

Nanomaterials Inspiration from Ancient Materials



Maryland Hall - Home of Materials Science at JHU

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Special thanks to
Yi Ding, Anant Mathur, Greg Fritz, Young-Ju Kim



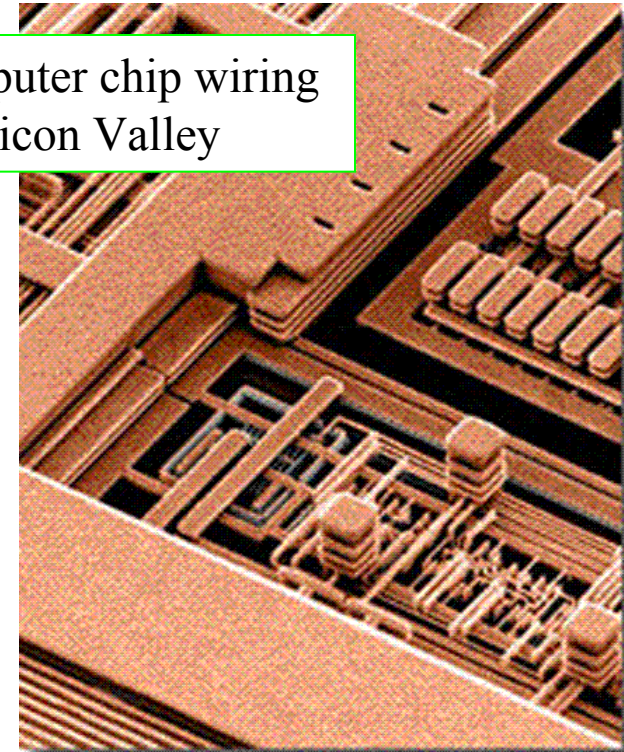
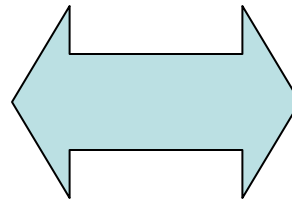
JOHNS HOPKINS
UNIVERSITY



Theme



Steelmaking in Bethlehem, PA

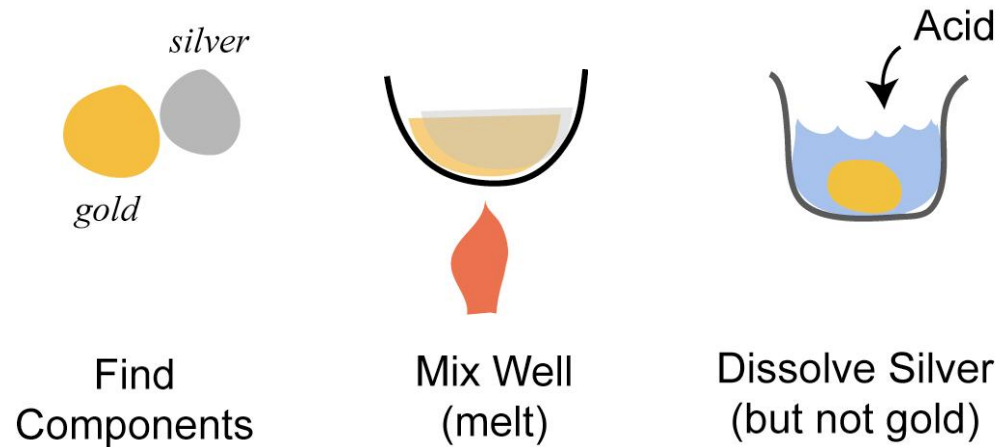


Computer chip wiring in Silicon Valley

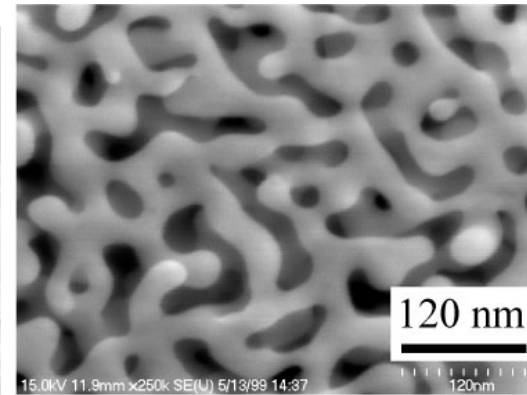
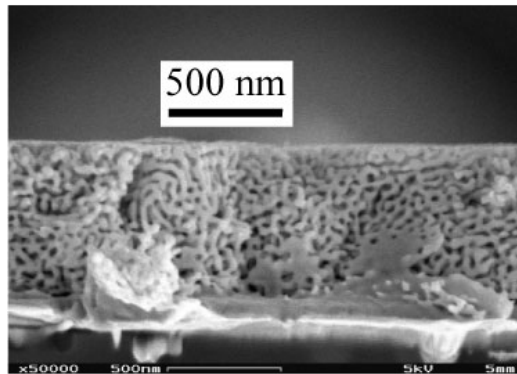
How can traditional (metallurgical) technologies inform nanotechnology, and vice versa?



Dealloying: A Method to Create Nanoporosity



Nanoporosity:
Ligament widths
and spacings are of
order 10 nm



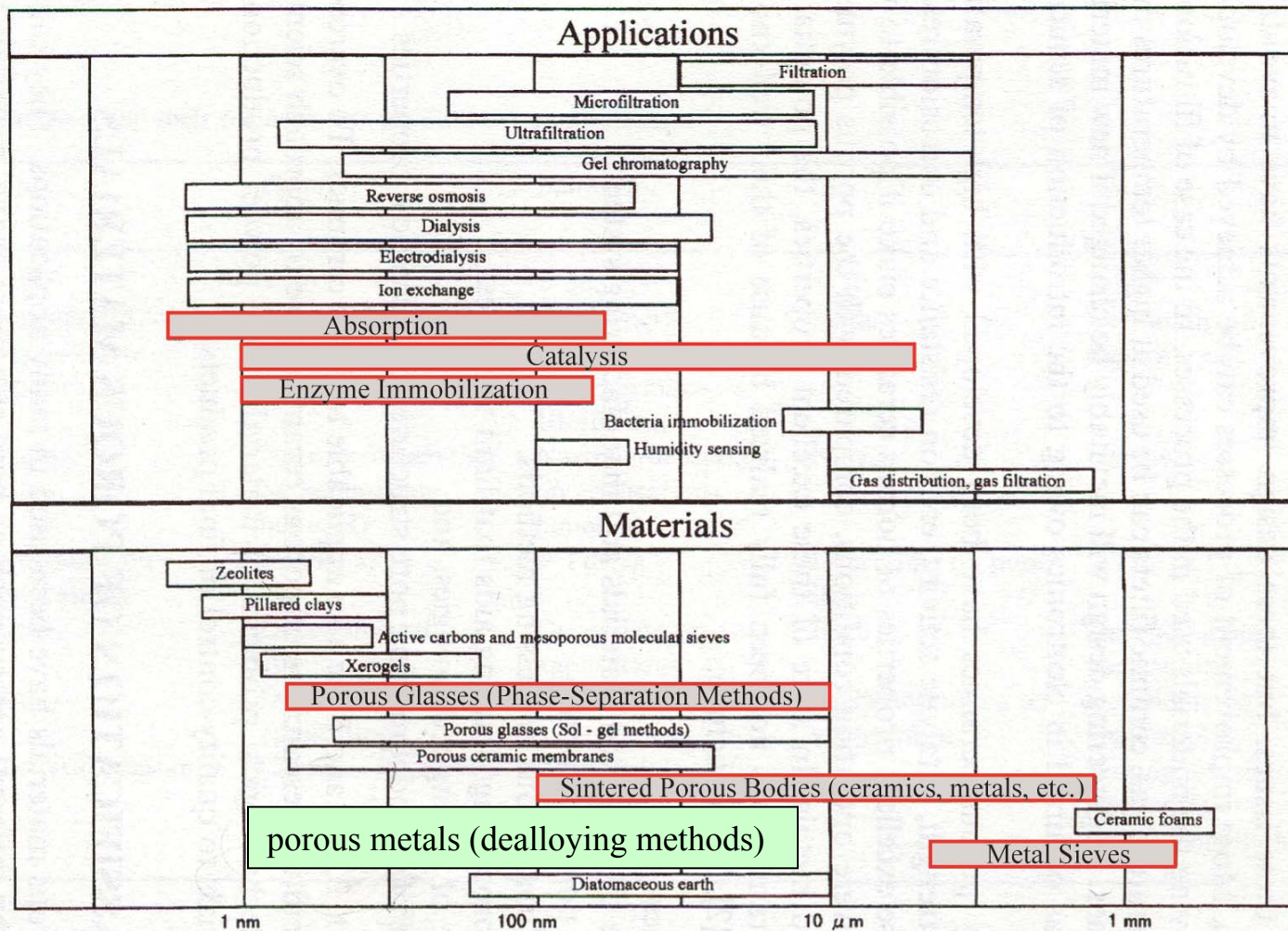
“Nanoporous Gold” (NPG)

History of NPG

- “Depletion gilding” was known to the ancient Incas
- Origin of current interest:
Corrosion
 - Dealloying is seen during corrosion of many technologically important brasses, stainless steels, and Cu-Al alloys

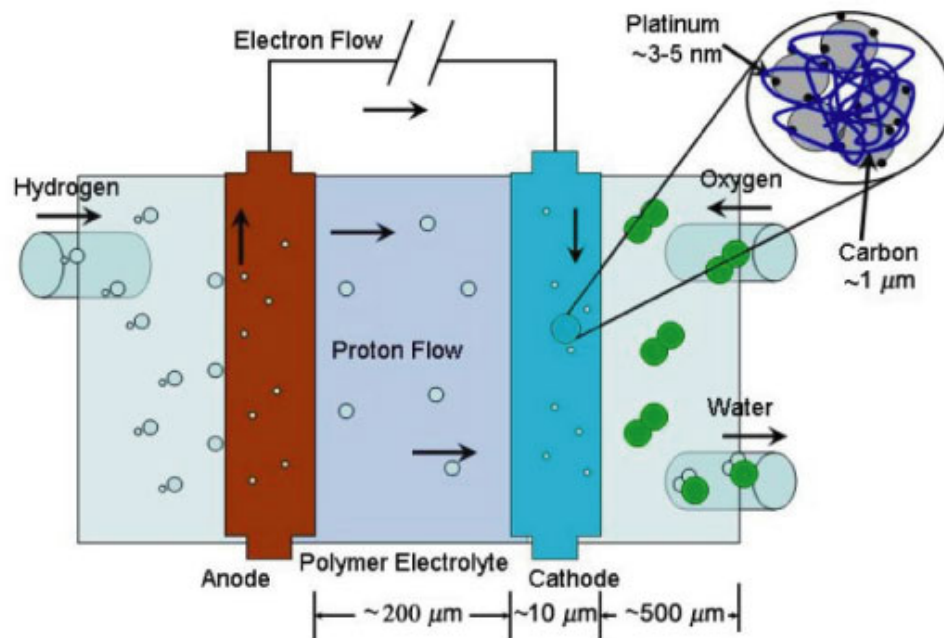


Modern Context of Nanoporous Metals



from K. Ishizaki, Porous Materials: Process Technology and Applications, (Kluwer), 1998.

Fuel Cells : An application for nanoporous metals?



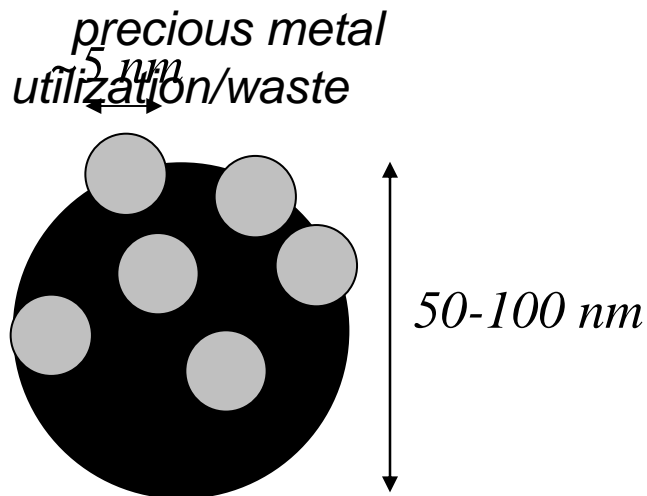
Cathode and anode must

- (a) be conductive
allows electron flow
- (b) be porous
allows reactant gas flow
- (c) have a very high surface area catalyst
optimizes precious metal use

Materials Design of Precious Metal Fuel Cell Catalysts

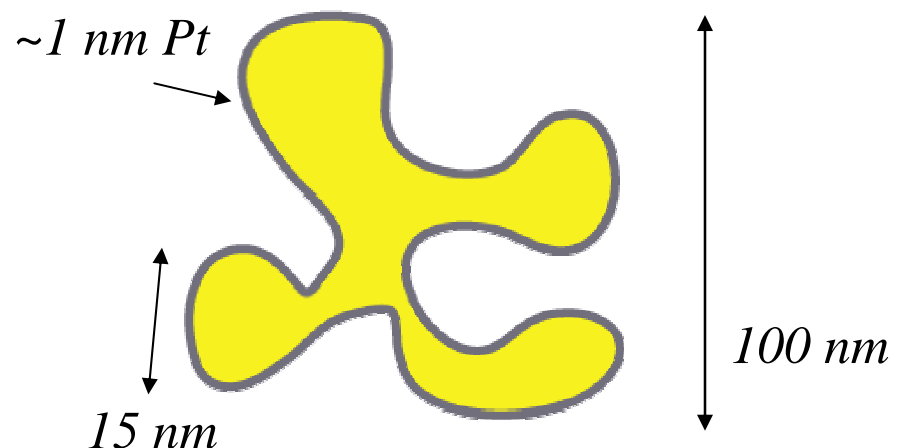
Nanoparticles

- High surface area/volume
- Immobilization by physisorption
 - thermal stability issues*
- No intrinsic in-plane conductivity
- Processing leads to “thick” (>10 microns) catalyst layers



Mesoporous Metal Membranes

- High surface area/volume
- Immobilization by epitaxy
 - thermal stability issues good?*
- High intrinsic in-plane conductivity
 - proton conduction still a problem*
- Processing leads to thin (100 nm) catalyst layers



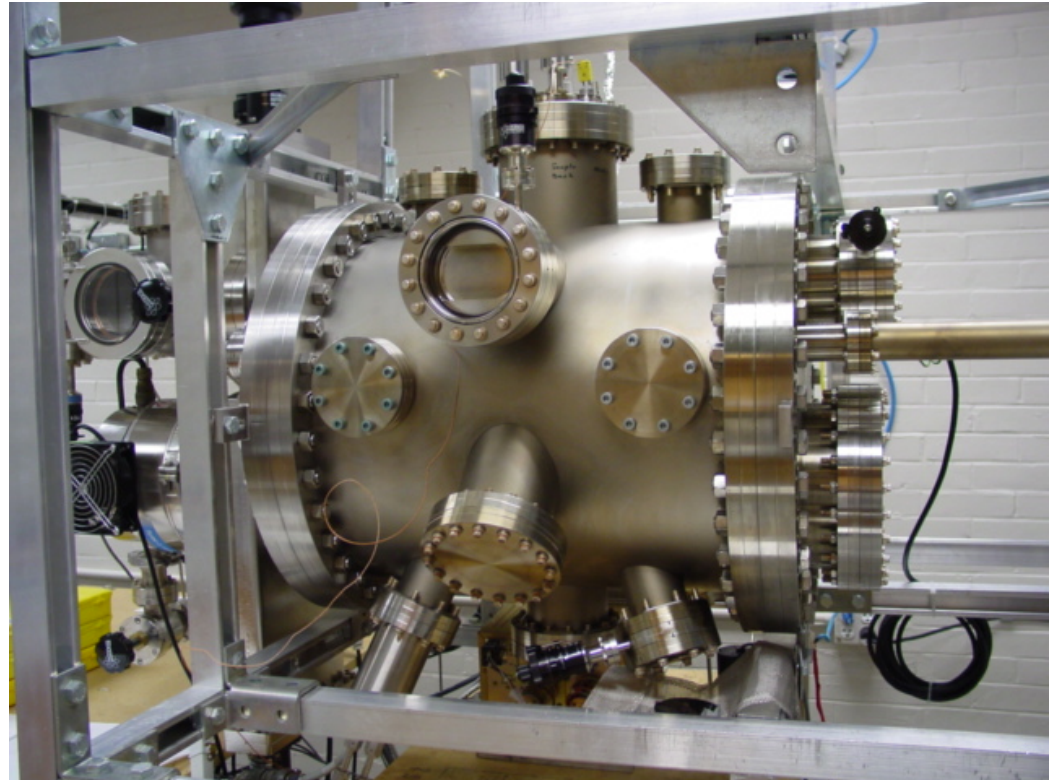
Making NPG Films: Thin-Film Fabrication

Minuses → expense

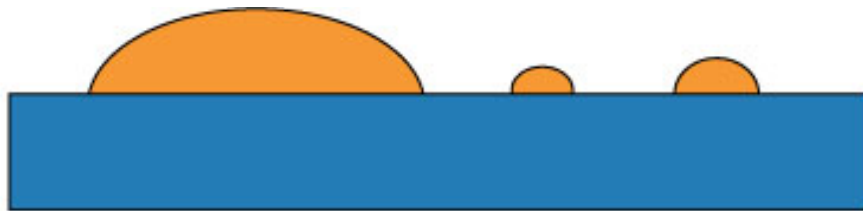
- Requires ultra-high vacuum
- Much of the material that is evaporated is wasted
- Time consuming

Plusses

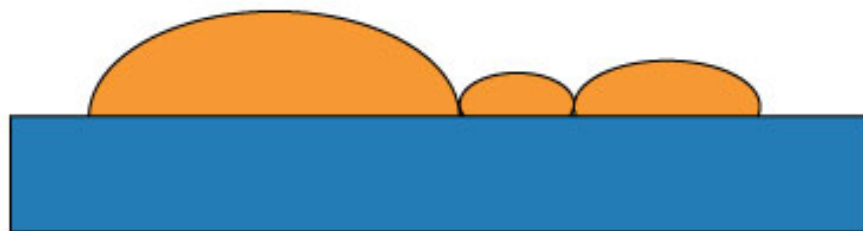
- Extremely clean ($< 10^{-10}$ Torr)
- Very small features (< 0.1 micron) with great precision



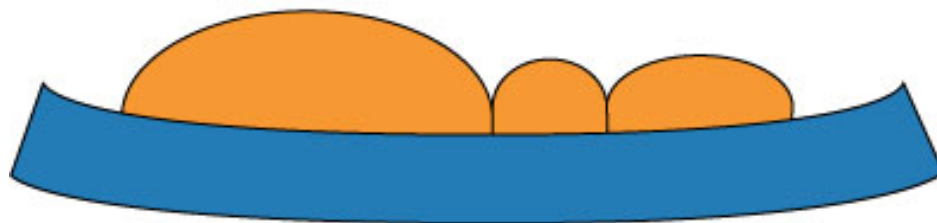
Stress Evolution in Volmer-Weber Growth



islanding

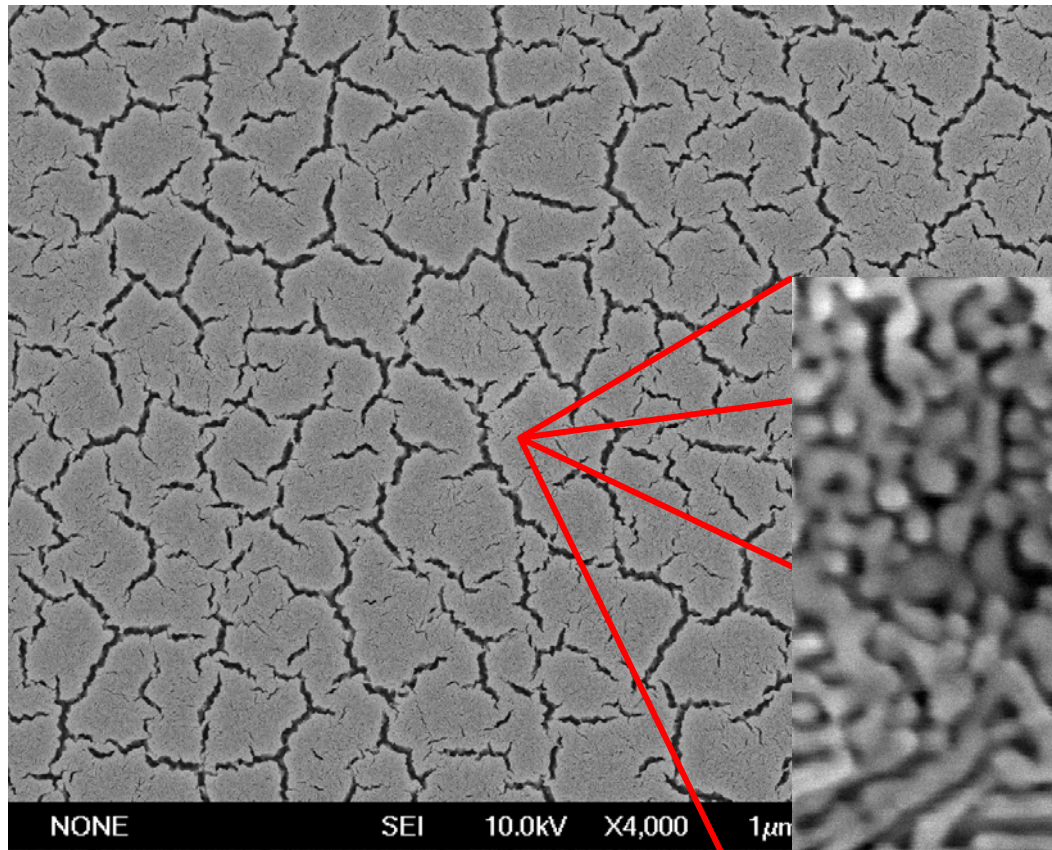


coalescence (~100 nm grains)
system wants to create grain boundaries

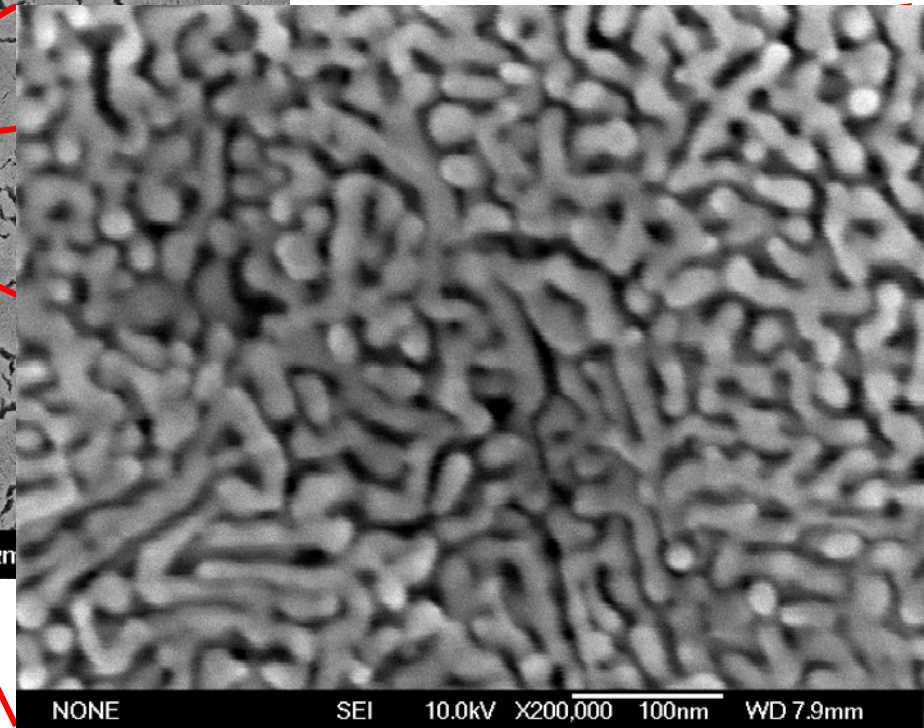


substrate: compression
film: tension

Cracking in Dealloyed Silver Gold Thin Films



4,000x



200,000x

Wouldn't it be nice....?

To have a porous gold film with the following properties:

- Thin (< 200 nm)
- Doesn't crack upon dealloying
- Not attached to a substrate



Gold Leaf: An Old Technology



<http://shofu.pref.ishikawa.jp>

Gold Leaf: The Historical Perspective

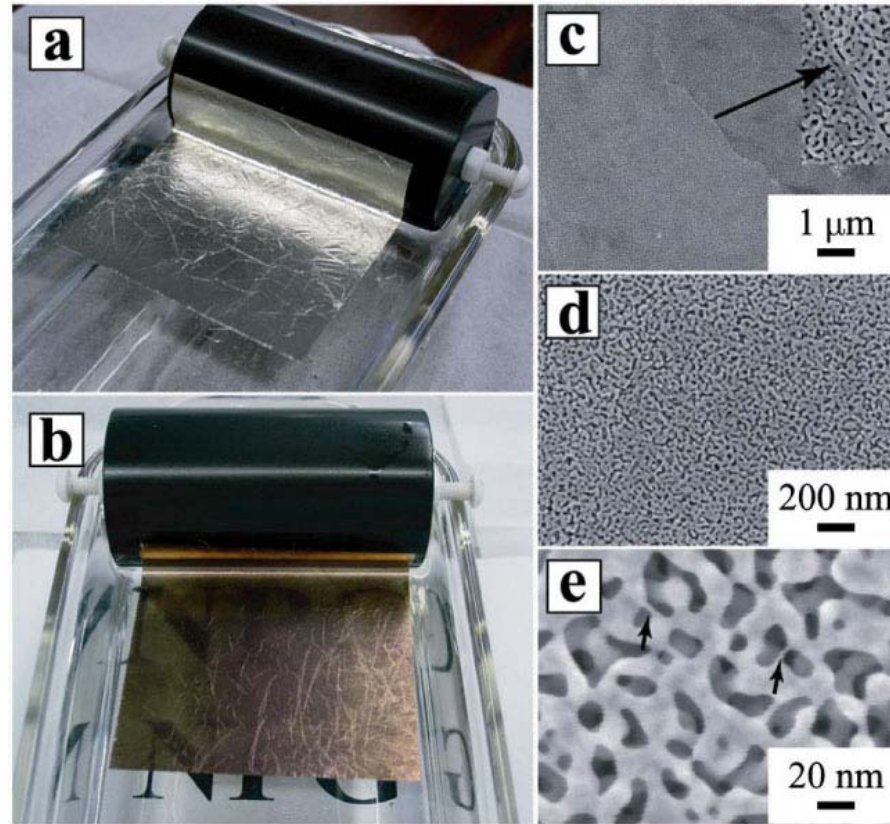
Progress of Materials and Materials Processing

1. Stone bashing (> 10,000 years)
2. Fire (> 10,000 years)
3. Melting metal (> 5,000 years)
4. Gold Leaf (bashing + fire + metal) (> 4,000 years)

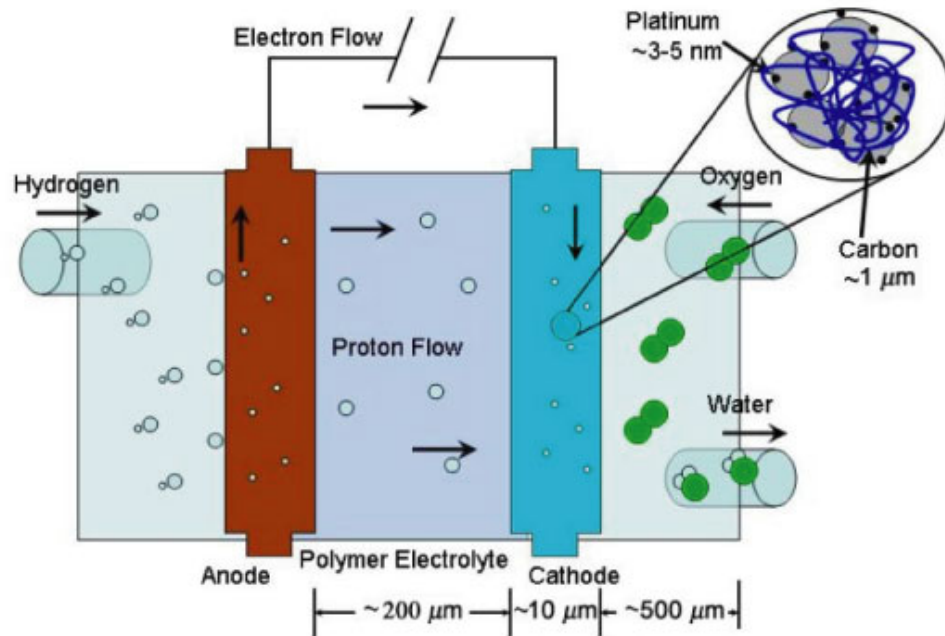


Nanoporous Gold “Leaf”

silver/gold leaf, 100 nm thick, 35 at. % Au, 3 3/8” x 3 3/8” : note color change!



Catalytic Applications of Nanoporous Gold



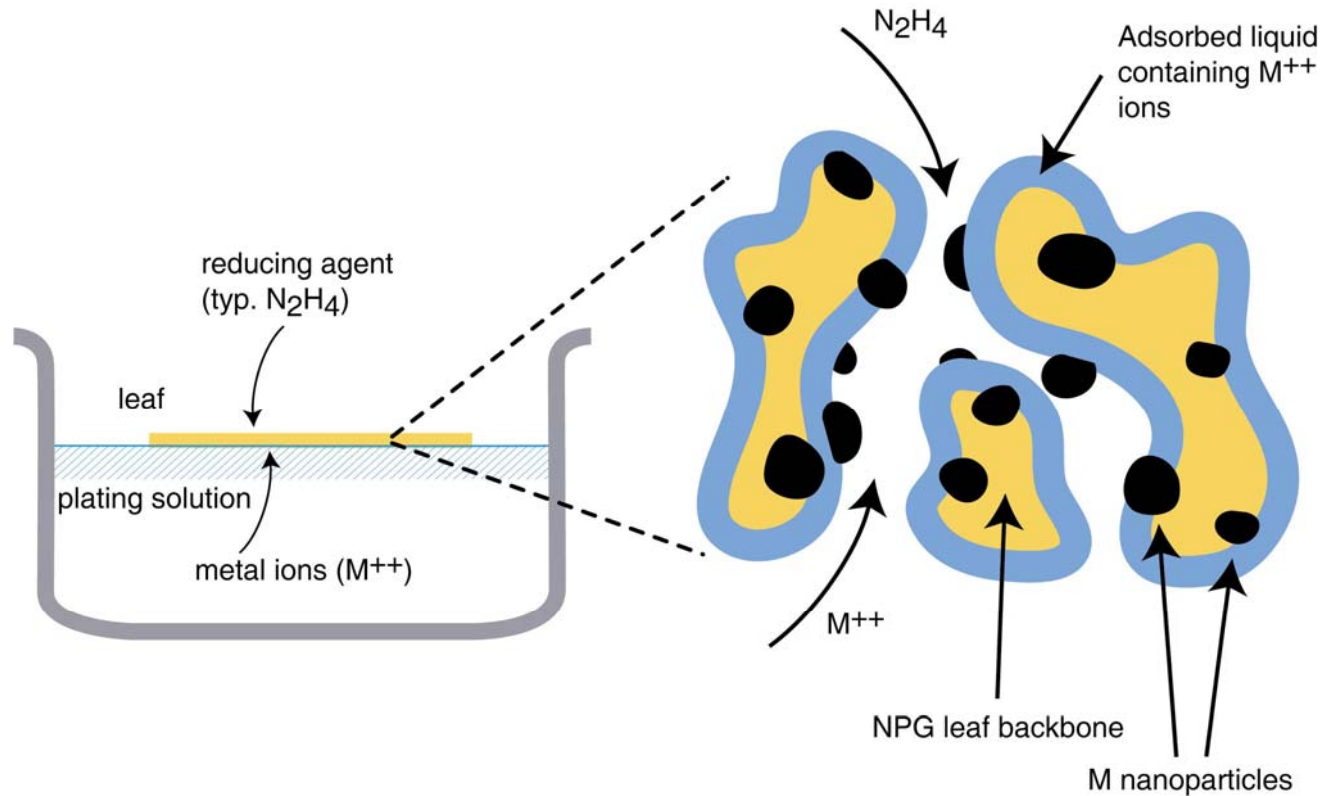
Cathode and anode must

- (a) be conductive
- (b) be porous
- (c) contain a very high surface area of catalyst both in electrical contact (to the current load), and in ionic contact (to the polymer electrolyte) → thin is good

Nanoporous gold leaf fits the bill, but is not catalytic itself. But what about Pt-plated NPG....

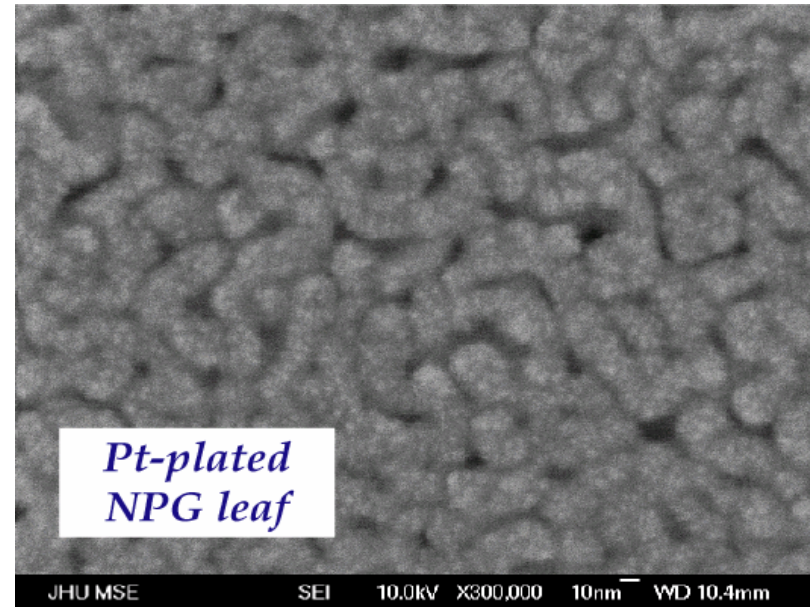
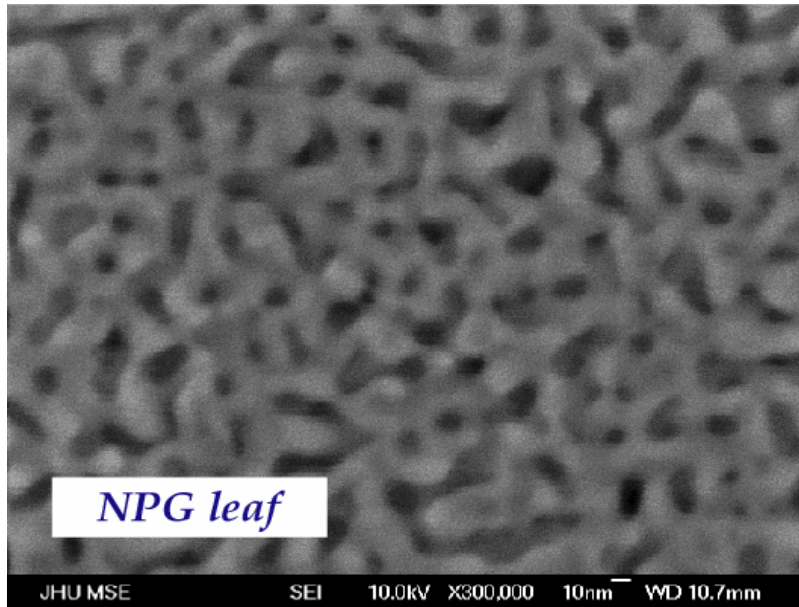
Electroless Plating of NPG Leaf to form Nanocomposites

Take advantage of the fact that leaf floats on water.



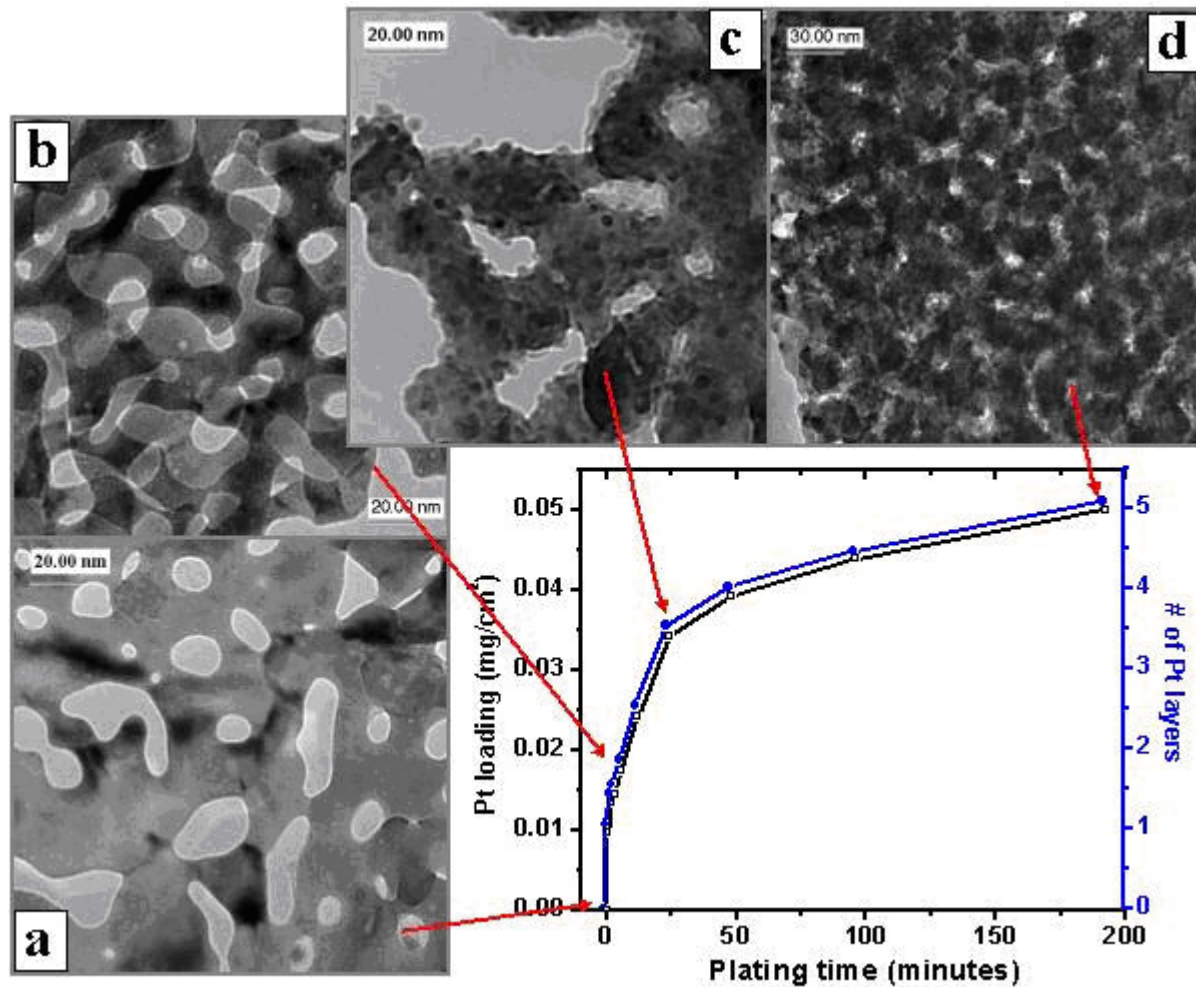
Plating should be confined to within the pores, and should self-limit
-- an advantage over typical electroless or electrochemical plating
To date, we have plated **Pt**, **Ni**, **Co**, and **Ag**

Pt-Plated Nanoporous Gold Leaf



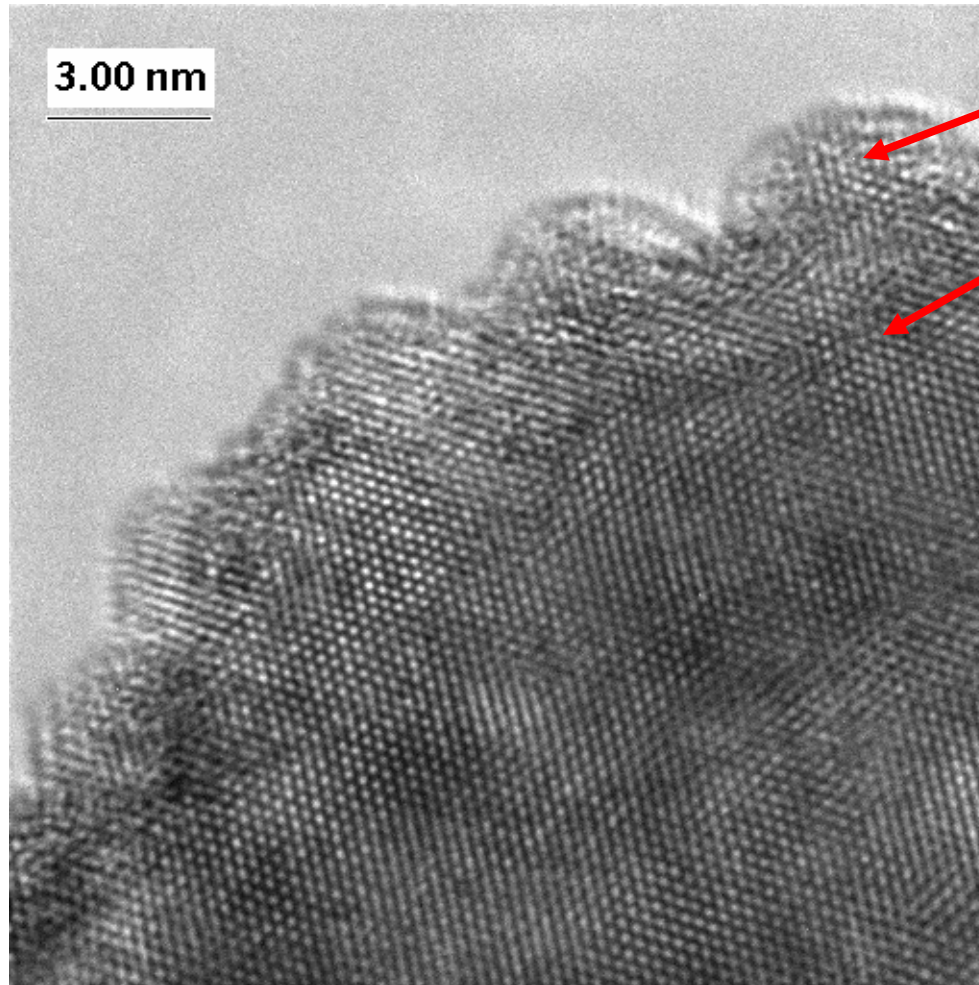
In SEM, coatings look nanoparticulate, dense, and conformal.

Growth Kinetics of Pt-NPGL



Deposition may be controlled to within 0.01 mg/cm² (1 ml) using only room temperature benchtop chemistry. Deposition stops prior to filling of pores. (?!)

HRTEM of Pt-NPGL

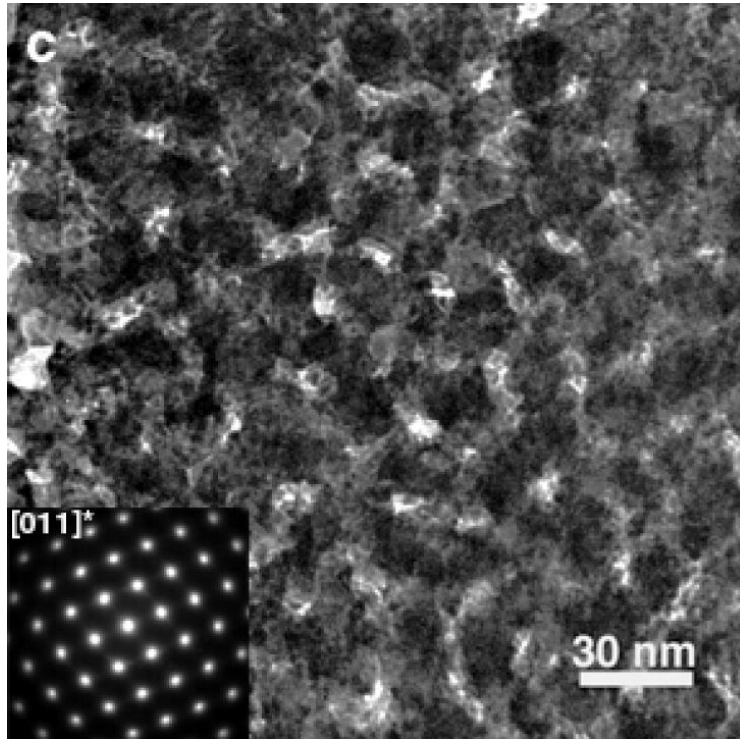


Pt

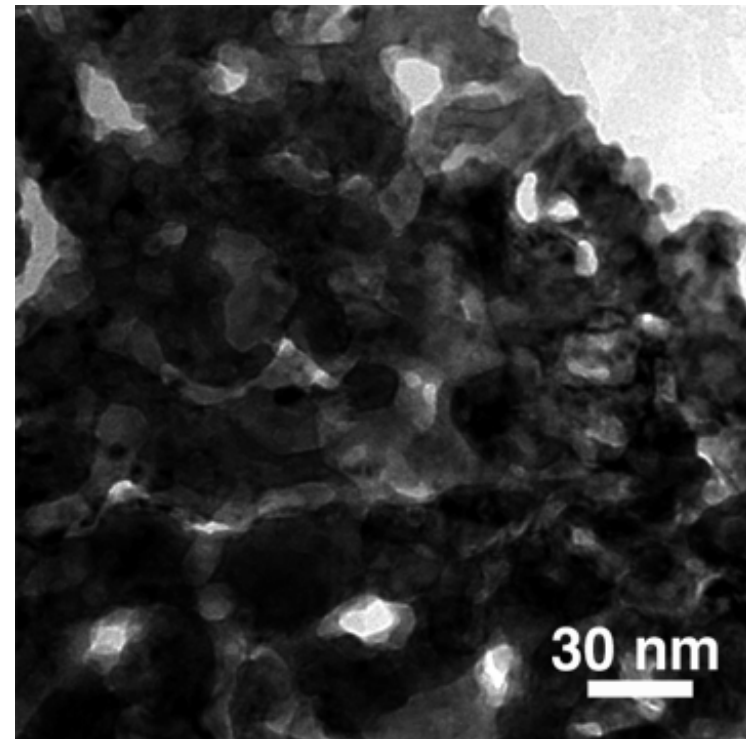
Porous Gold

Particle growth seems to
“self-limit”

HRTEM of Pt-NPG



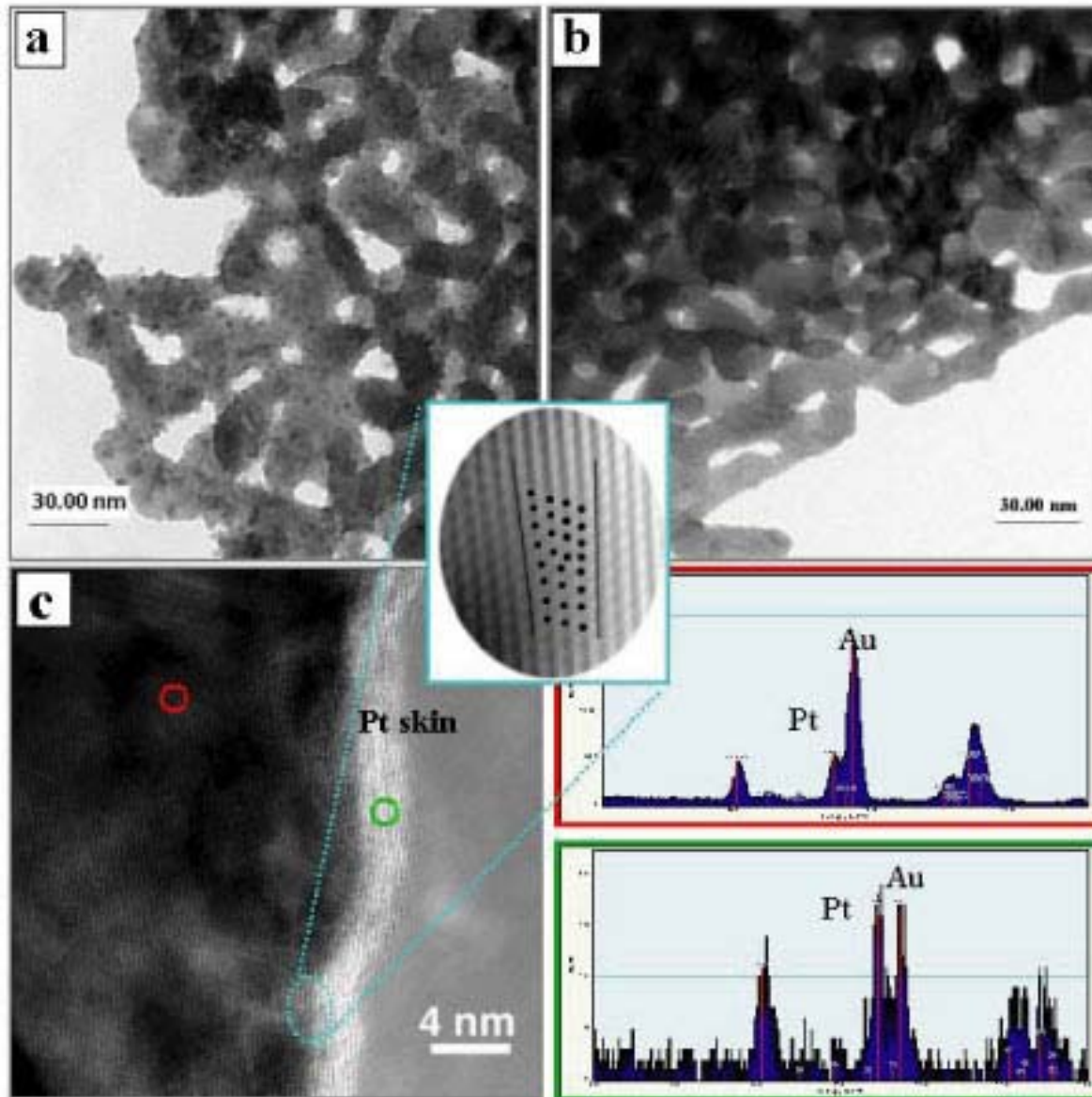
before



after

Where did all the islands go?

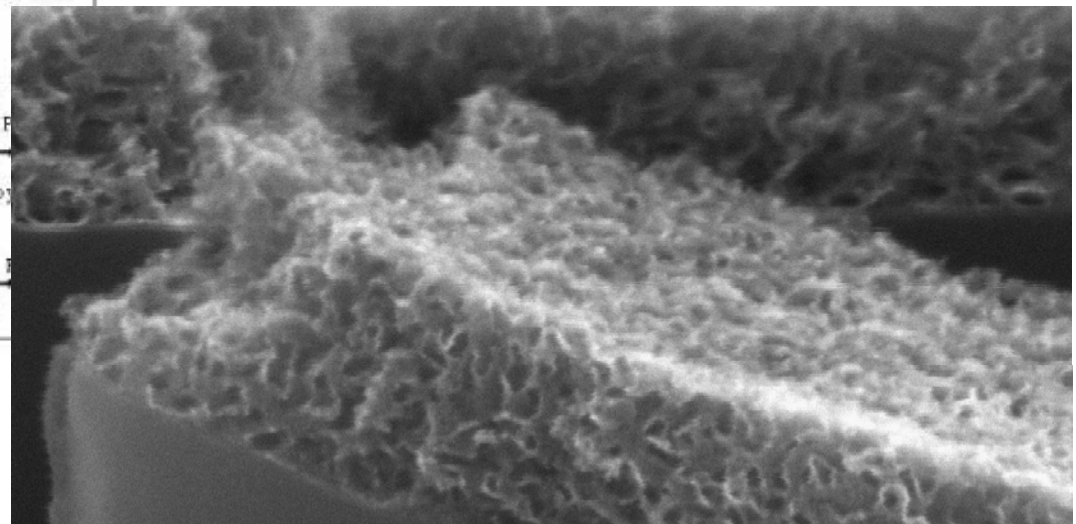
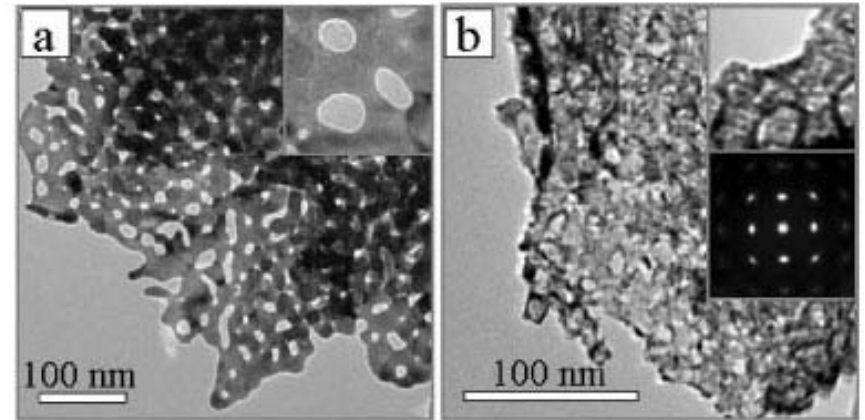
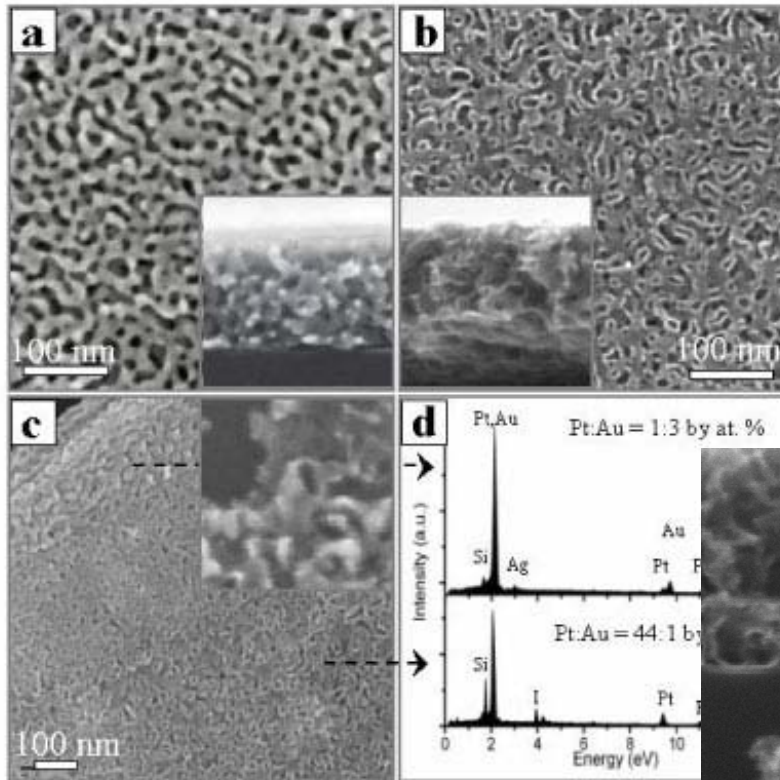
Formation of an Epitaxial Pt skin on NPG



Dislocations at the Pt/Au interface relieve stress more efficiently than islanding.

hypothesis – initial SK growth is metastable

Nanotubular Mesoporous Pt – A doubly bicontinuous mesoporous metal



dissolving Au with KI/I_2 etch leaves behind a 1 nm thick mesoporous Pt

Summary

- Nanoporous materials are emerging as an important “nanotechnology”
- Familiarity with traditional materials processing technology is still relevant
- *Nanoporous gold has a bright future!*

Thanks!

Nanostructured Organic Electronics: Where Silicon Has Never Gone Before

Howard E. Katz

Department of Materials
Science and Engineering

Johns Hopkins University

Acknowledgments

- Cheng Huang
- Kevin See
- Jia Huang
- Jia Sun
- Jennifer Bai



National Science Foundation
WHERE DISCOVERIES BEGIN



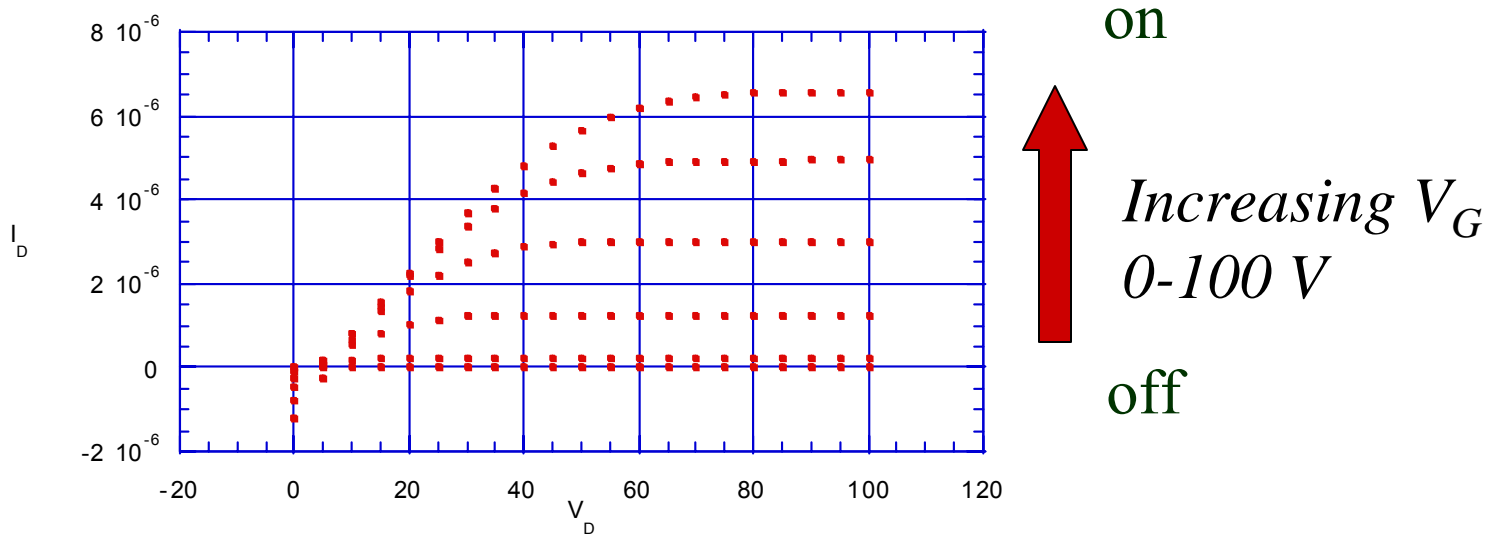
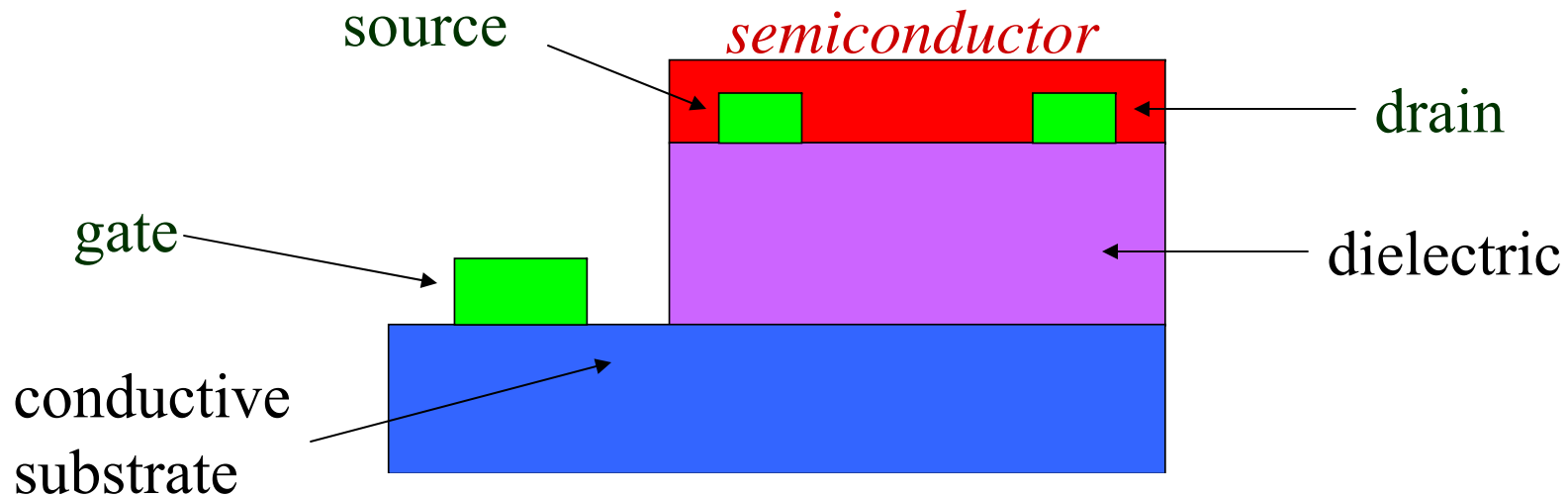
Kenan Fund

- Daniel Reich (Physics)
- Stuart Kirschner (Physics)
- James West (Electrical Engineering)
- Joseph Miragliotta (JHUAPL)
- Alan Becknell (JHUAPL)
- P. Gopalan (Wisconsin)



Outline

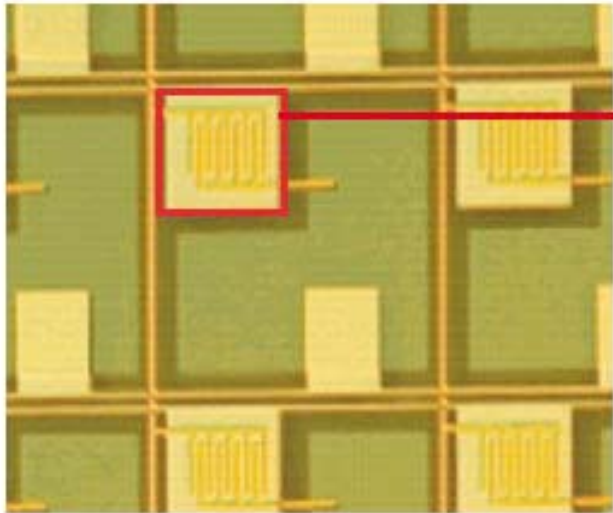
- Applications and demonstrations of organic transistors and circuits
- Solution deposition of oligomers
- Organic semiconductor diodes
- Circuits through charge writing
- Vapor sensors based on organic transistors



Special Features of Organic FETs

- covalent integration with molecules
- moderate temperature processing
- large area coverage, solution deposition
- mechanical and thermal compatibility with plastic substrates
- rational control of polarity and threshold voltage using organic substituents

Applications (flexibility and low cost)

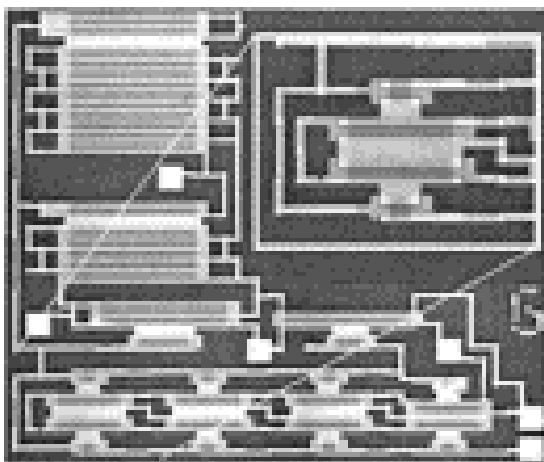


display pixel from
SONY (2004)



Source: Philips Research

flexible display
Philips (2004)



RFID circuit from 3M (2003)

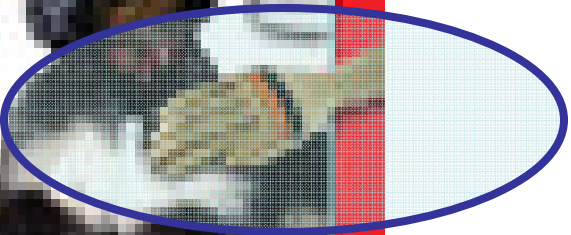
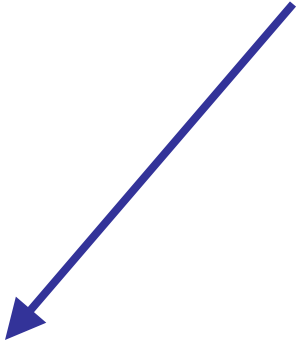


Roll-printed
transponder
Circuits (PolyIC)

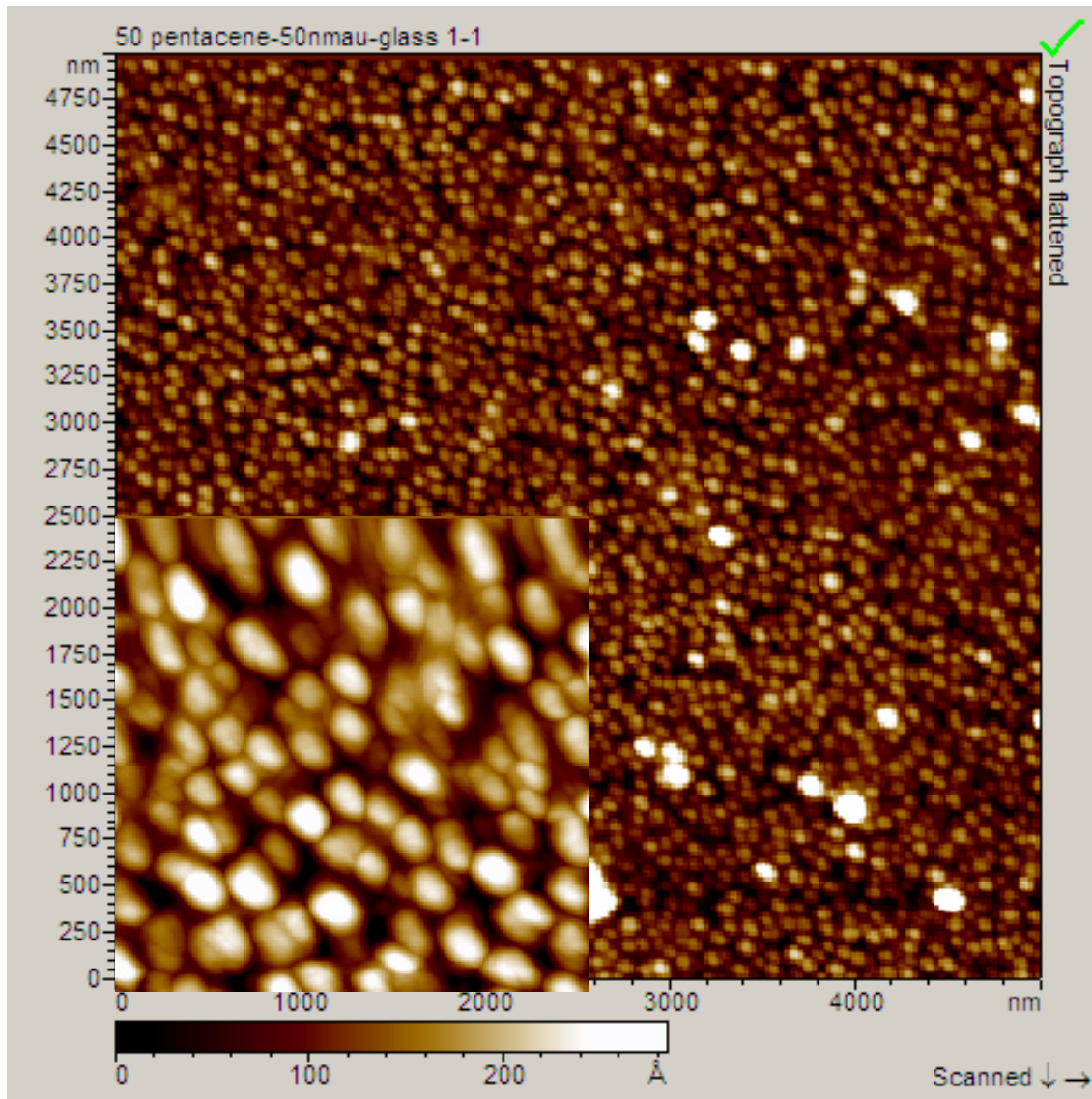
Sensitive Skin with Organic Transistors



T. Someya

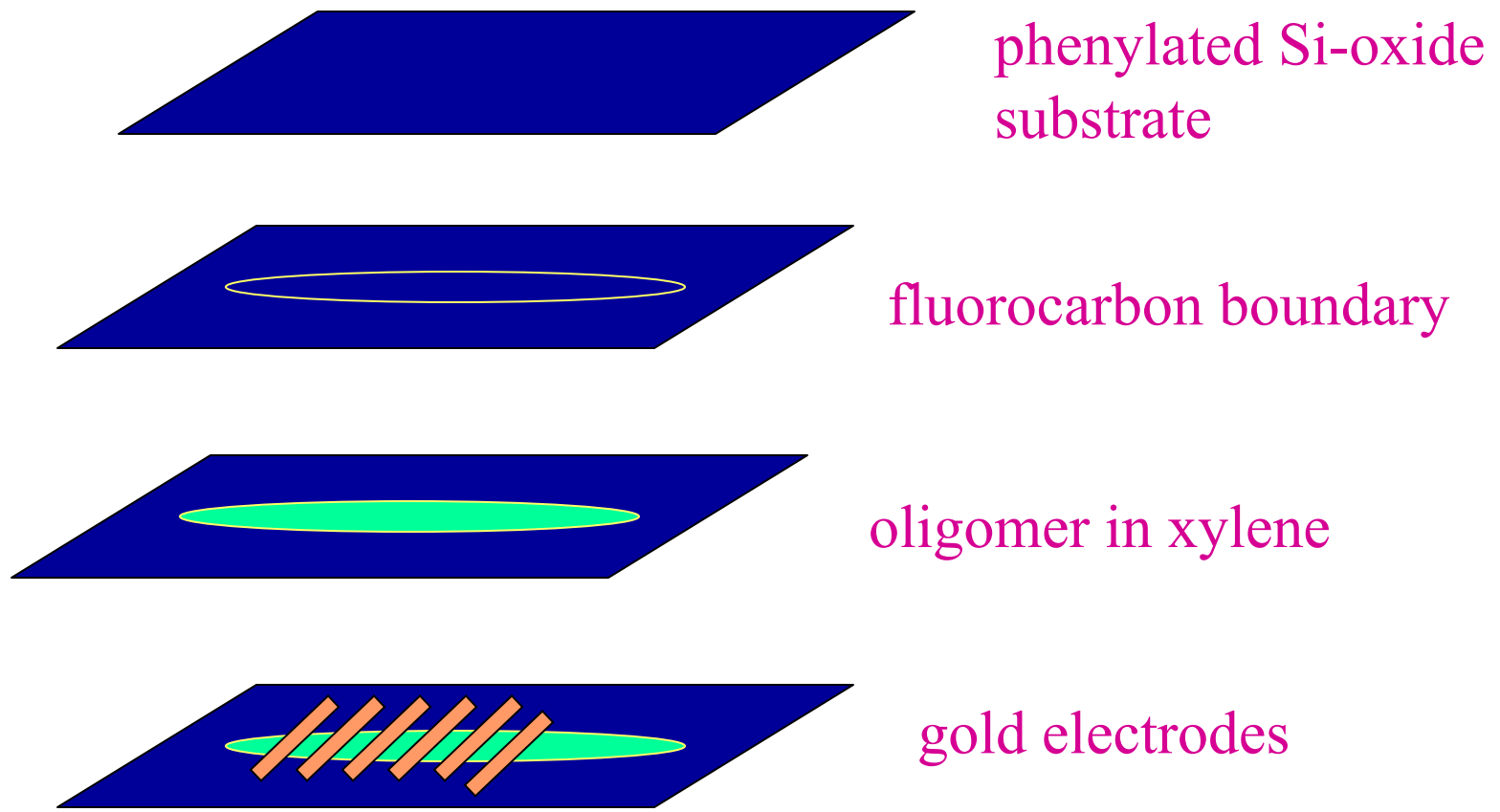


AFM image of 50nm pentacene sublimed on 50nm Au

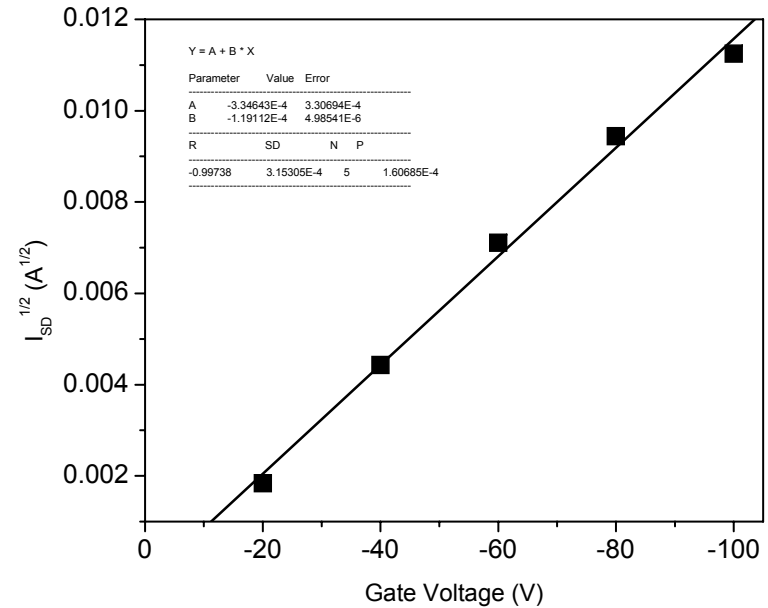
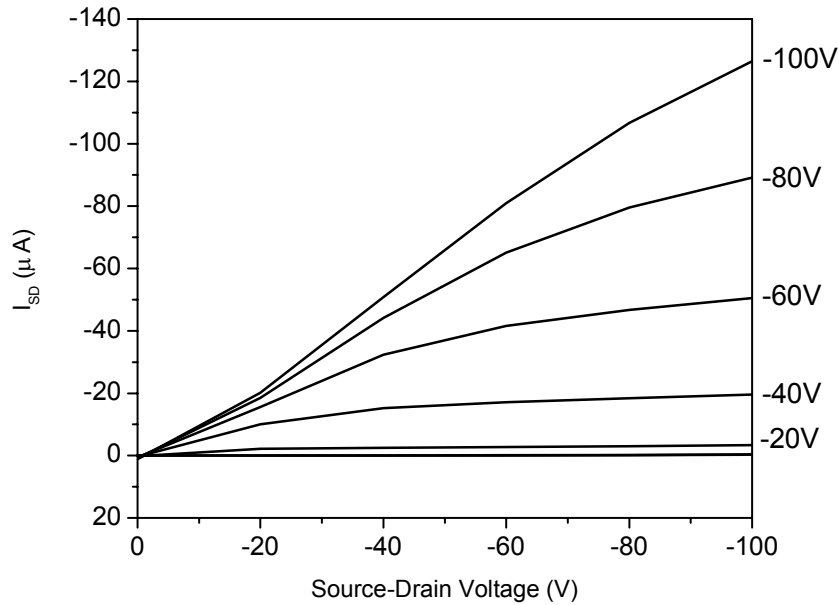


A $5 \times 5 \mu\text{m}$ AFM image of 50nm pentacene/50nm Au/glass. Inset is $1 \times 1 \mu\text{m}$ image.

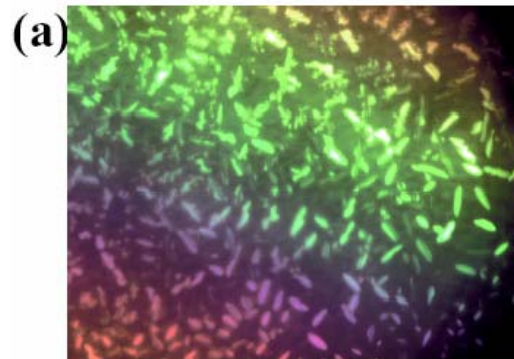
Solution Phase Oligomer Deposition



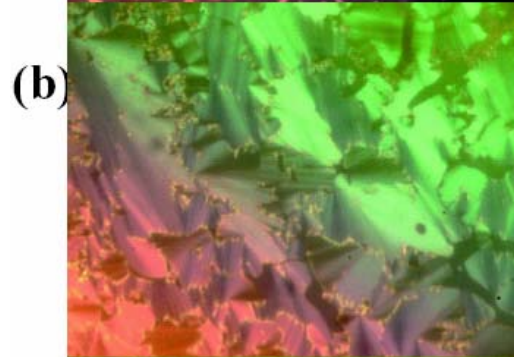
Characteristics of 6PTTP6 Solution-deposited, Small-area FET



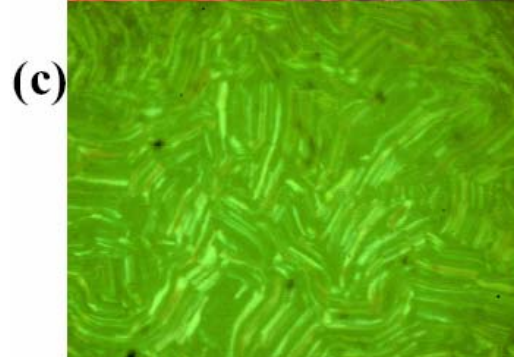
6PTTP6 Mesophases



240 degrees

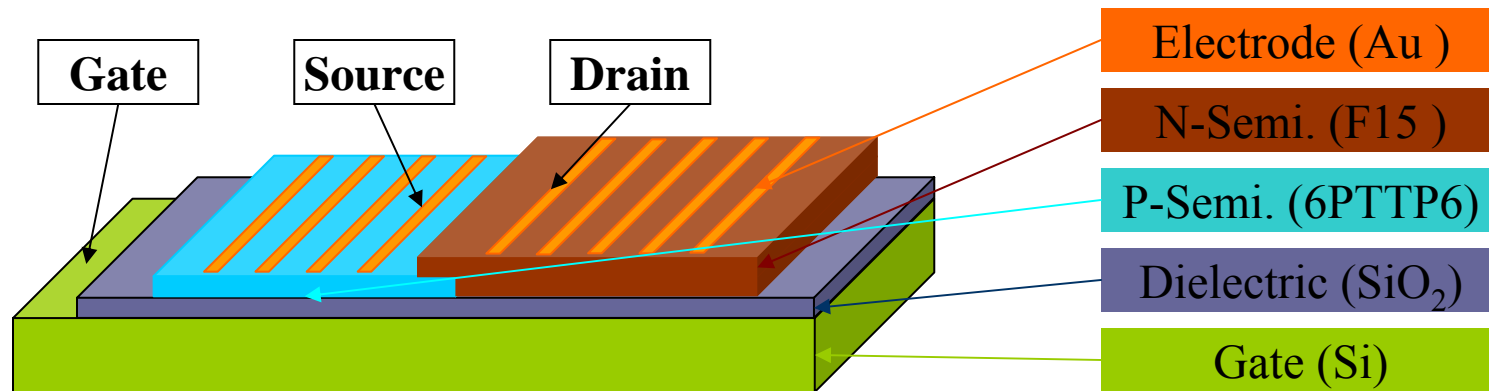


230 degrees, SA

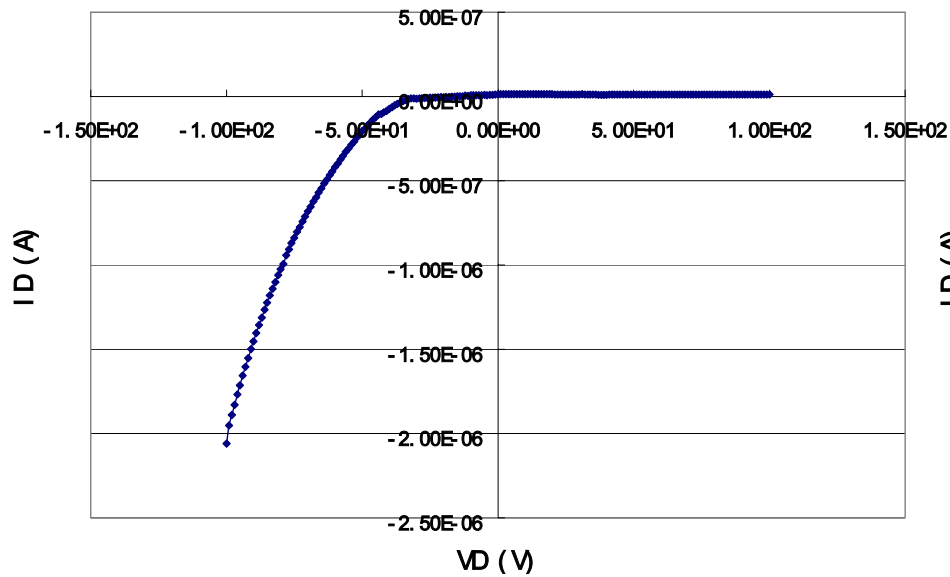


200 degrees, SB/SF

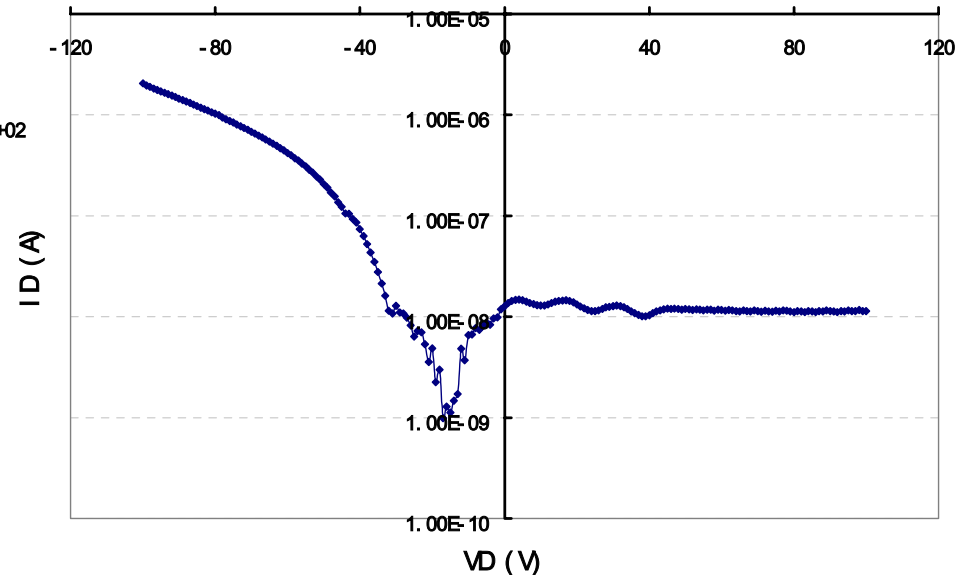
Structure of Organic Diodes with Gate



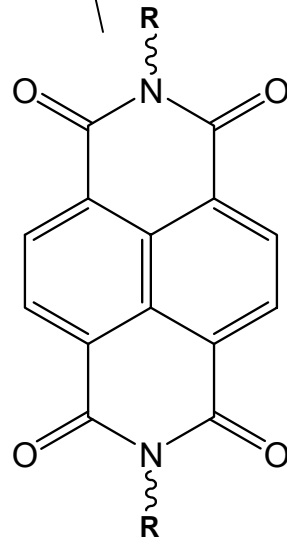
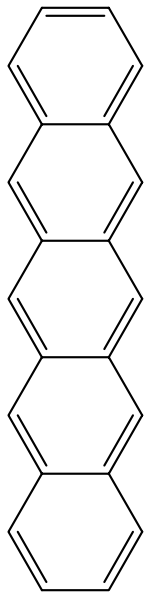
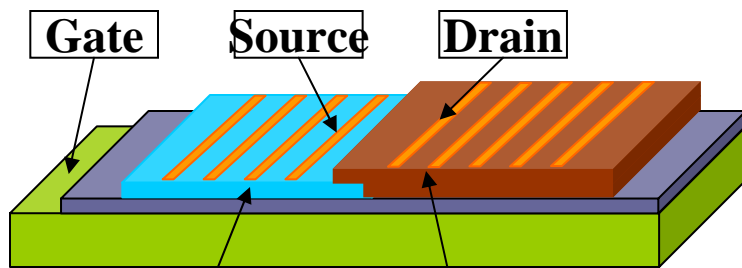
di ode 6pttp6-f15 082305 wi de overlap test 2 from -100 to 100



Di ode 6pttp6-f15 082305 wi de-overl ap test 2

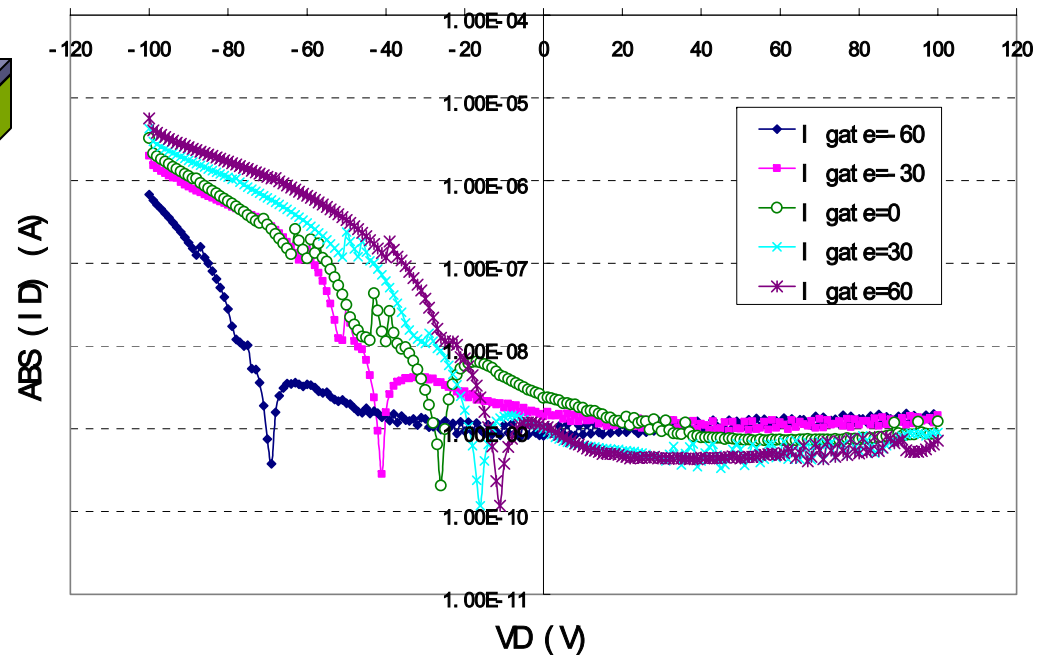


NTCDI-F7 “Lateral” Diode with Pentacene: Gate-dependent, Log Scale

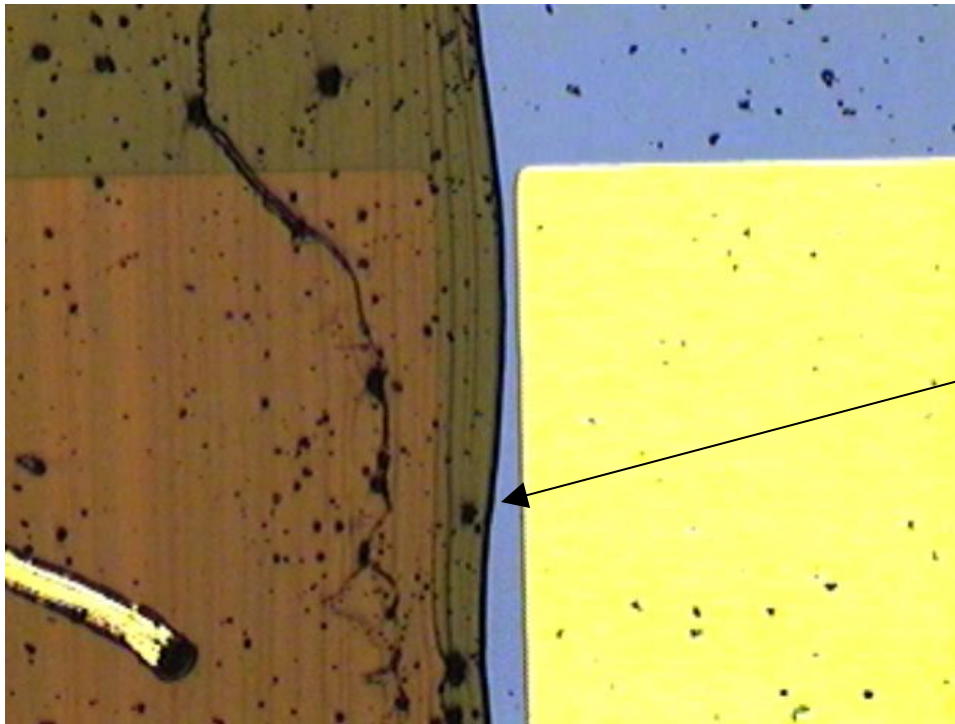


NTCDI-F7

Diode pentacene-f7 sample 071105 wide overlap with gate



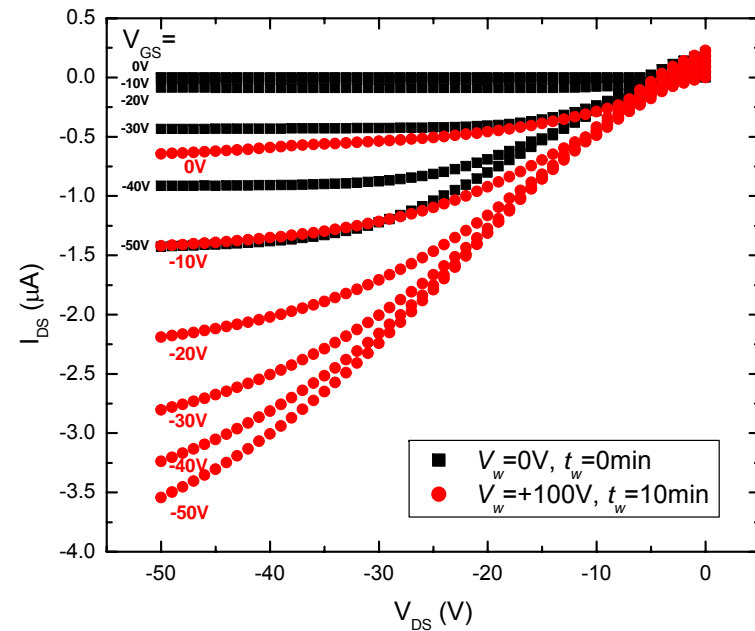
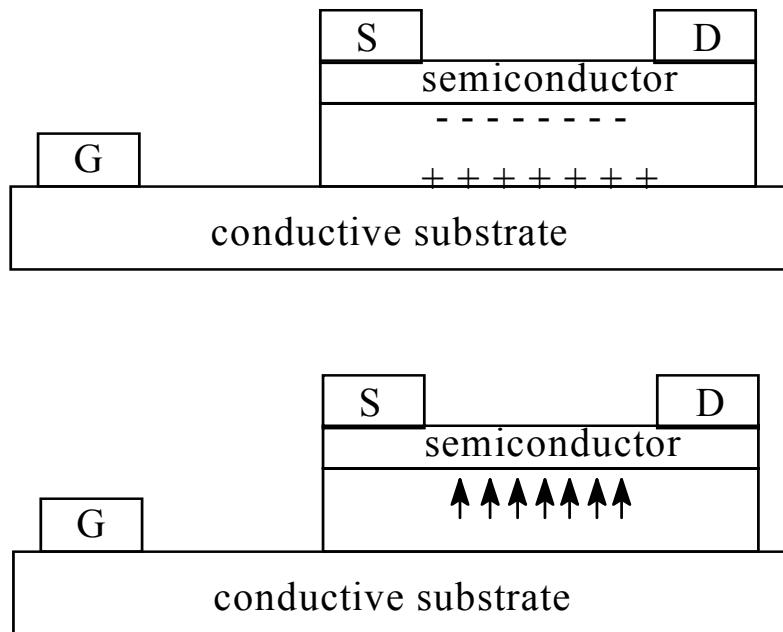
Organic pn Diode Junction



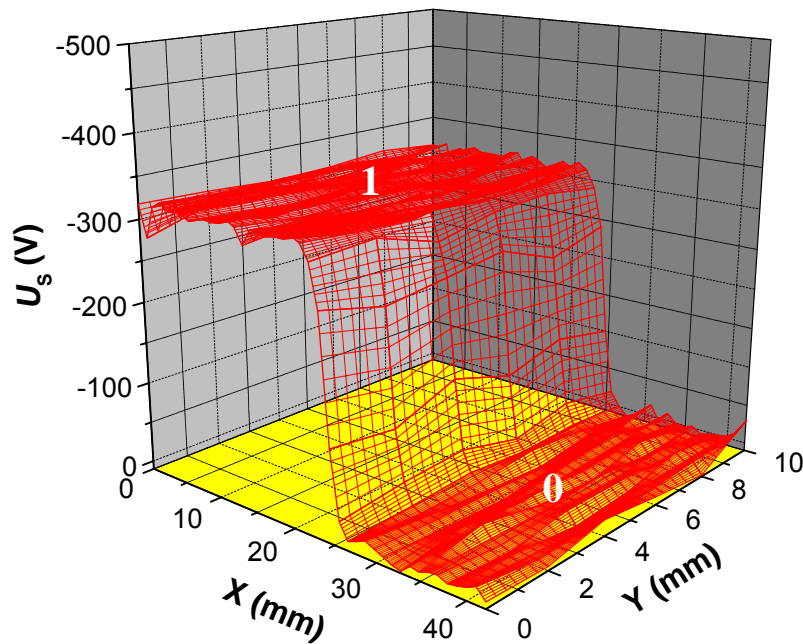
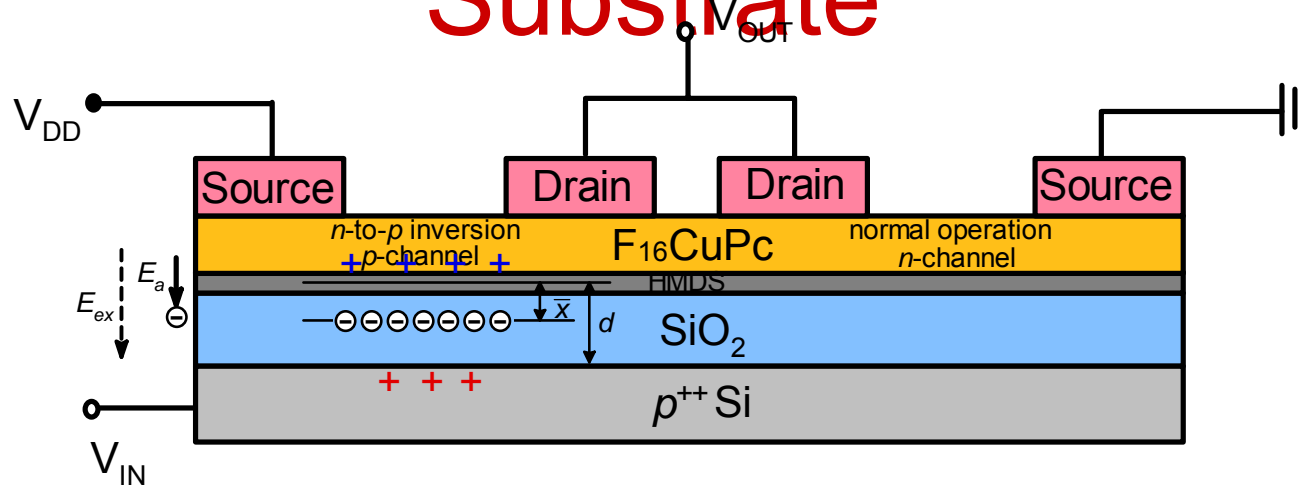
*nanoscale junction
between semiconductors!*

100 micron gap between electrodes

Many Transistors out of One: Putting a Charge into the Device!

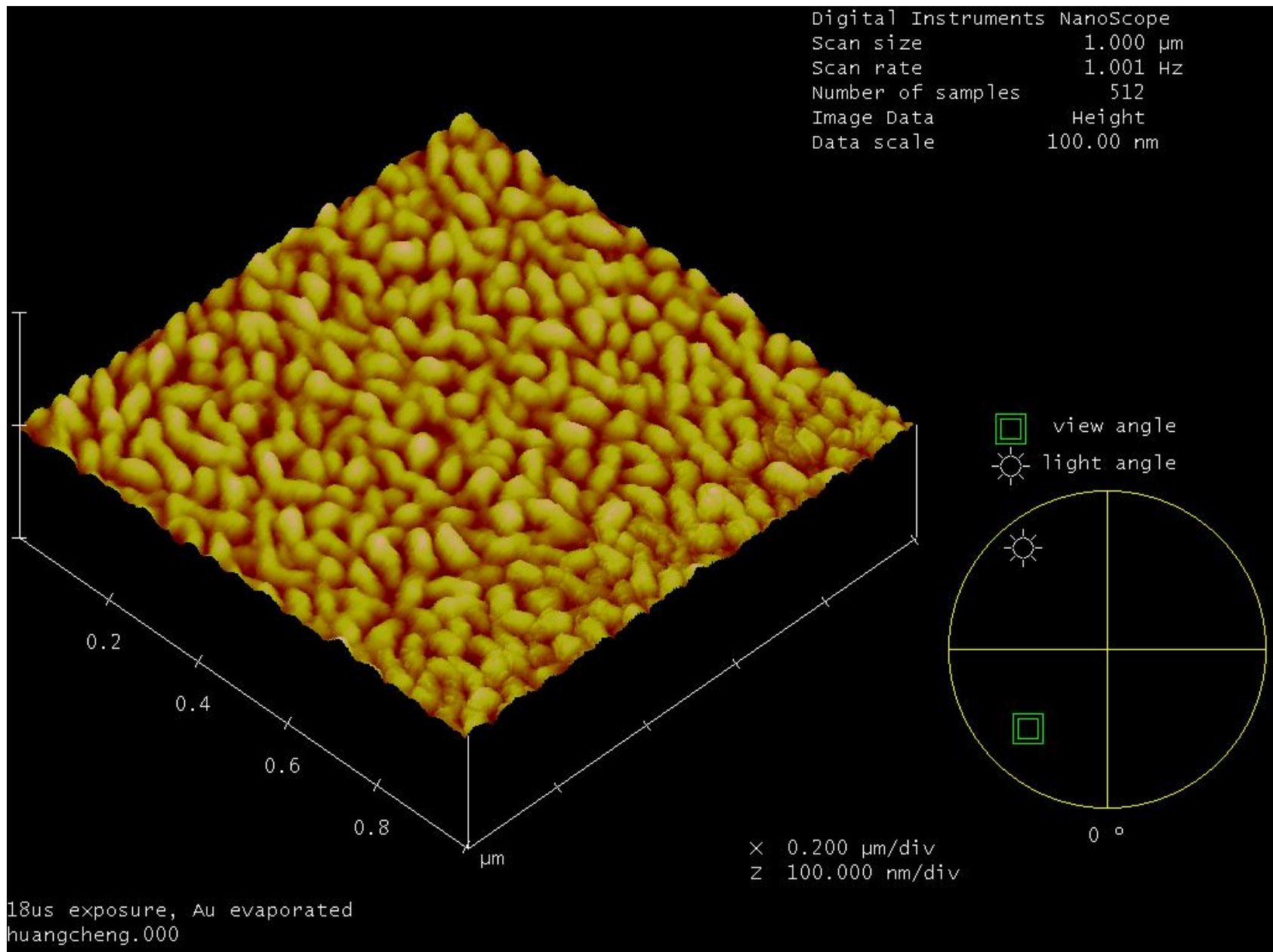


Patterned Charging of OFET Substrate

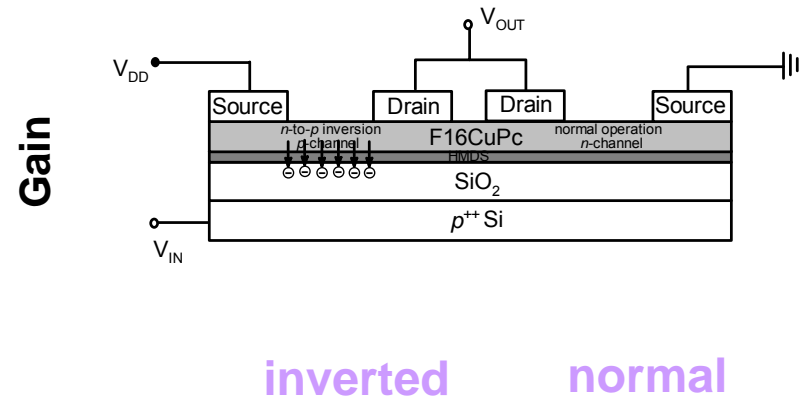
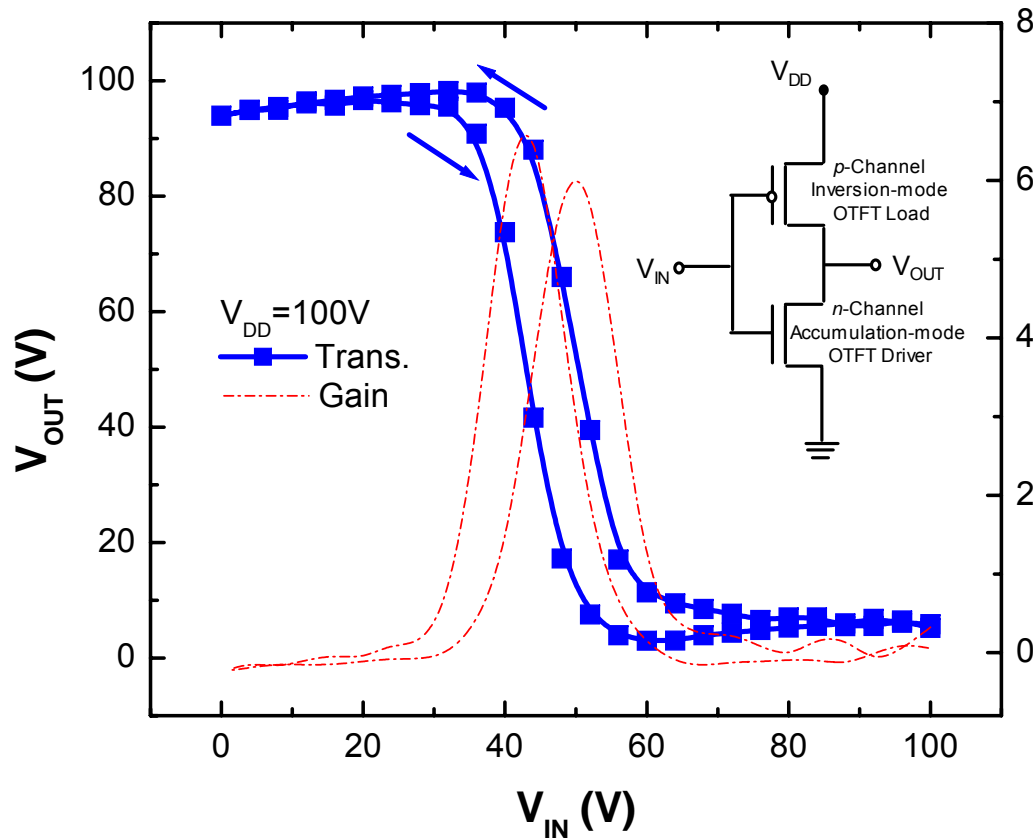


Kelvin probe mapping
of surface potential

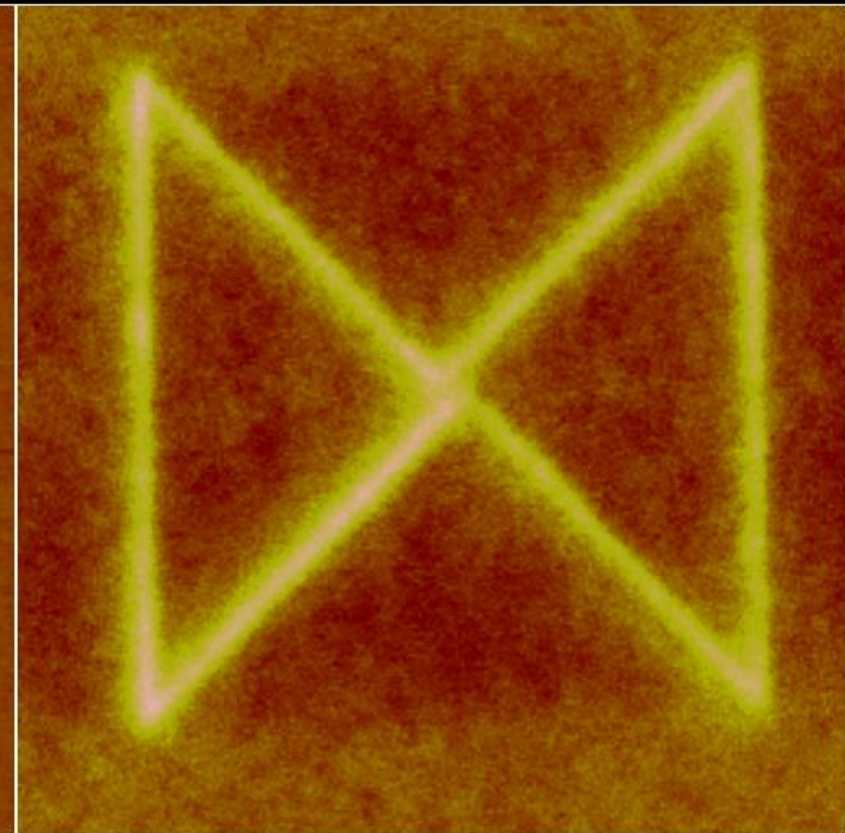
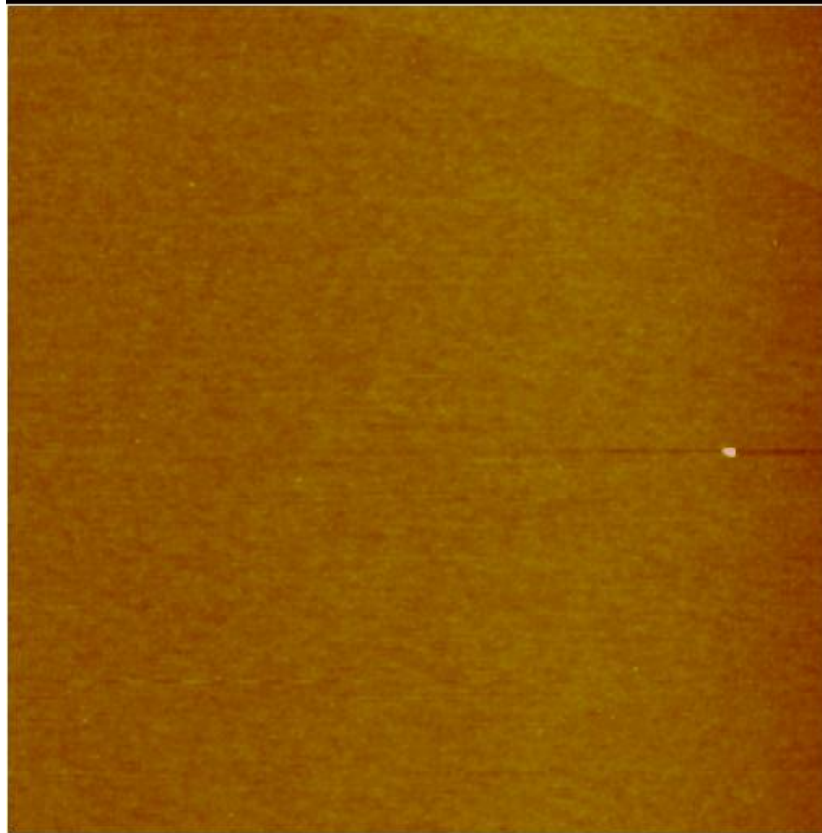
AFM Topographic Image of 25nm F₁₆CuPc Organic Semiconductor Thin Film



F16-CuPc Complementary Inverter



Electrostatic Potential Image of 300nm SiO₂ Dielectric Thin Film by AFM Nano-Charging and Nano-Scanning



0 6.00 μ m 0

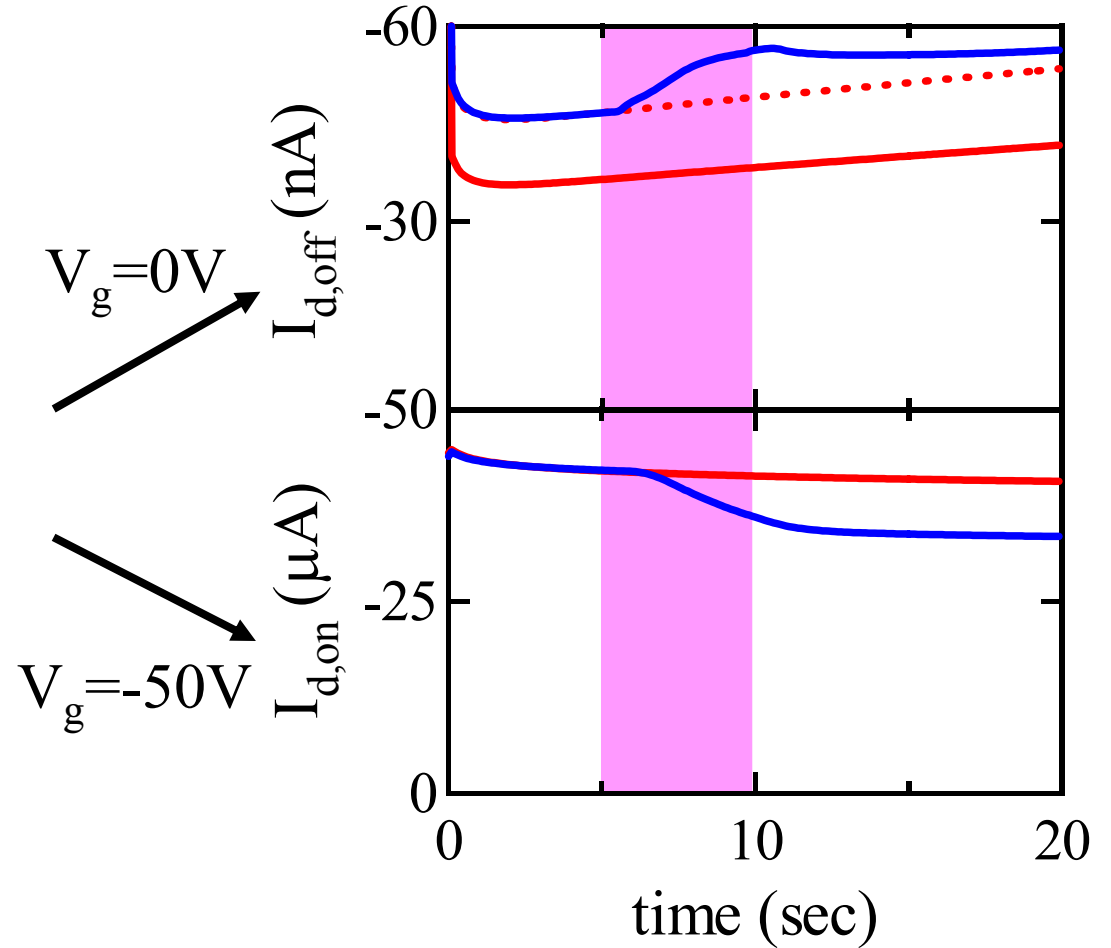
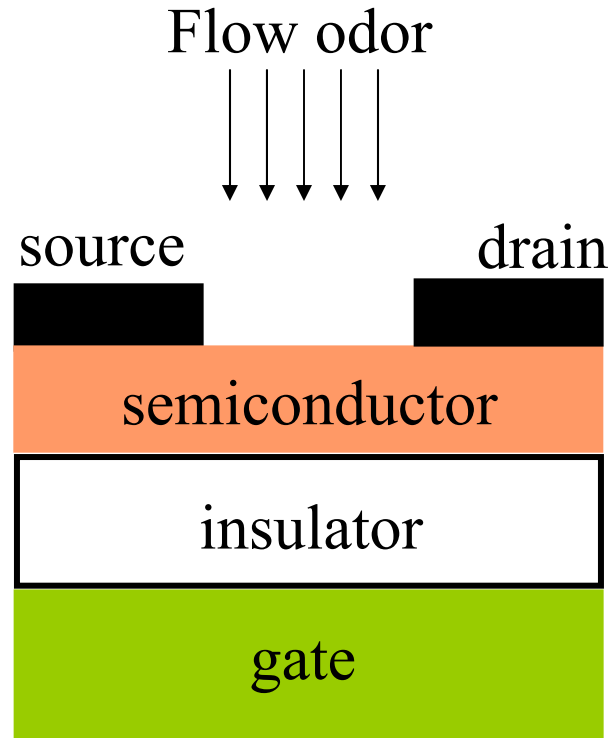
Data type Height
Z range 10.00 nm

6.00 μ m

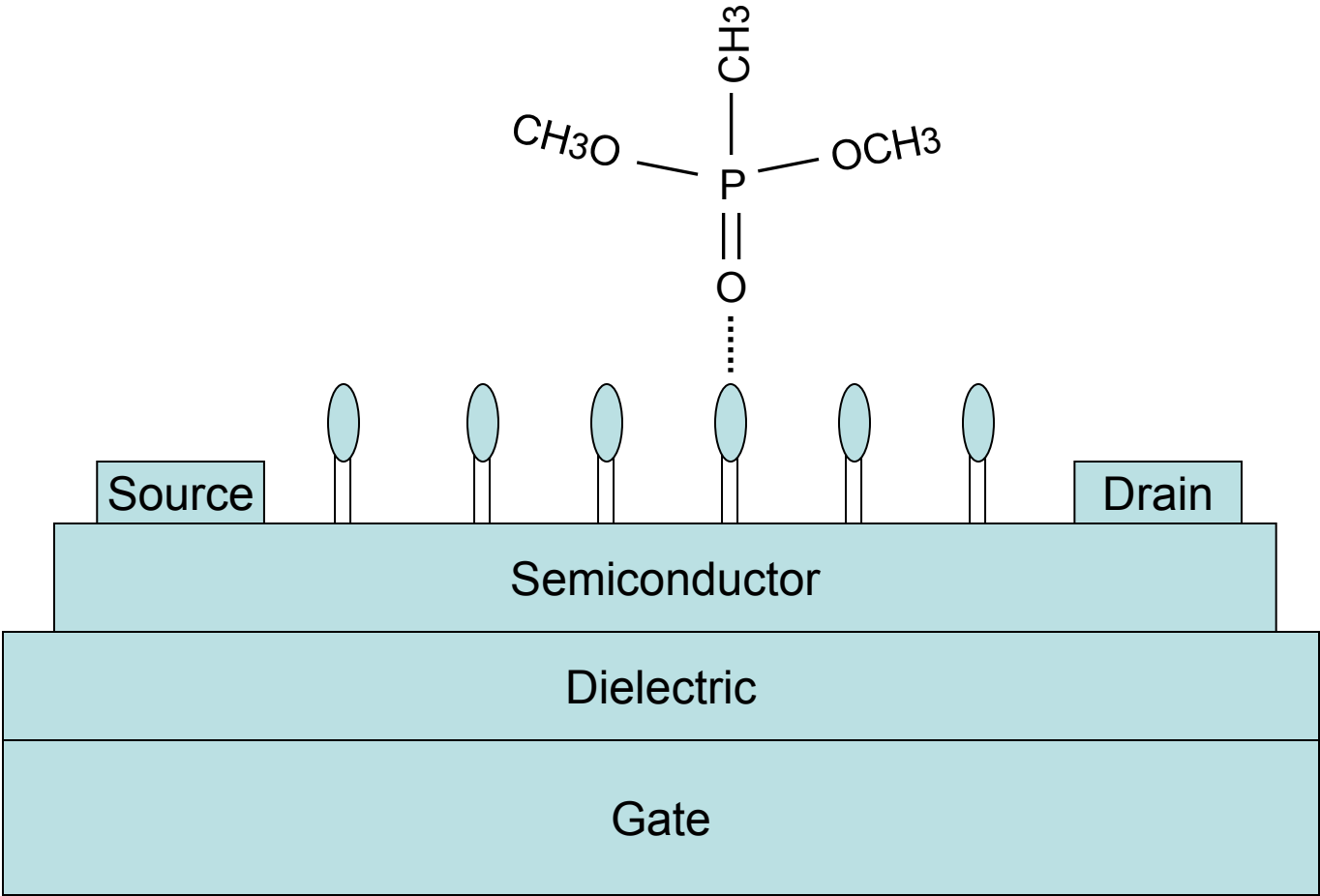
Data type Frequency
Z range 5.000 Hz

pattern_tri7.001
5v, 50nm, after 7v injection, letter M

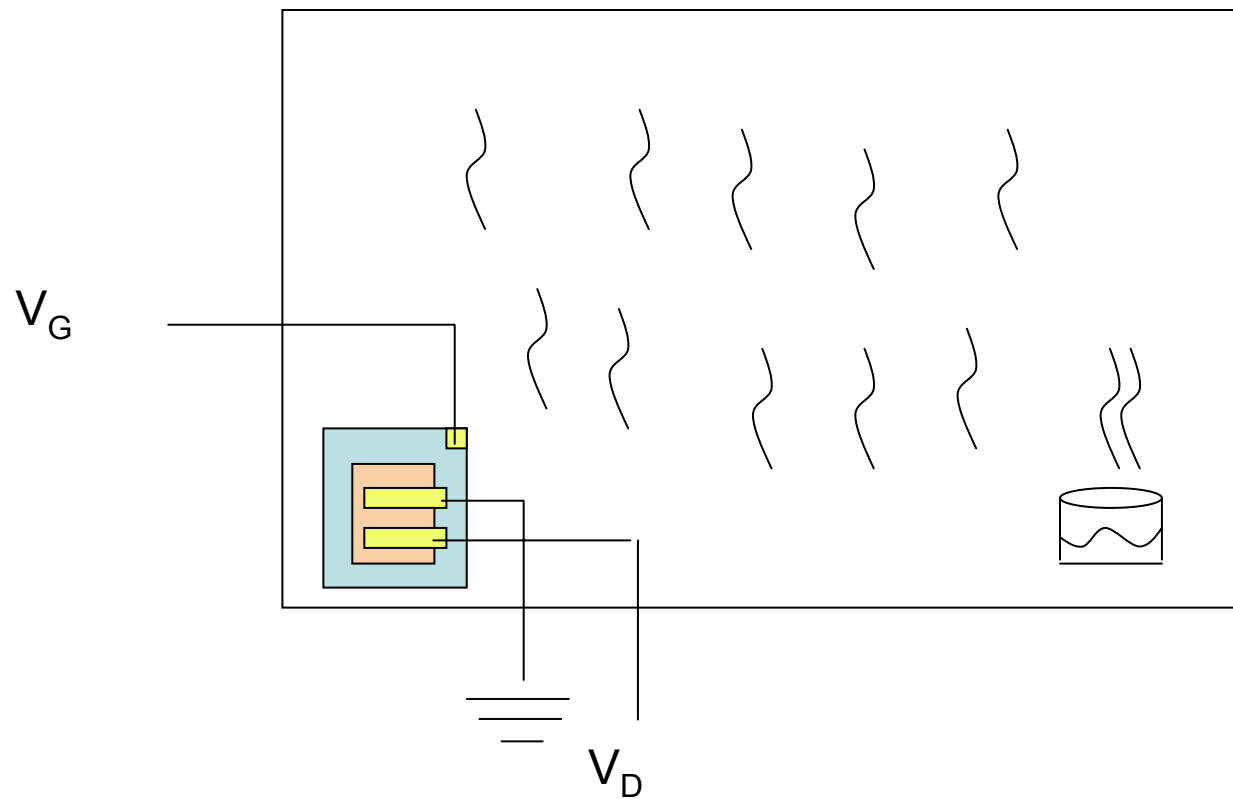
OFETs as Vapor Sensors



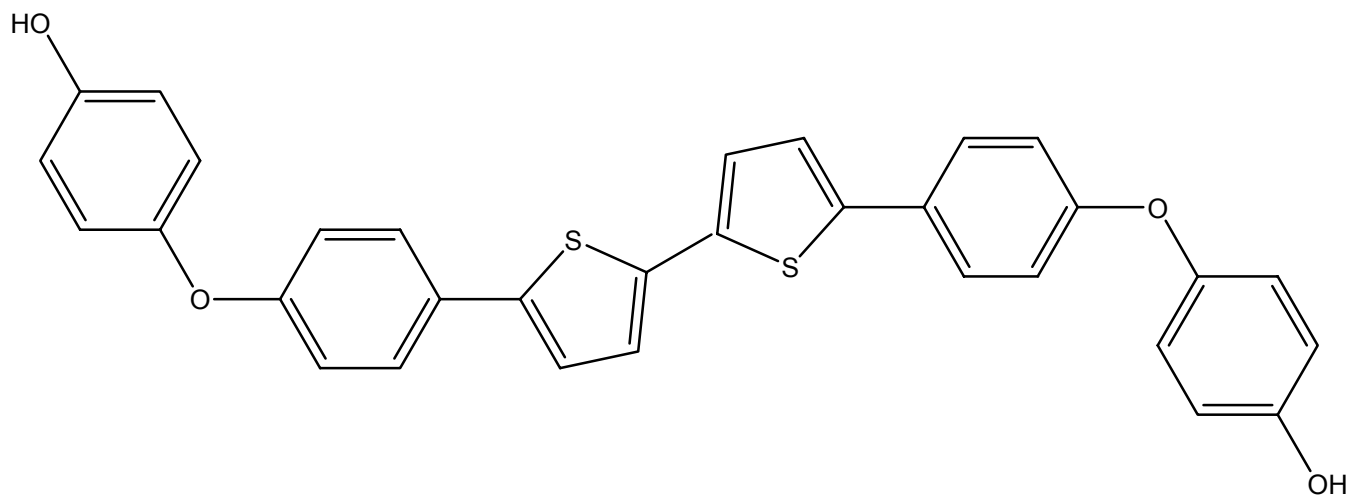
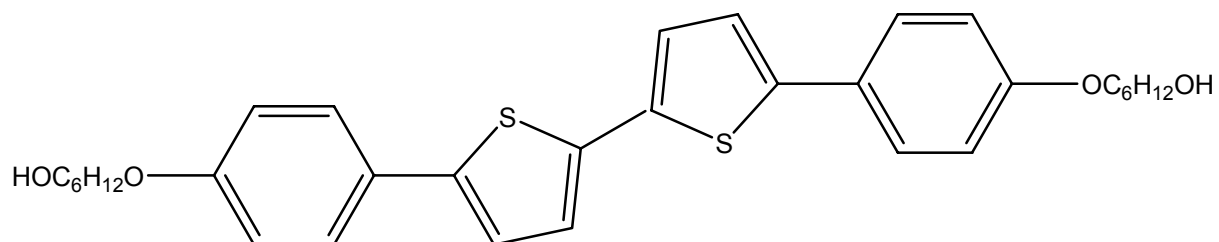
DMMP, a phosphonate
of environmental interest



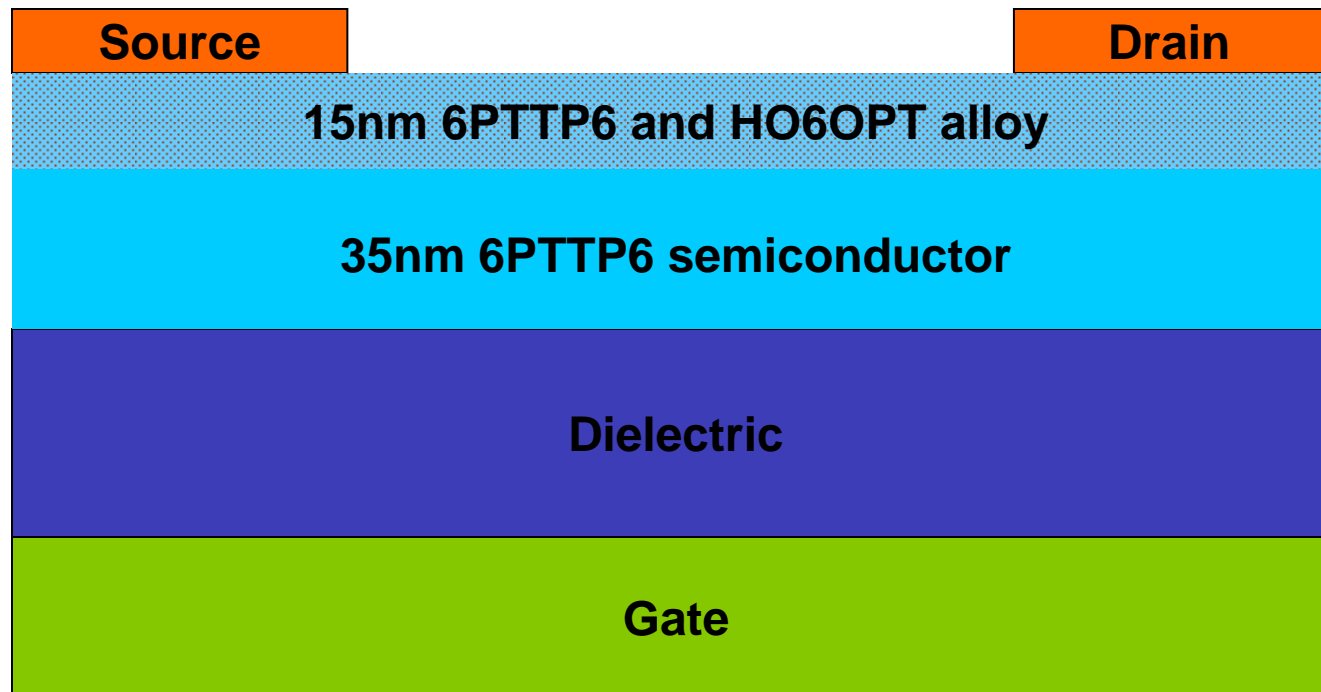
Setup for Preliminary Data



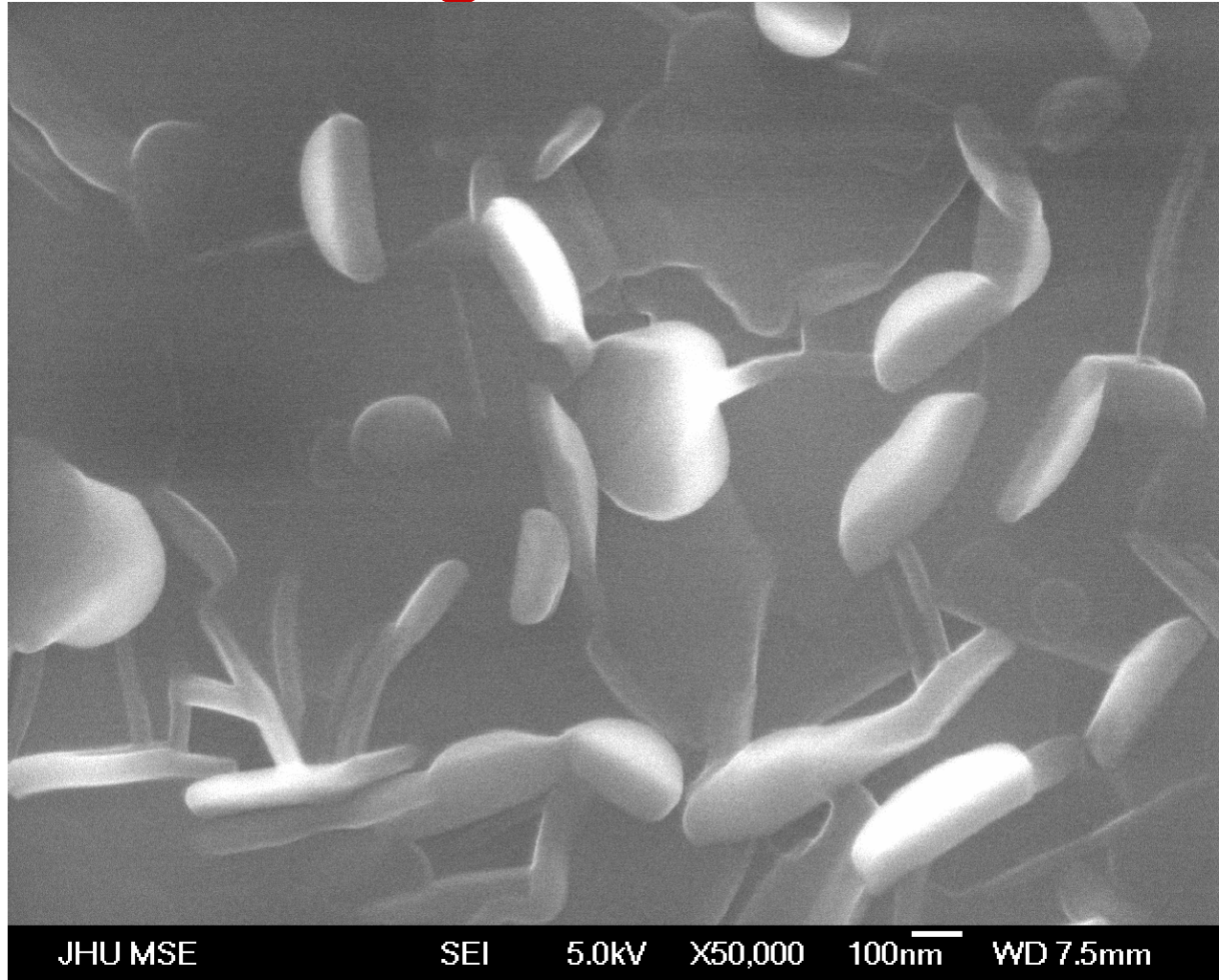
Hydroxy PTTP Derivatives



Structure of the alloy OFET sensor with 6PTTP6 and HO6OPT as semiconductor materials



6pttp6-100nm-50k Magnification



Two Layer Alloy-50nm-50k

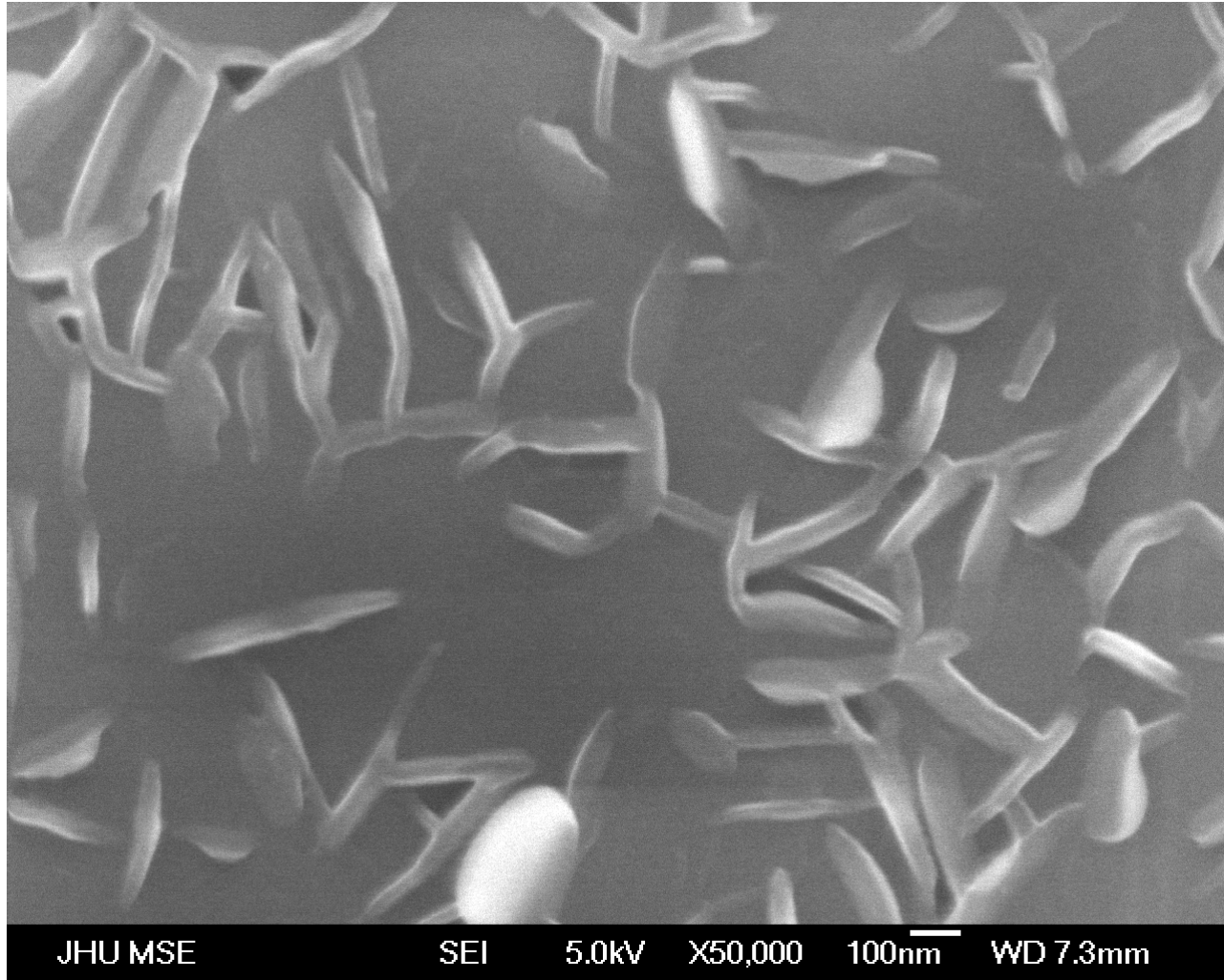
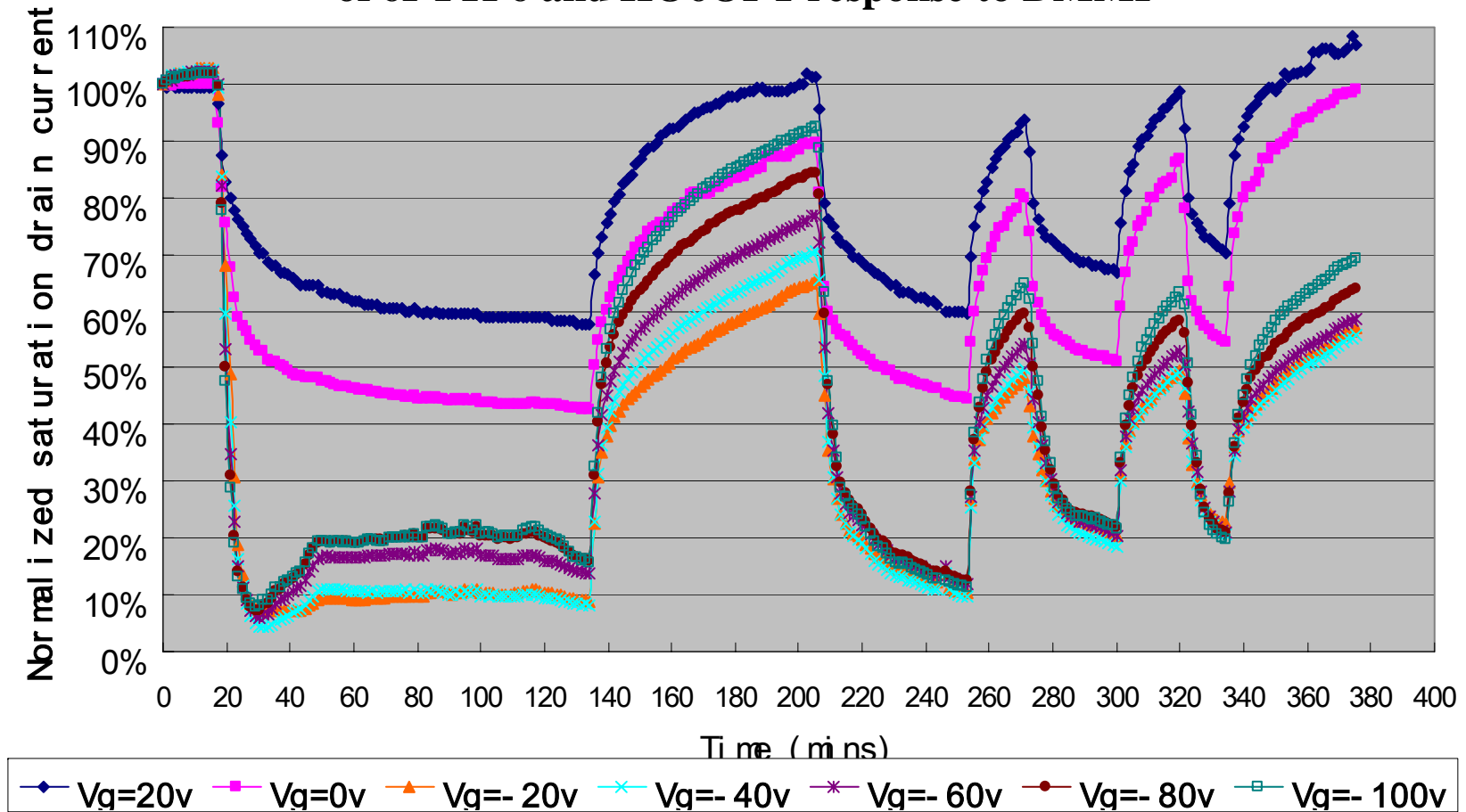
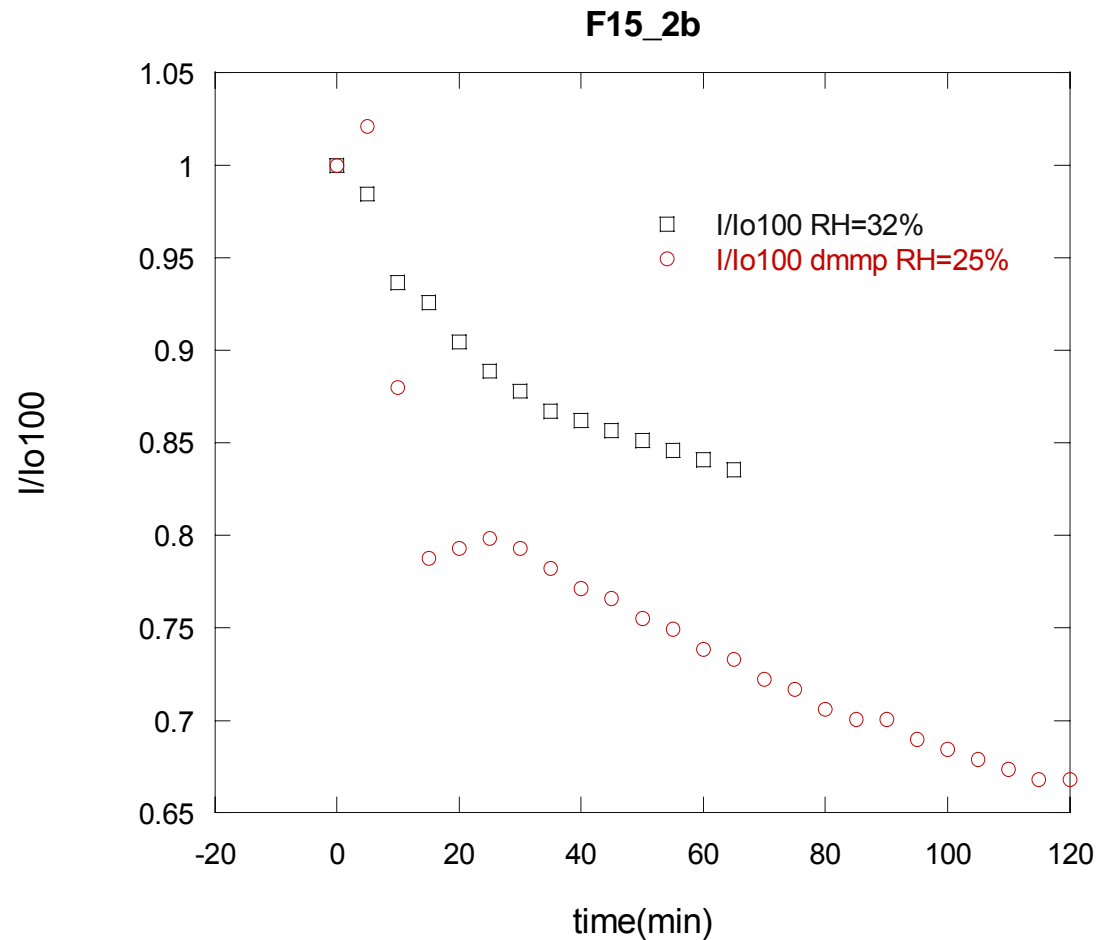


Figure 2. Normalized saturation drain current of an alloy sensor of 6PTTP6 and HO6OPT response to DMMP



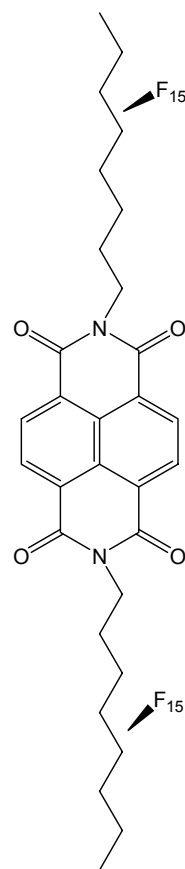
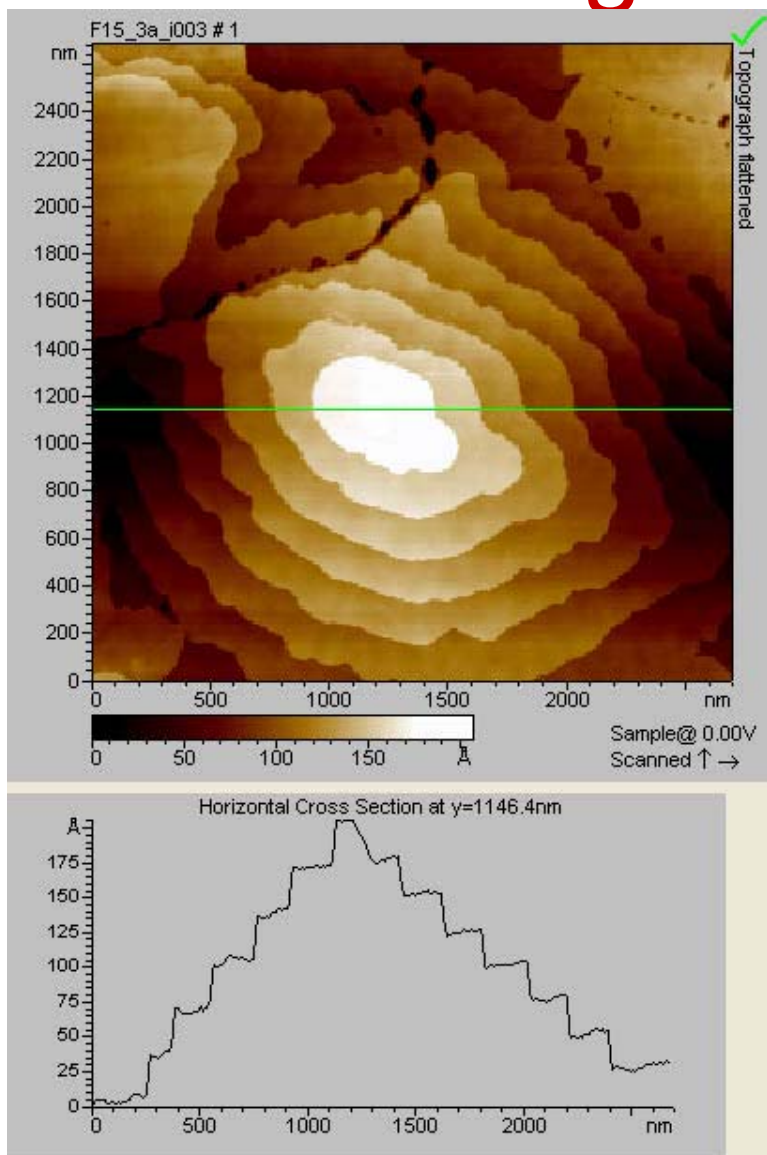
DMMP Response of NTCDI-F15

electron-carrying semiconductor



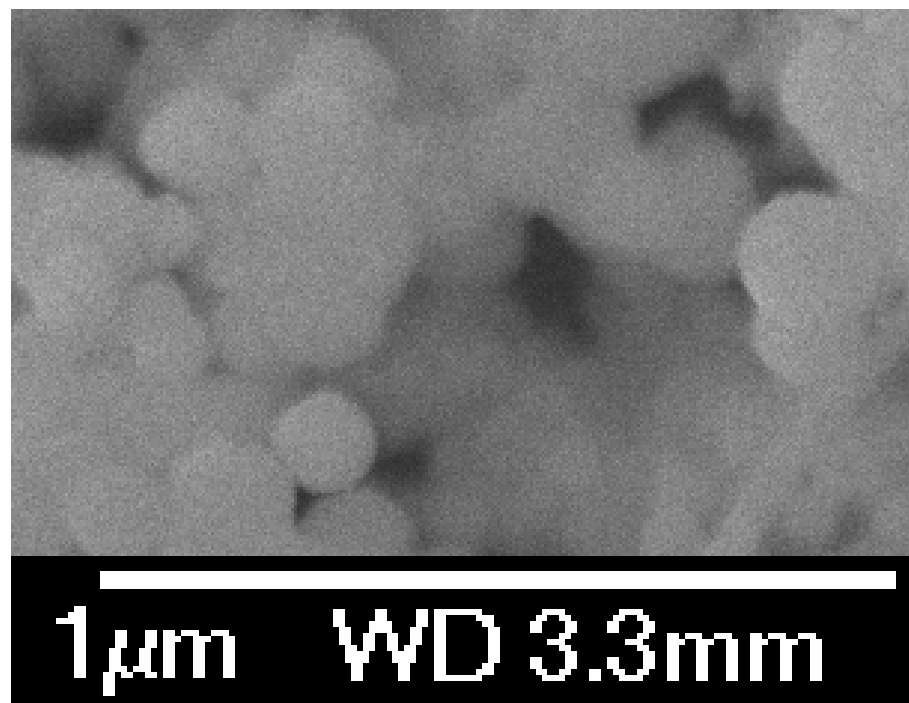
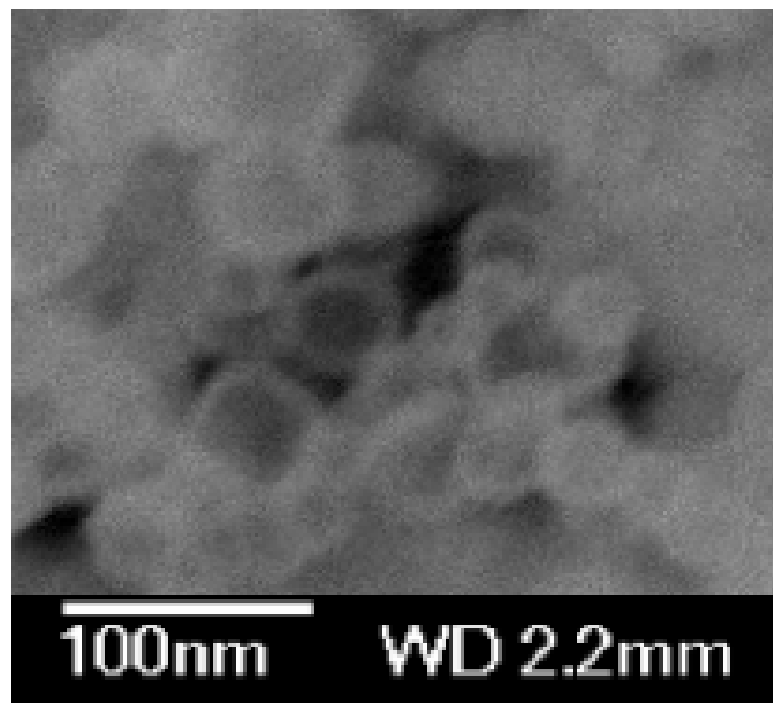
response in <5 minutes to 10% of saturated vapor (hundreds of ppm), again limited by diffusion of the vapor. Note greater current change with DMMP even though humidity is less.

AFM of NTCDI-F15—Deposition at High Substrate T



25-30 Angstrom
molecular length!

SEM Images of Dansylamide dye-doped (left) and Nitrophenyl dye-doped (right) carboxyl-functionalized silica nanoparticles for biophotonic imaging applications (J. Bai and H.E. Katz, Dept. of MSE)

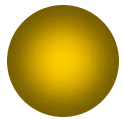


Multifunctional Nanoparticles

Peter C. Searson

Department of Materials Science and Engineering
Johns Hopkins University

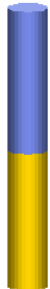
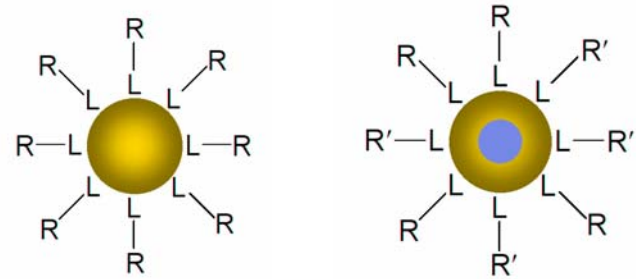
Spherical Particles and Nanowires



spherical particles

isotropic

single or mixed functionality

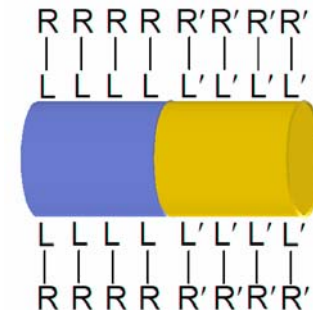


asymmetric particles

anisotropic

multicomponent

multifunctional



degrees of freedom

shape anisotropy, aspect ratio

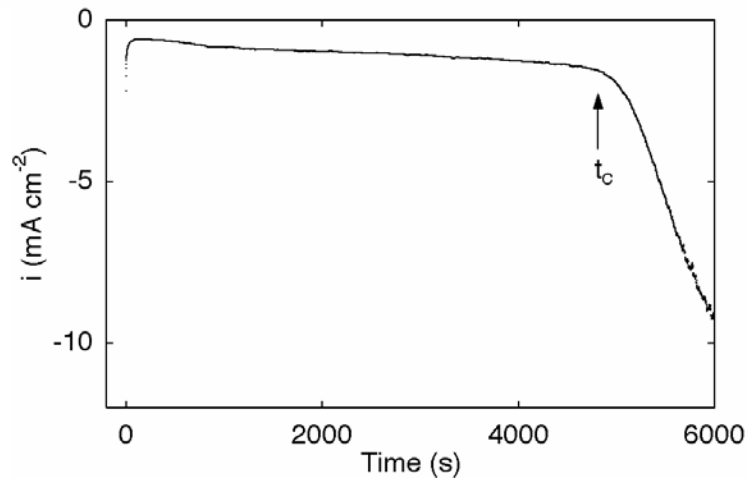
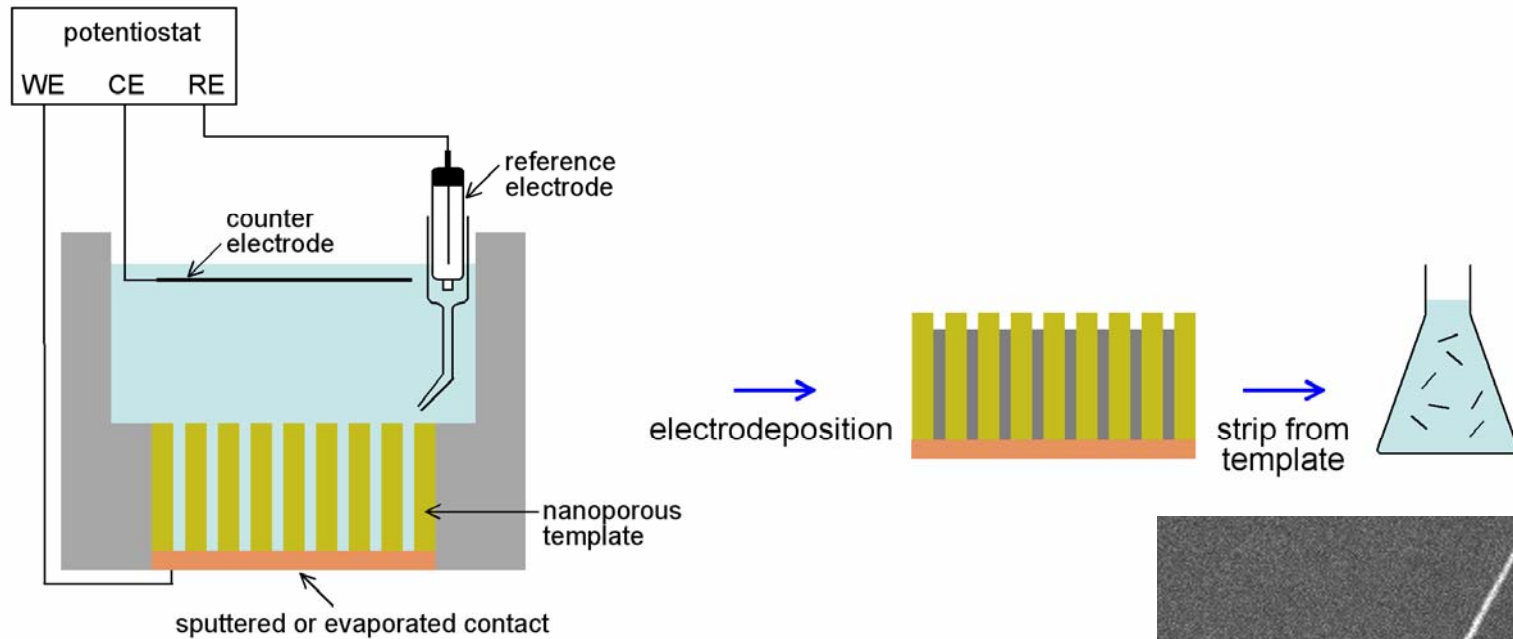
interlayer coupling

spatial multifunctionality

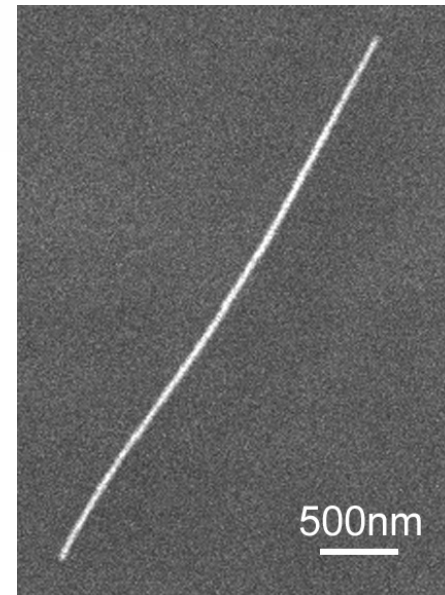
→ building blocks with more complex functions

→ more complex architectures

Electrochemical Template

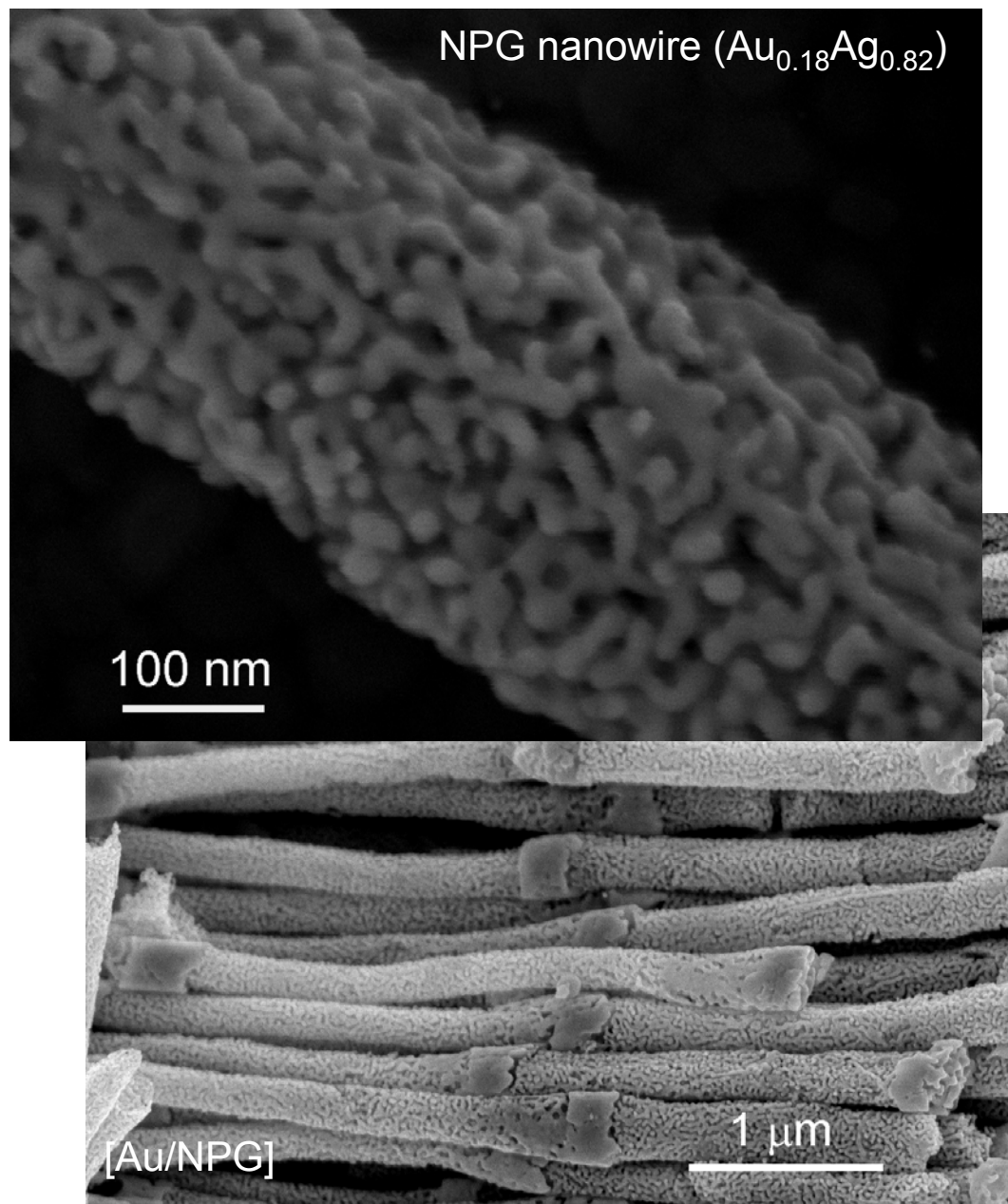
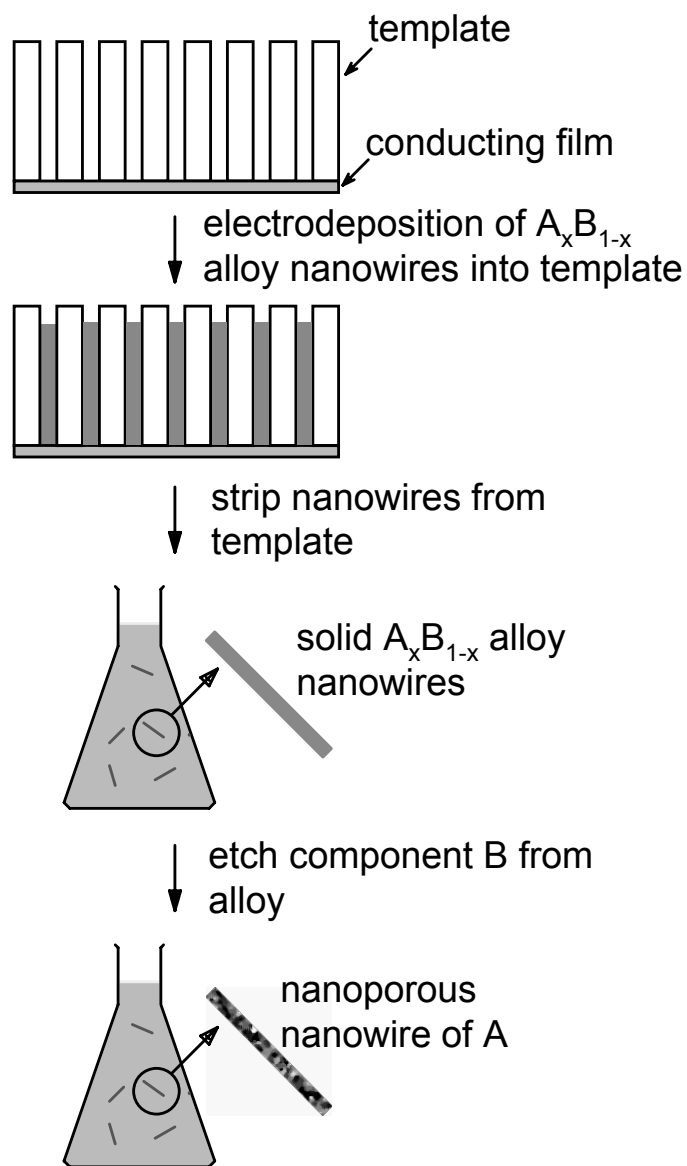


I - t curve for deposition of 30 nm CoPt nanowires into 6 μm polycarbonate template ($N \approx 6 \times 10^8 \text{ cm}^{-2}$)

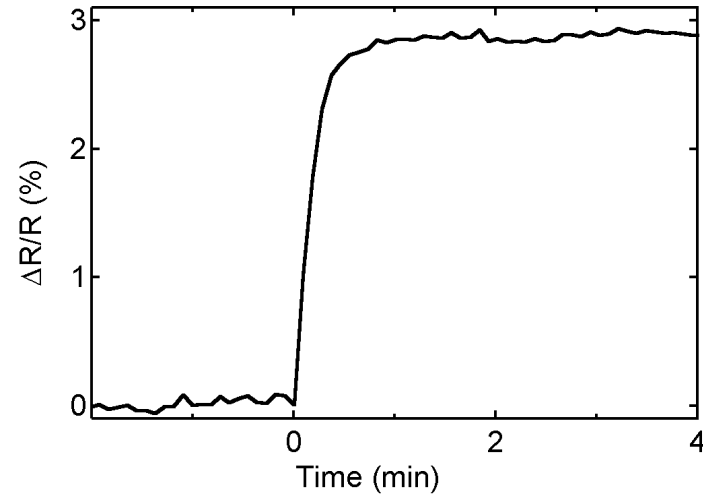
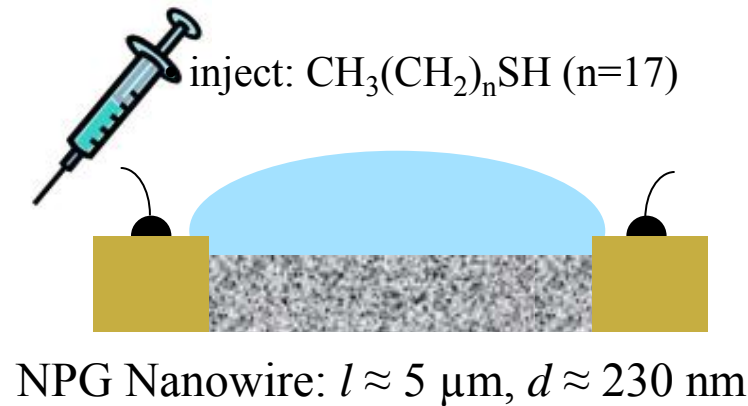


$\text{Co}_{0.65}\text{Pt}_{0.35}$ nanowire: $\ell = 4 \mu\text{m}$, $d = 30 \text{ nm}$

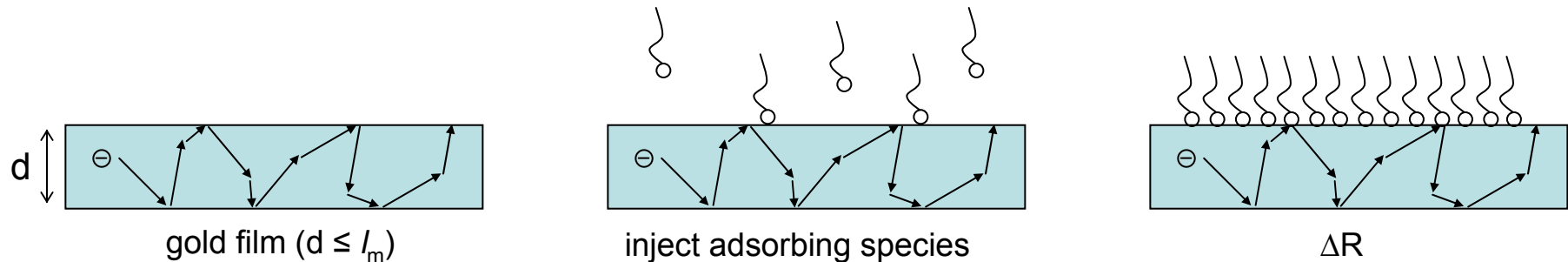
Nanoporous Nanowires



Single Nanowire Sensors



10 μL of 1 mM ODT, coverage, $\theta = 1$

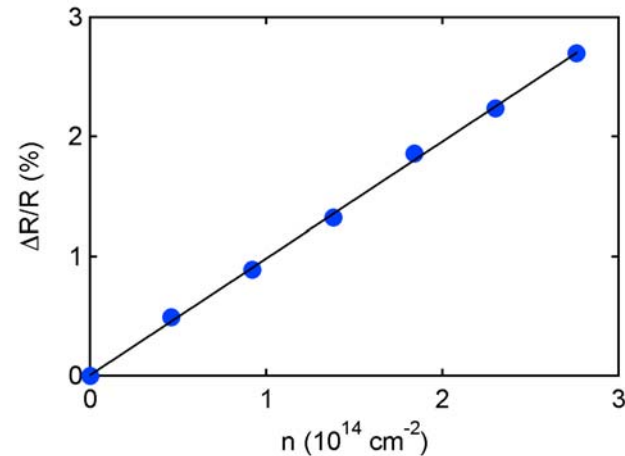
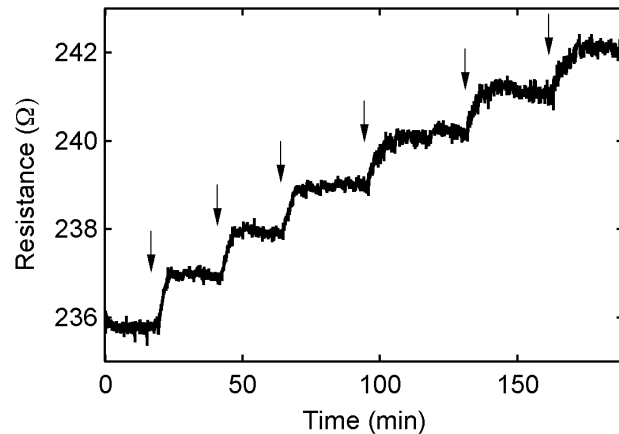


Ideal clean surface: **specular (elastic) scattering** - no change in momentum \rightarrow no resistance change

Real surface (defects, adsorbates, etc): **diffusive scattering** - change in momentum \rightarrow resistance change

e.g. Wissmann, Tracts in Modern Physics, Vol. 77, Springer-Verlag (1975).

Single Nanowire Sensors



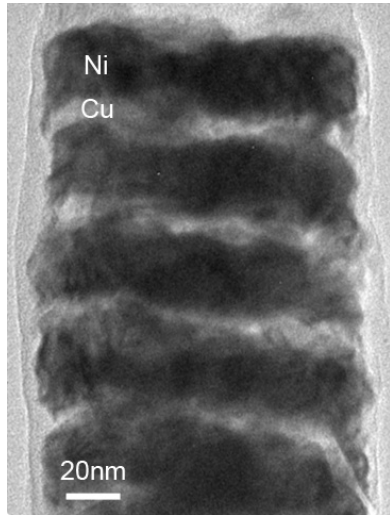
Sequential injection of 5×10^{-11} moles ODT
 monolayer coverage: $4.6 \times 10^{14} \text{ cm}^{-2}$

$$\left. \frac{d(\Delta R/R)}{dn} \right|_{n \rightarrow 0} = \frac{Al_m}{d}$$

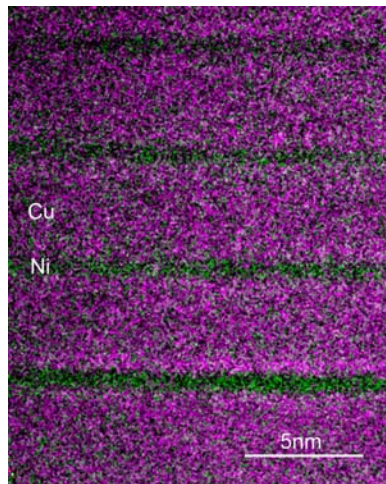
$$d(\Delta R/R)/dn = 1.0 \times 10^{-16} \text{ cm}^2$$

- ODT on Au (40 nm): $0.2 \times 10^{-16} \text{ cm}^2$
- CO on Ni(10 nm): $0.5 \times 10^{-16} \text{ cm}^2$
- CO on Cu(10 nm): $2 \times 10^{-16} \text{ cm}^2$

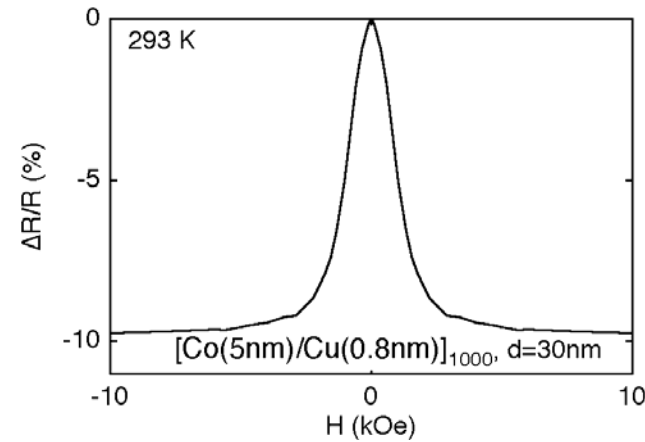
Multicomponent FM/NM Multilayer Nanowires



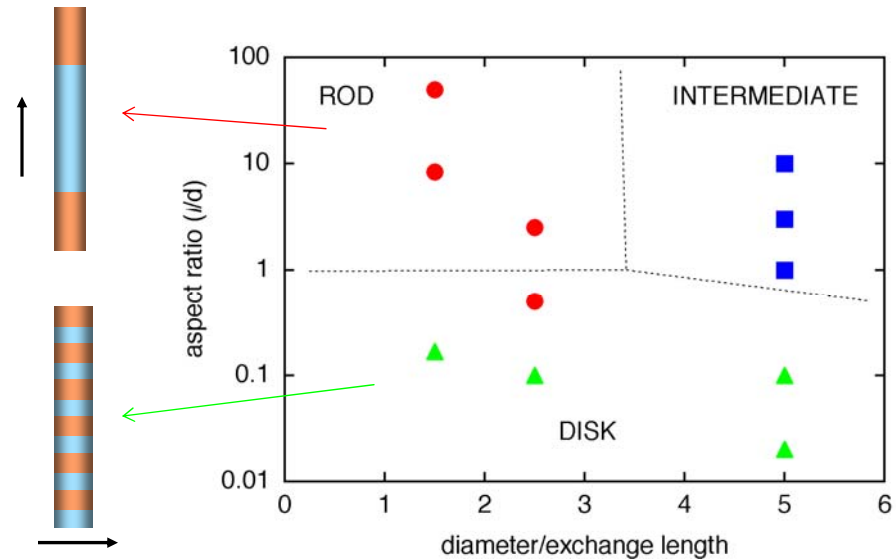
HRTEM image
[Ni(20nm)/Cu10nm], d=120nm



EELS image
[Ni(1nm)/Cu(4nm)], d = 30nm



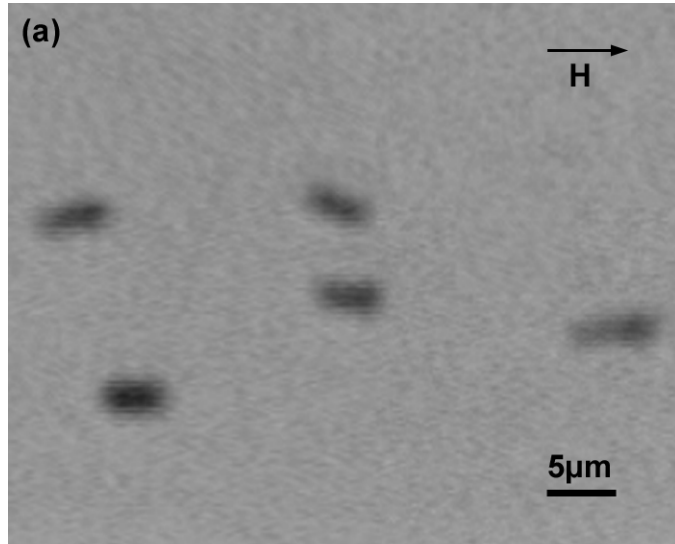
→ Nanowire GMR elements



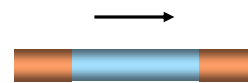
exchange length, $\lambda_{ex}(\text{Ni}) \approx 20 \text{ nm}$

Phys. Rev. B, Rapid Comm. **51**, 7381 (1995).
Appl. Phys. Lett. **82**, 3310-3312 (2003).

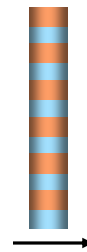
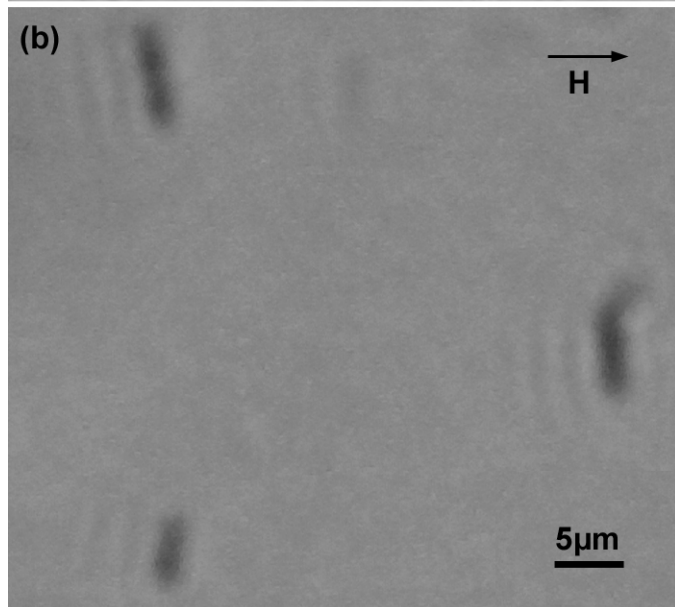
Exploiting Shape Anisotropy in FM/NM Multilayer Nanowires



nanowire suspensions in octadecane/hexadecane (1:1)
 $l = 6 \mu\text{m}$, $d = 100 \text{ nm}$
composition: 50% Ni, 50% Cu

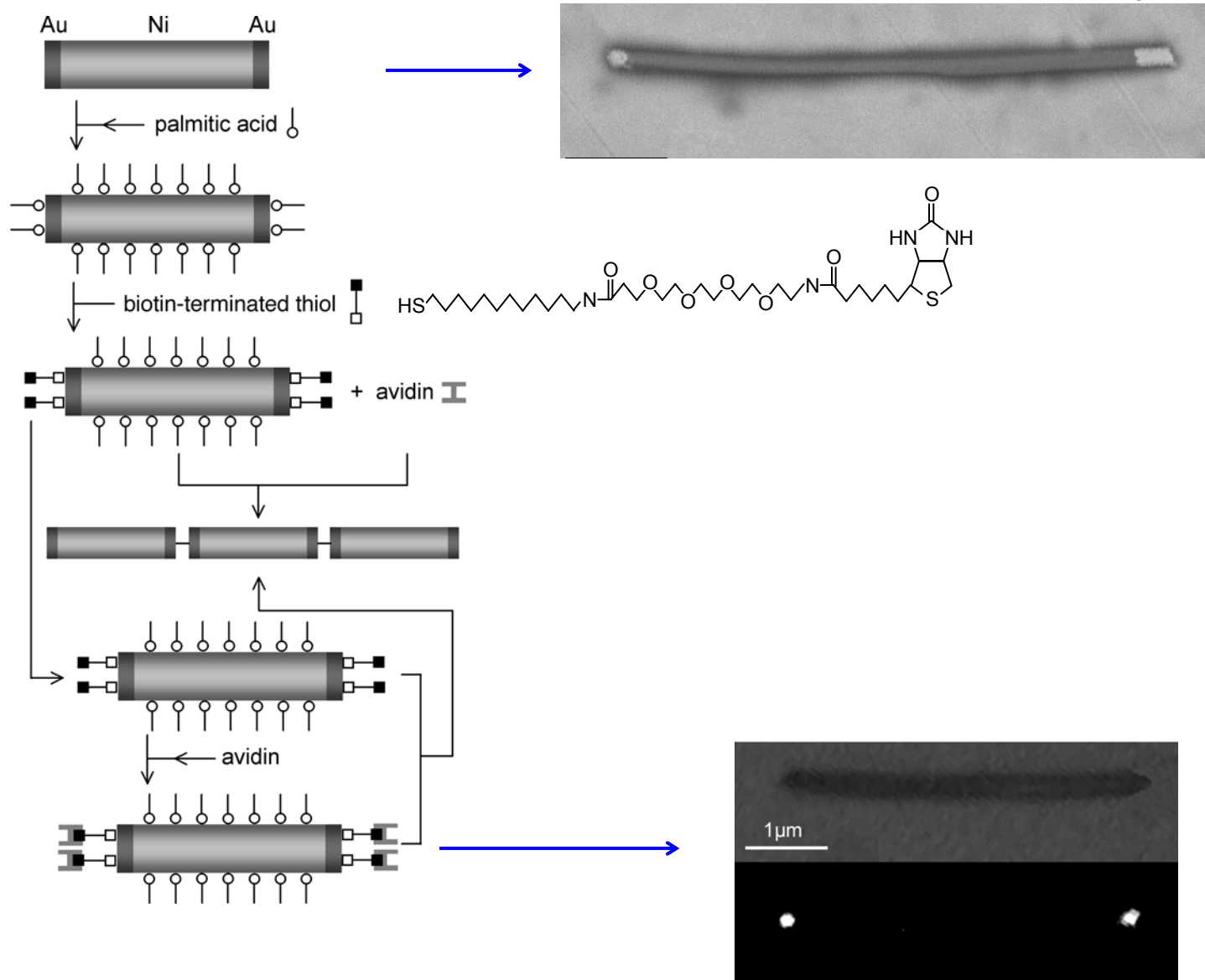


$[\text{Ni}(1000\text{nm})/\text{Cu}(1000)]_3$

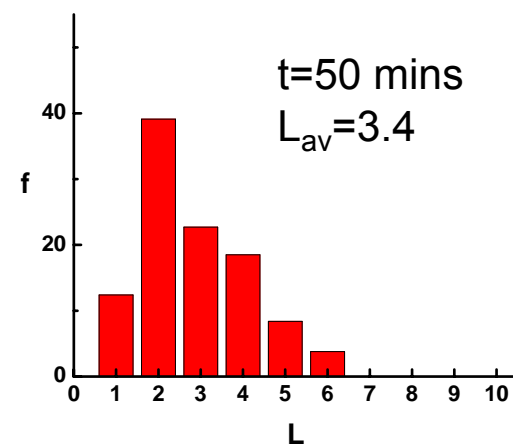
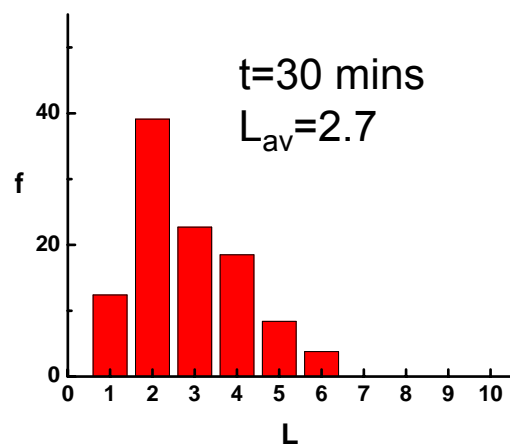
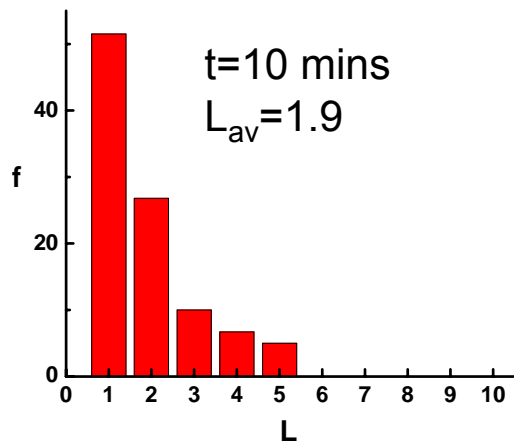
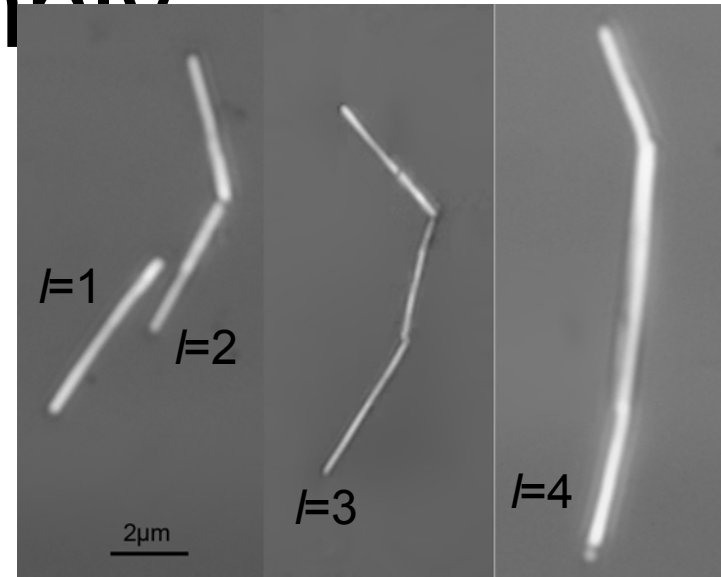
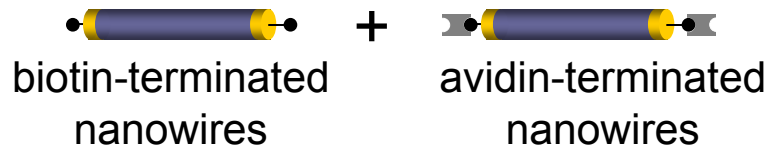


$[\text{Ni}(10\text{nm})/\text{Cu}(10)]_{300}$

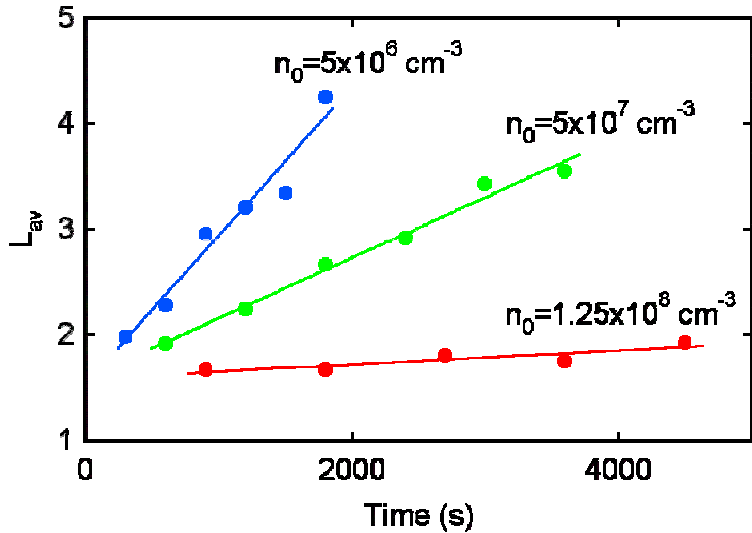
Nanowire Self-Assembly



Nanowire Self-Assembly



Rate of Assembly



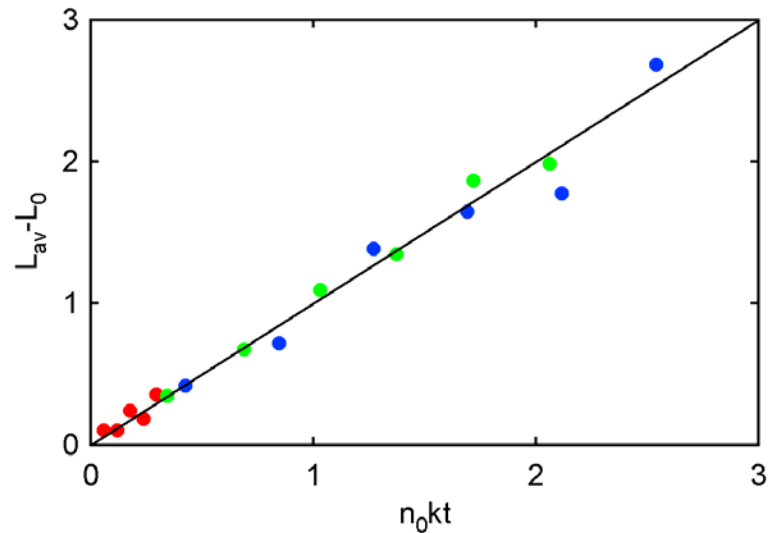
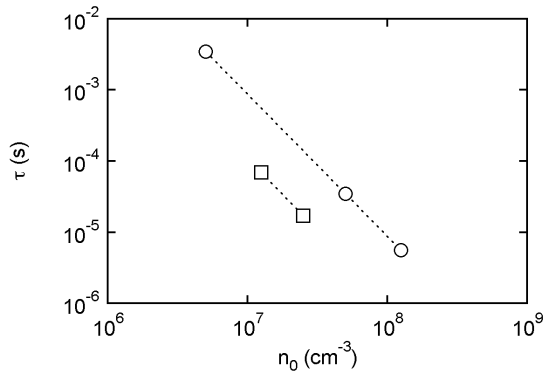
Model

Assume that attachment is dependent on the collision rate, defined by respective rate

constants

Note: analogous to Smoluchowski model for diffusion limited aggregation

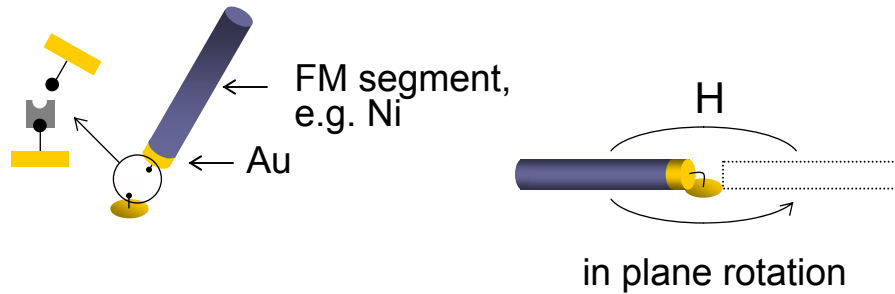
SOLUTION: $L_{av} - L_0 = n_0 kt$



Adv. Mater. **17**, 2765-2768 (2005).

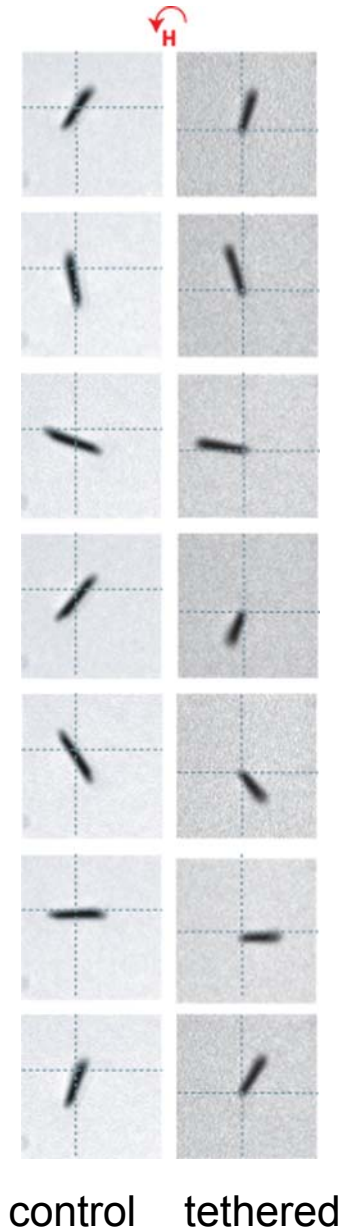
J. Phys. Chem. **110**, 211-217 (2006).

Rotation of Tethered Nanowires

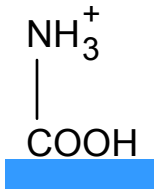
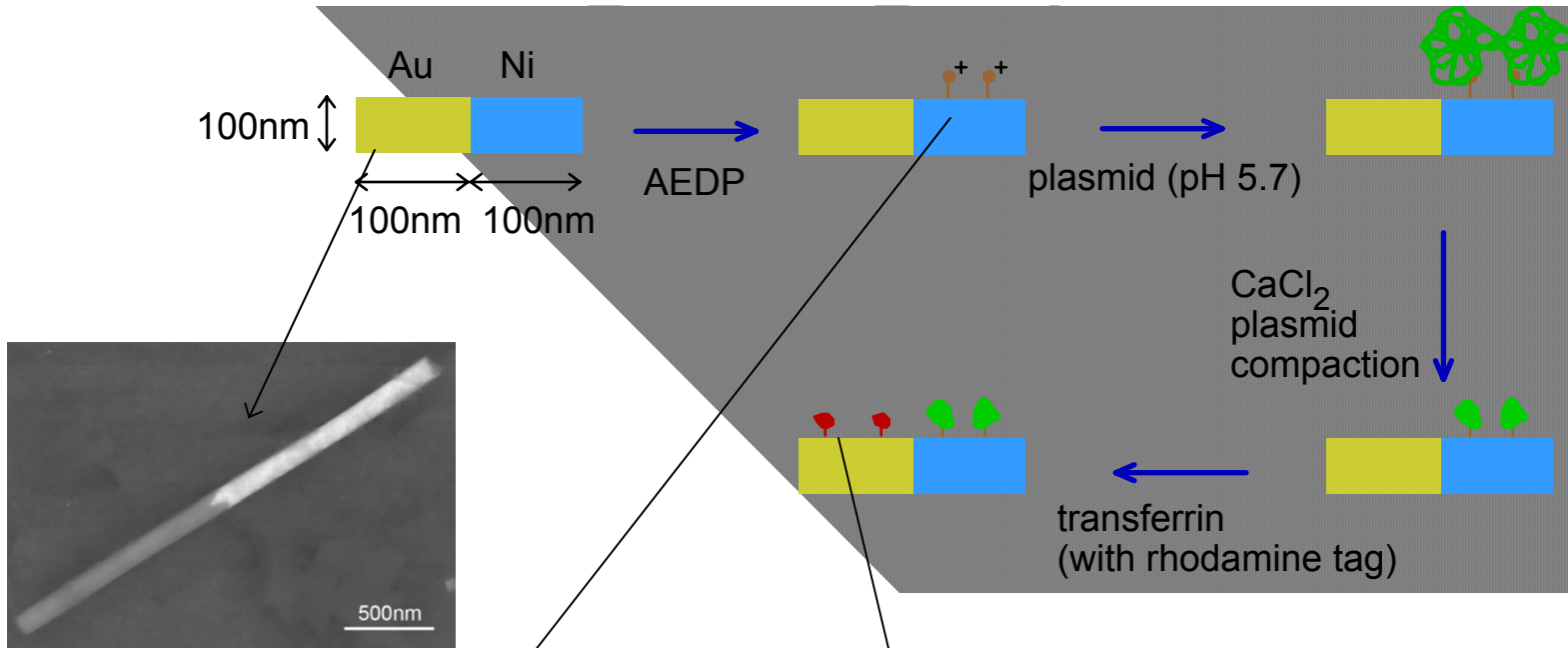


QuickTime™ and a Cinepak decompressor are needed to see this picture.

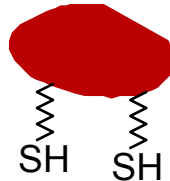
Nanowire motors, switches, ...?



Selective Functionalization for



3-[2-aminoethyl]dithio] propionic acid (AEDP)

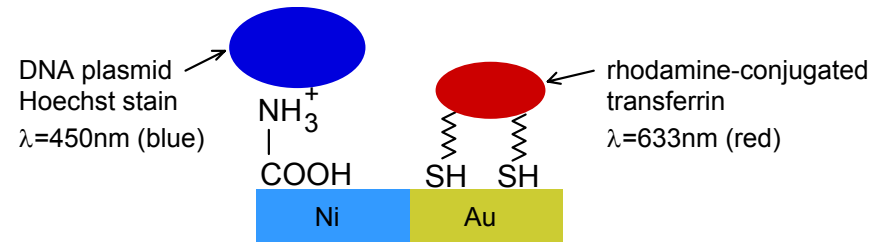
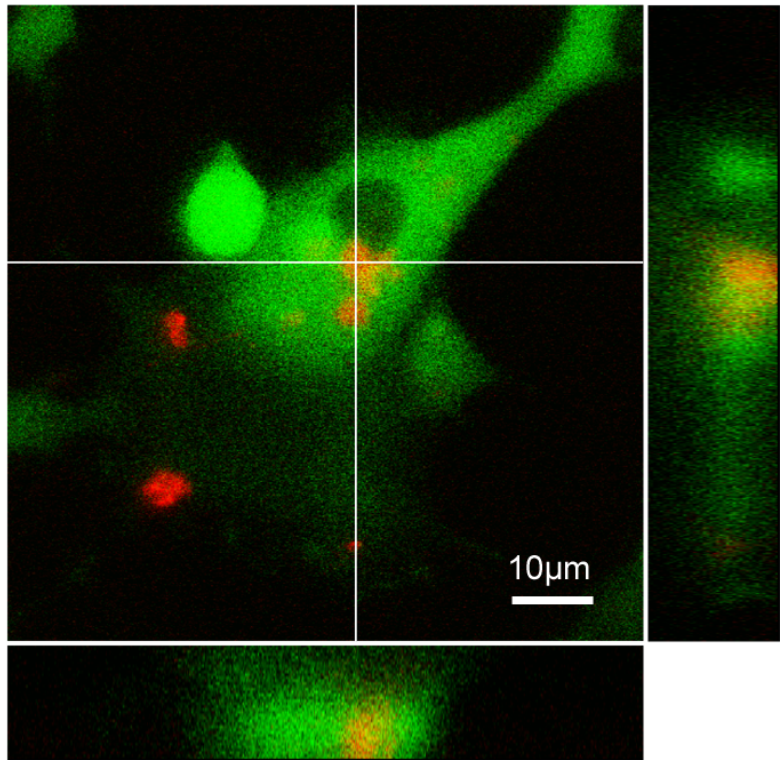


transferrin - cell targeting protein
 rhodamine tag (red emission)
 fraction of $-\text{NH}_2 \rightarrow -\text{SH}$

- plasmid**
- GFP reporter gene (green emission)
 - Luciferase reporter gene

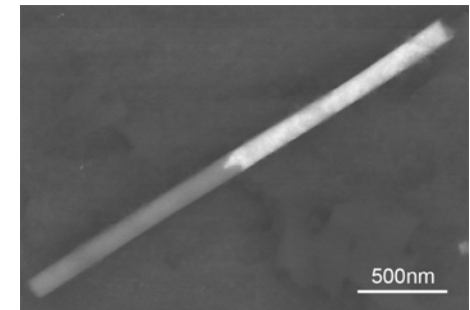
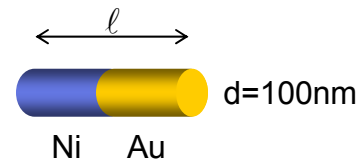
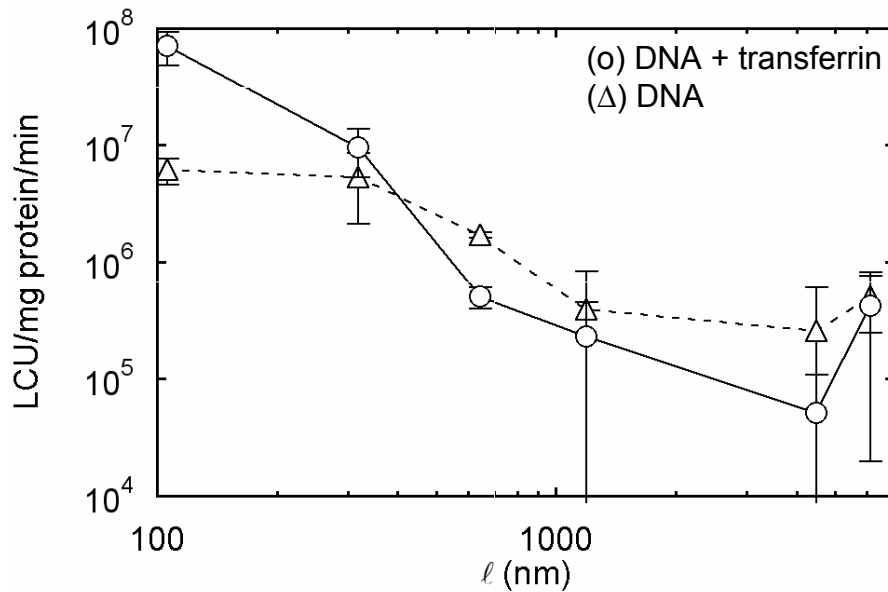
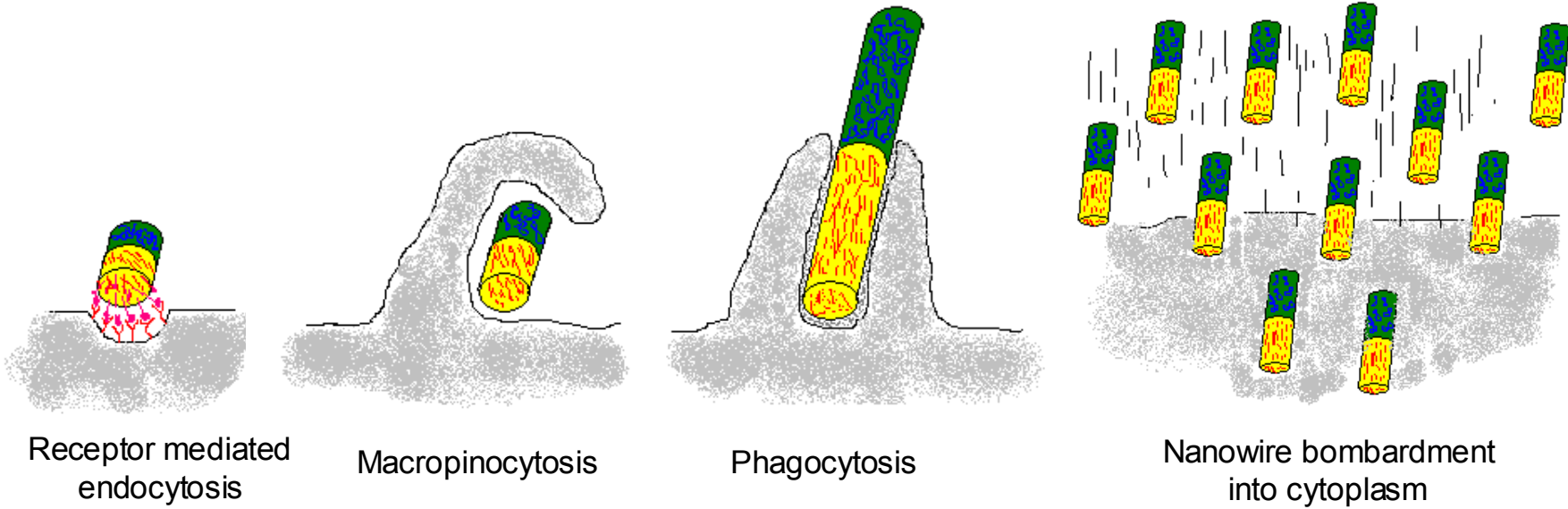
Nature Materials **2**, 668 - 671 (2003).
Nanotechnology **16**, 484-487 (2005).

Confocal Microscopy



- stacked confocal microscope images of live HEK293 cells
 - red: rhodamine (633nm) - transferrin (Au segments)
 - green: GFP (543nm) fluorescent protein expressed during transfection
- orthogonal sections: confirm that the nanorods are inside the cells.

Dependence on Nanoparticle Size



S. D. Conner and S. L. Schmid, *Nature*, 422, 37-44 (2003).
 M. Marsh and H. T. McMahon, *Science*, 285, 215-220 (1999).

Summary

The ability to control shape, composition, morphology, and surface chemistry is important in exploiting multifunctional nanoparticles and building blocks

Important properties include:

shape anisotropy

interlayer coupling

spatial multifunctionality

controlled morphology