
A series of ***spectra*** in 2 InP NWs as Temperature increases.



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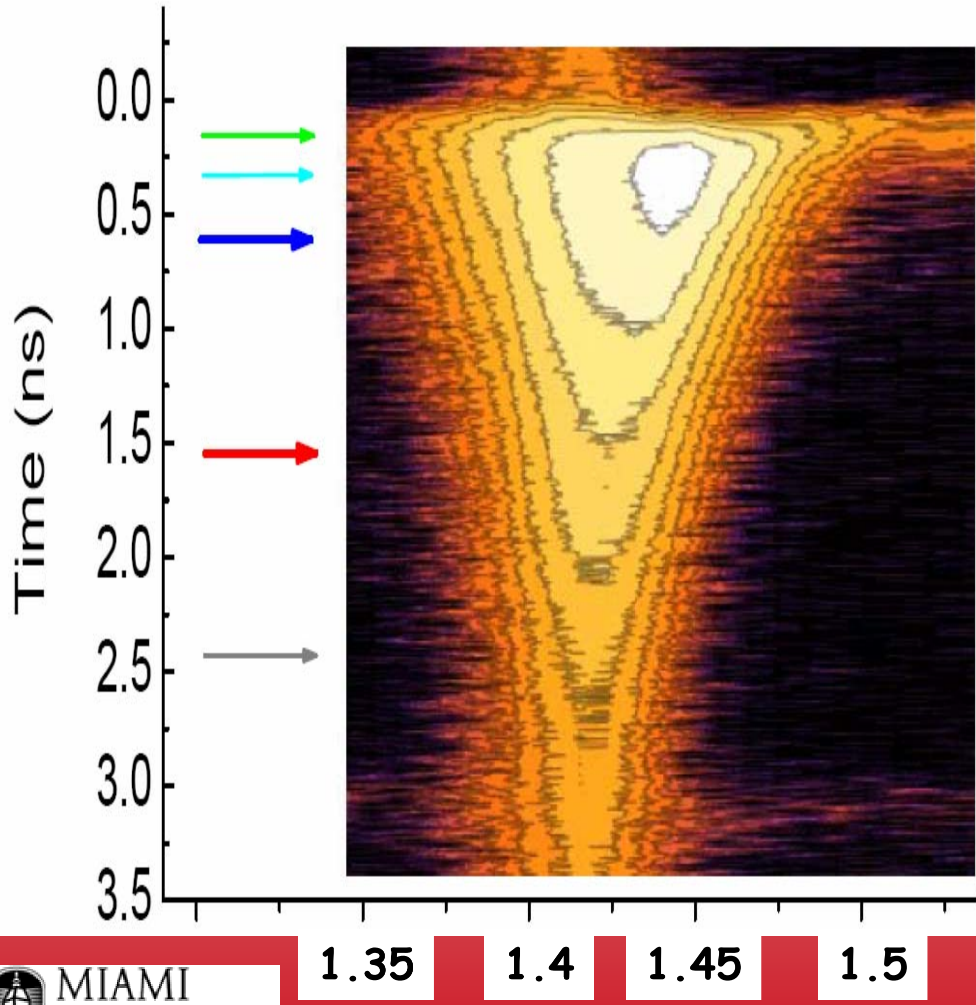
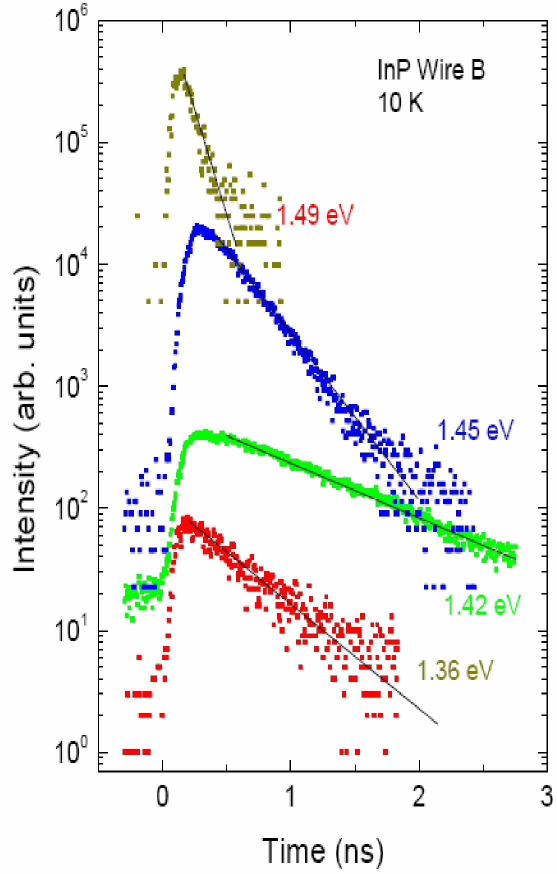
InP NW Photoluminescence Spectra over Time





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NOW….

Onto NW Devices and BioSensors !!

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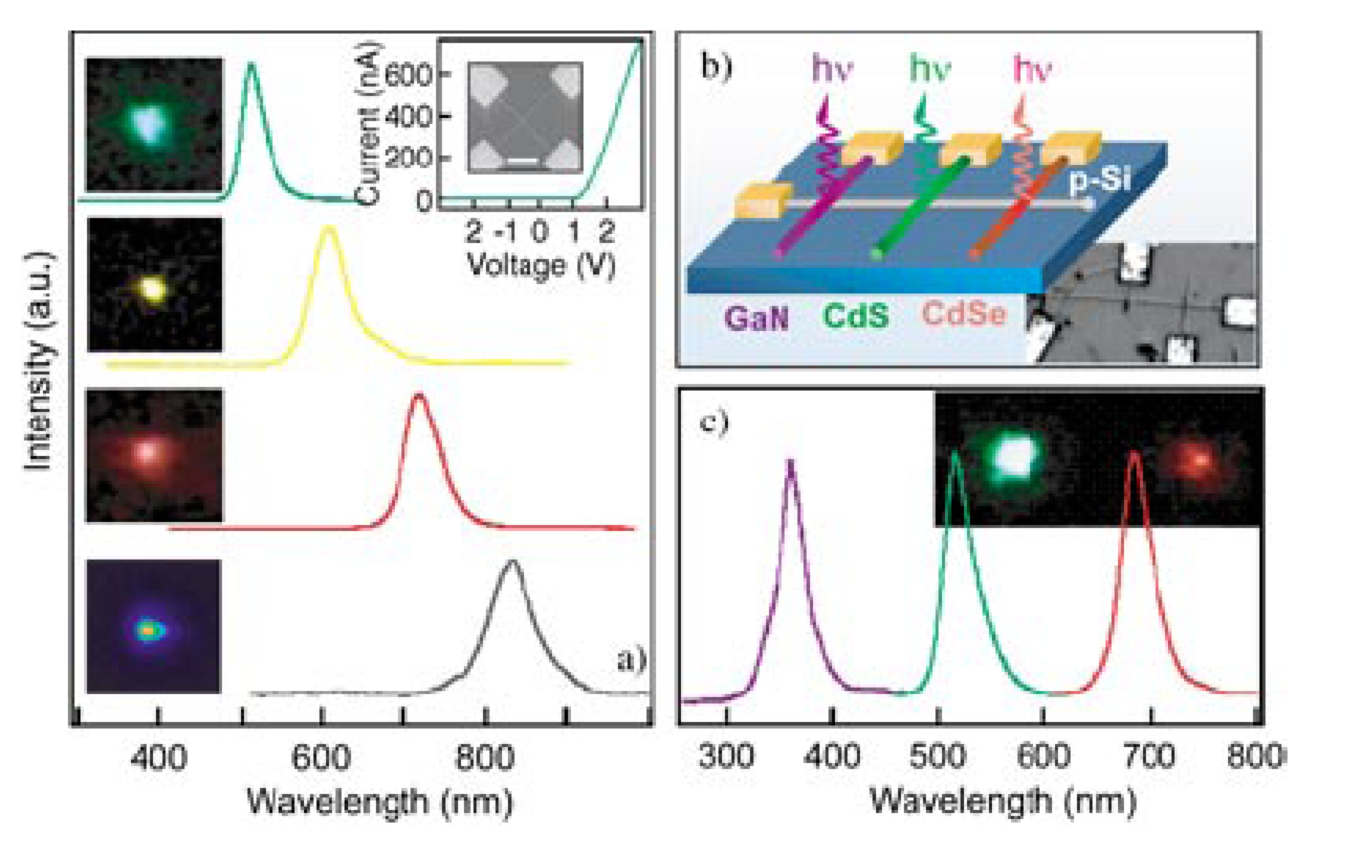
NW of Different Materials as PhotoEmitters



From: H. Jackson, UC

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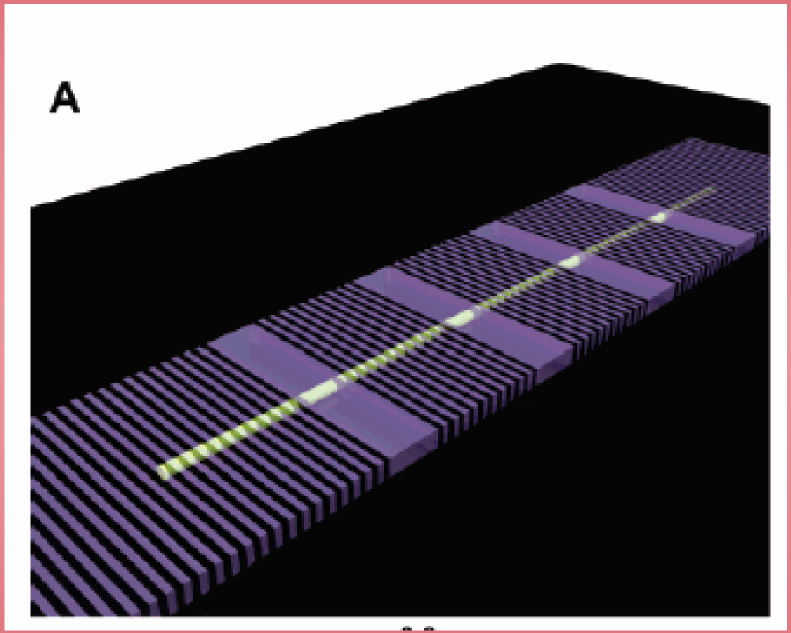
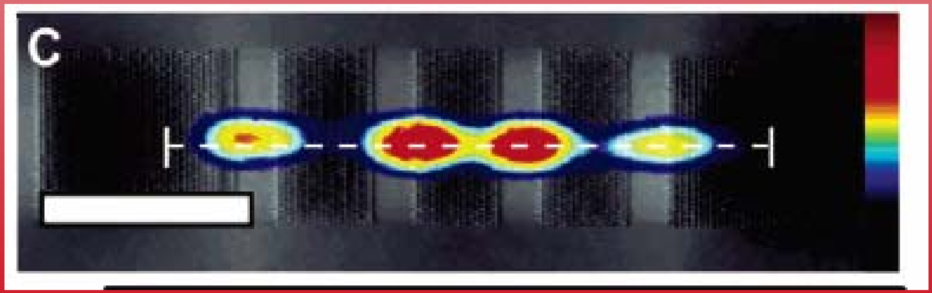
NW LEDs and Lasers



From: H. Jackson, UC



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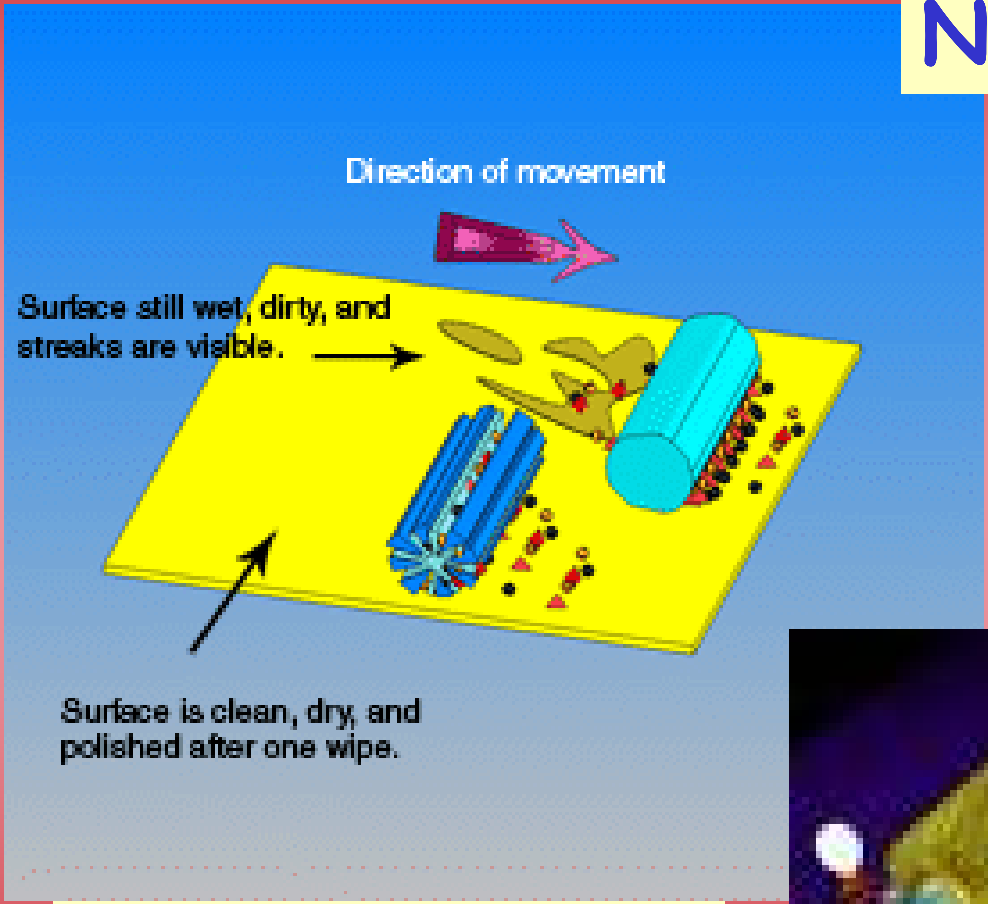
Nanowires are also finding use in:

- Filters – air and water – a woven filter of NWs can filter out ultra-small particles
- Stronger materials that are still flexible – for police and armed forces protection
- Latest report: for making electricity on a small scale !

And of course, in my area of interest →

Other NW Applications include:

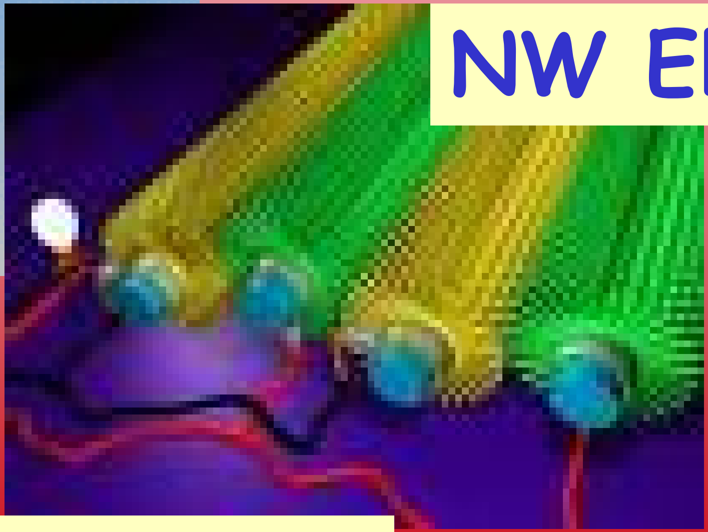


NanoFiber Mop

NW Solar Cell

www.newscientist.com

NW Electricity



www.azonano.com

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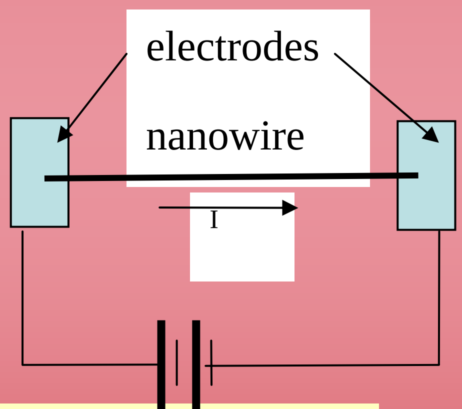
Nanowires as Biosensors !

From: H. Jackson, UC

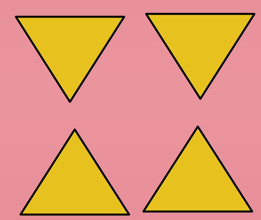
Nanowire BioSensor Schematic

Nanowire Sensor



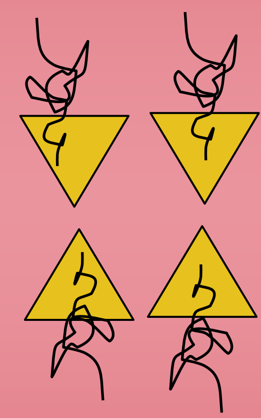
High sensitivity

Bowtie Resonator



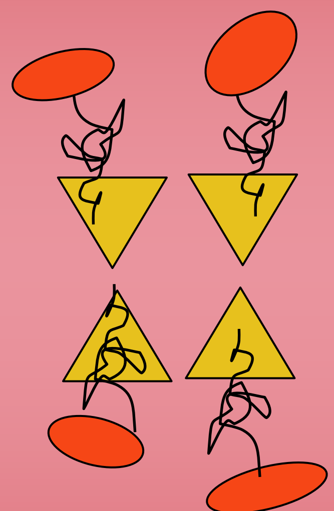
- **~10^4 Enhancement at resonance**

"Dressed" Bowtie



Ligands added

Bowtie with Toxins



Toxins captured, surface plasmon resonance changed

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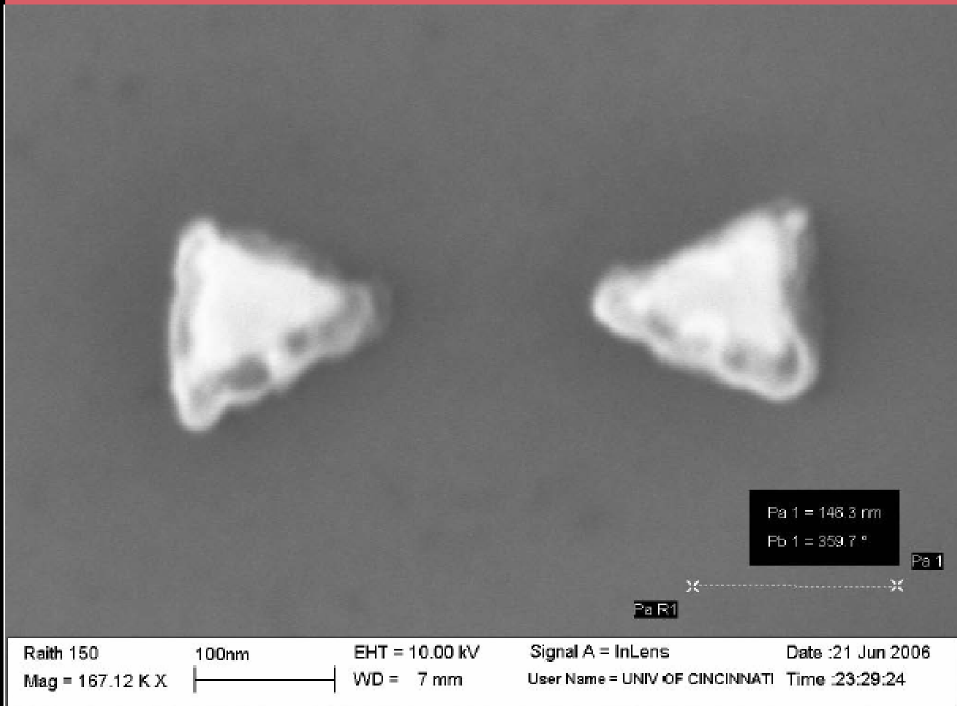
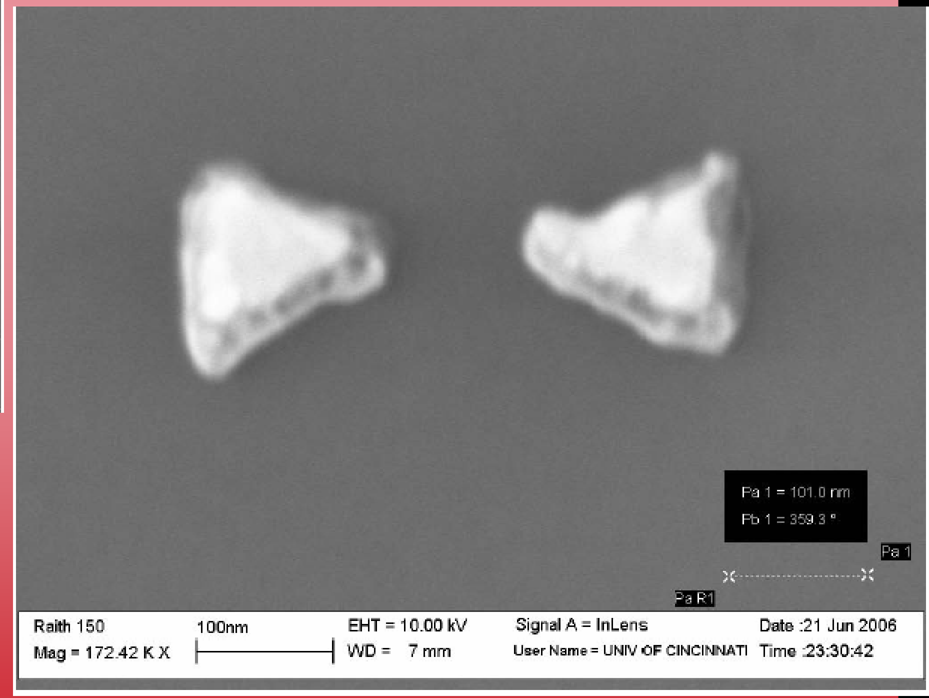
Bowtie Plasmonic Resonators





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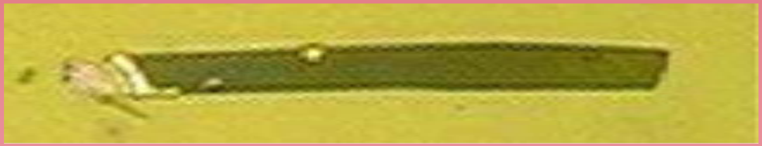
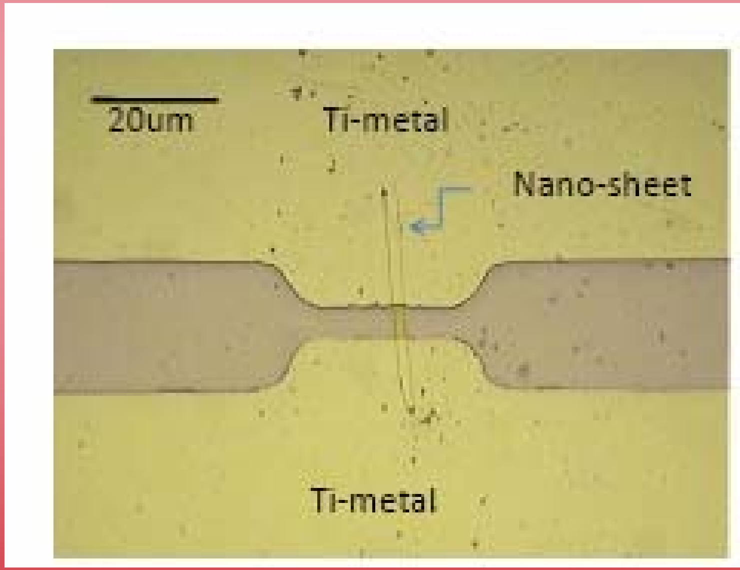
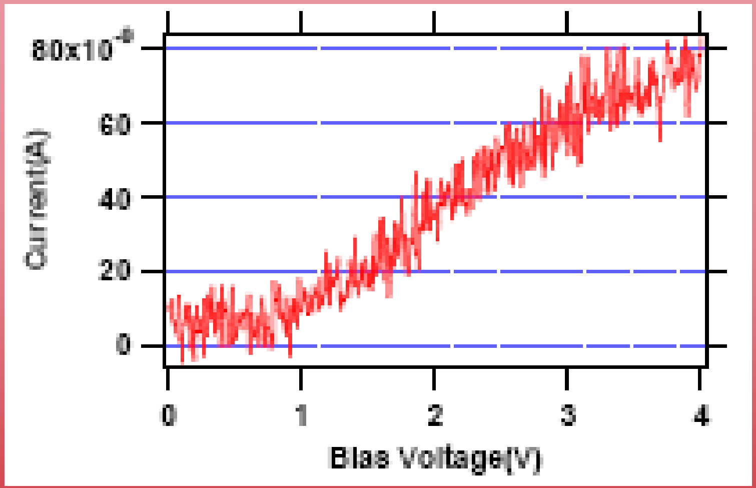
First Device Structure: CdS Nanosheet w/ Electrodes







Current vs. Voltage

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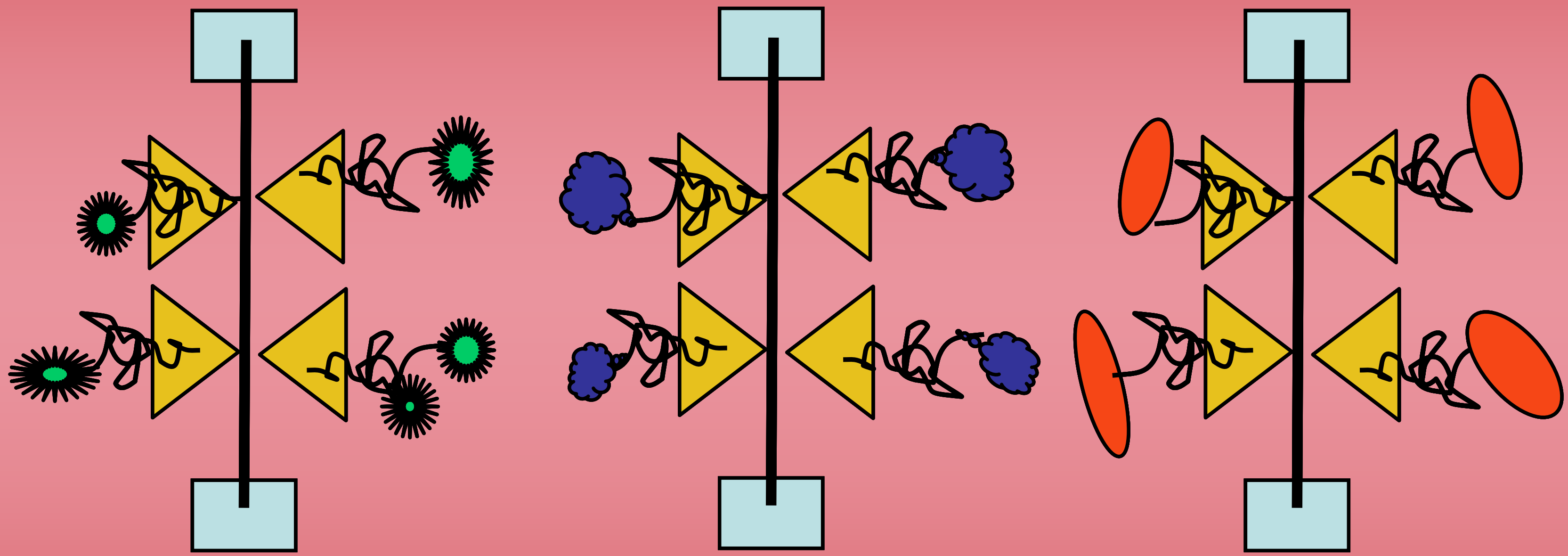
Imagine a biosensor array?!



A different chemical species detected on each biosensor !

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Conclusion

"The National Nanotechnology Initiative is a big step in a vitally important direction. It will send a clear signal to the youth of this country that the hard core of physical science (particularly physics and chemistry) and the nanofrontiers of engineering have a rich, rewarding future of great social relevance. The coming high tech of building practical things at the ultimate level of finesse, precise right down to the last atom, has the potential to transform our lives. Physics and chemistry are the principal disciplines that will make this all happen. But they are hard disciplines to master, and far too few have perceived the rewards at the end of the road sufficient to justify the effort. The proposed NNI will help immensely to inspire our youth."

Richard E. Smalley
Gene and Norman Hackerman Professor of Chemistry and Professor of Physics
Rice University Center for Nanoscale Science and Technology

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Thanks to my collaborators at Miami:

Graduate Students :

Neil Smith, Senthil Rajagopal, Siwei Cao, & Erich See

Undergraduate Students:

Katie Beddow, Jesse Manders, Colin Boyle, & Caroline Scacca

Colleagues at University of Cincinnati:

Graduate Students	Faculty
Melodie Fickenscher	Leigh Smith
T.B. Hoang	
S. Perenga	Howard Jackson
Ashu Mishra	

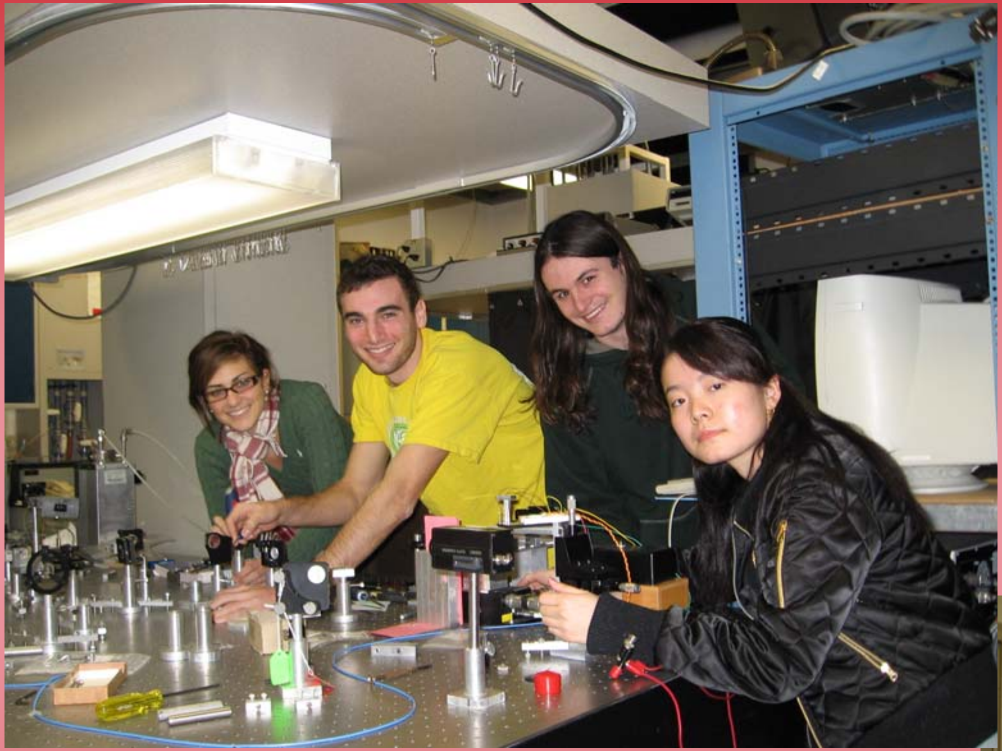
Thanks to NSF & DOE for their support

Thanks to Synthesis Colleagues:

Chenupati Jagadish's Group: Australian National University

Collegues: KIST (Korean Institute of Science & Technology

JYR 2008 Nano Group



Caroline Scacca
Jesse Manders
Colin Boyle
Siwei Cao

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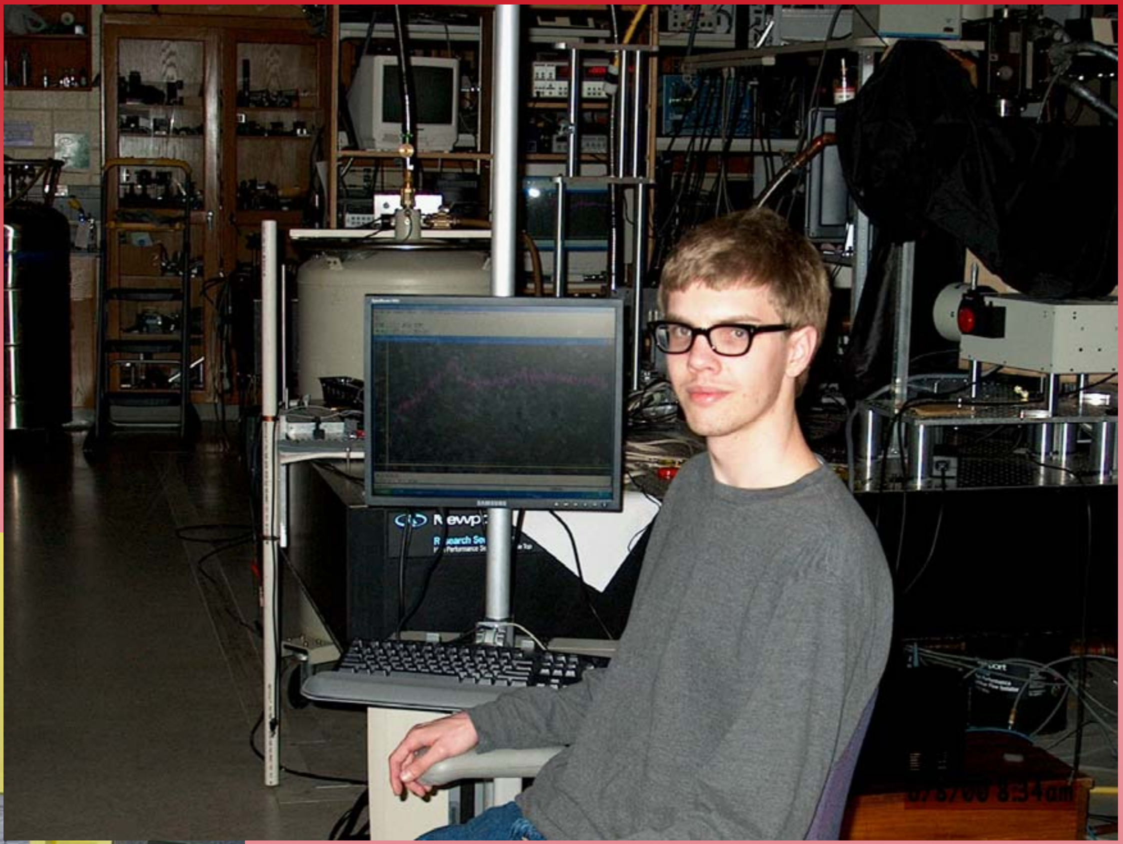
Grad Students



Erich See

Siwei Cao

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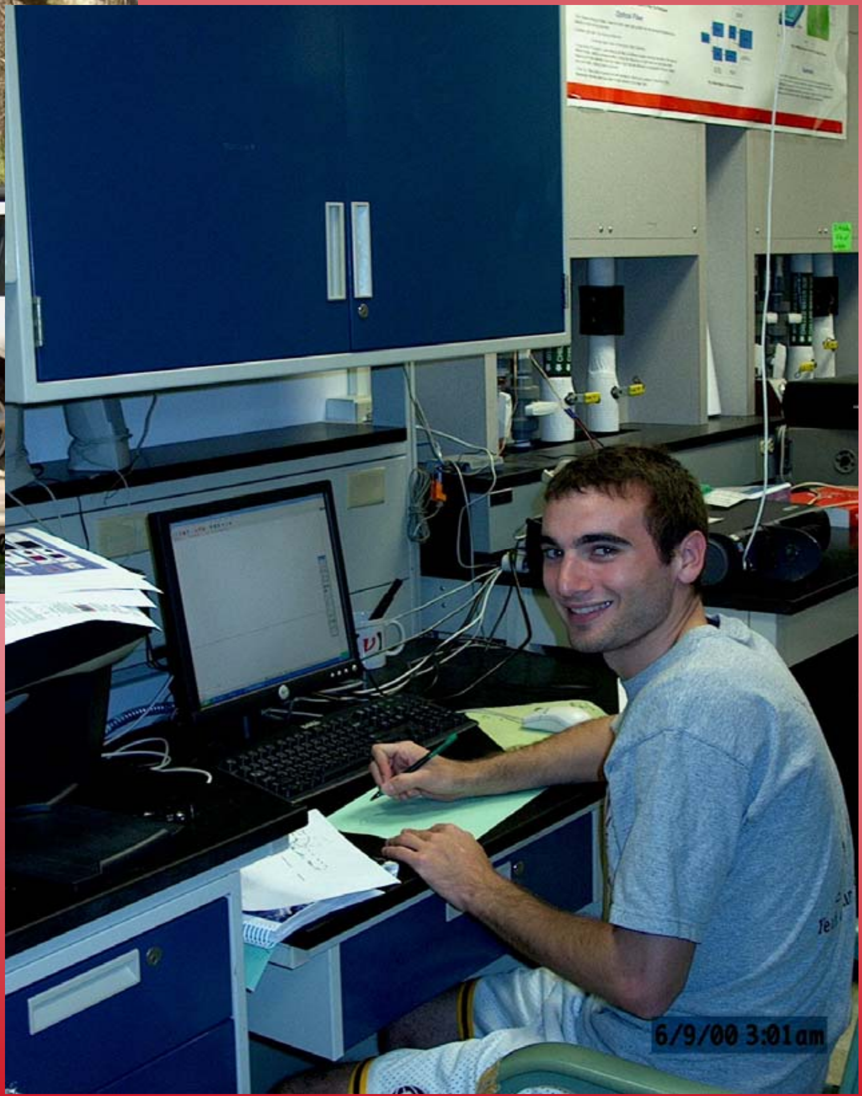
Jesse Manders
Off to NIST



Colin Boyle
Off to Australia

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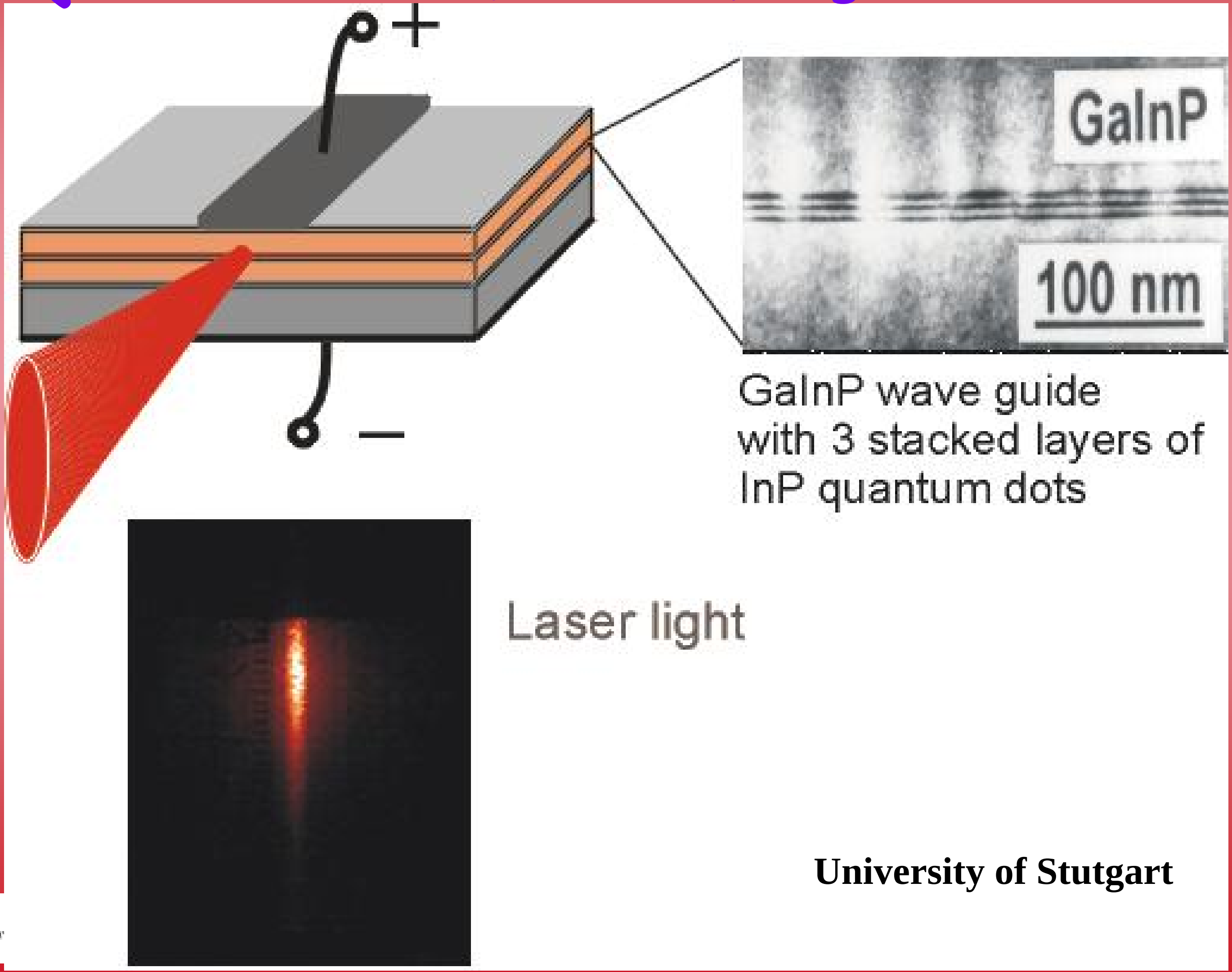
Uses for QDs Include:
InP QD Laser (where QDs grow on surfaces)



GaInP wave guide with 3 stacked layers of InP quantum dots

University of Stutgart

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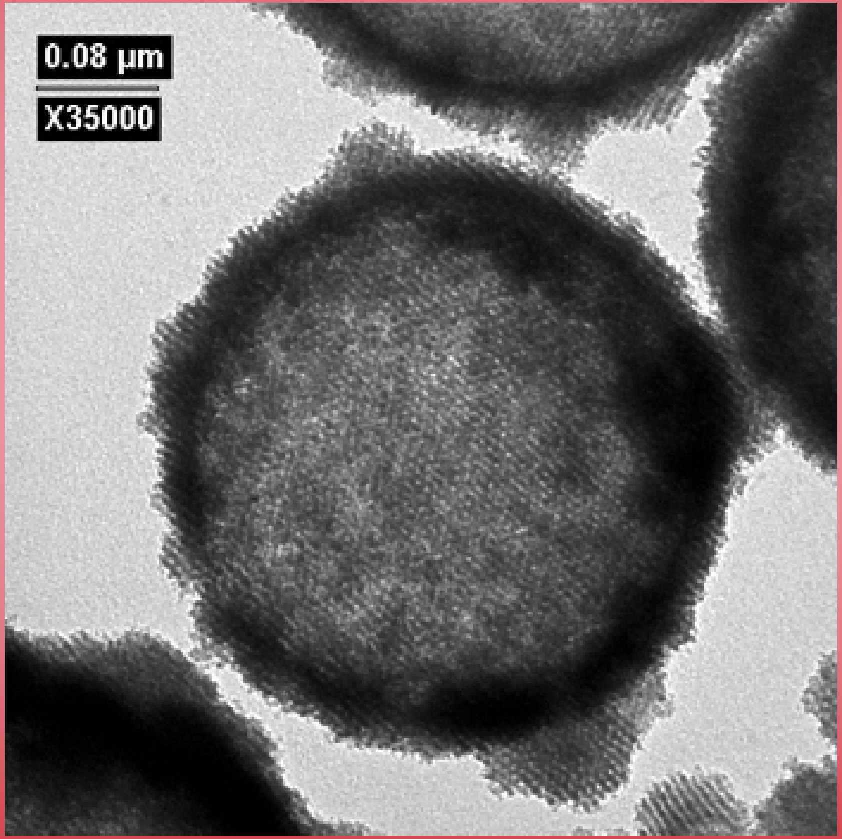
Applications of Nanoscience: Medicine



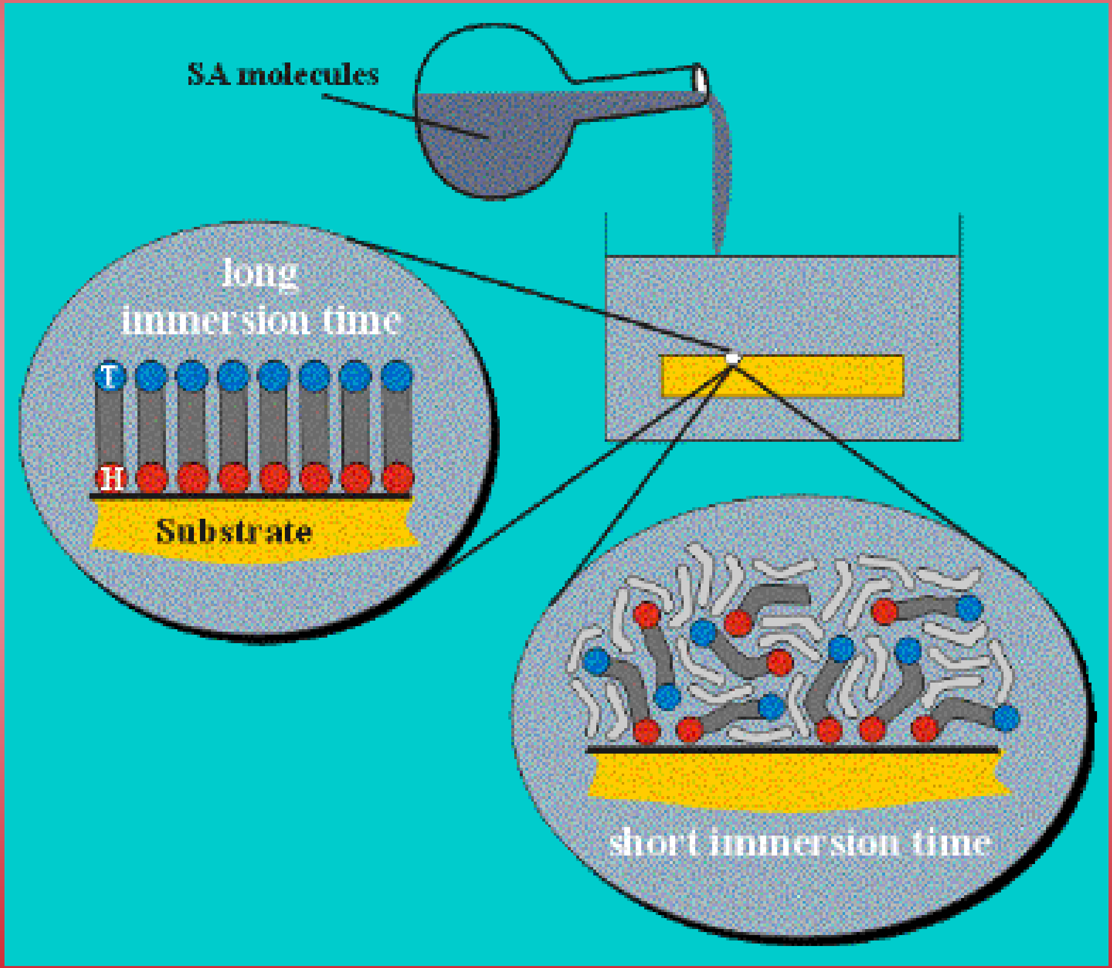
Drug Delivery

TEM image of the hexagonally-templated hollow ZnS on Silica Spheres

braungroup.beckman.uiuc.edu/Dongyeon.html

Bottom Up Approach – Self Assembly

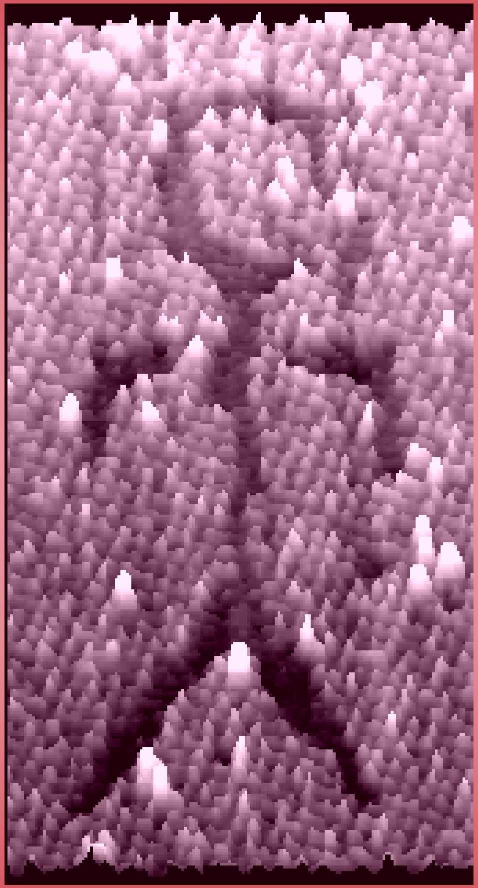
Self-assembled monolayers (SAM)



chemistry.st-and.ac.uk/staffmember.php?id=mb

Self-Assembly & STM

Note: STM means Scanning Tunneling Microscope



Molecular **NanoMan** logo (line thickness 1-3 nm), written with STM into a layer of self assembled molecules.

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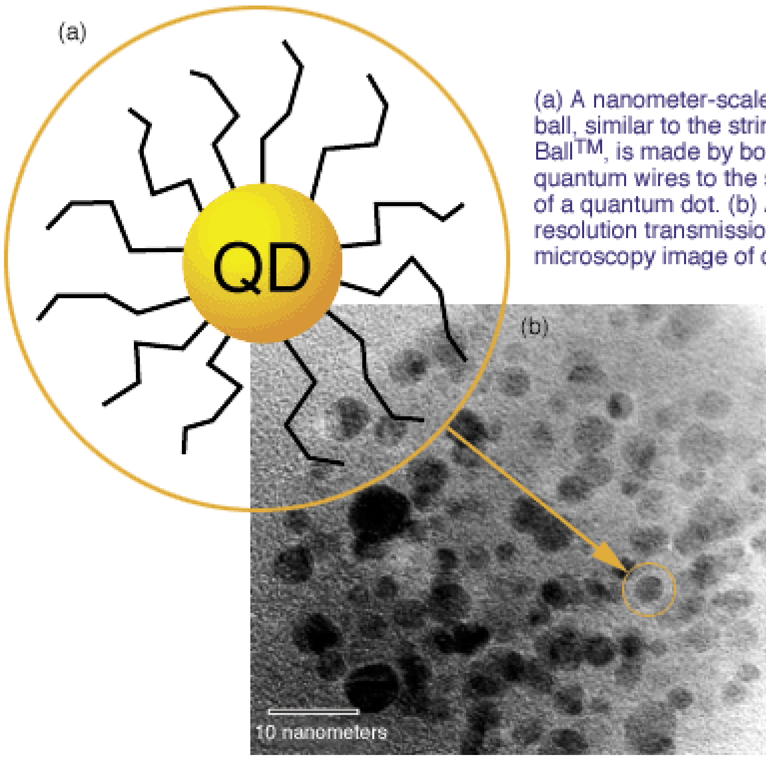
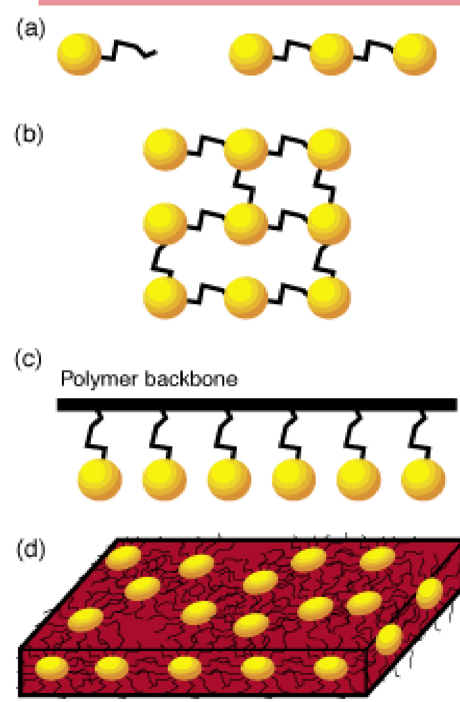
www.nano.geo.uni-muenchen.de/.../molecwrite.html

Spherical QDs with Molecular Tethers form Building Blocks for Sensors



(a) A nanometer-scale quantum ball, similar to the stringy Koosh Ball™, is made by bonding quantum wires to the surface of a quantum dot. (b) A high-resolution transmission electron microscopy image of quantum dots.



With molecular tethers to link them together, quantum dots become the building blocks of nanostructures. They can be linked together as (a) molecules, (b) lattices, (c) attached to a polymer backbone, or (d) incorporated into a polymer thin film.

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CNTs Uses:

- Similar to nanowires for nanoscale electronics
- As a strengthener in polymers and other materials
- As a probe -- in sensors

QuickTime™ and a
TIFF (LZW) decompressor
are needed to see this picture.

Sensor design to left

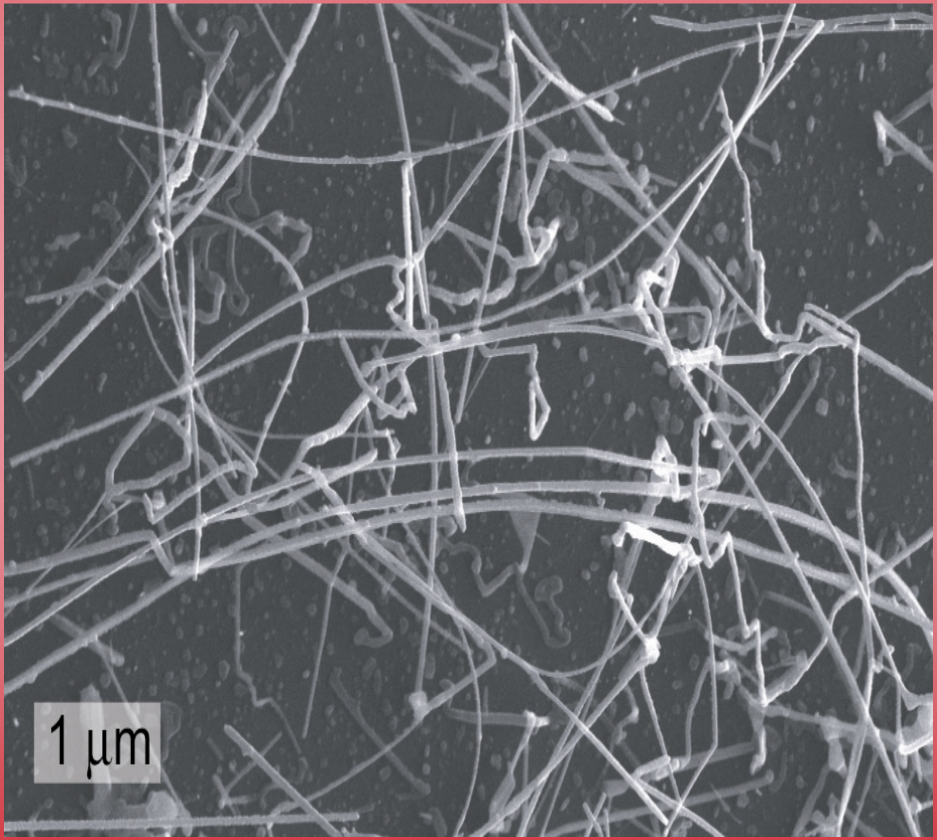
To right, CNTs grown in sensor gap, then used to detect temperature

QuickTime™ and a
TIFF (LZW) decompressor
are needed to see this picture.

IEEE Trans Nanotech, Jan. 2007

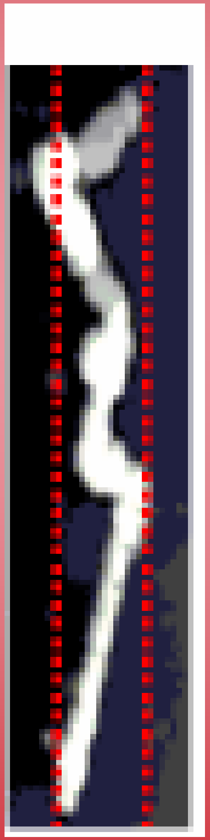
CdS Nanowires

SEM Image

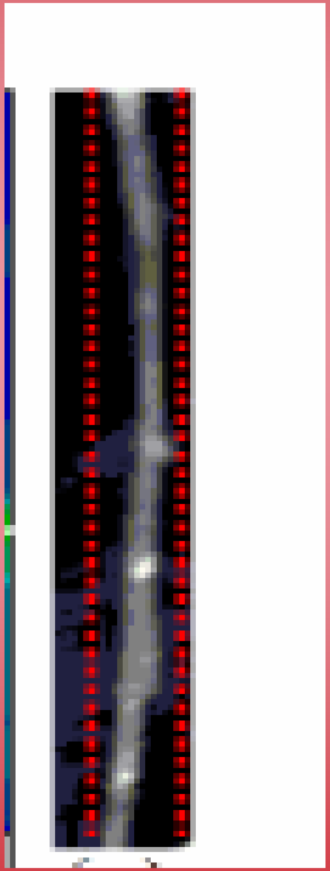


CdS nanowires grown with 50 nm Au catalysts

AFM Images



14 mm long



17 mm long

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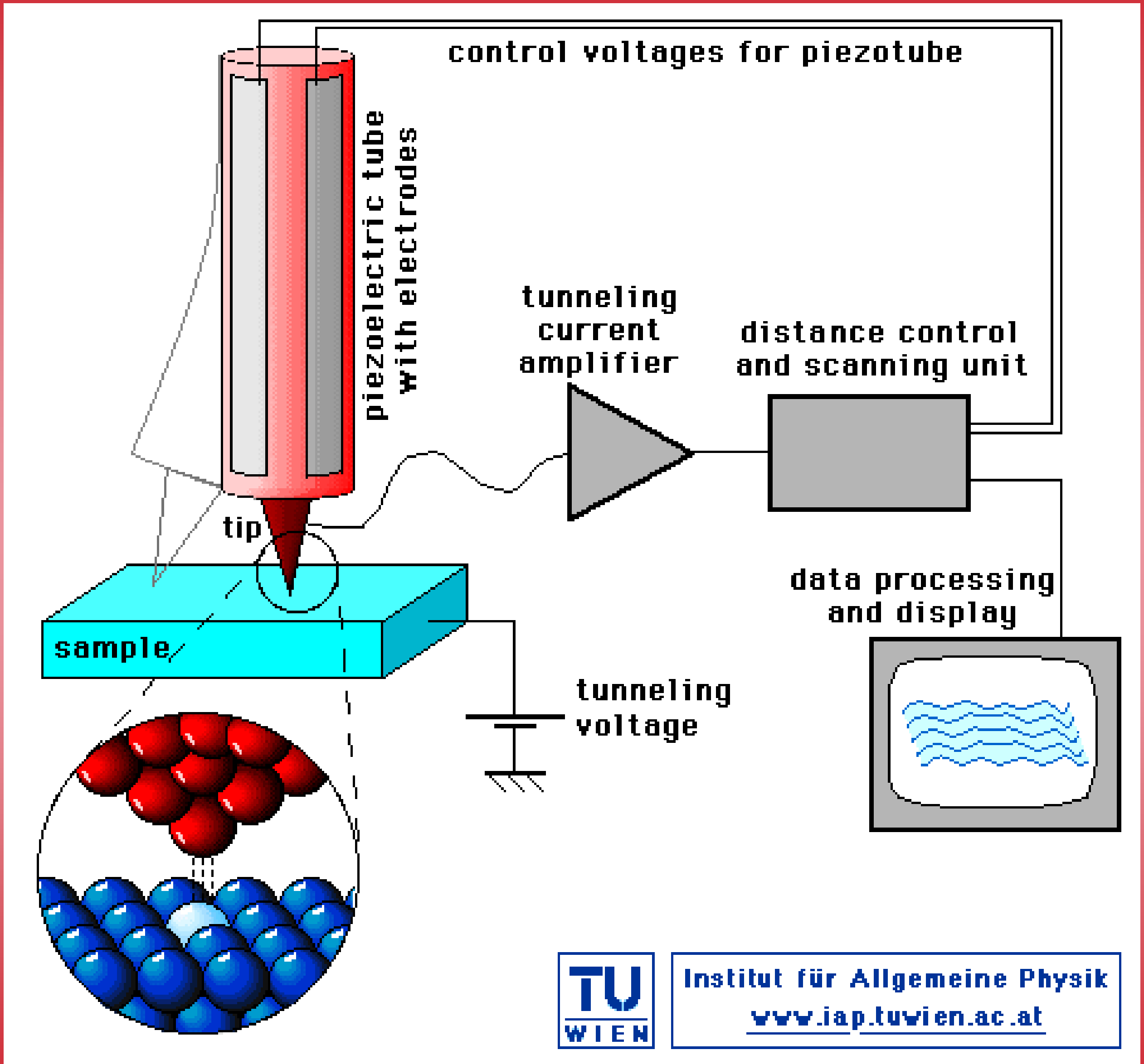
STM

- Scanning tunneling microscope



http://www.iap.tuwien.ac.at/www/surface/STM_Gallery/stm_schematic.html

Other cool sites…

- http://www.almaden.ibm.com/vis/stm (Interesting STM images)
- http://www.nobel.se/physics/educational/microscopes/scanning/ (Interesting STM images)

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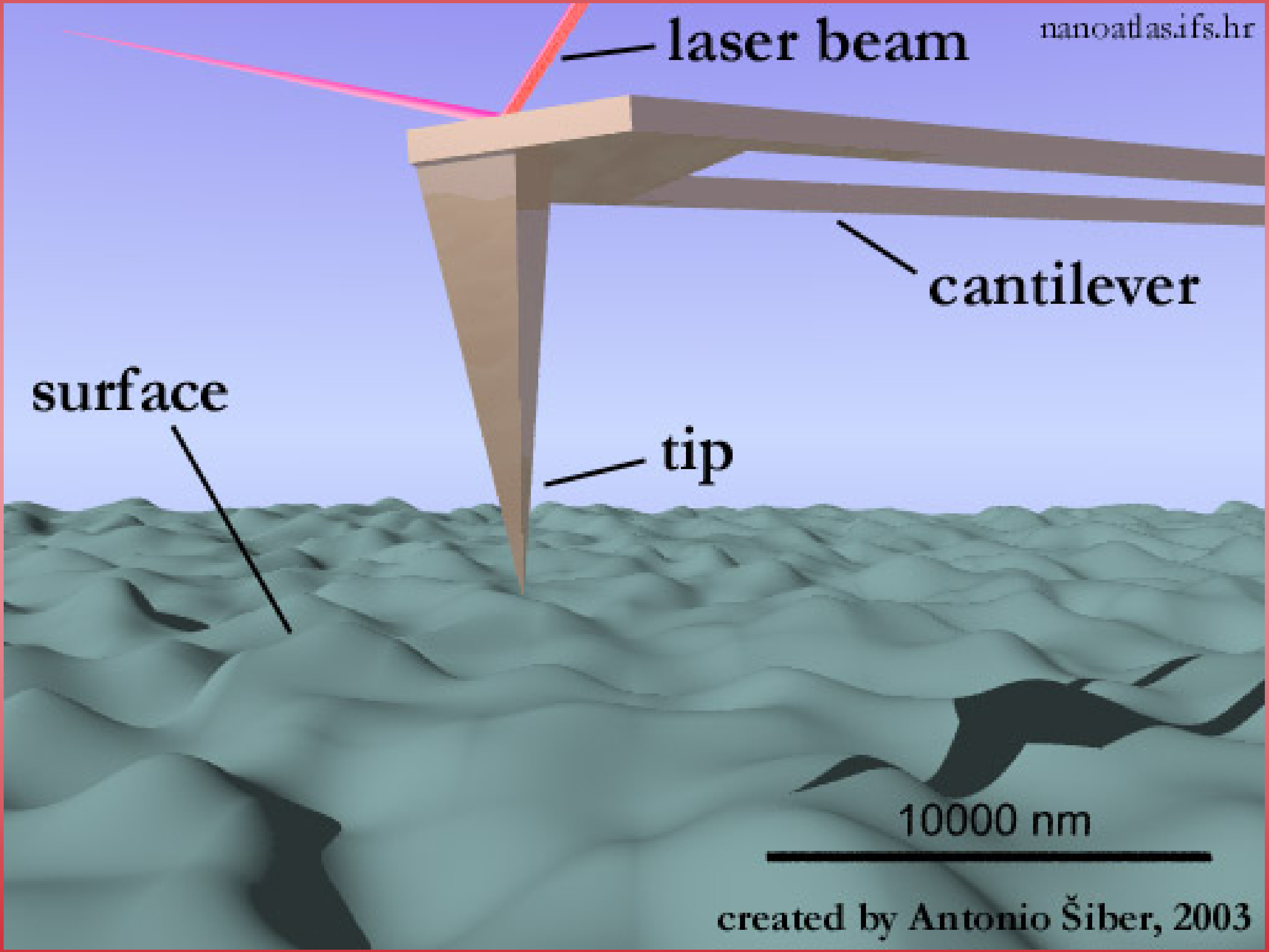
Atomic Force Microscopy



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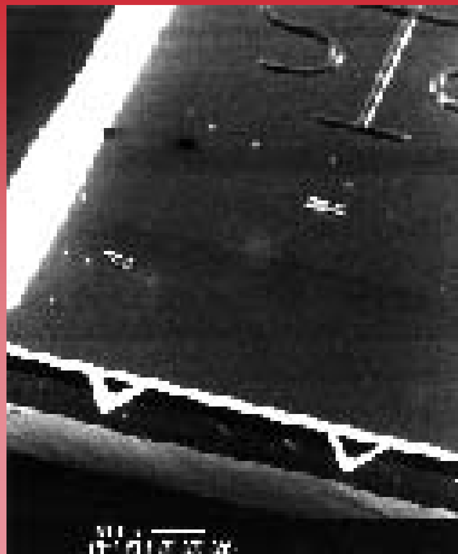
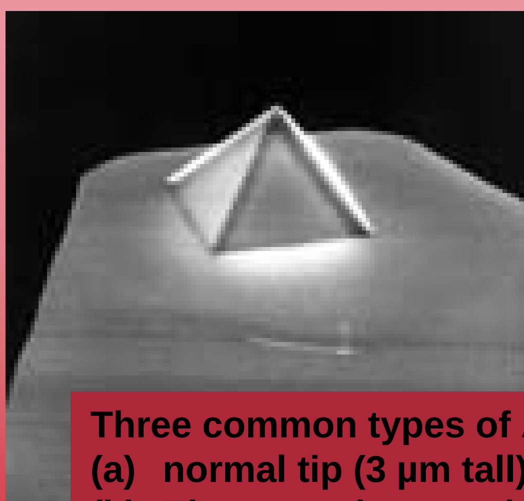
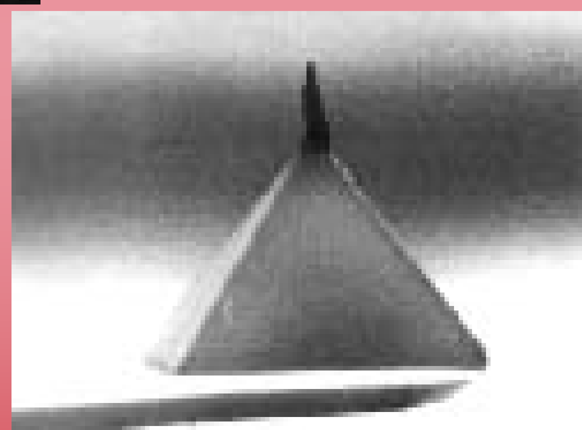


Wafer & TIP

- Si or SiN – 10 nm at end
  – ~100 atoms

Electron micrograph of two 100 μm long V-shaped cantilevers (by Jean-Paul Revel, Caltech; cantilevers from Park Scientific Instruments, Sunnyvale, CA).





Three common types of AFM tip.
(a) normal tip (3 μm tall); (b) supertip; (c) Ultralever (also 3 μm tall).
(b) Electron micrographs by Jean-Paul Revel, Caltech.

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http://stm2.nrl.navy.mil/how-afm/how-afm.html

Non-Contact Mode – Solid Lipid Nanoparticles

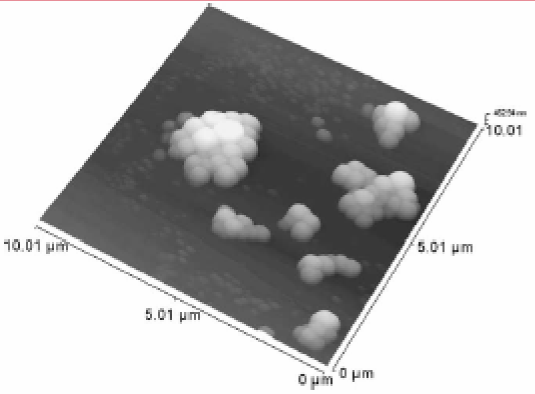
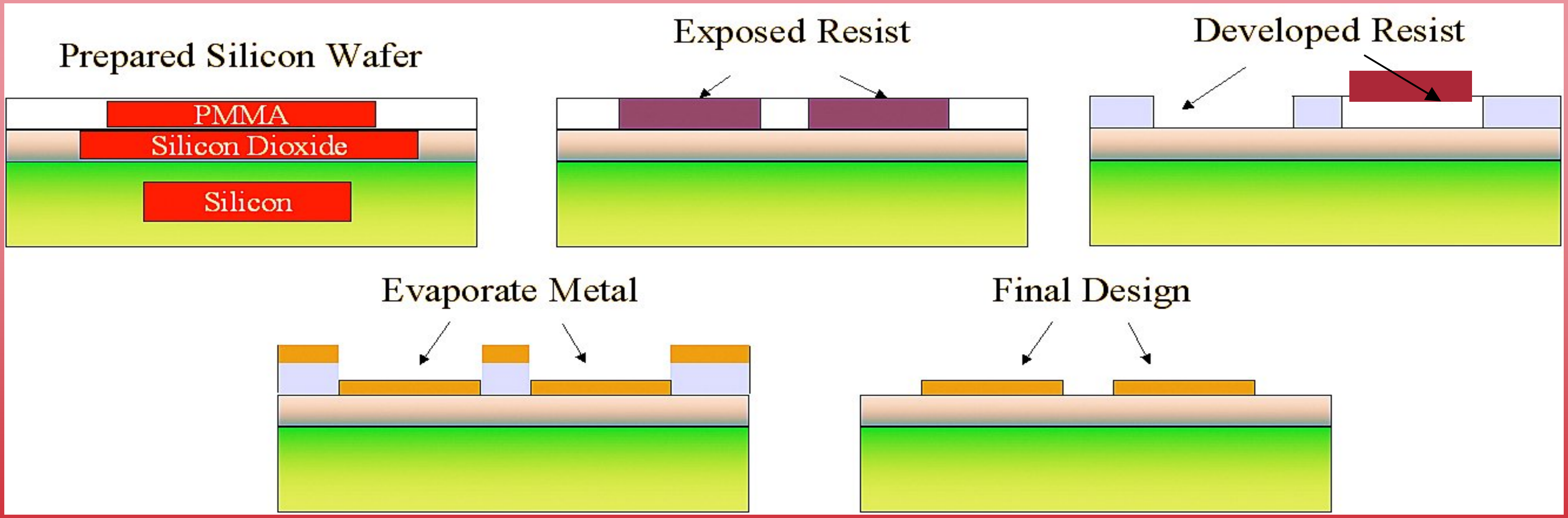


Fig. 10. Non-contact-mode AFM image of the solid lipid nanoparticles formed by βCD21C_6 on mica at scan size 10 μm.

Top-Down Approach: Electron-beam or Optical Lithography

- Exposure and development process to fabricate a nanoscale structure



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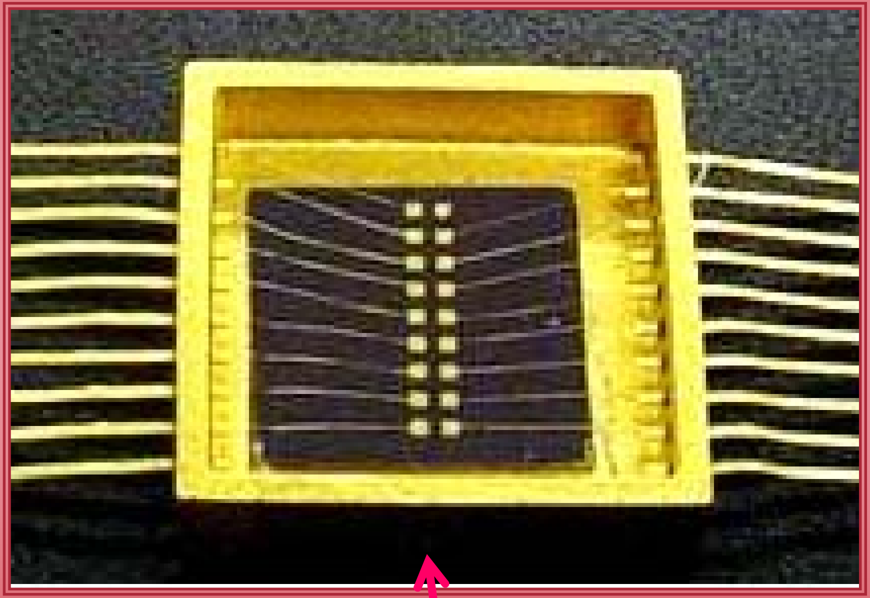
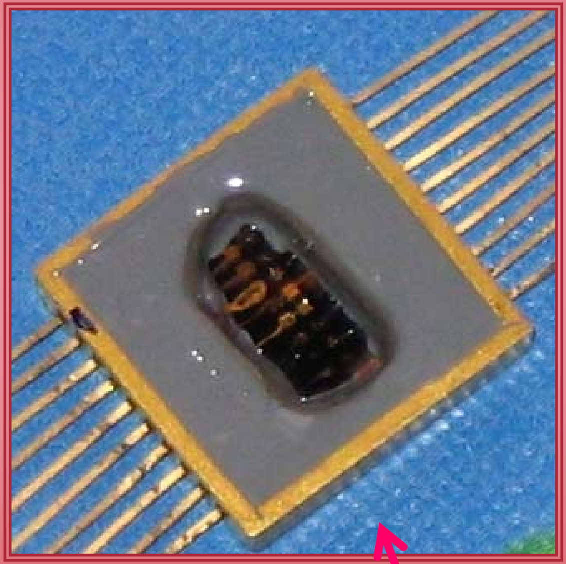
Incorporating Electrodes into a Device





Gold squares are 300 mm and electrodes are in between them !

When epoxy is added, then we can add the molecules and the experiment begins.

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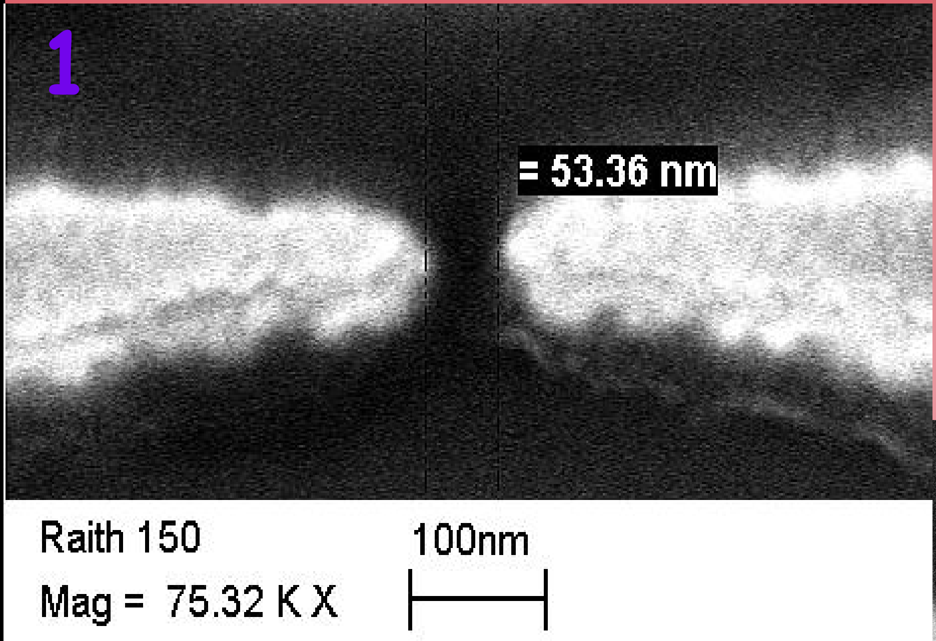
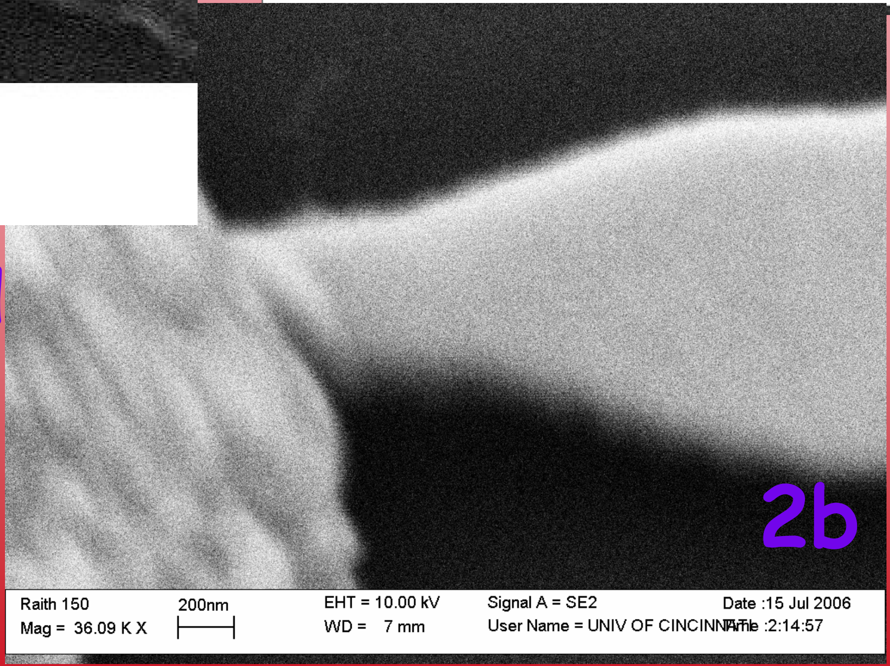
Electrodes for Single Molecules



Step 2: Grown shut for 3 nm gap

Step 1: Fabricated with lithography



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The "bottom up" approach holds the most promise:

Types of nanoscale building blocks:

- Quantum Dots - QDs
- Nanowires - NWs
- Carbon Nanotubes - CNTs
- Nanosheets - NSs

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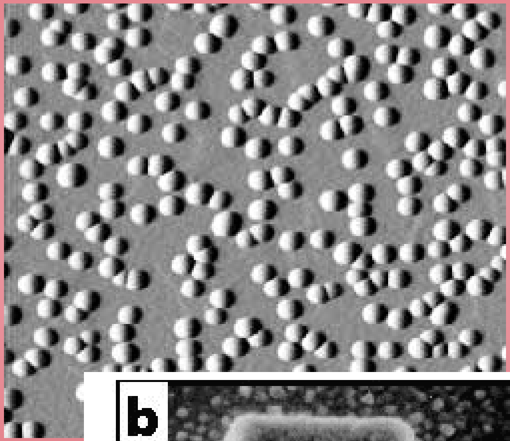
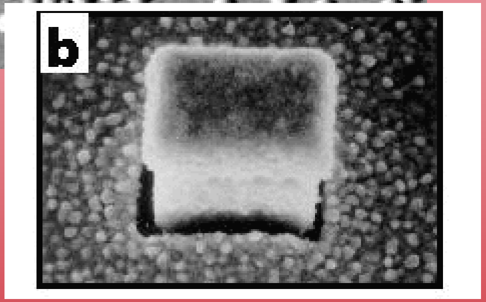
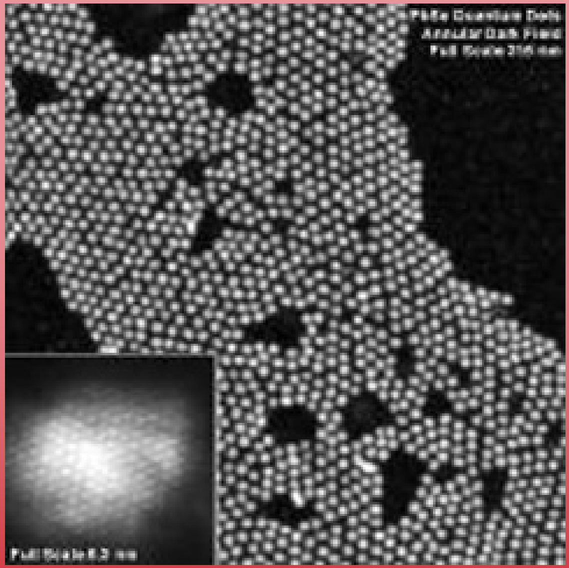
QDs come in all shapes and sizes!

nppp.ipl.nasa.gov/topics/
Top.quant.dot.htm





www.scifi.com/sfw/issue203/
drexler3.jpg



www.aep.cornell.edu/ gif/QdotsPbSe.jpg

qt.tn.tudelft.nl/news/
NN6fig1b.gif

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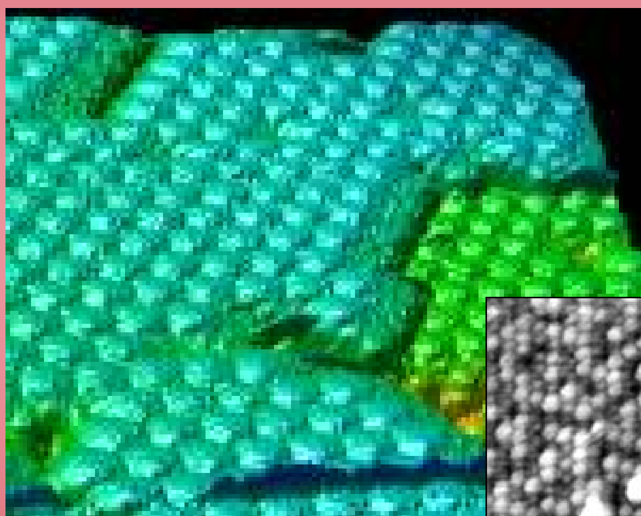
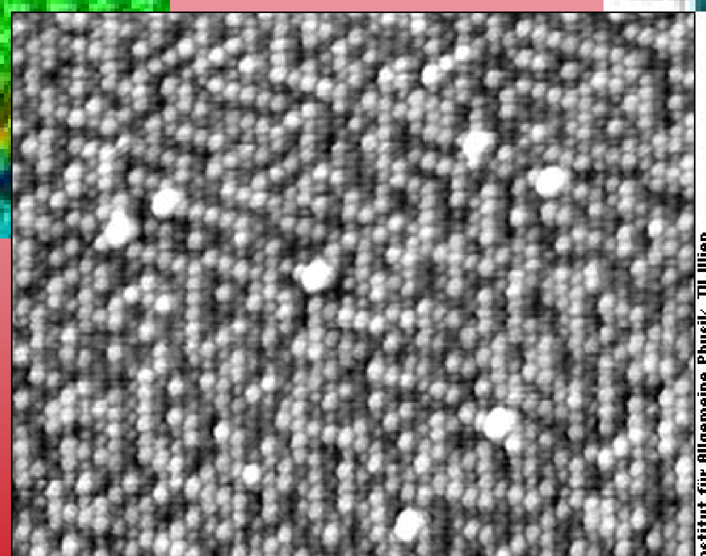
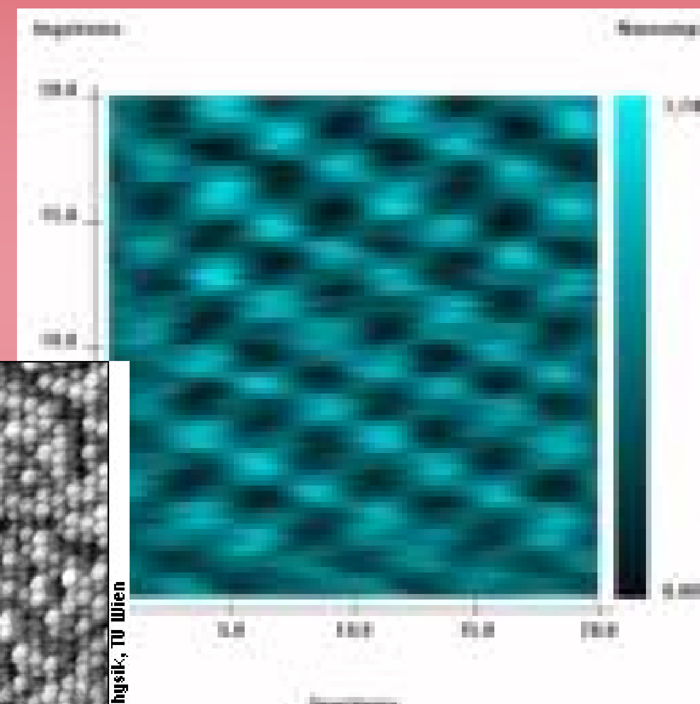
Looking at & Manipulating Atoms… STMs & AFMs







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