Nanomaterials Inspiration from Ancient Materials

Maryland Hall - *Home of Materials Science at JHU*

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U.S. Department of Energy, BES/HFI under grant DE-FG02-05ER15727

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

NSF

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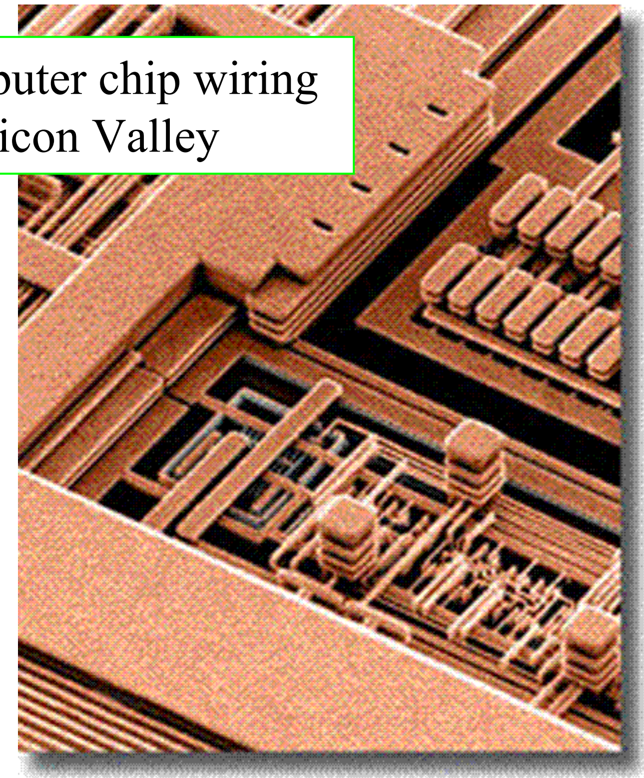
Theme

Steelmaking in Bethlehem, PA

Computer chip wiring in Silicon Valley



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

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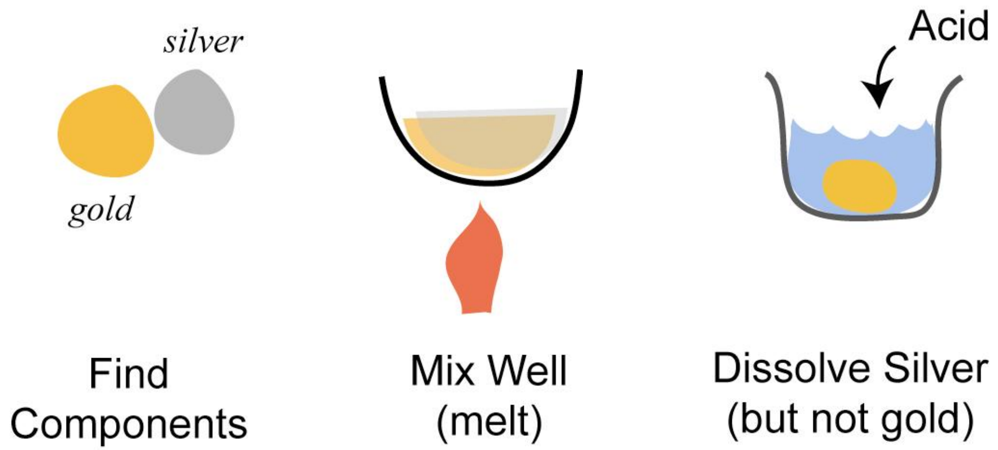
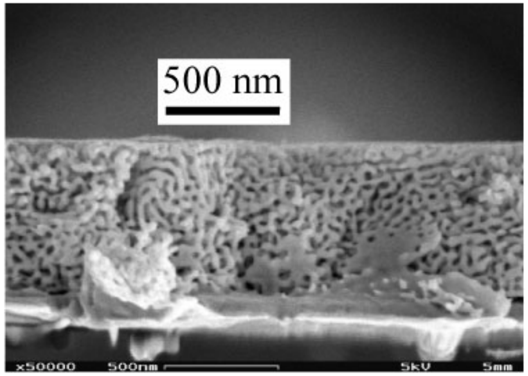
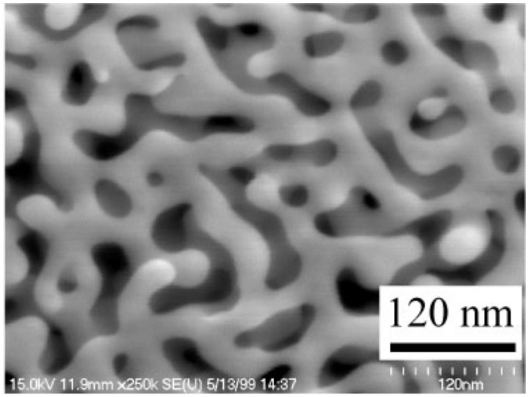
Dealloying: A Method to Create Nanoporosity



Nanoporosity:
Ligament widths and spacings are of order 10 nm



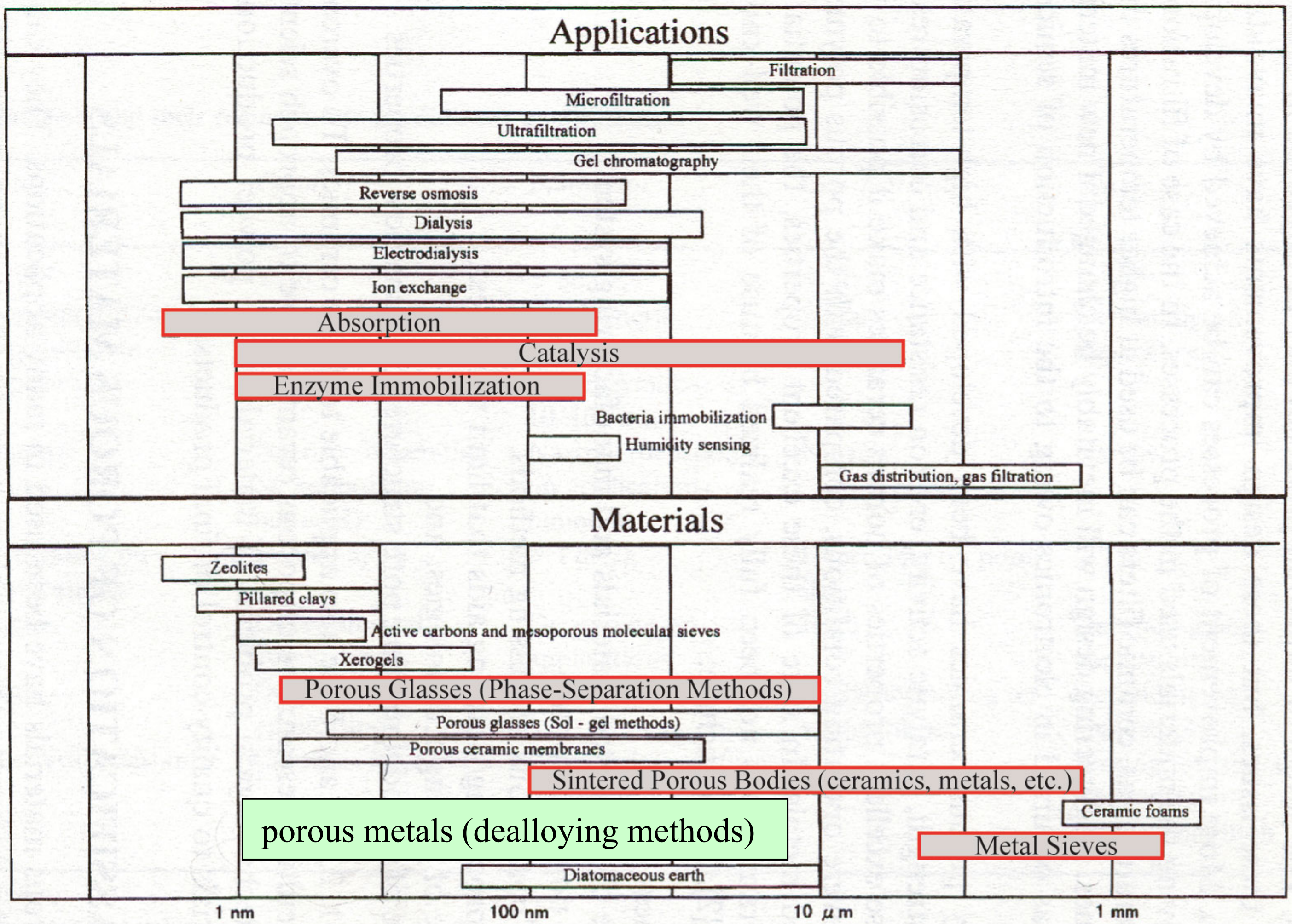


“Nanoporous Gold” (NPG)

History of NPG

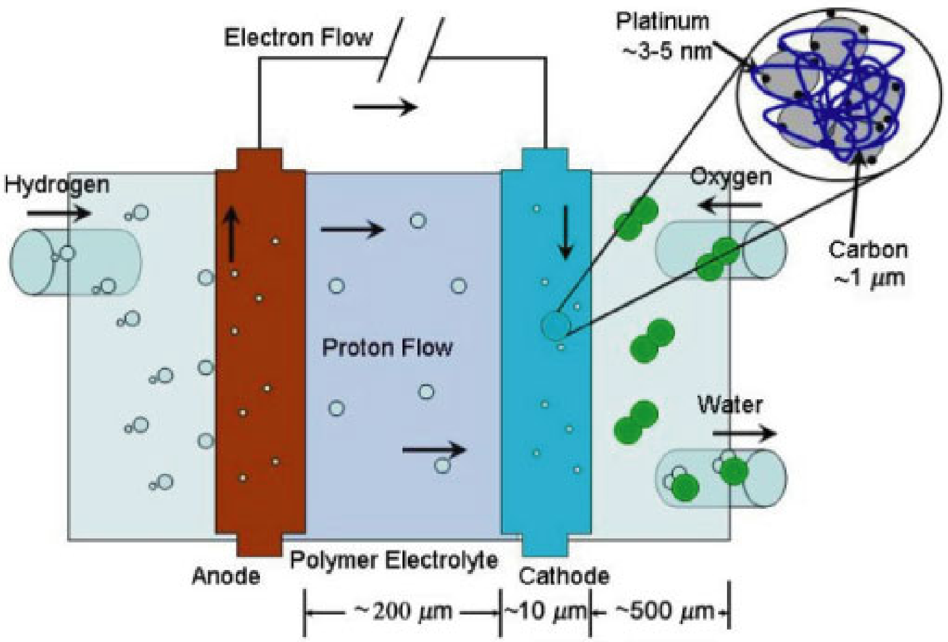
- "Depletion gilding" was known to the ancient Incas
- Origin of current interest: ***Corrosion***
  - Dealloying is seen during corrosion of many technologically important brasses, stainless steels, and Cu-Al alloys

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

http://www.eere.energy.gov/hydrogenandfuelcells/fuelcells/types.html#pem

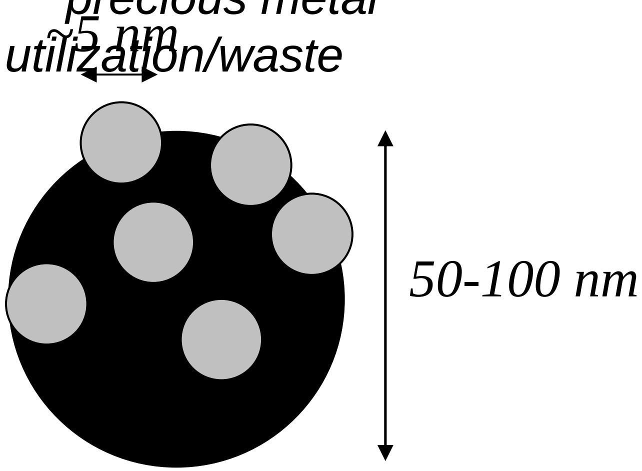
Materials Design of Precious Metal Fuel Cell Catalysts

Nanoparticles

- High surface area/volume
- Immobilization by physisorption

    thermal stability issues
- No intrinsic in-plane conductivity
- Processing leads to “thick” (>10 microns) catalyst layers

    precious metal utilization/waste

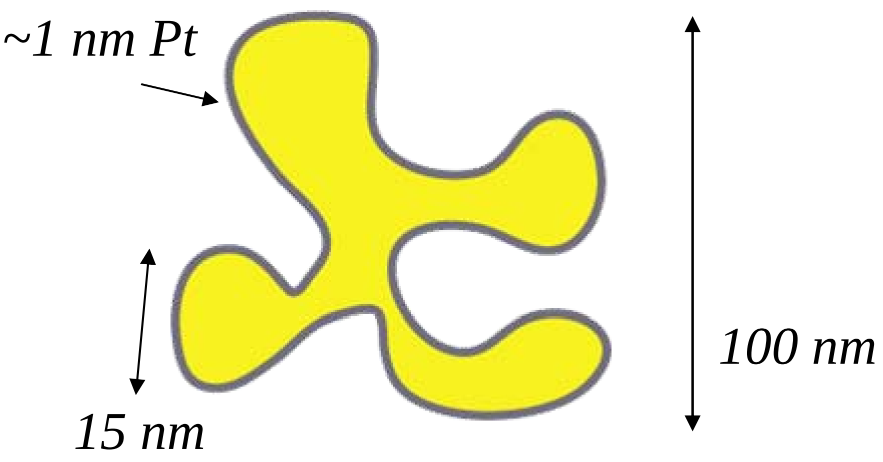


Mesoporous Metal Membranes

- High surface area/volume
- Immobilization by epitaxy

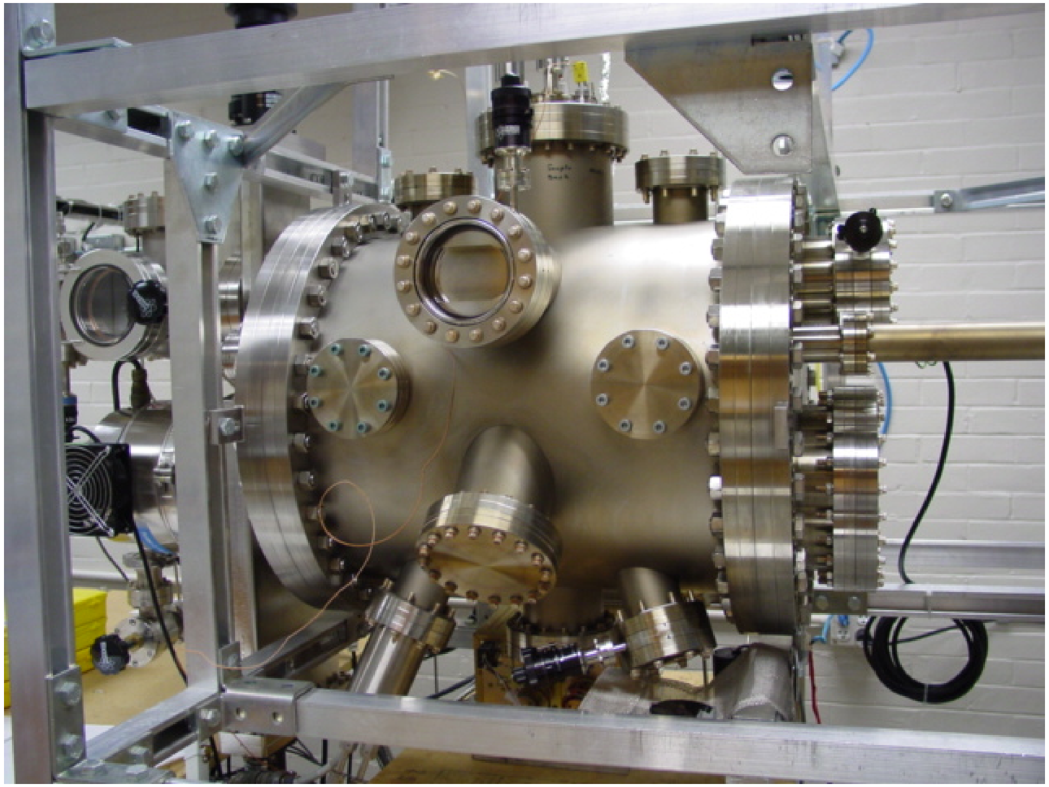
    thermal stability issues good?
- High intrinsic in-plane conductivity

    proton conduction still a problem
- Processing leads to thin (100 nm) catalyst layers



Making NPG Films: Thin-Film Fabrication

Minuses → expense

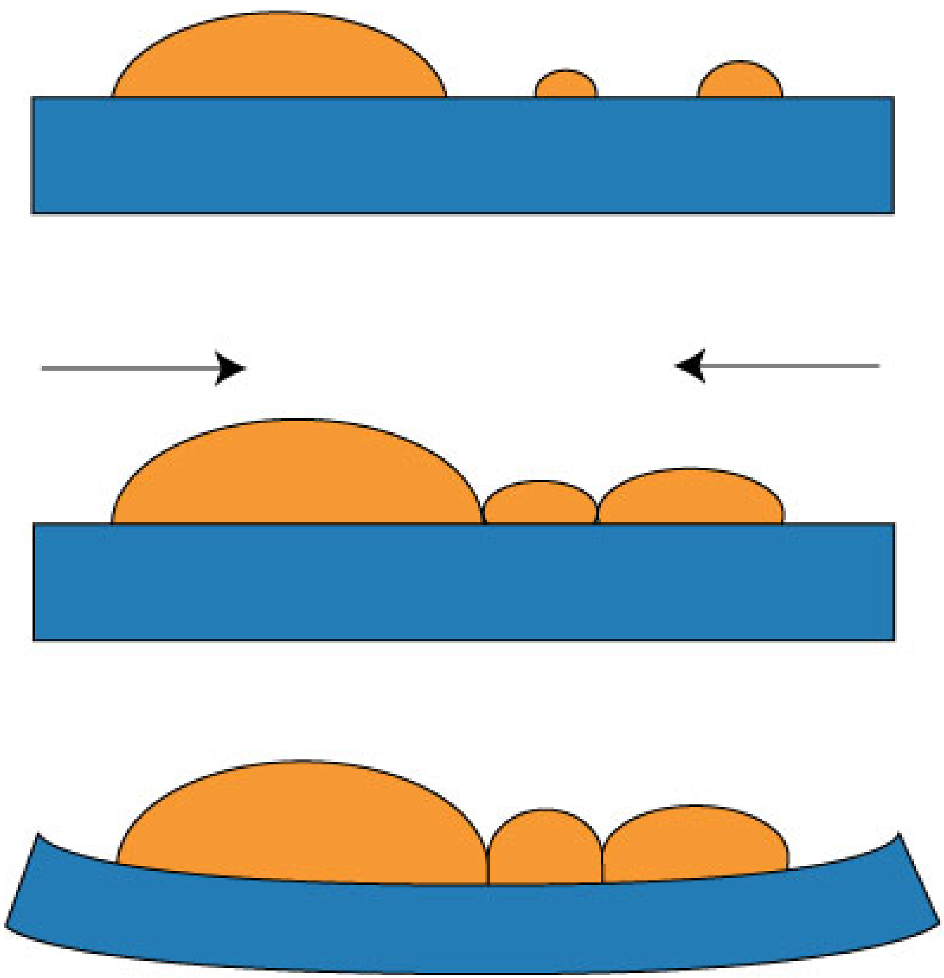


- Requires ultra-high vacuum
- Much of the material that is evaporated is wasted
- Time consuming

Plusses

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

Stress Evolution in Volmer-Weber Growth

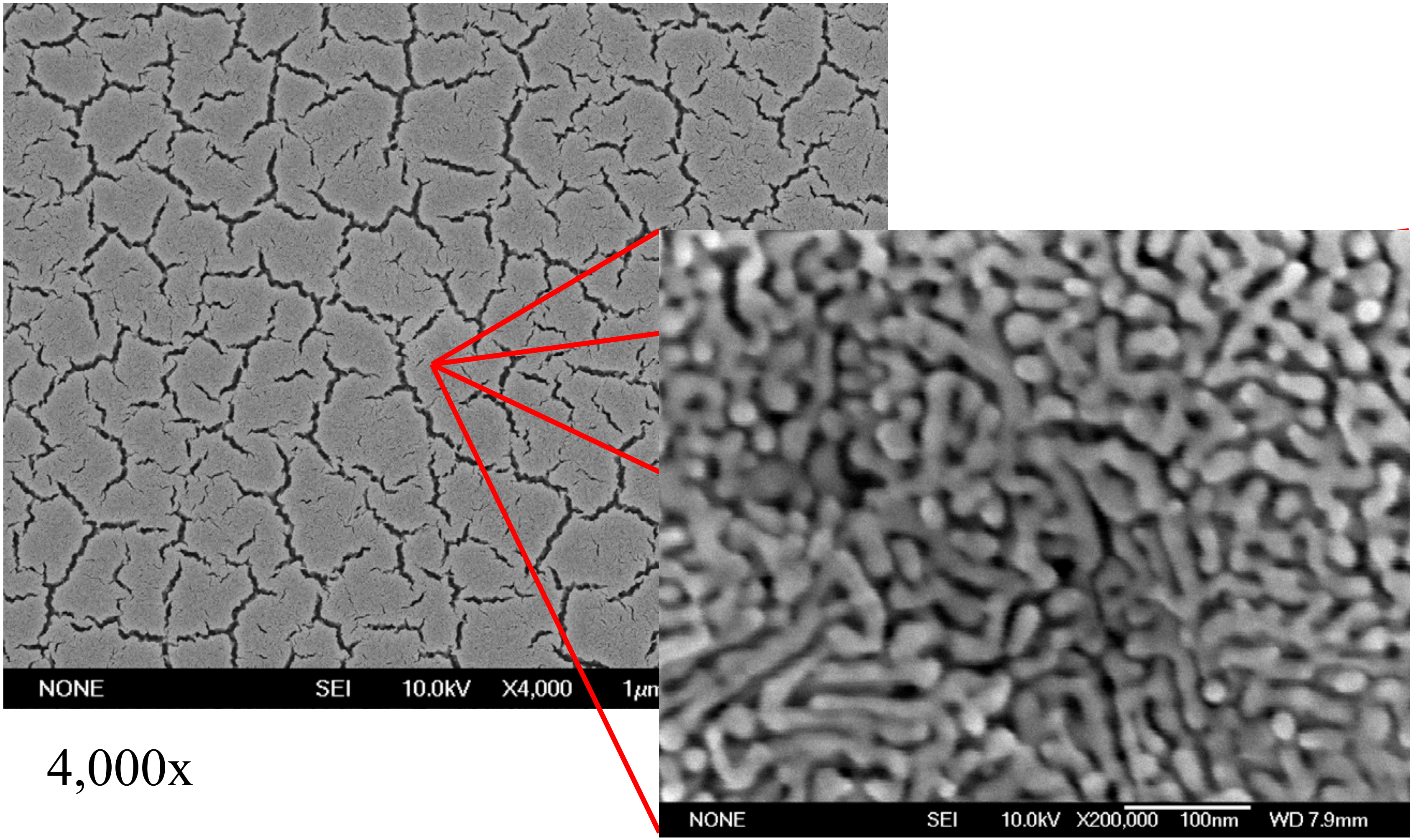


islanding

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

substrate: compression
film: tension

Cracking in Dealloyed Silver Gold Thin Films



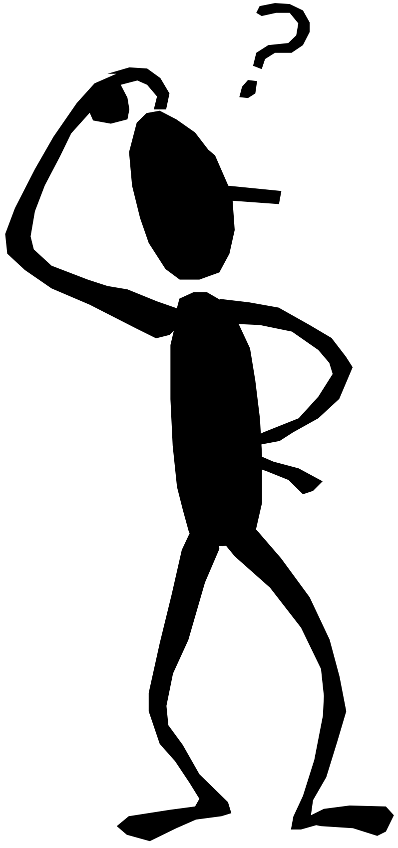
4,000x

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

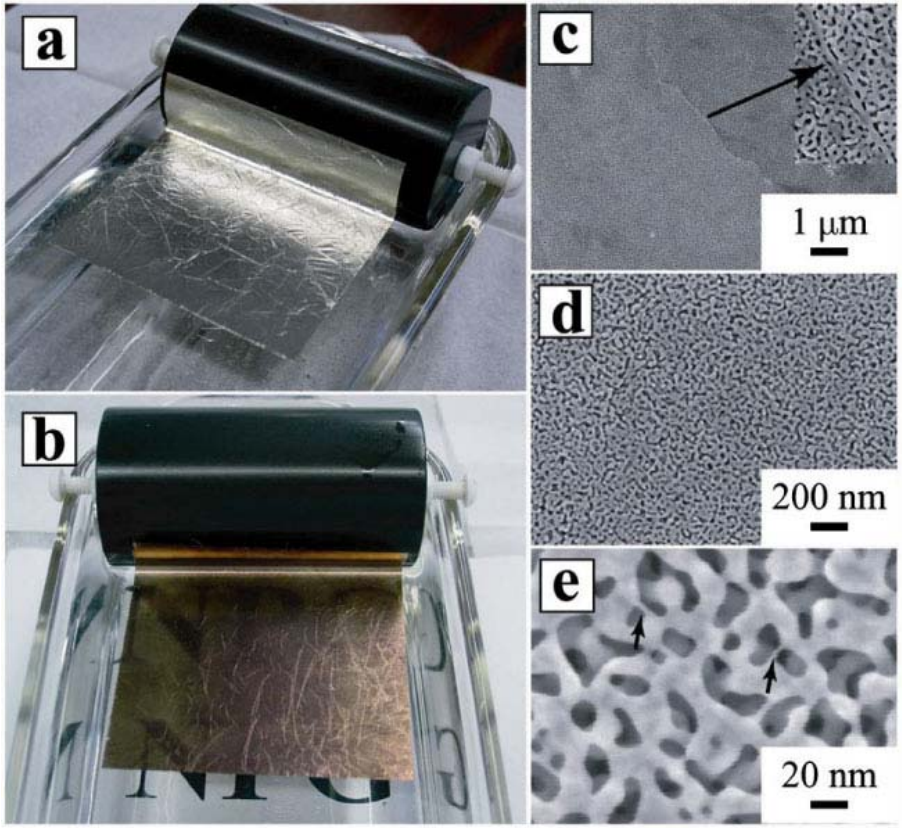
Gold Leaf: The Historical Perspective

Progress of Materials and Materials Processing

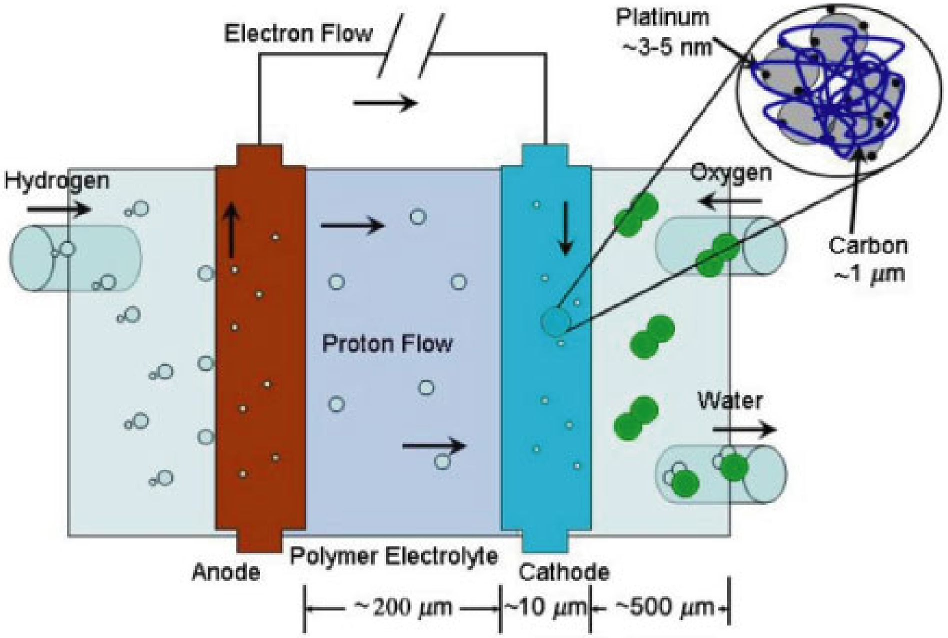
1. Stone bashing (> 10,000 years)
2. Fire (> 10,000 years)
3. Melting metal (> 5,000 years)
4. Gold Leaf (bashing + fire + metal) (> 4,000 years)

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

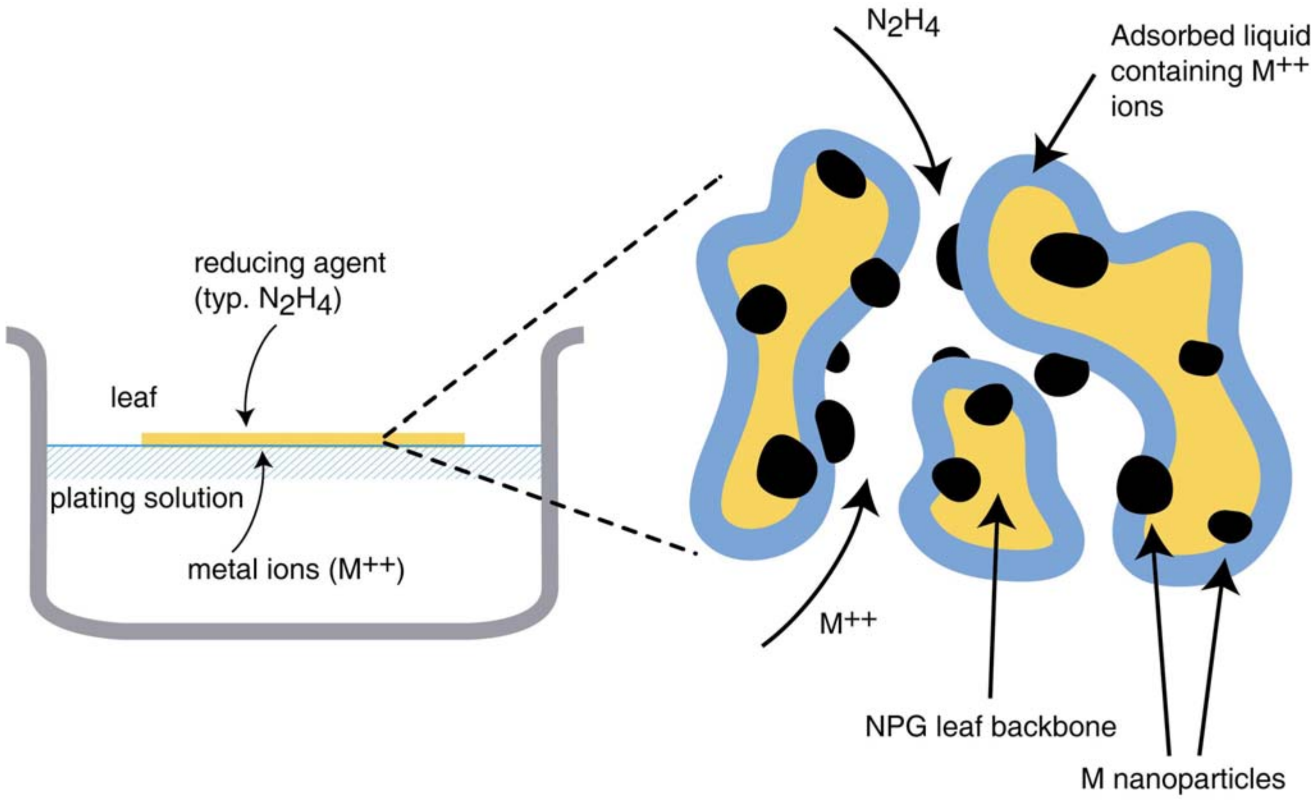
(a) be conductive
(b) be porous
(c) contain a very high surface area of catalyst both in electrical contact (to the current load), and in ionic contact (to the polymer electrolyte) → thin is good

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

http://www.eere.energy.gov/hydrogenandfuelcells/fuelcells/types.html#pem

Electroless Plating of NPG Leaf to form Nanocomposites

Take advantage of the fact that leaf floats on water.

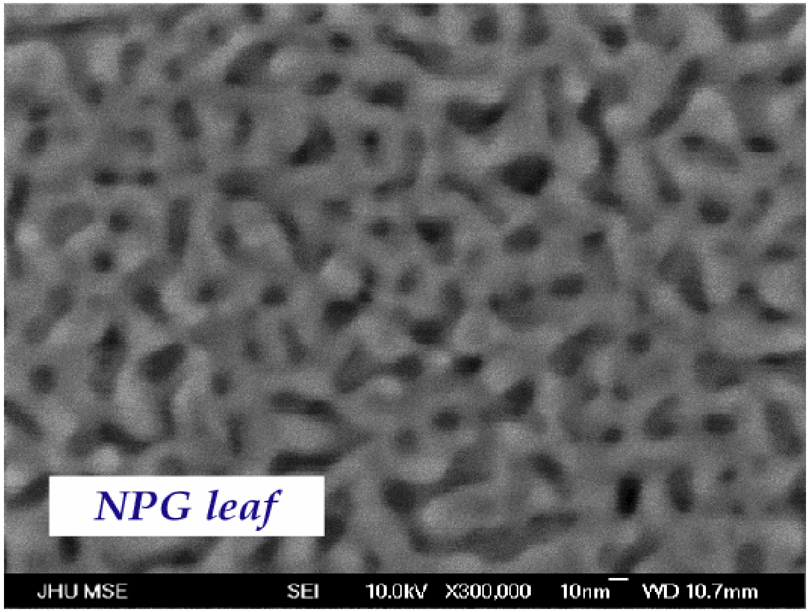


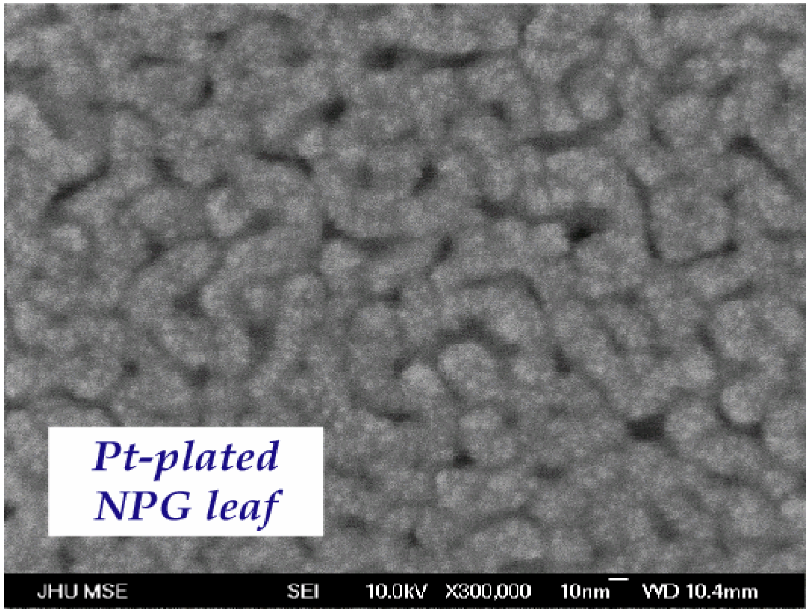
Plating should be confined to within the pores, and should self-limit

-- an advantage over typical electroless or electrochemical plating

To date, we have plated **Pt**, Ni, Co, and **Ag**

Pt-Plated Nanoporous Gold Leaf

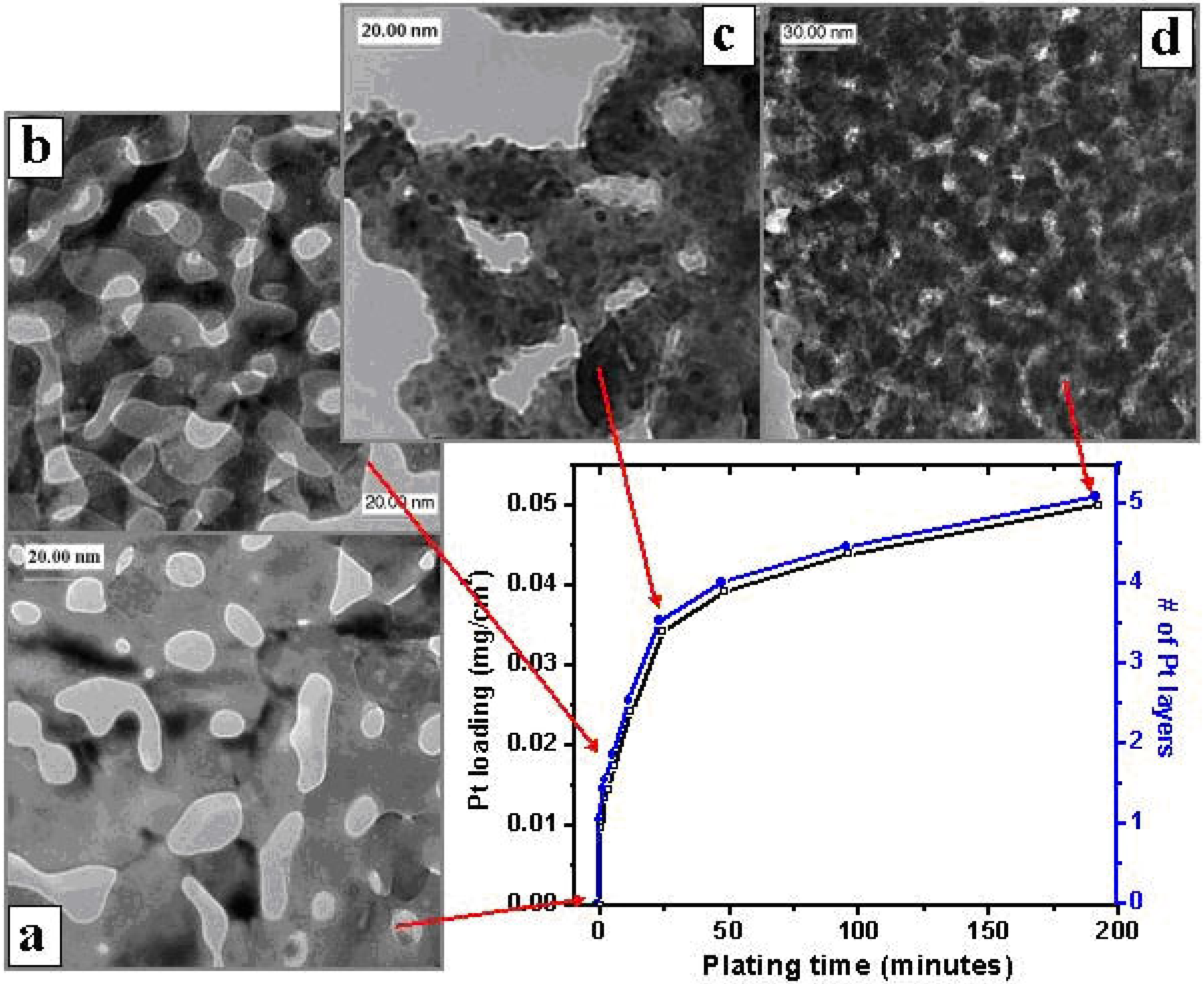




In SEM, coatings look nanoparticulate, dense, and conformal.

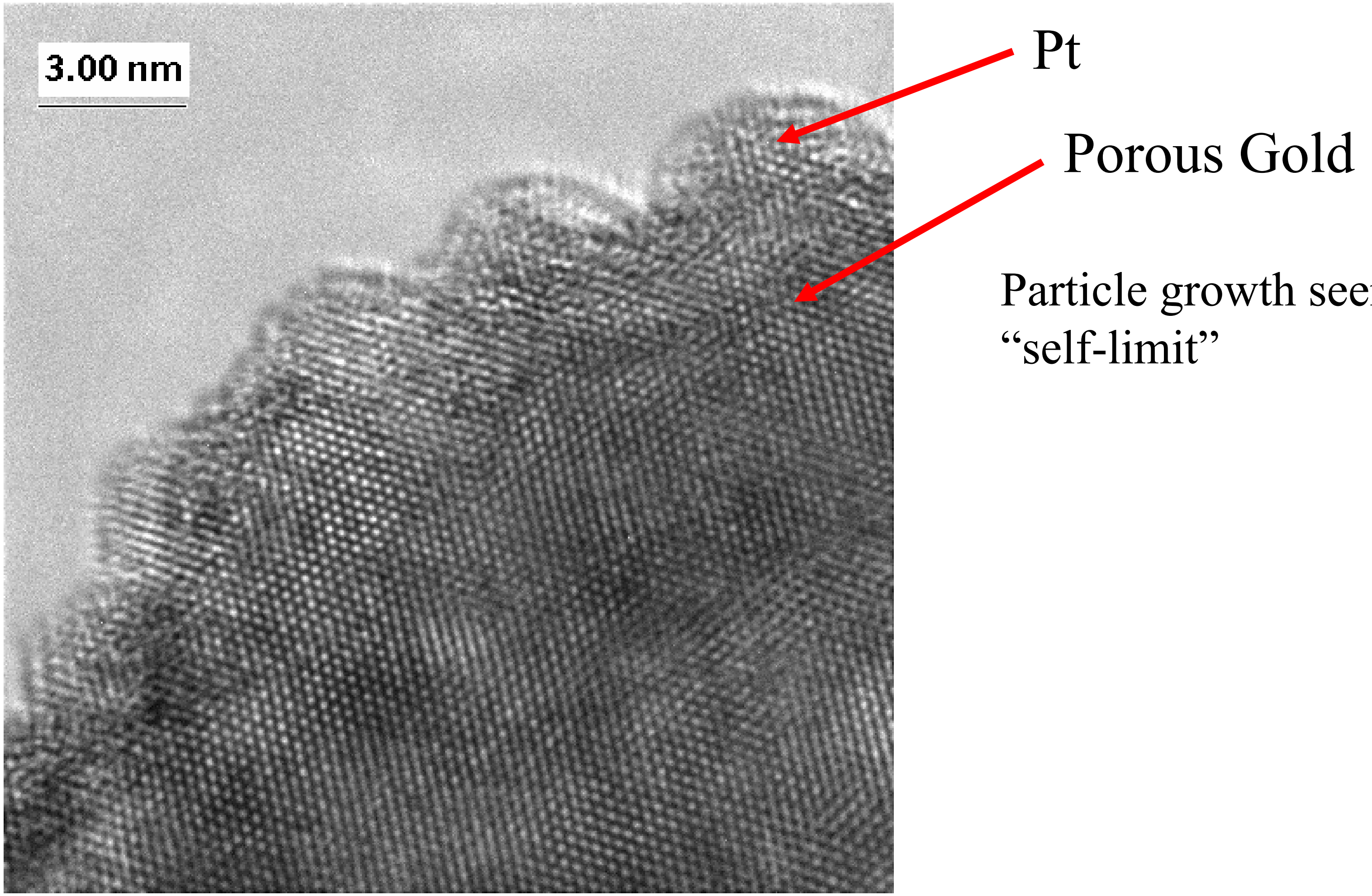
Y. Ding, M. Chen, J. Erlebacher, "Metallic Mesoporous Nanocomposite Materials for Electrocatalysis," *J. Amer. Chem. Soc.*, **126** (2004), 6876.

Growth Kinetics of Pt-NPGL



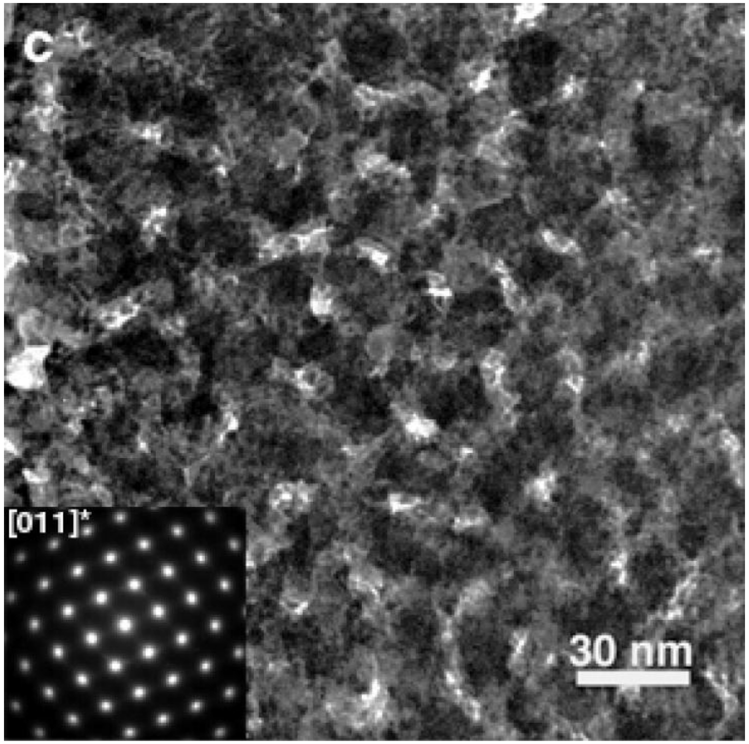
Deposition may be controlled to within 0.01 mg/cm² (1 ml) using only room temperature benchtop chemistry. Deposition stops prior to filling of pores. (?!)

HRTEM of Pt-NPGL

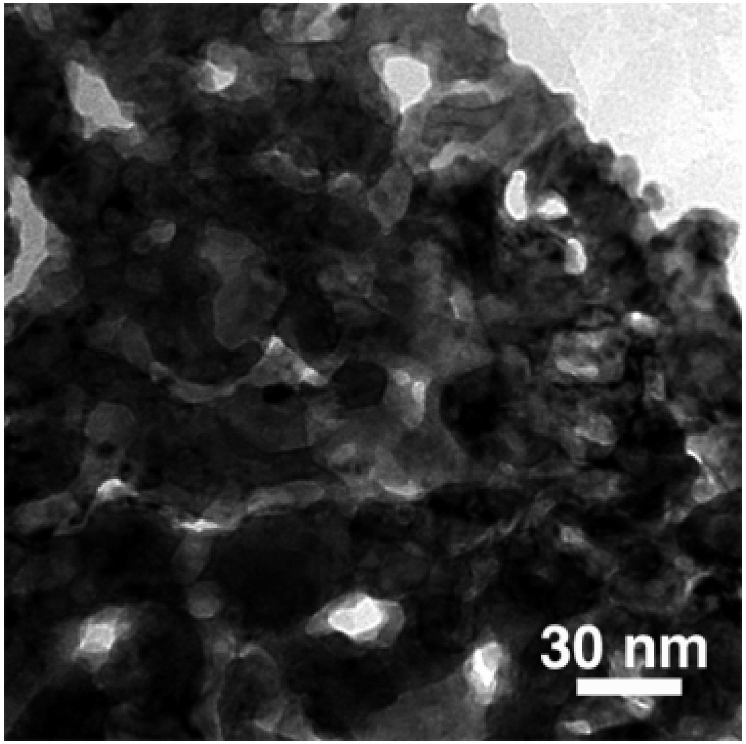


Particle growth seems to "self-limit"

HRTEM of Pt-NPG



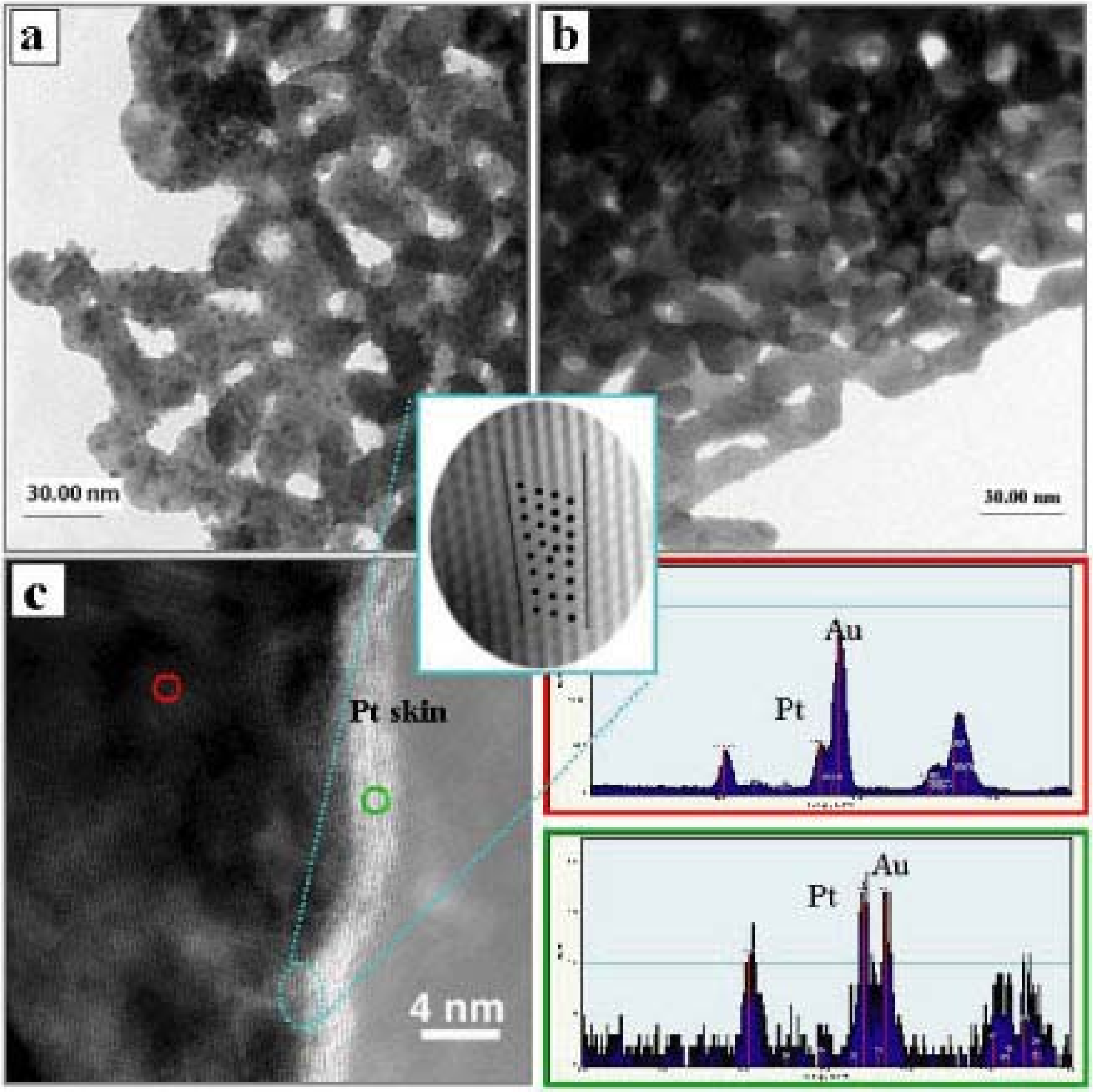
before



after

Where did all the islands go?

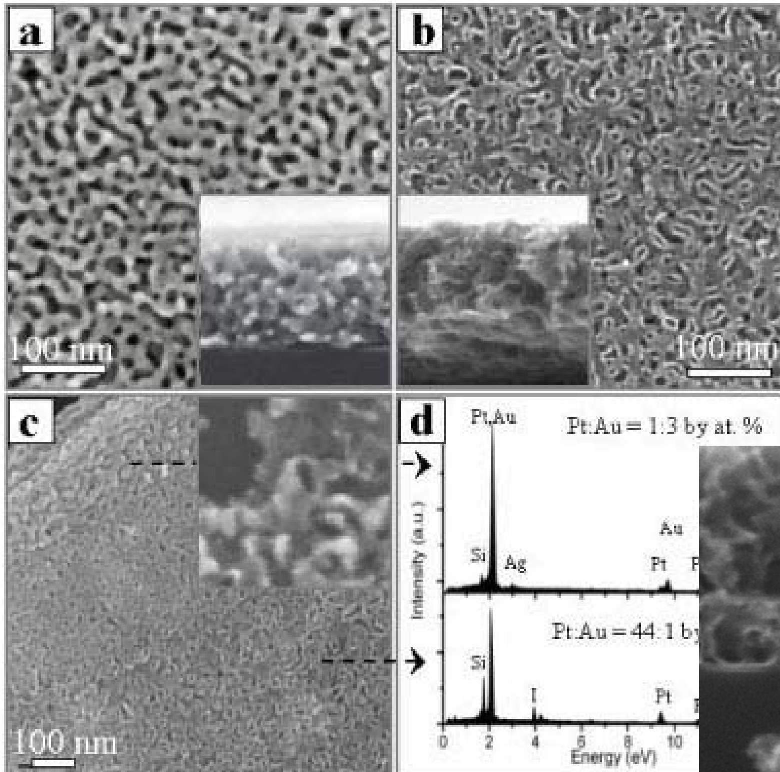
Formation of an Epitaxial Pt skin on NPG

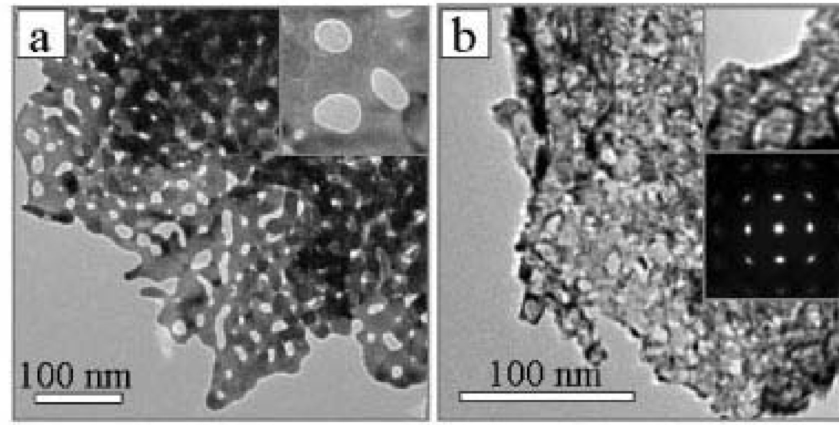


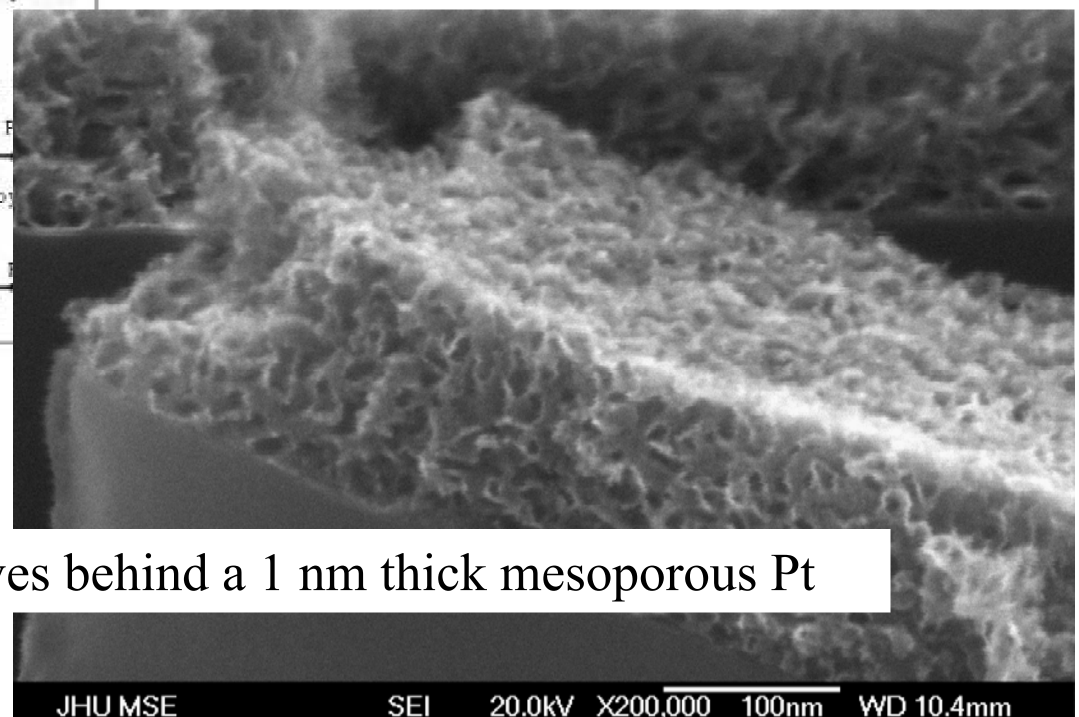
Dislocations at the Pt/Au interface relieve stress more efficiently than islanding.

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

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- Jia Sun
- Jennifer Bai

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- Stuart Kirschner (Physics)
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- Alan Becknell (JHUAPL)
- P. Gopalan (Wisconsin)

National Science Foundation
WHERE DISCOVERIES BEGIN

APL The Johns Hopkins University
Applied Physics Laboratory

Kenan Fund

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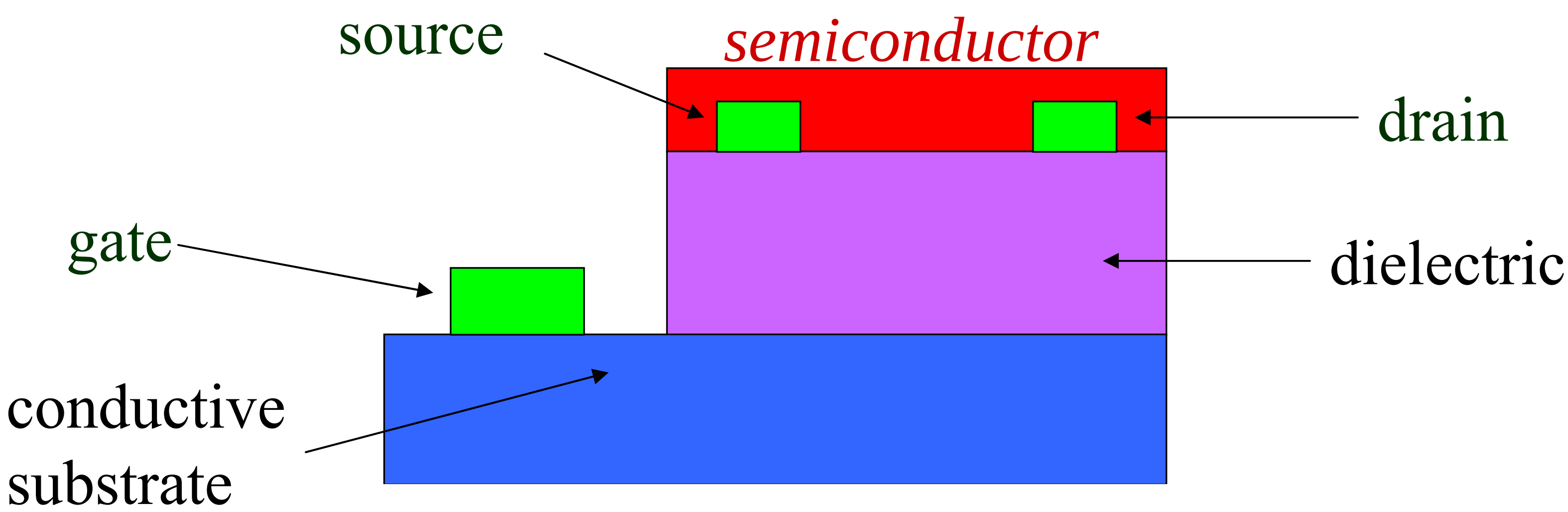
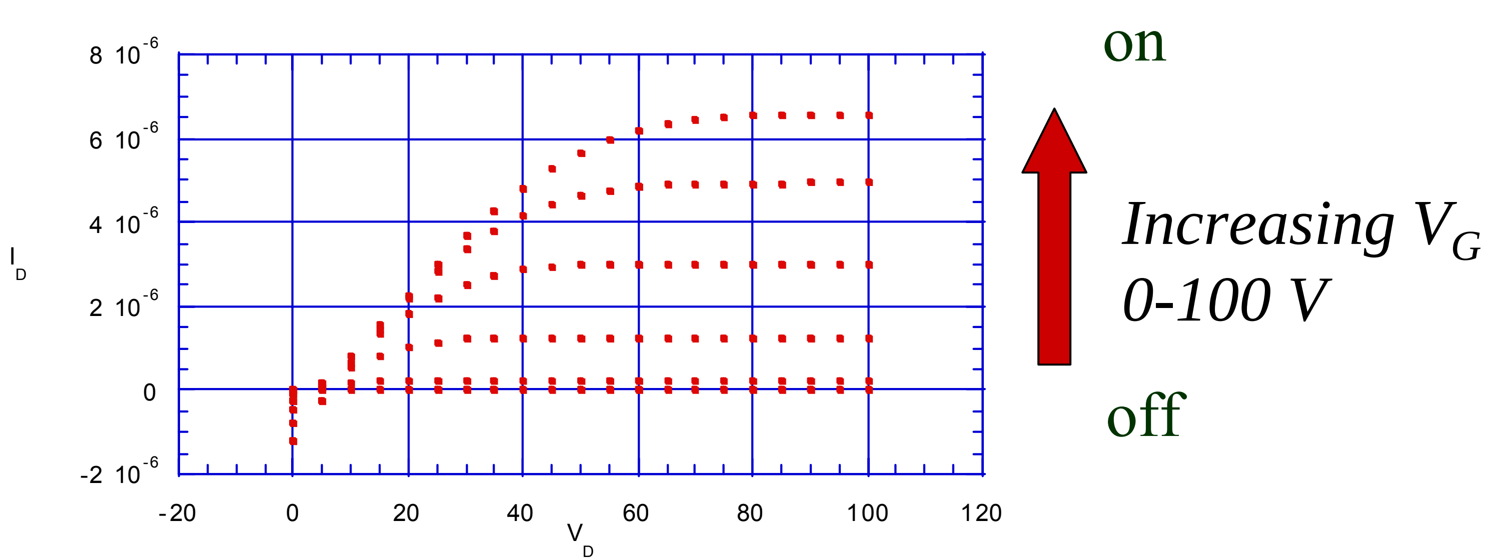
Outline

- 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

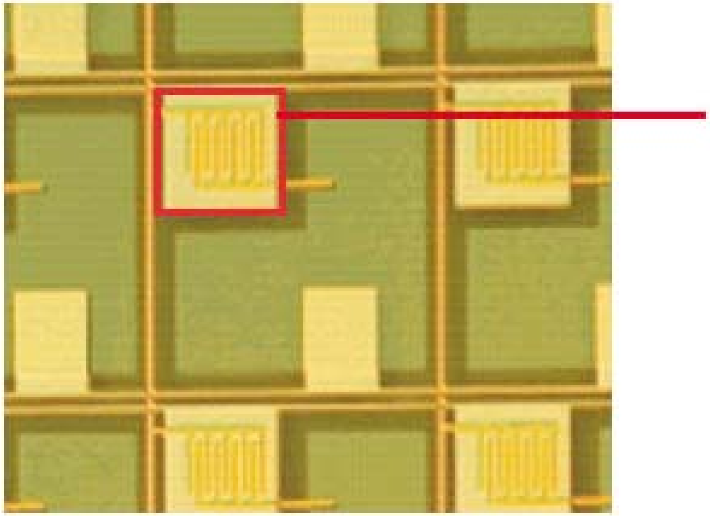

source
semiconductor
drain
gate
dielectric
conductive
substrate


8 10-6
6 10-6
4 10-6
2 10-6
0
-2 10-6
I_D
-20
0
20
40
60
80
100
120
V_D
on
Increasing V_G
0-100 V
off

Special Features of Organic FETs

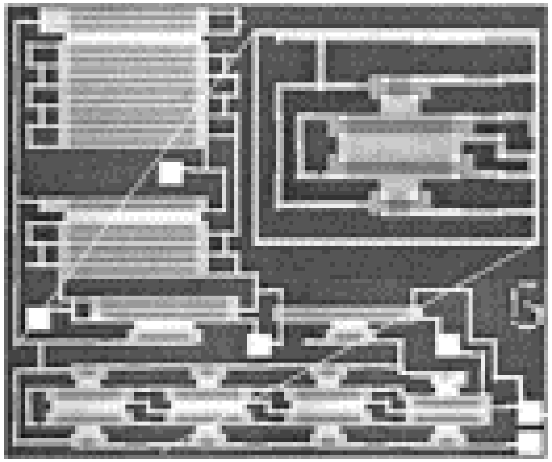
- covalent integration with molecules
- moderate temperature processing
- large area coverage, solution deposition
- mechanical and thermal compatibility with plastic substrates
- rational control of polarity and threshold voltage using organic substituents

Applications (flexibility and low cost)



flexible display Philips (2004)

display pixel from SONY (2004)



RFID circuit from 3M (2003)

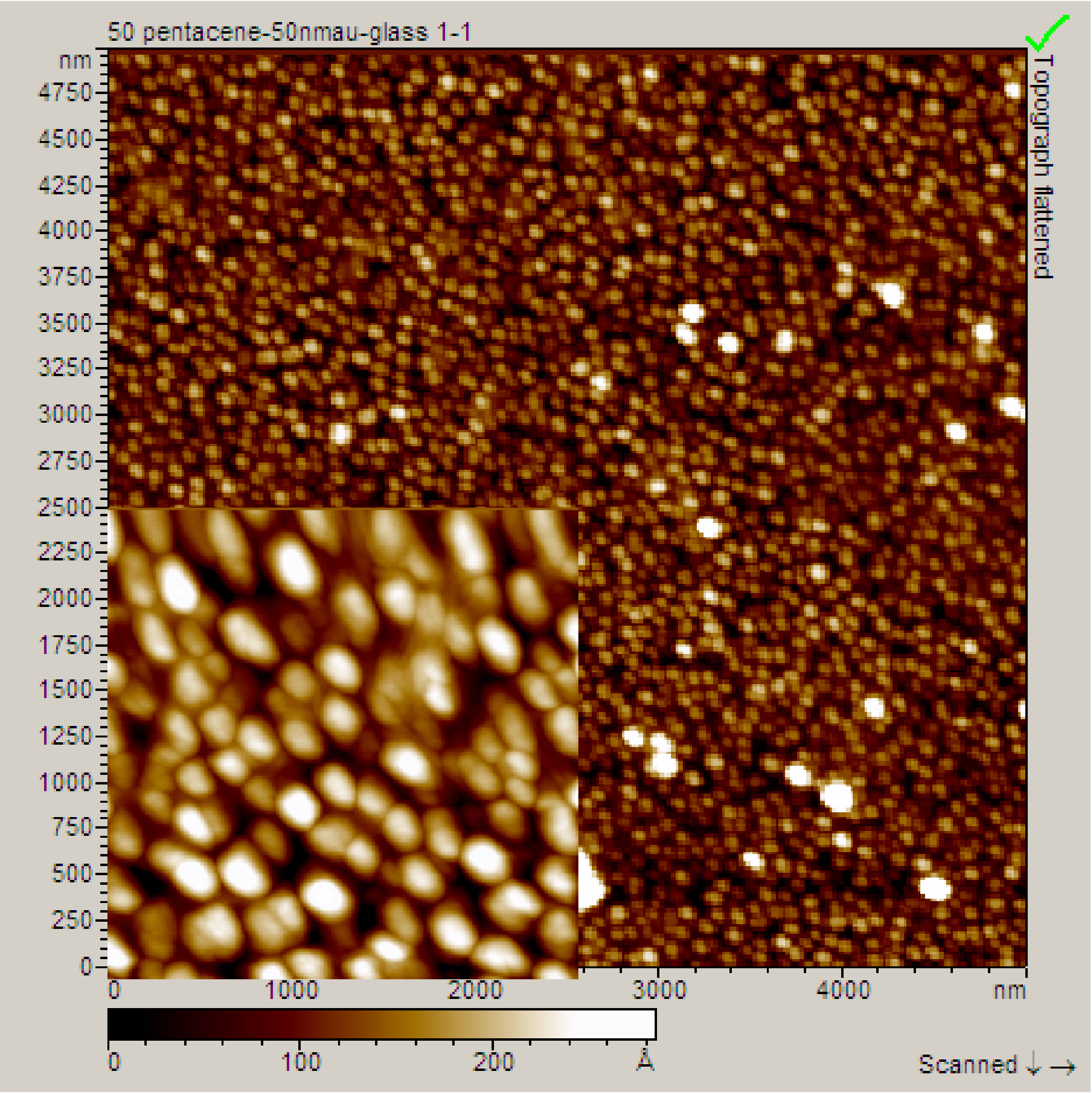
Roll-printed transponder Circuits (PolyIC)

Sensitive Skin with Organic Transistors

T. Someya

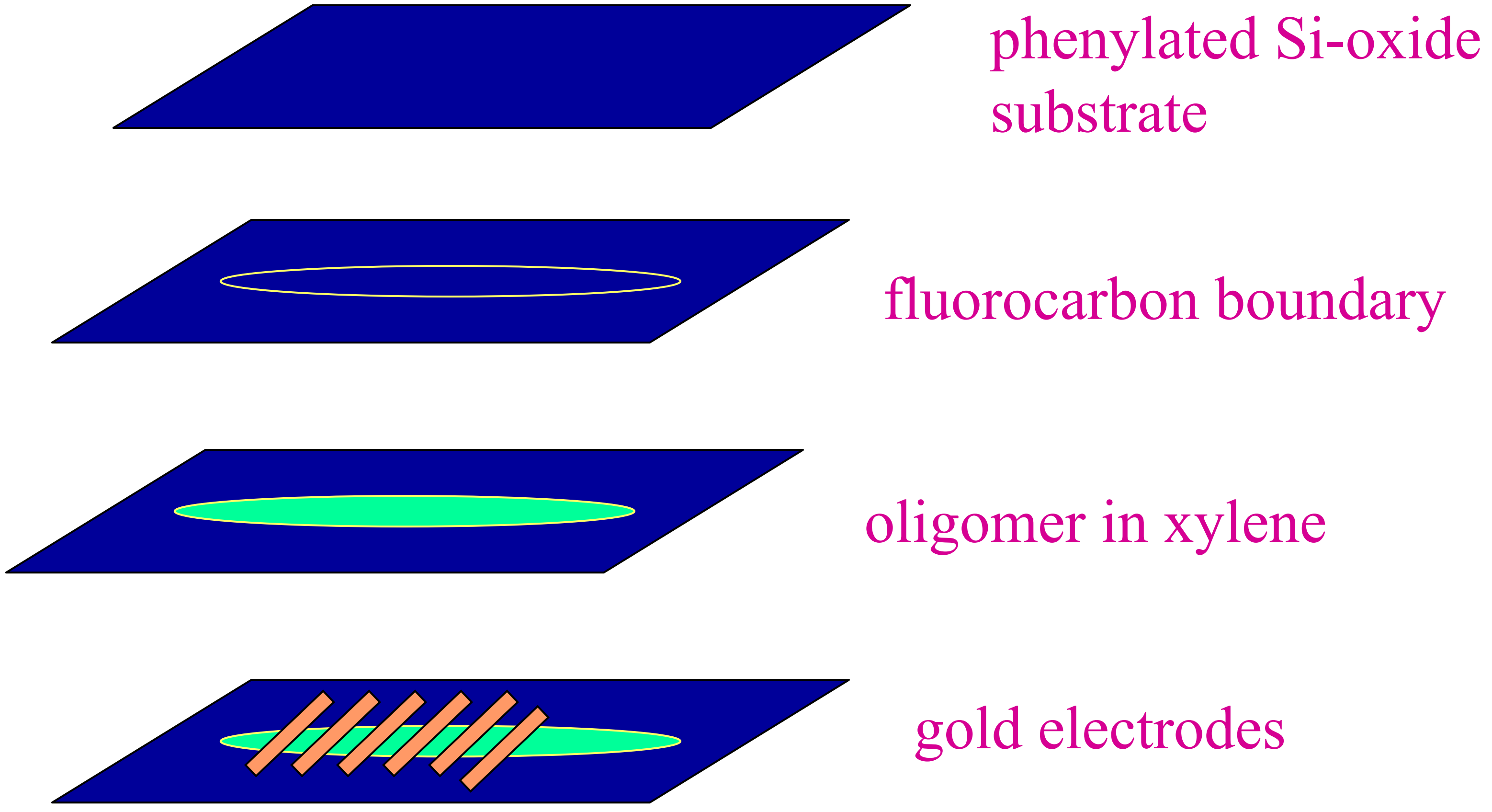

TIME
THE MOST AMAZING
INVENTIONS
OF 2005

AFM image of 50nm pentacene sublimed on 50nm Au

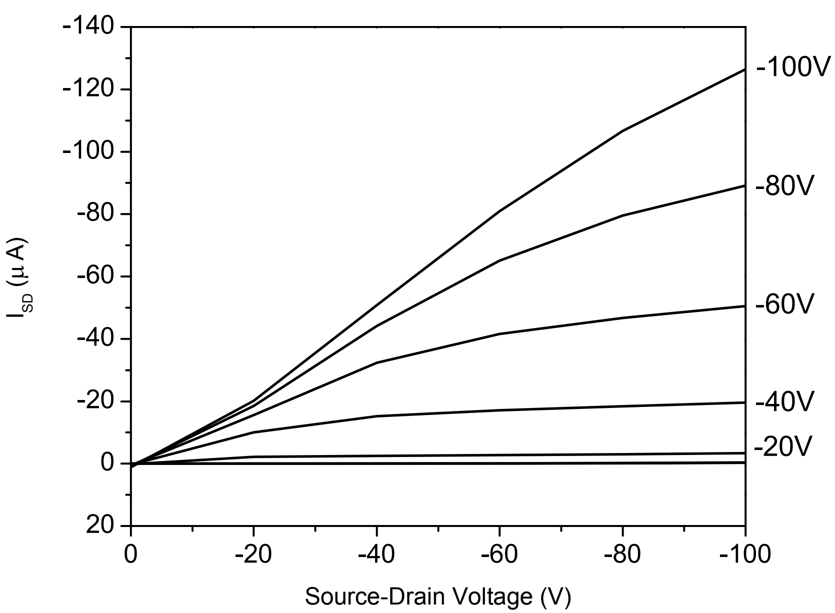


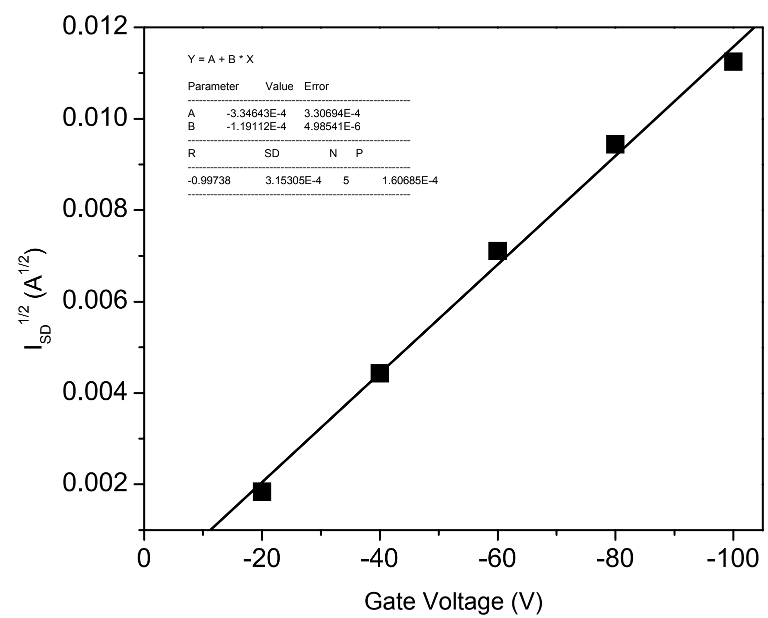
A 5 × 5µm AFM image of 50nm pentacene/50nm Au/glass. Inset is 1 × 1 µm image.

Solution Phase Oligomer Deposition

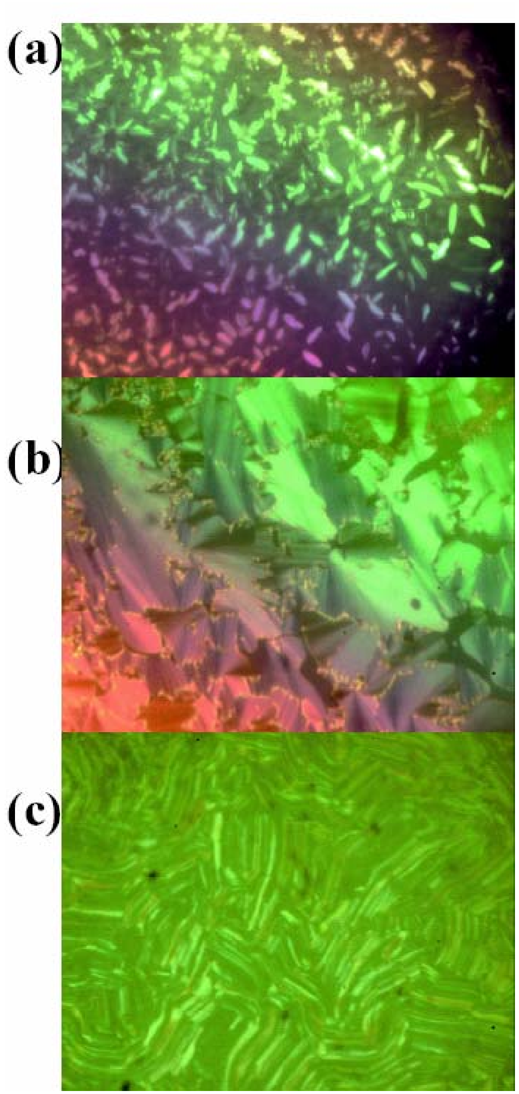


Characteristics of 6PTTP6 Solution-deposited, Small-area FET





6PTTP6 Mesophases

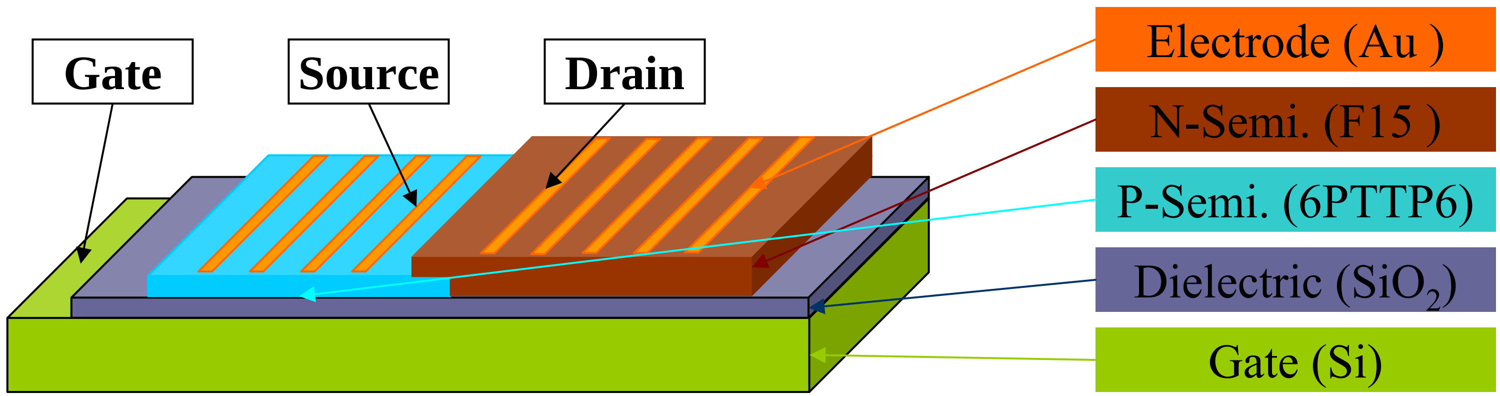


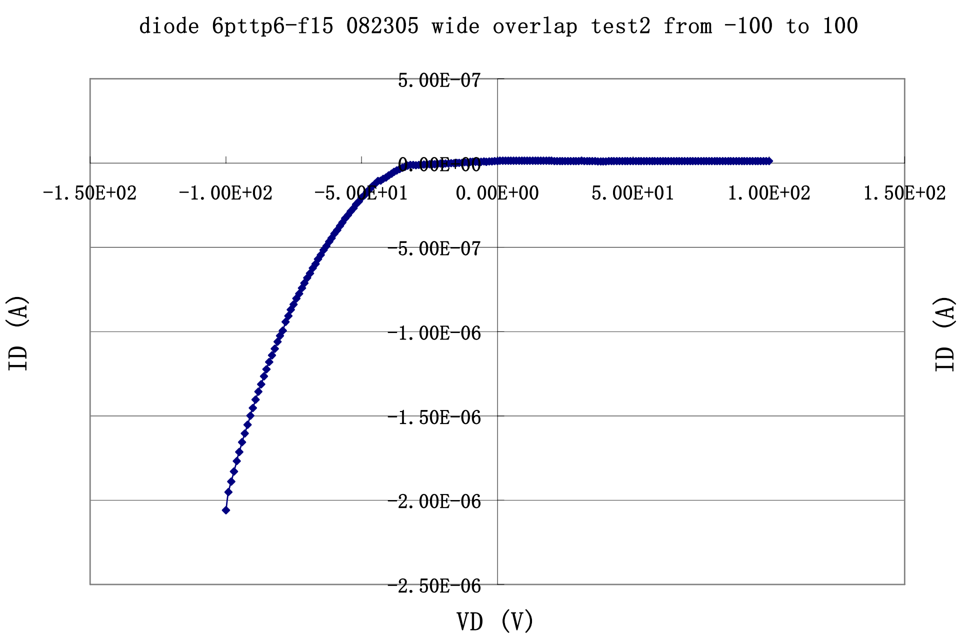
240 degrees

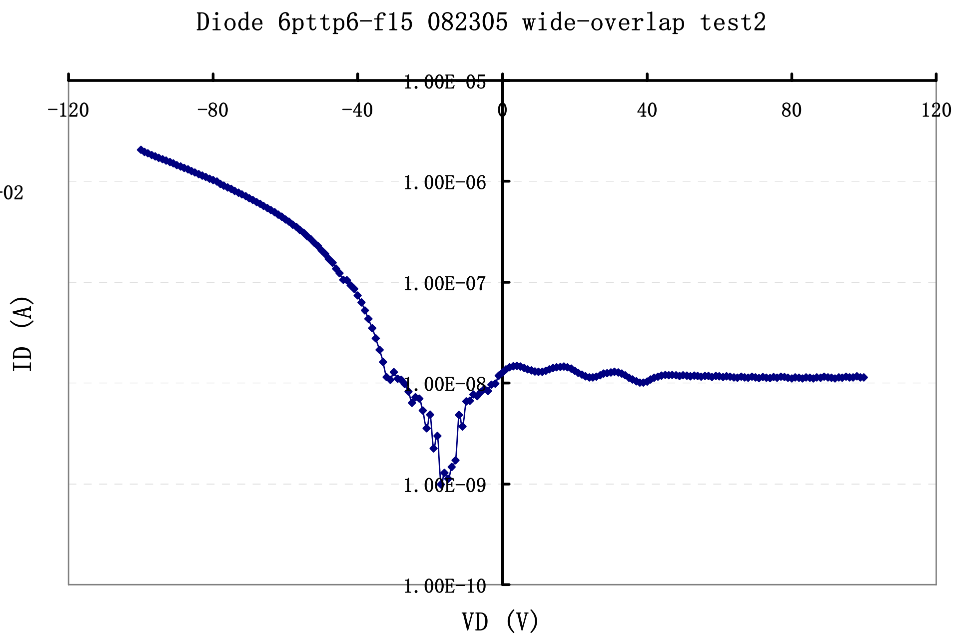
230 degrees, SA

200 degrees, SB/SF

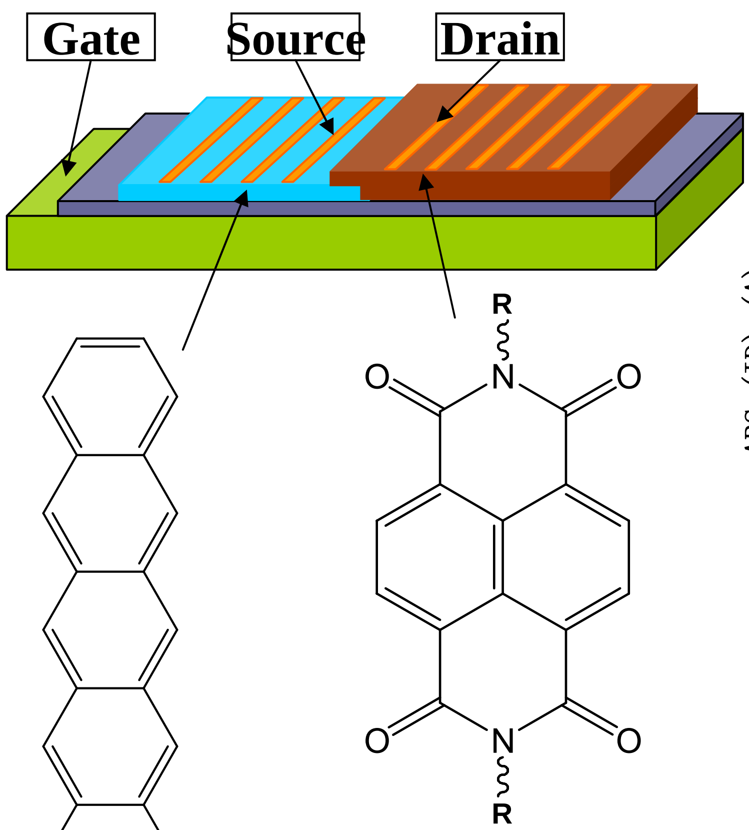
Structure of Organic Diodes with Gate





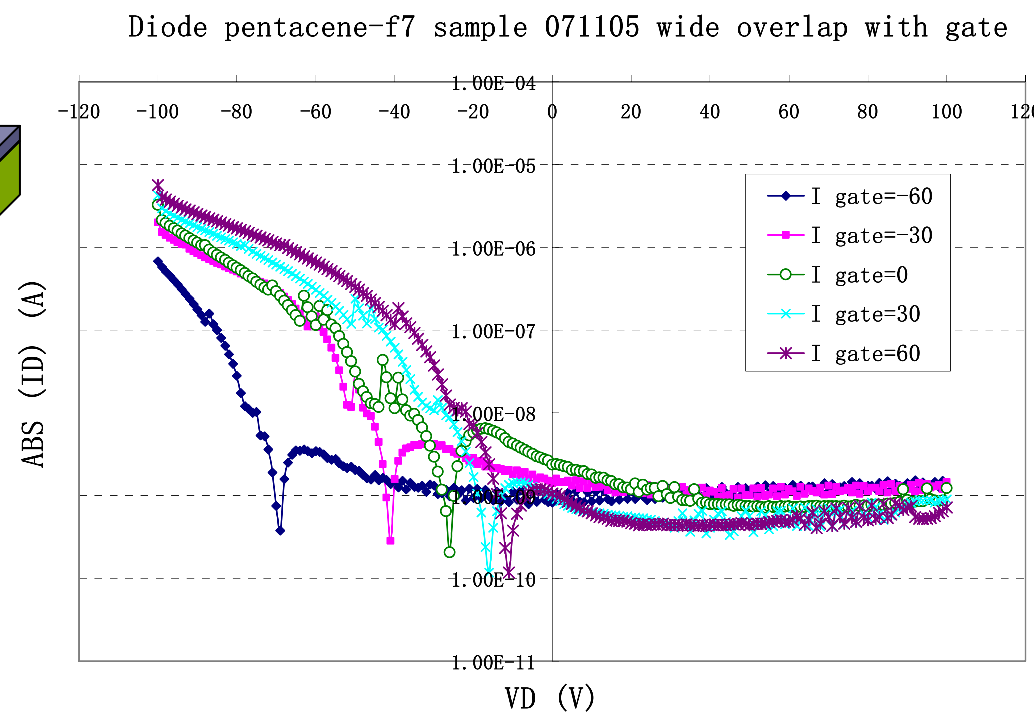


NTCDI-F7 “Lateral” Diode with Pentacene: Gate-dependent, Log Scale

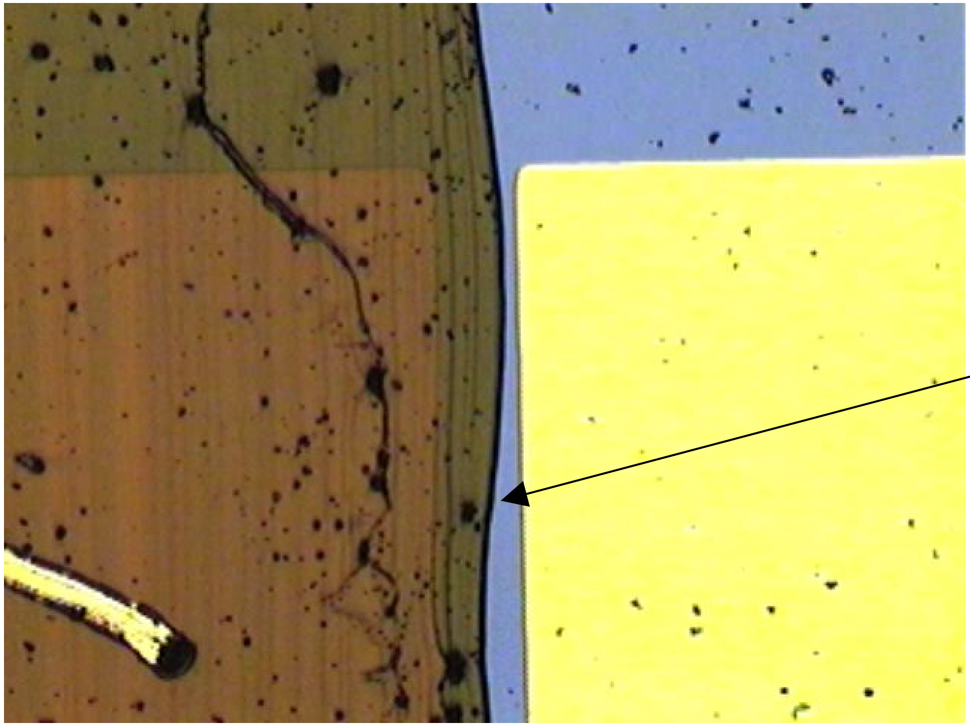


$R = C_4H_2F_7$

NTCDI-F7



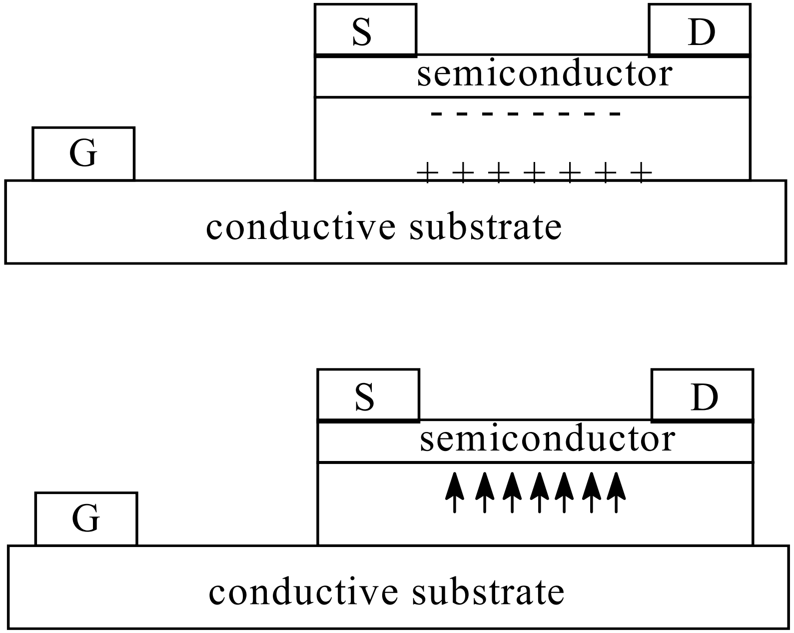
Organic pn Diode Junction

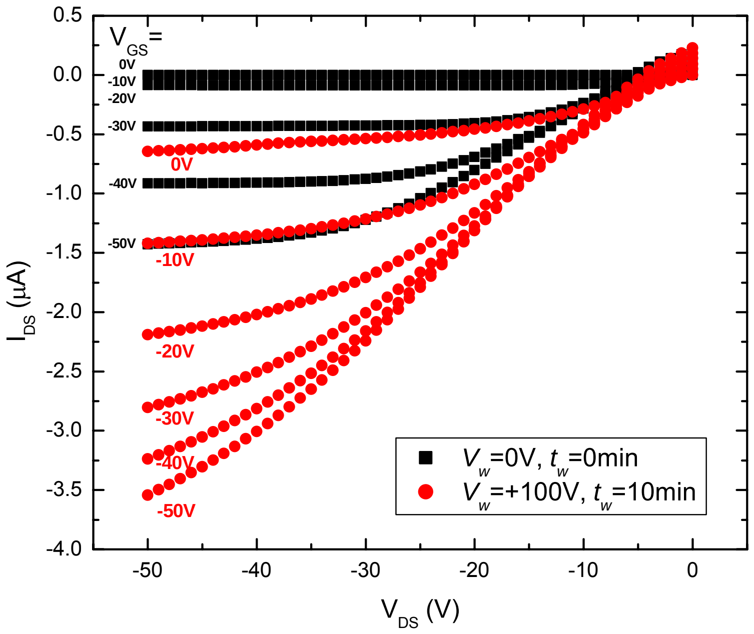


nanoscale junction between semiconductors!

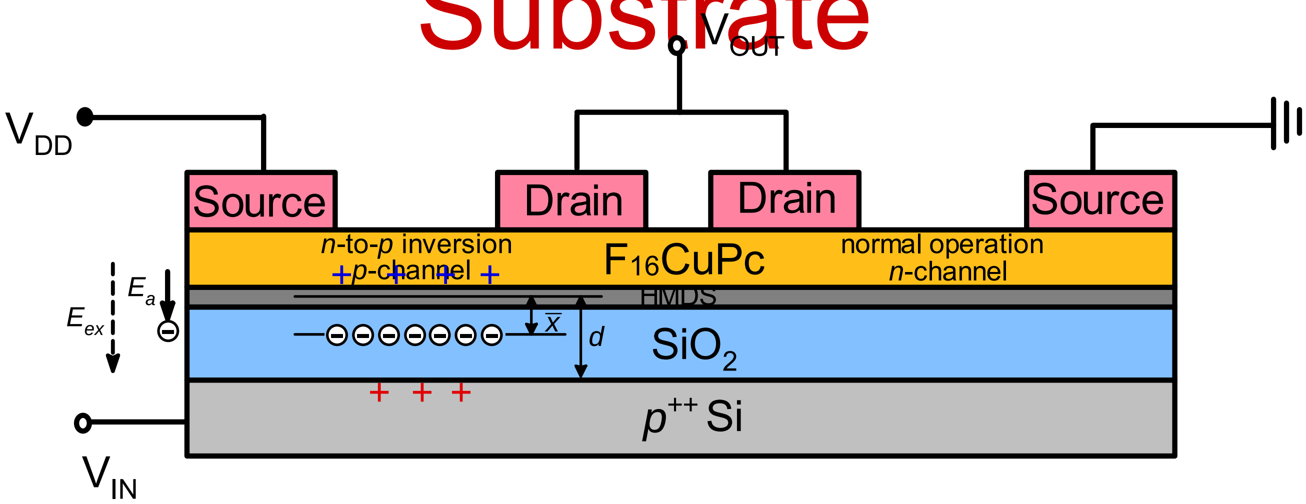
100 micron gap between electrodes

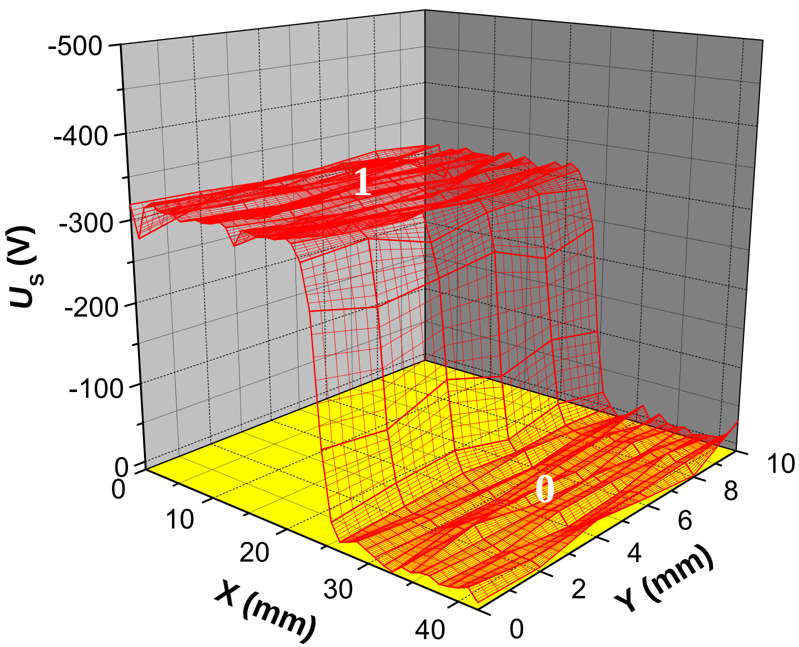
Many Transistors out of One: Putting a Charge into the Device!





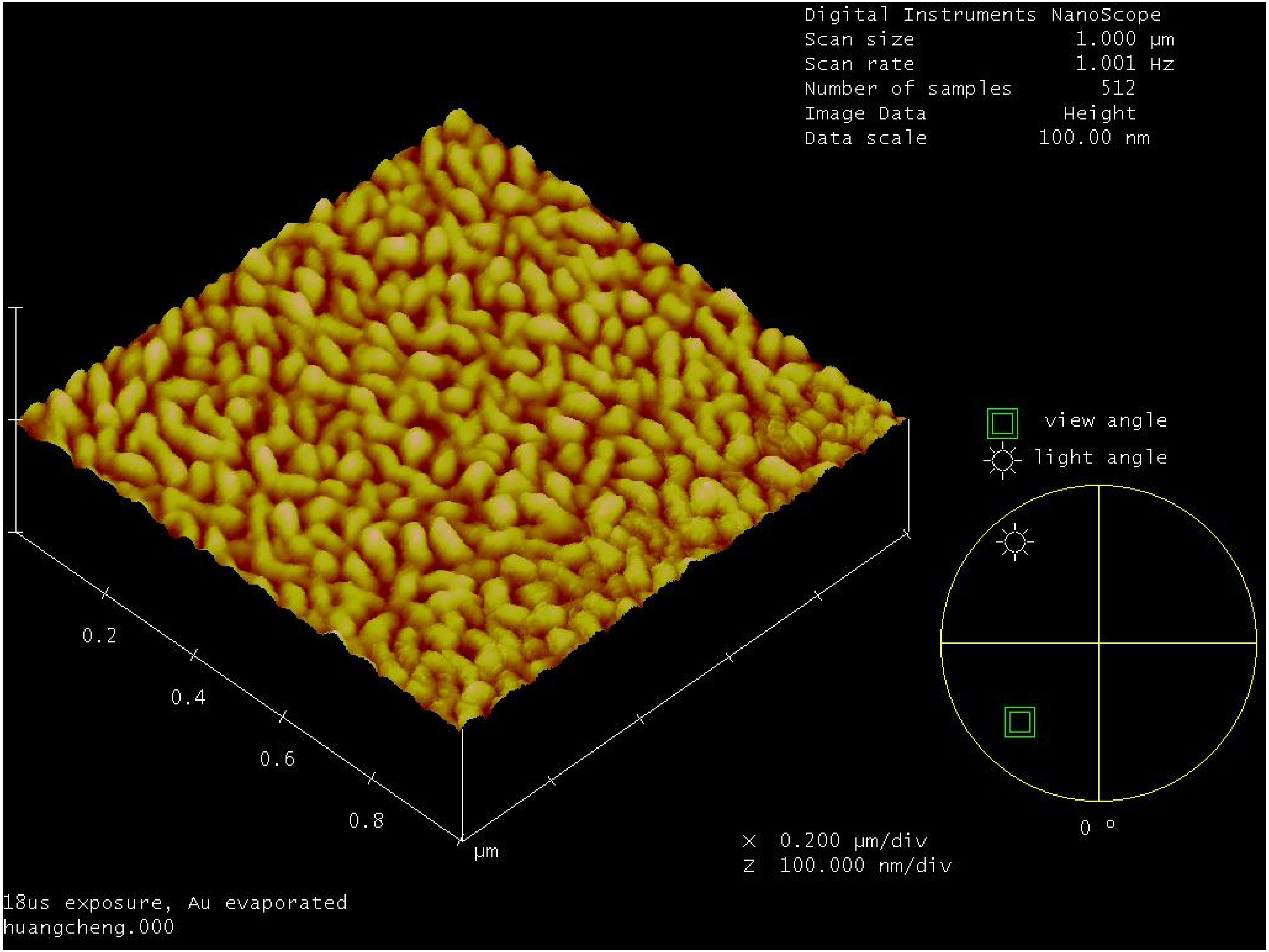
Patterned Charging of OFET Substrate



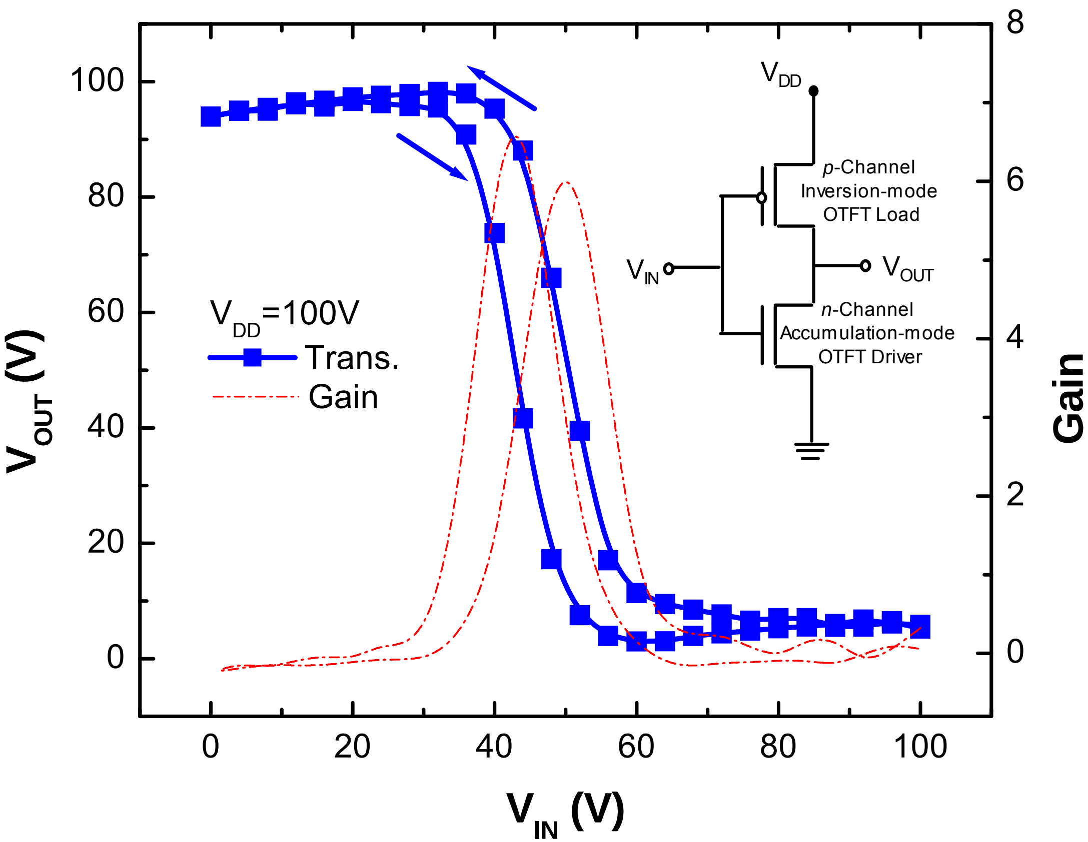


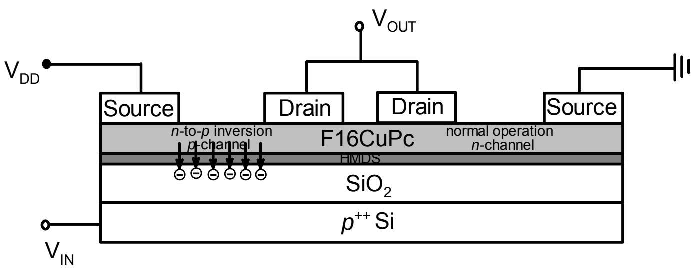
Kelvin probe mapping of surface potential

AFM Topographic Image of 25nm $F_{16}CuPc$ Organic Semiconductor Thin Film



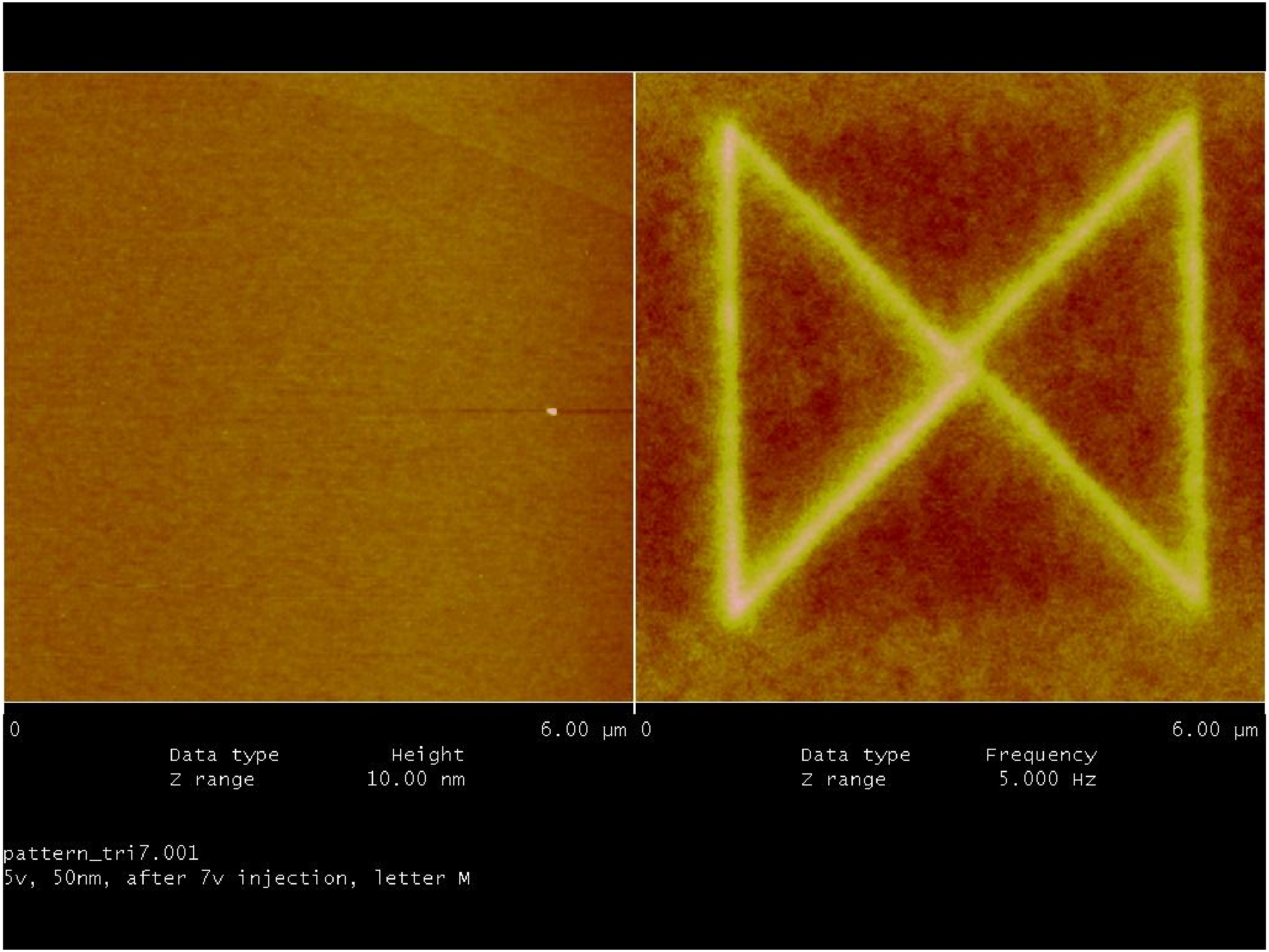
F16-CuPc Complementary Inverter



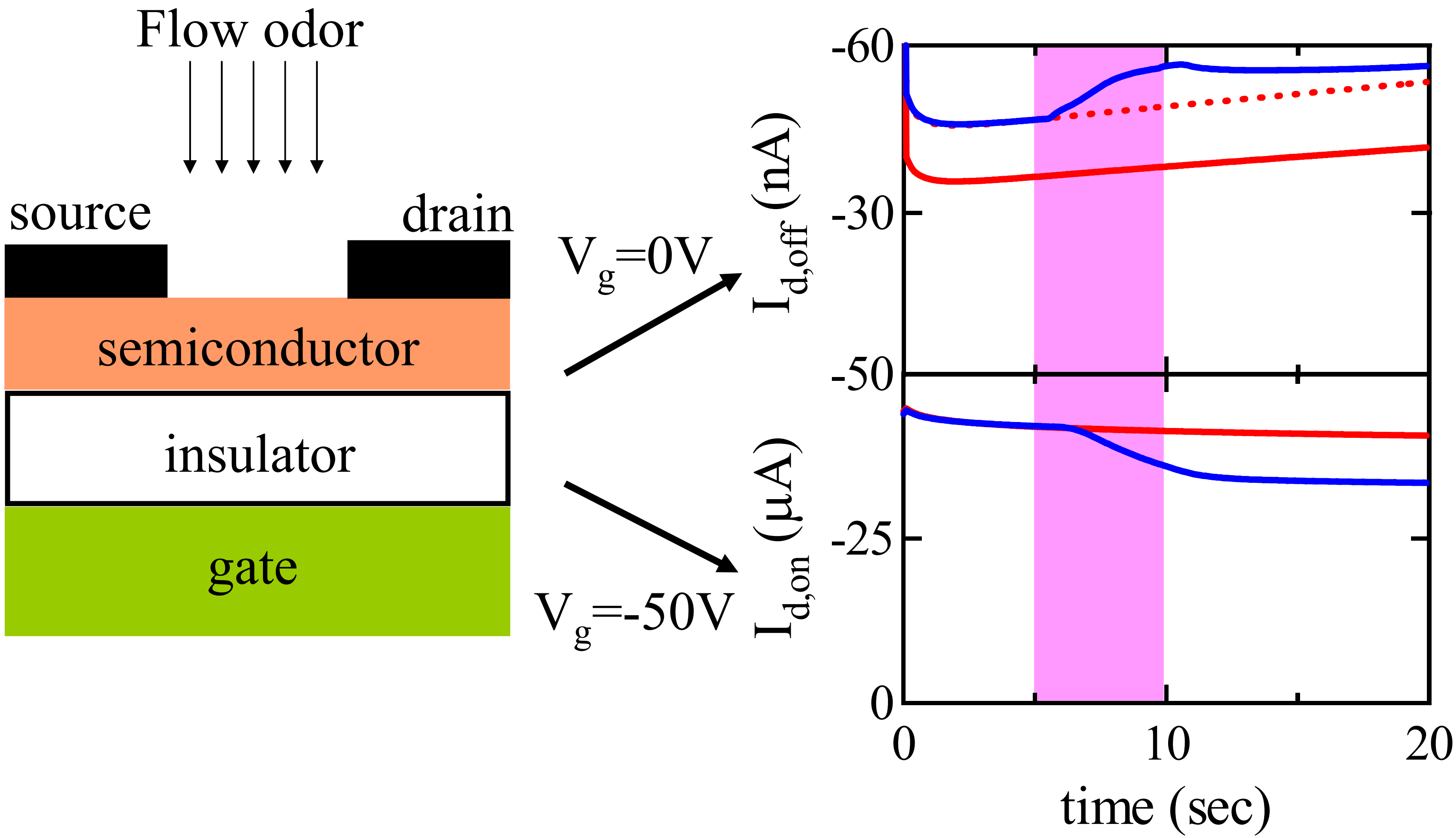


inverted normal

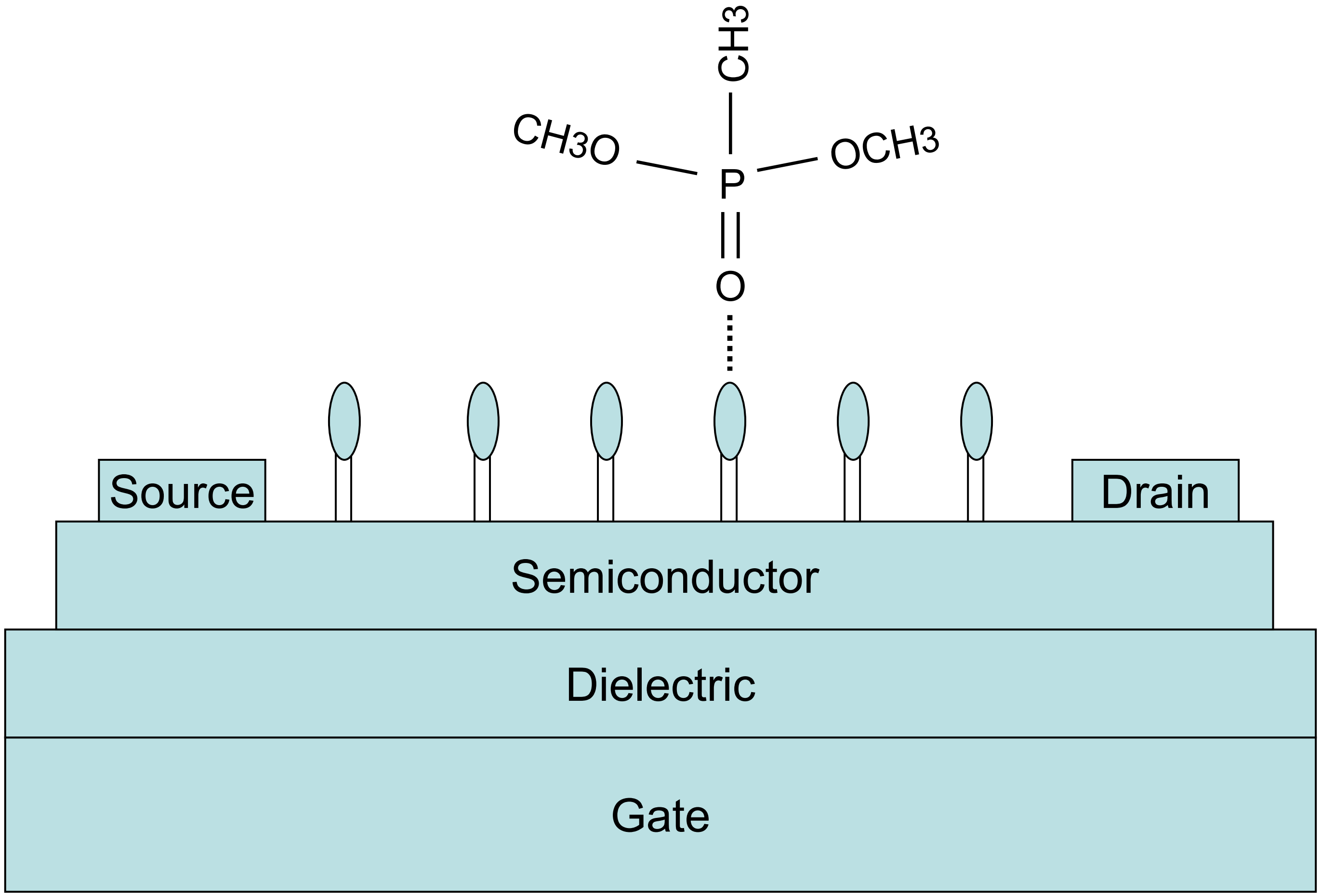
Electrostatic Potential Image of 300nm SiO_2 Dielectric Thin Film by AFM Nano-Charging and Nano-Scanning



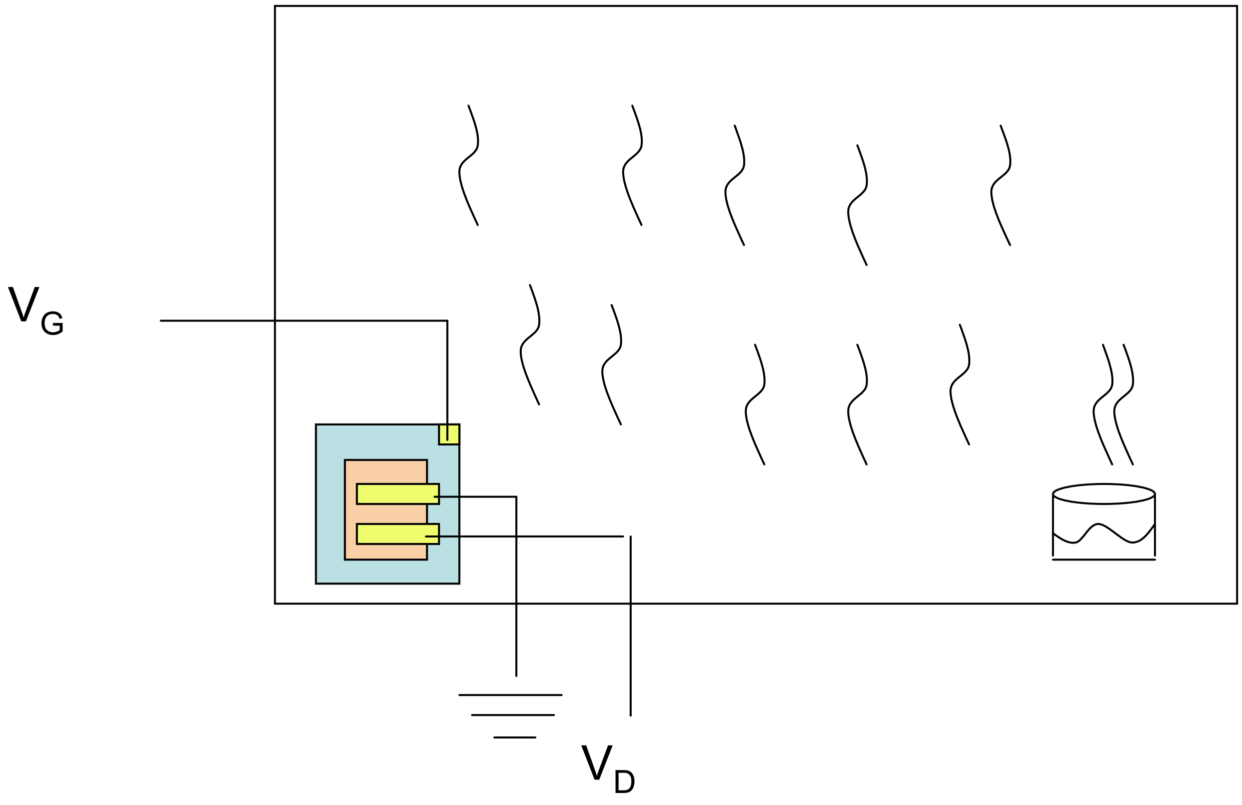
OFETs as Vapor Sensors



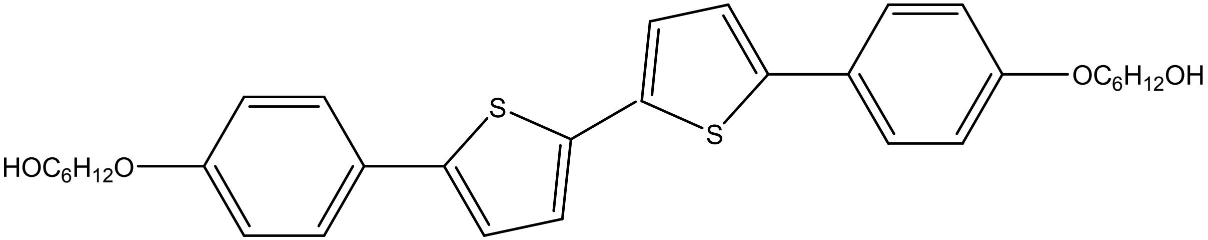
DMMP, a phosphonate
of environmental interest

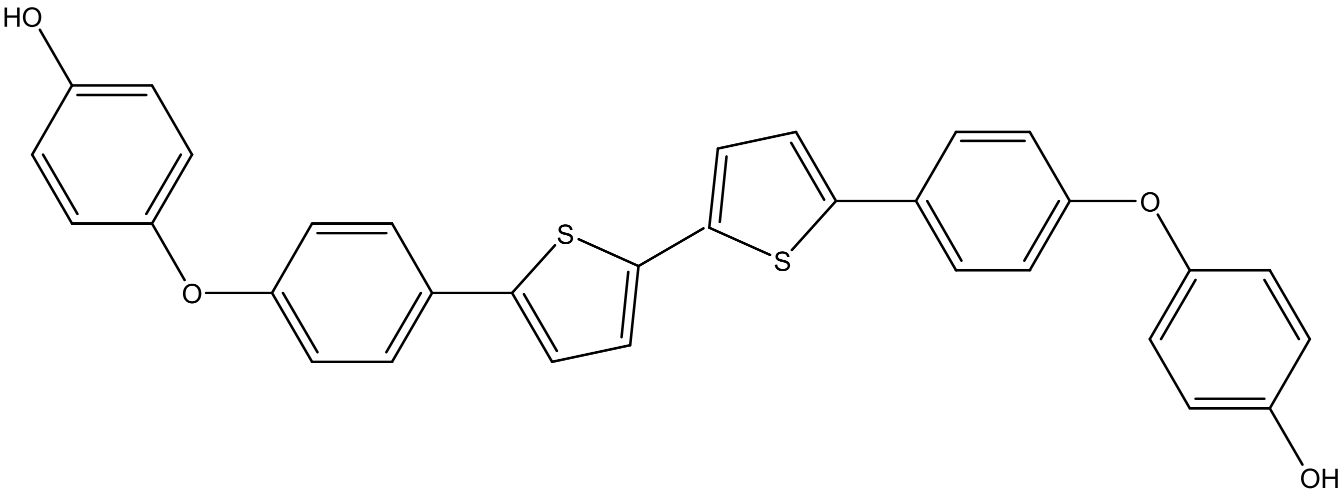


Setup for Preliminary Data

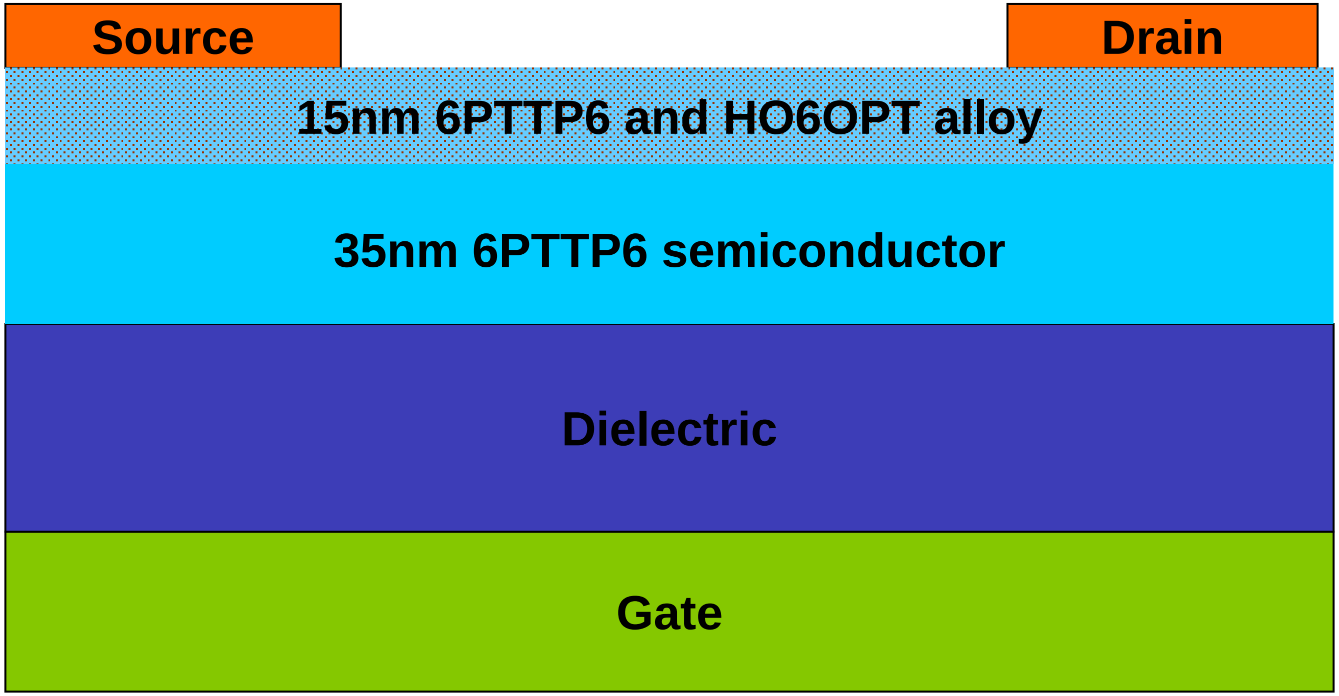


Hydroxy PTTP Derivatives

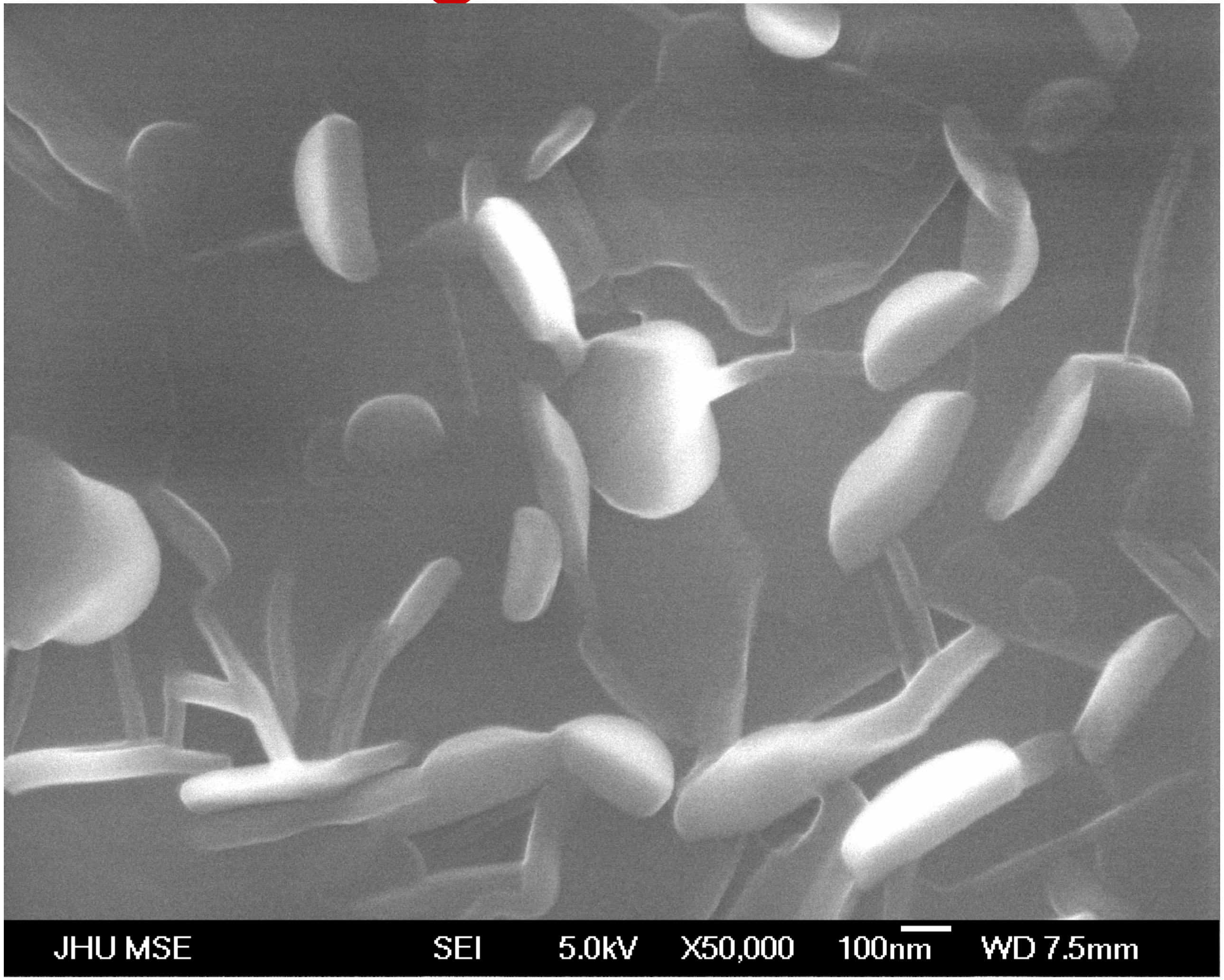




Structure of the alloy OFET sensor with 6PTTP6 and HO6OPT as semiconductor materials



6pttp6-100nm-50k Magnification



Two Layer Alloy-50nm-50k

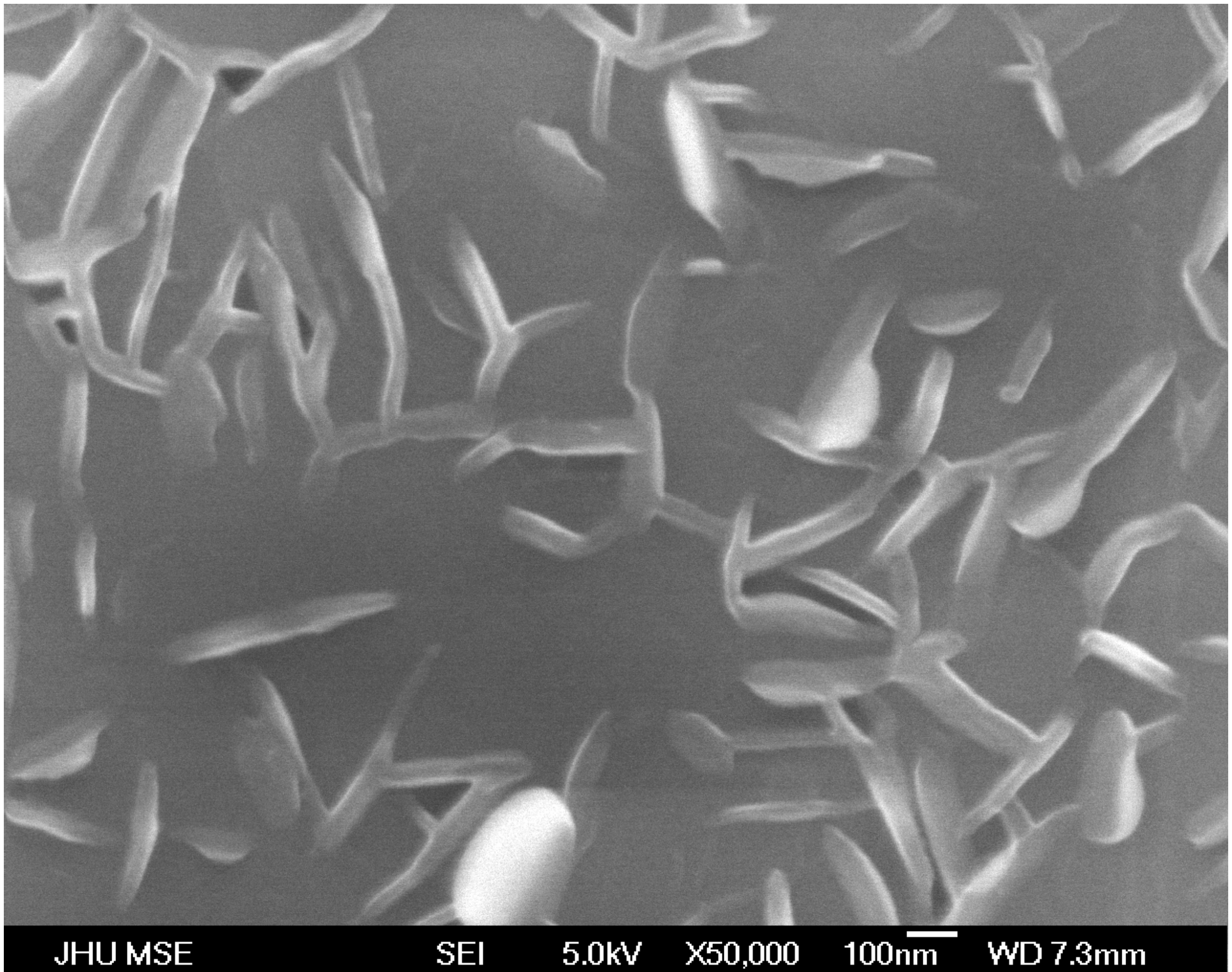
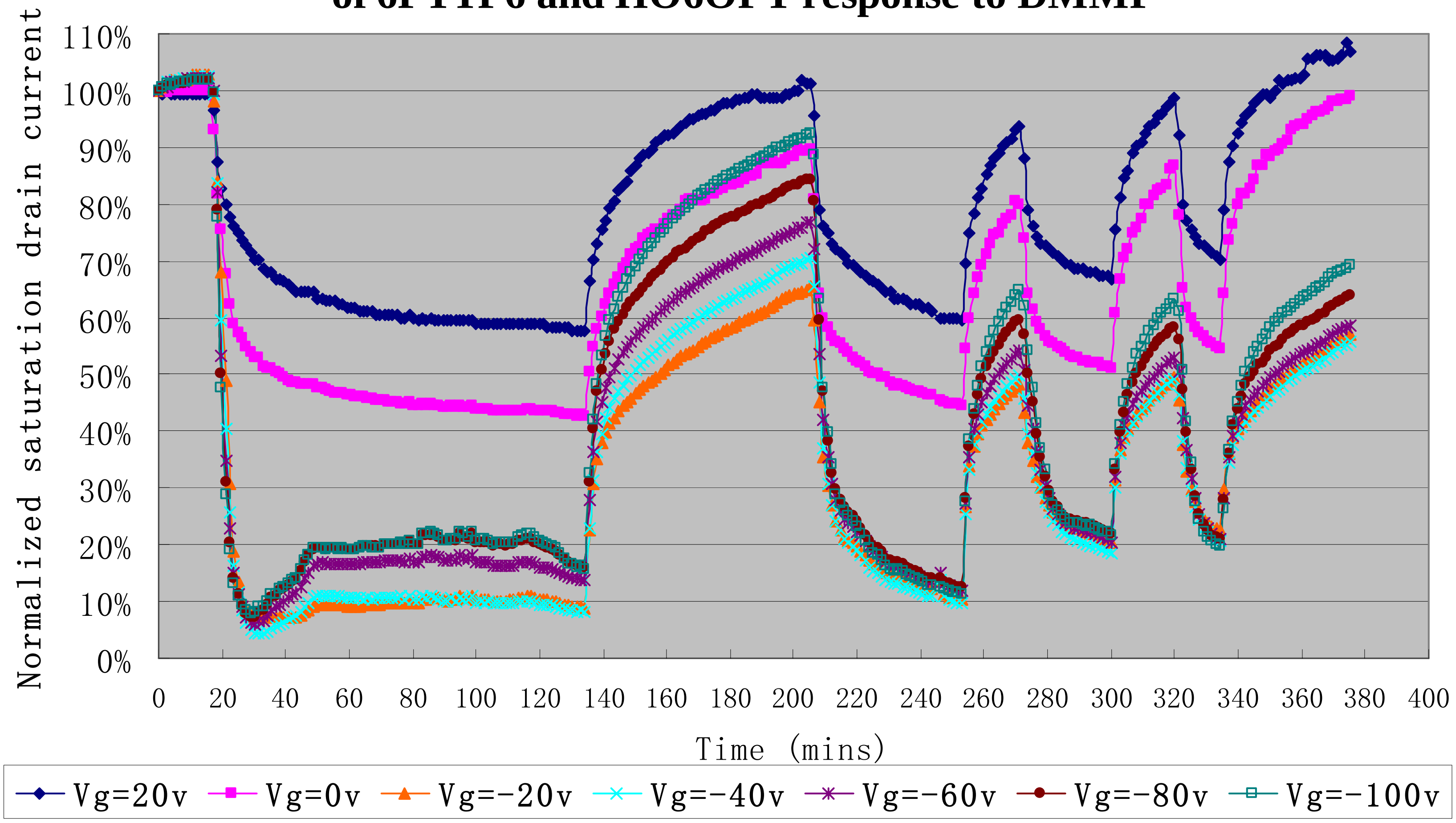
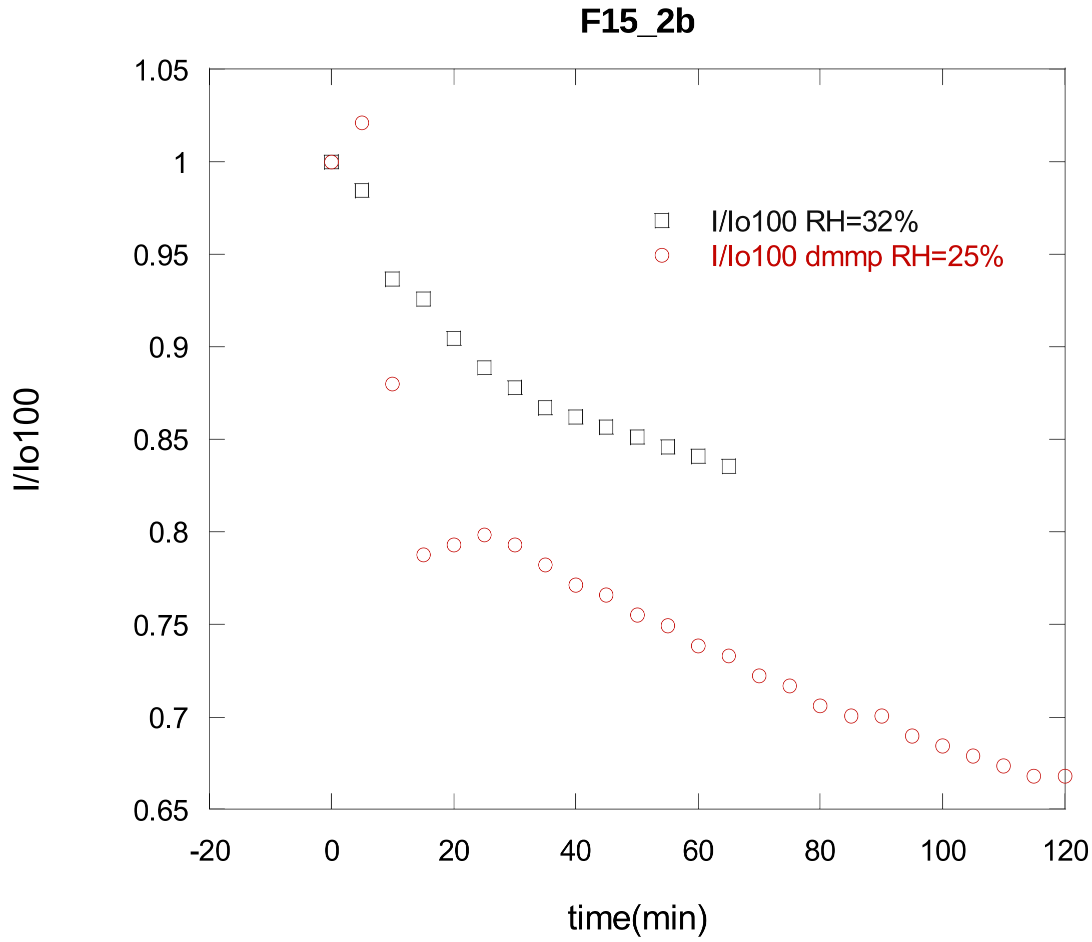


Figure 2. Normalized saturation drain current of an alloy sensor of 6PTTP6 and HO6OPT response to DMMP



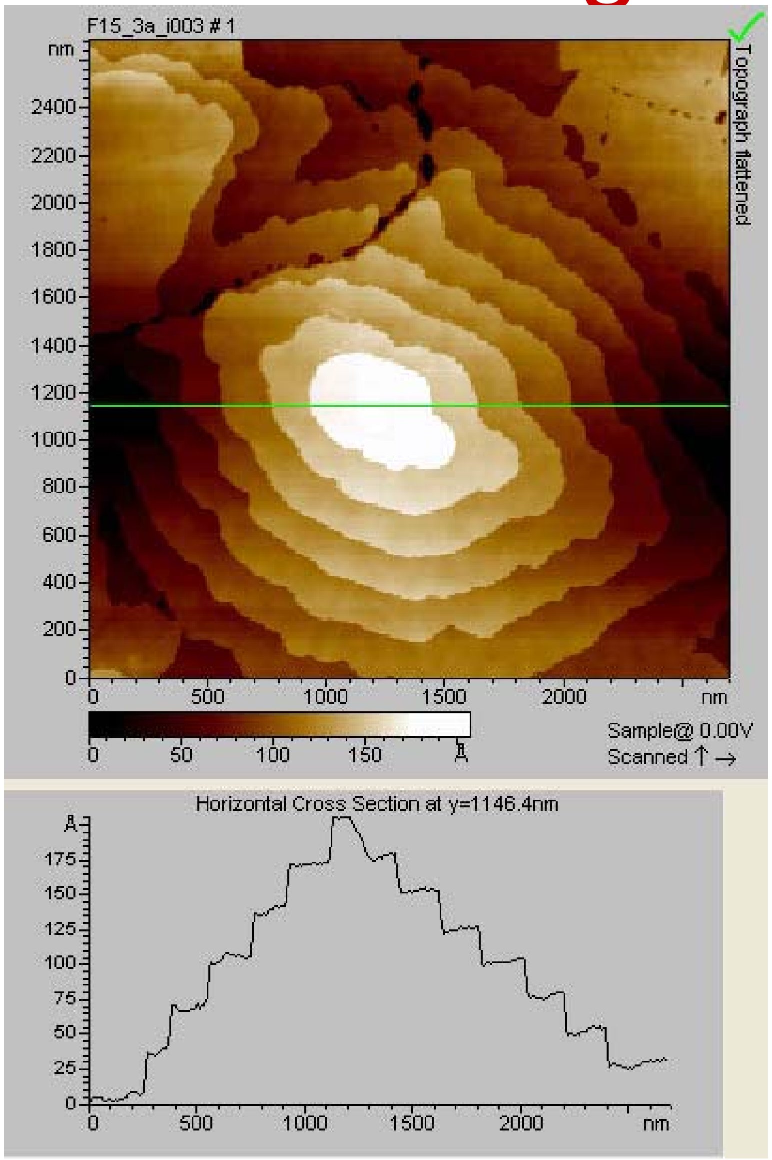
DMMP Response of NTCDI-F15

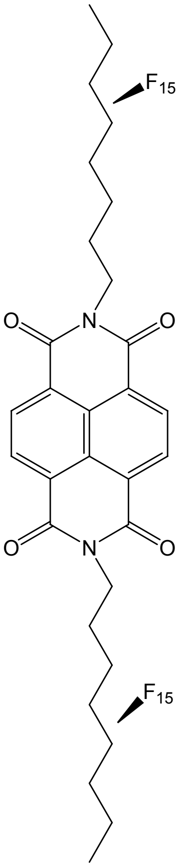
electron-carrying semiconductor



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

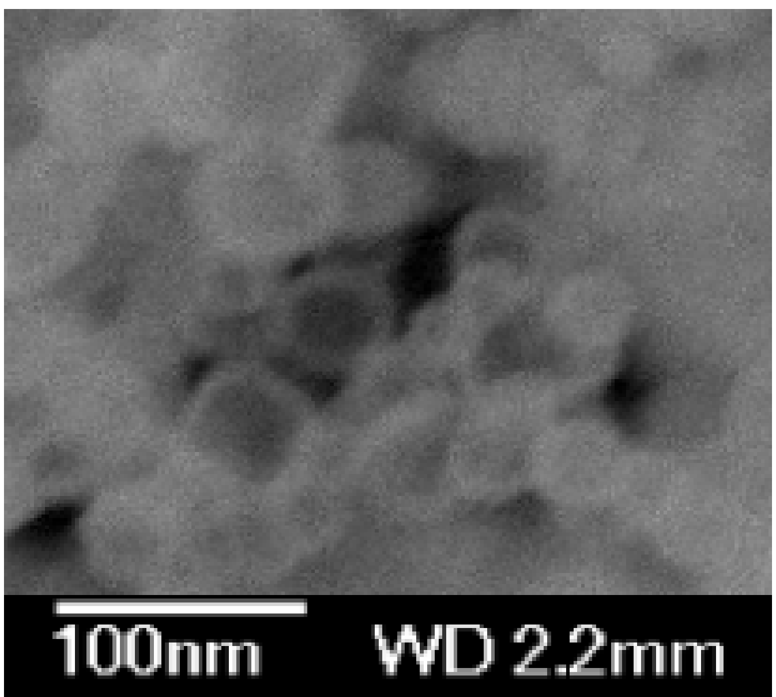


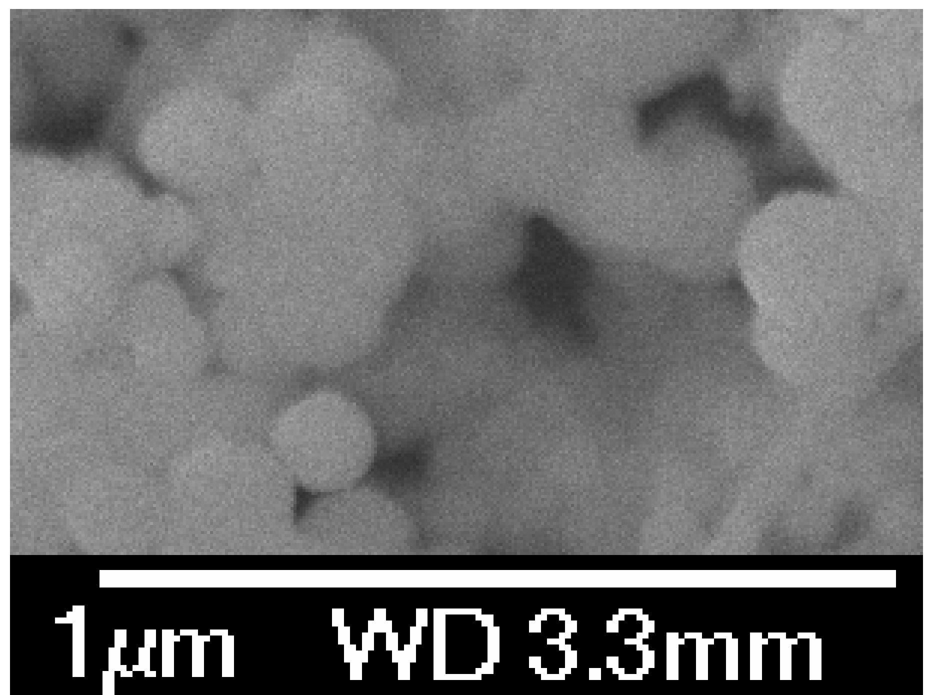


25-30 Angstrom molecular length!

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)



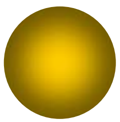


Multifunctional Nanoparticles

Peter C. Searson

Department of Materials Science and Engineering
Johns Hopkins University

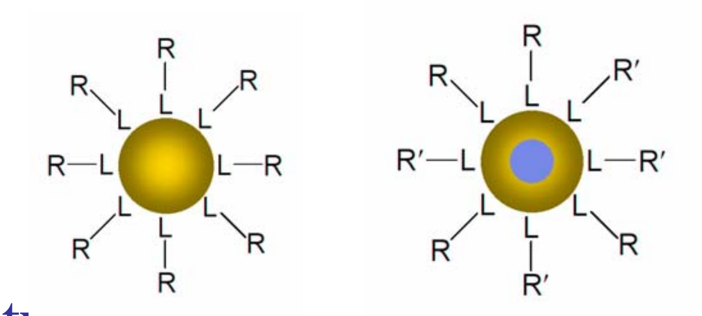
Spherical Particles and Nanowires

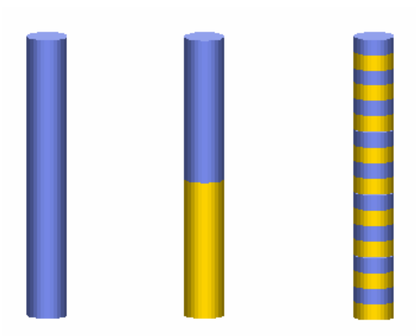


spherical particles

isotropic

single or mixed functionality



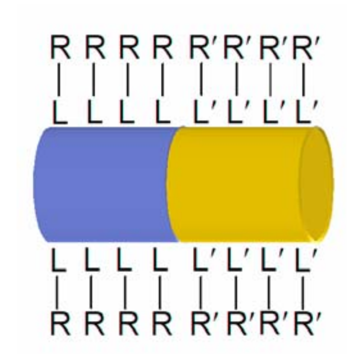


asymmetric particles

anisotropic

multicomponent

multifunctional



degrees of freedom

shape anisotropy, aspect ratio

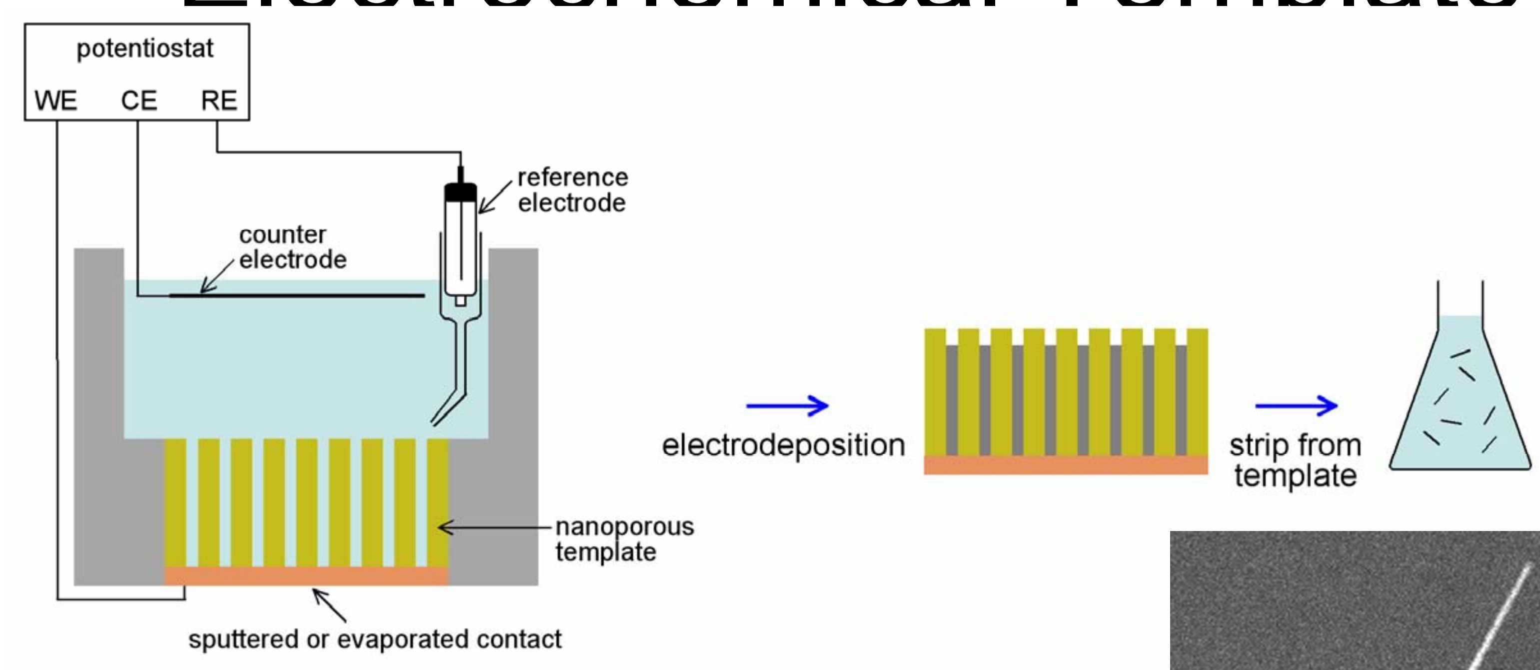
interlayer coupling

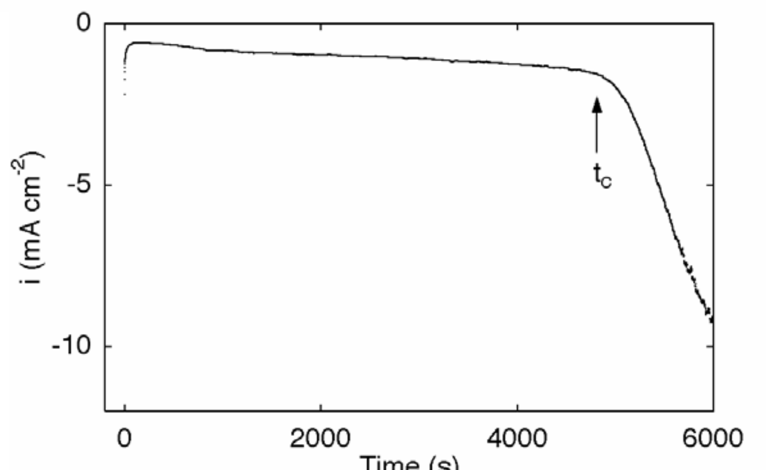
spatial multifunctionality

→ building blocks with more complex functions

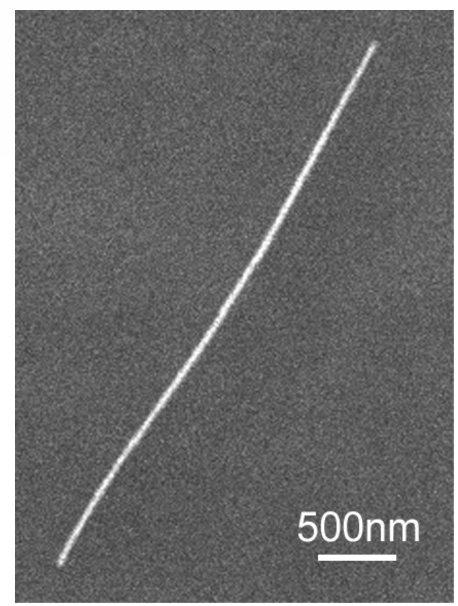
→ more complex architectures

Electrochemical Template





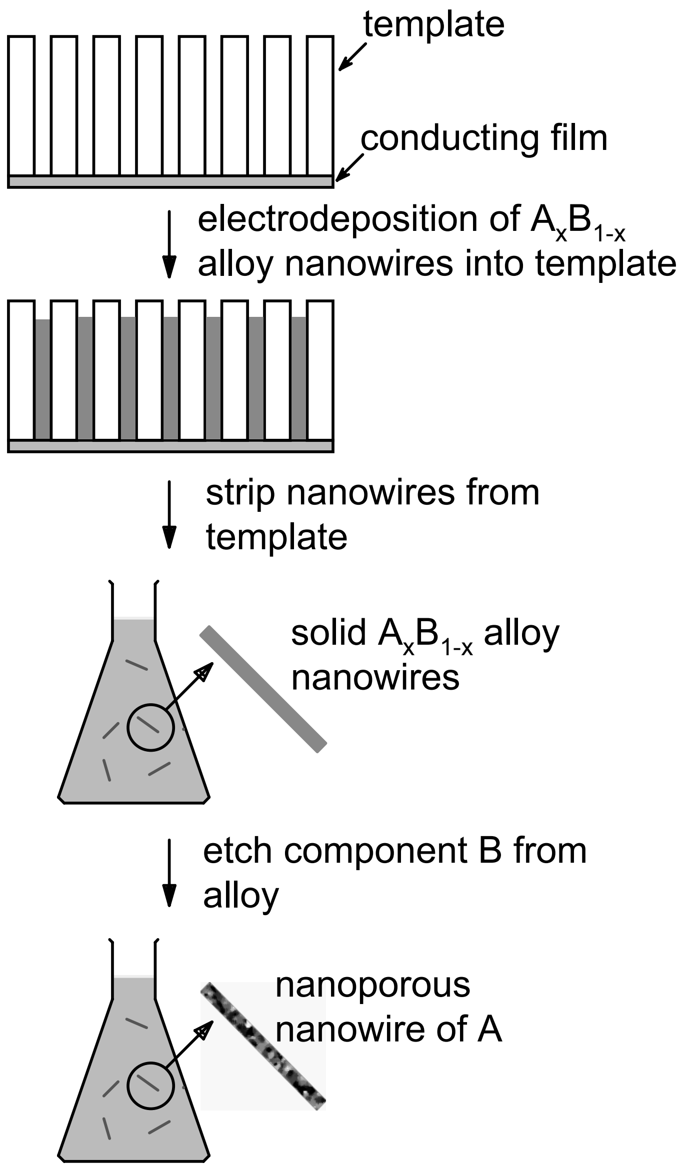
I - t curve for deposition of 30 nm CoPt nanowires into 6 μm polycarbonate template (N ≈ 6 x 10^8 cm^{-2})

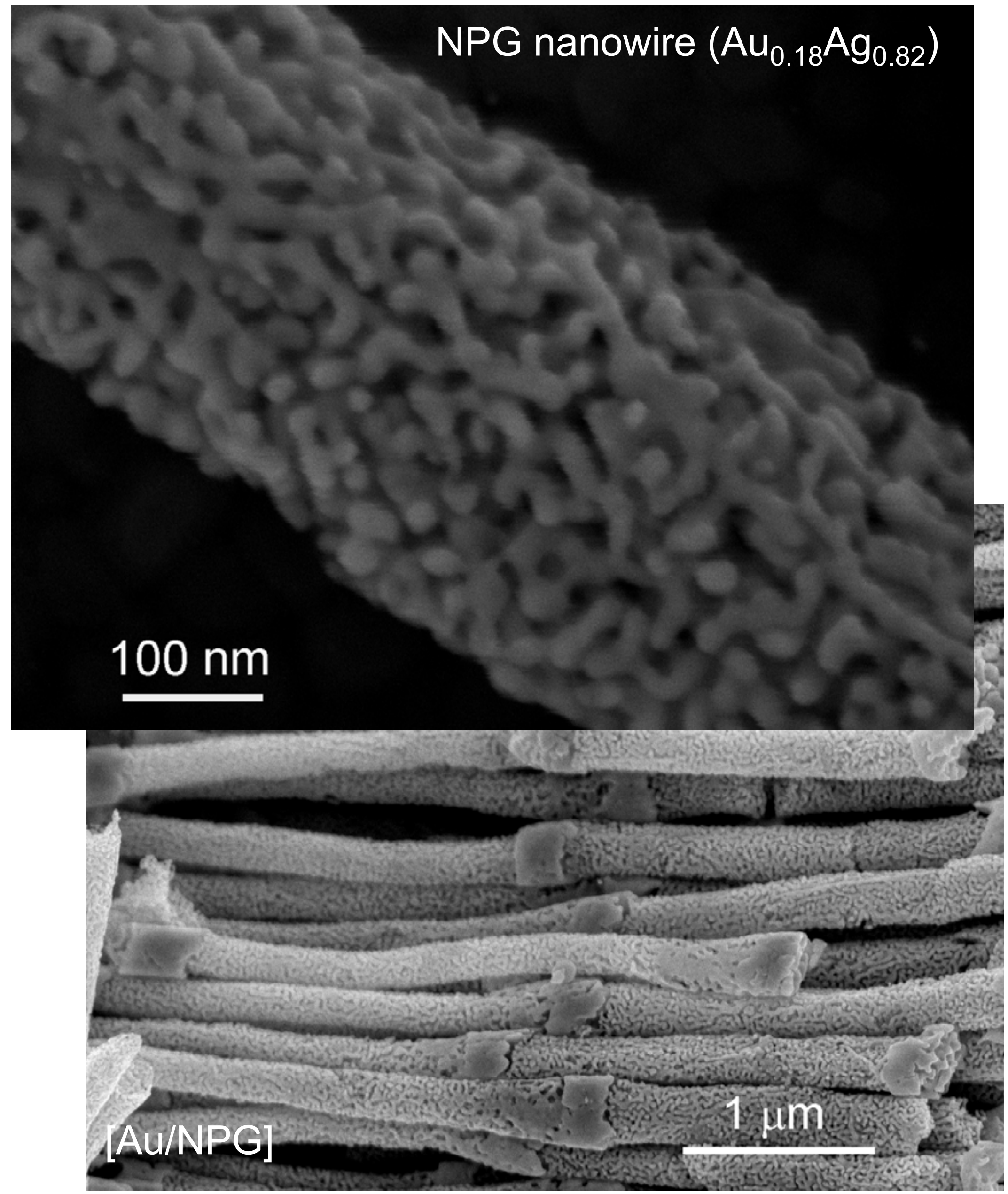


$Co_{0.65}Pt_{0.35}$ nanowire: ℓ = 4 μm, d = 30 nm

Appl. Phys. Lett., **84**, 3900-3902 (2004).

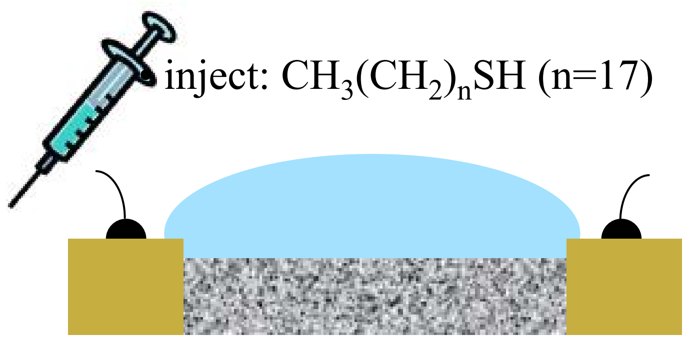
Nanoporous Nanowires



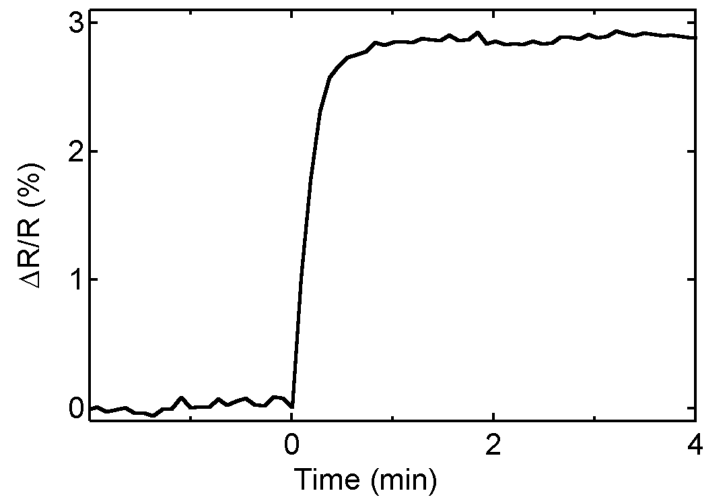


J. Phys. Chem. B. **107**, 4494-4499 (2003).

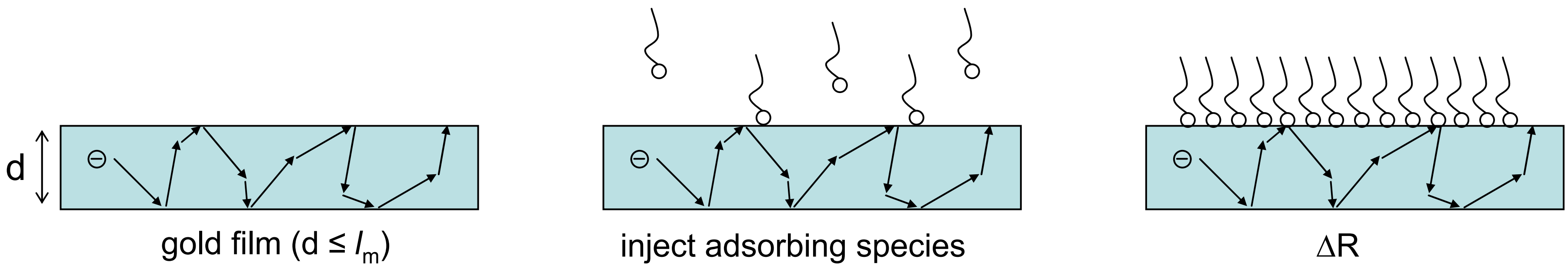
Single Nanowire Sensors



NPG Nanowire: $l \approx 5$ µm, $d \approx 230$ nm



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

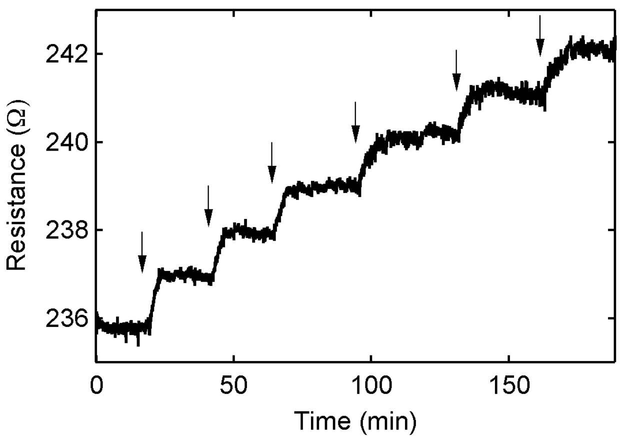


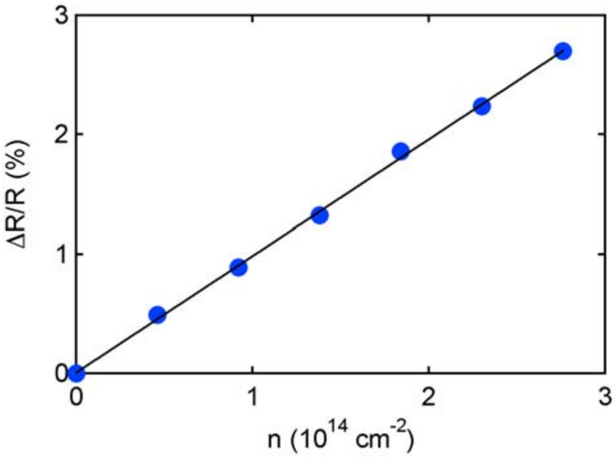
Ideal clean surface: specular (elastic) scattering - no change in momentum → no resistance change

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

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

Single Nanowire Sensors





Sequential injection of 5 x 10^{-11} moles ODT
monolayer coverage: 4.6 x 10^{14} cm^{-2}

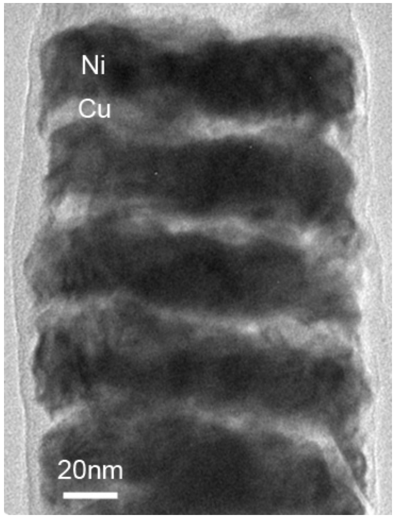
$$\left[\frac{d(\Delta R/R)}{dn}\right]_{n\to 0} = \frac{Al_m}{d}$$

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

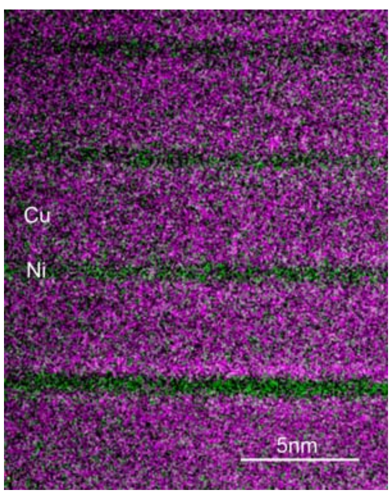
- ODT on Au (40 nm): $0.2 \times 10^{-16}\ cm^2$
- CO on Ni(10 nm): $0.5 \times 10^{-16}\ cm^2$
- CO on Cu(10 nm): $2 \times 10^{-16}\ cm^2$

J. Phys. Chem. **110**, 4318-4322 (2006).

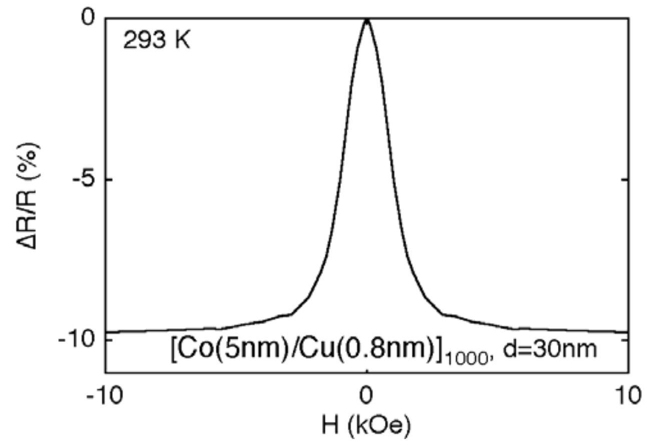
Multicomponent FM/NM Multilayer Nanowires



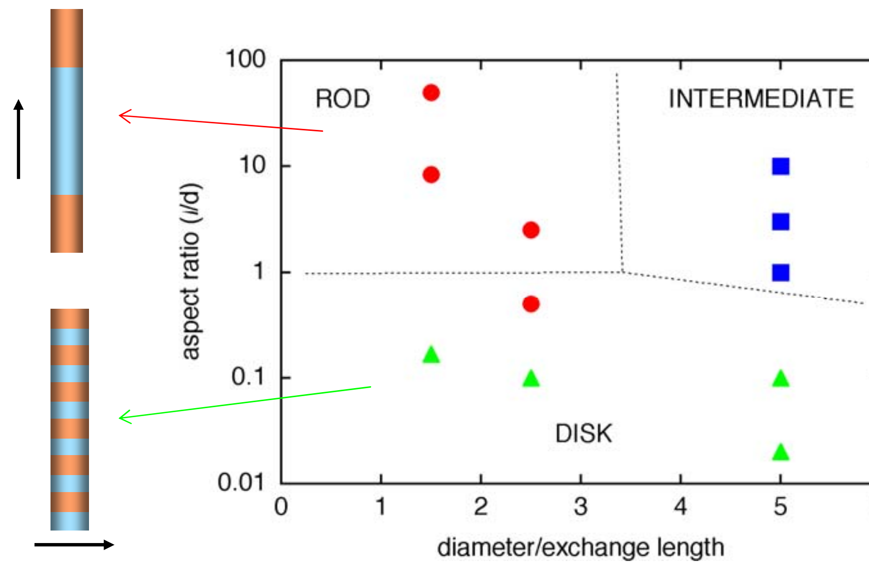
HRTEM image
[Ni(20nm)/Cu10nm)], d=120nm



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



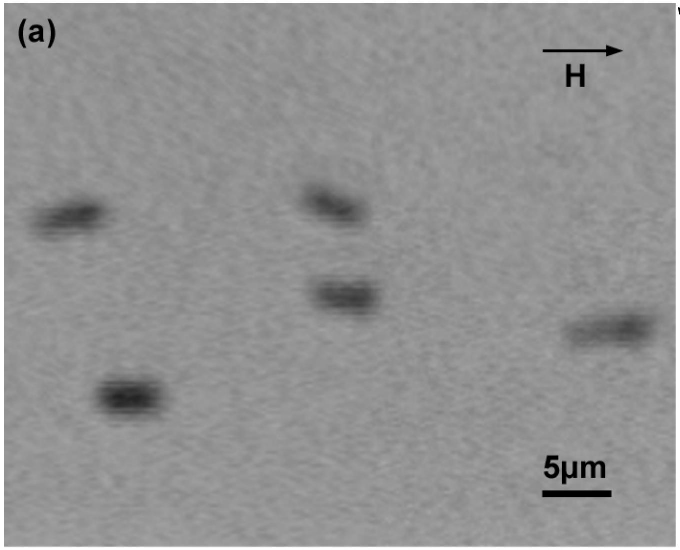
→ Nanowire GMR elements



exchange length, λ_{ex}(Ni) ≈ 20 nm

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

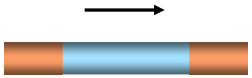
Exploiting Shape Anisotropy in FM/NM Multilayer Nanowires



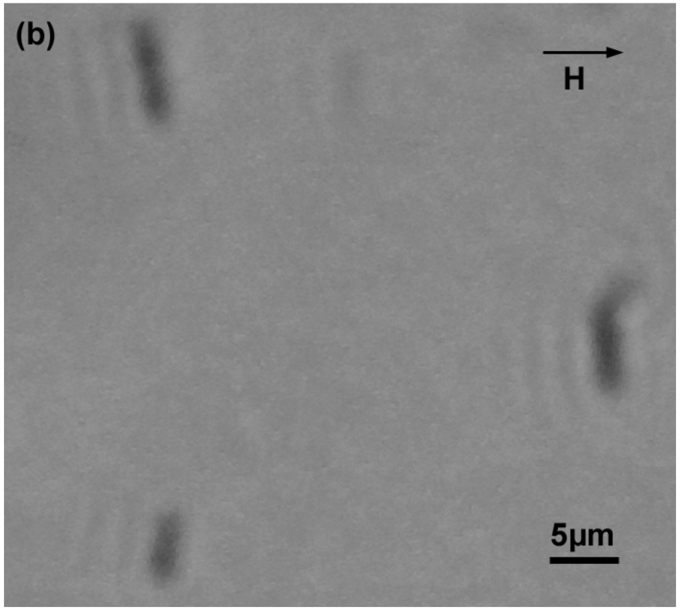
nanowire suspensions in octadecane/hexadecane (1:1)

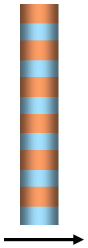
l = 6 µm, d= 100 nm

composition: 50% Ni, 50%Cu



[Ni(1000nm)/Cu(1000)]$_3$

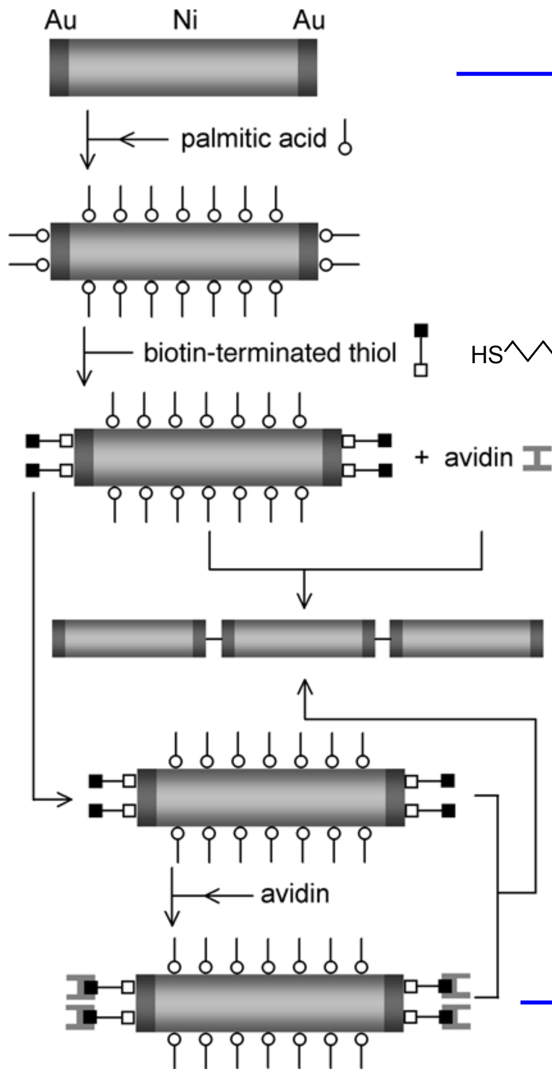


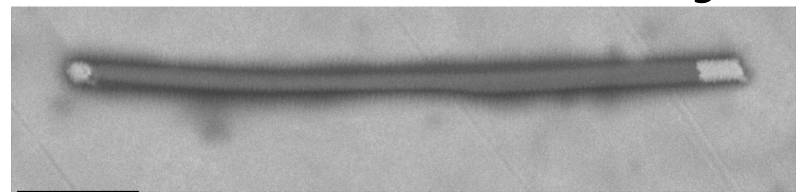


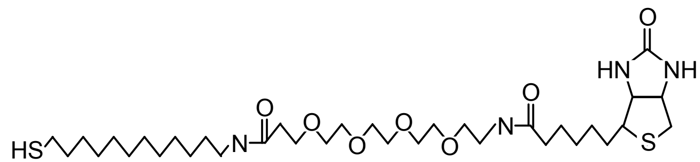
[Ni(10nm)/Cu(10)]$_{300}$

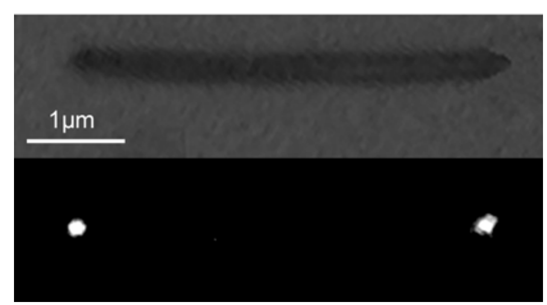
Appl. Phys. Lett. **82**, 3310-3312 (2003).
J. Appl. Phys. **93**, 8253-8255 (2003).

Nanowire Self-Assembly



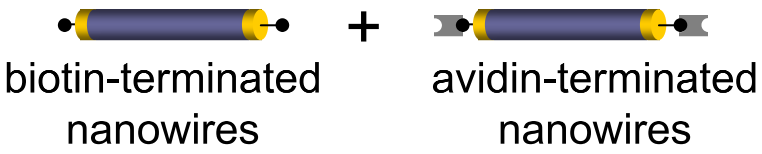


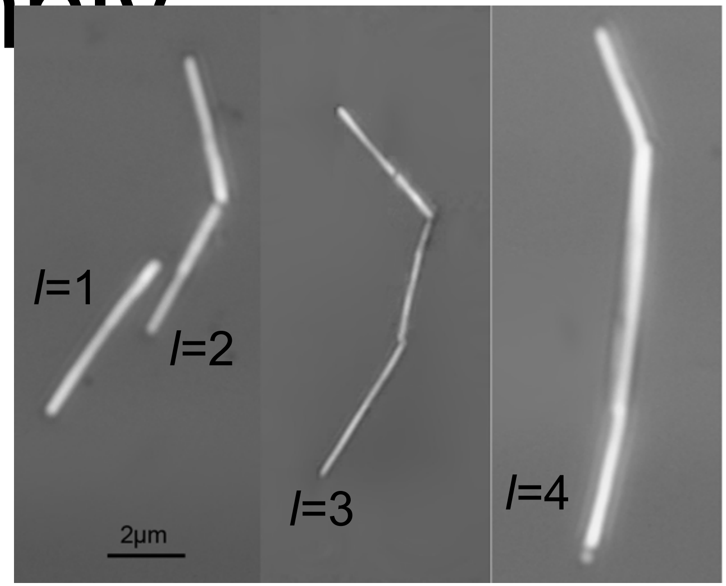


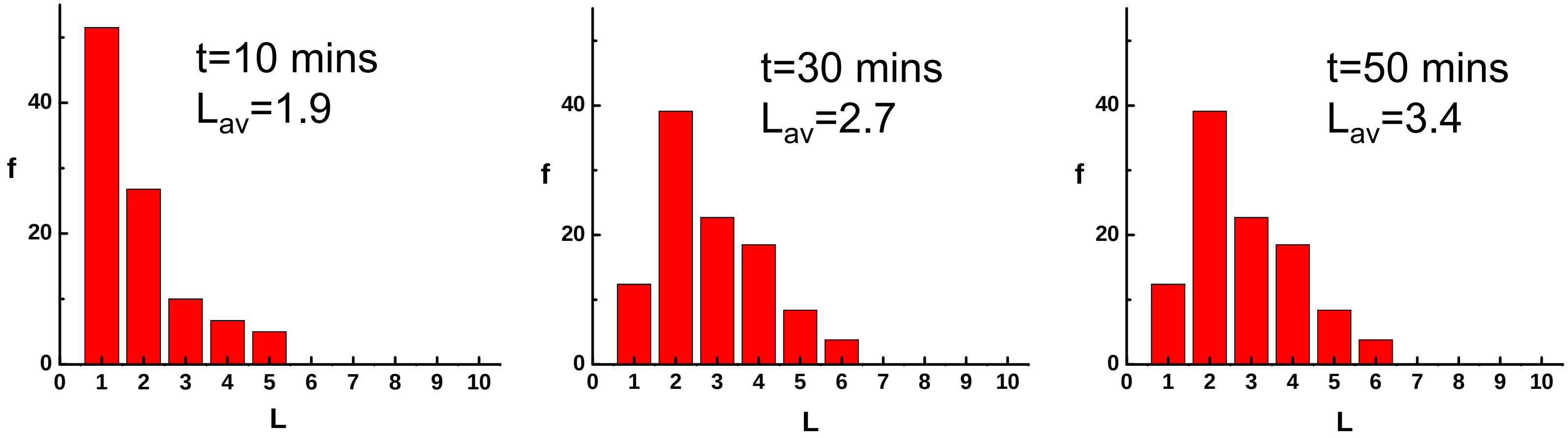


Adv. Mater. **17**, 2765-2768 (2005).

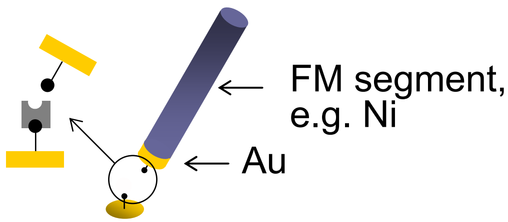
Nanowire Self-Assembly

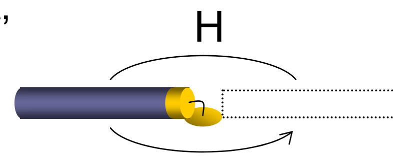




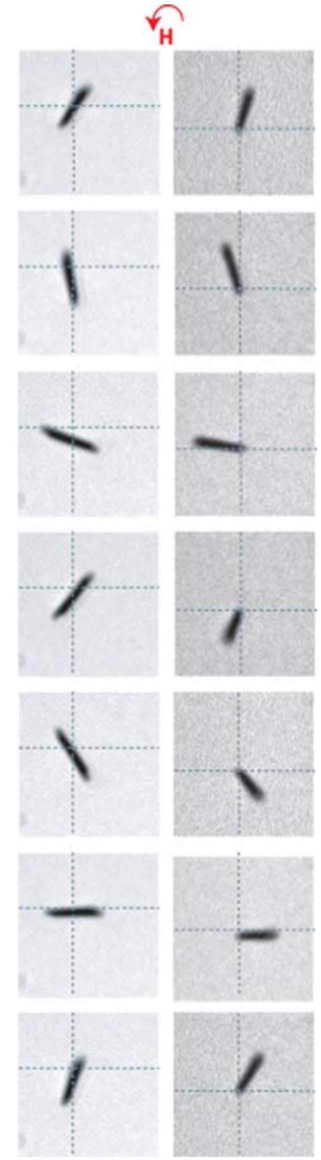


Rotation of Tethered Nanowires





in plane rotation

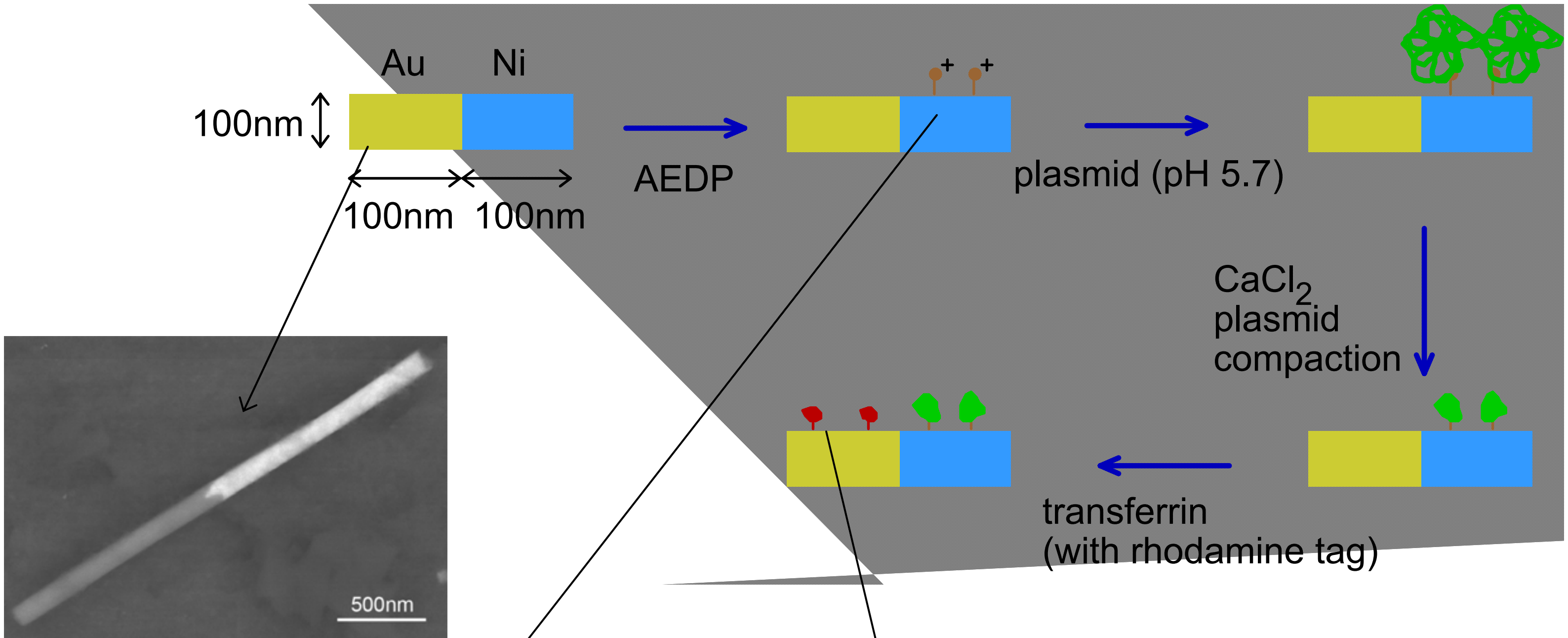


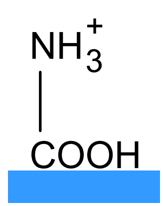
control tethered

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

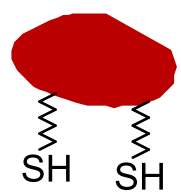
Nanowire motors, switches, …?

Selective Functionalization for





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

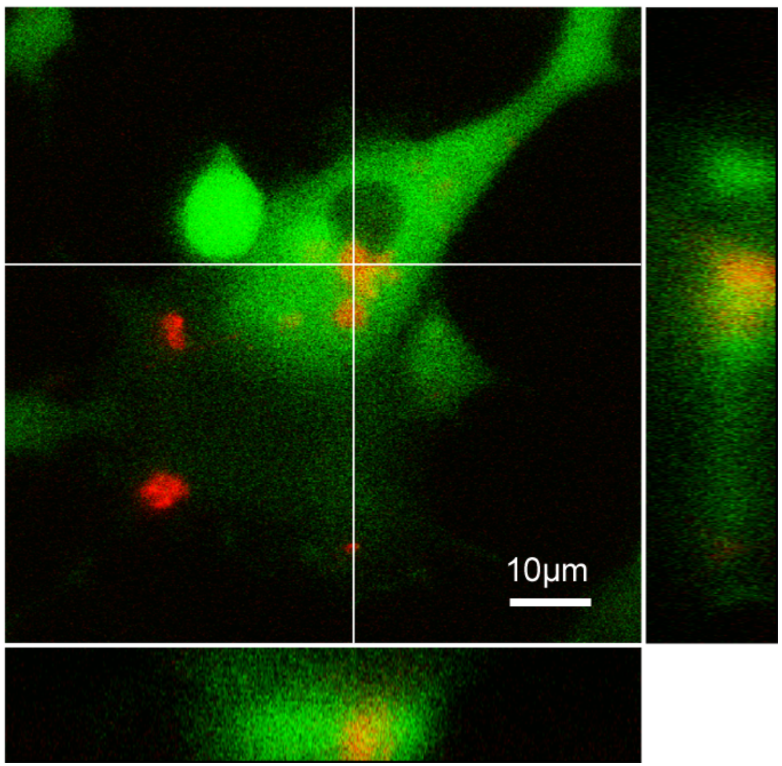


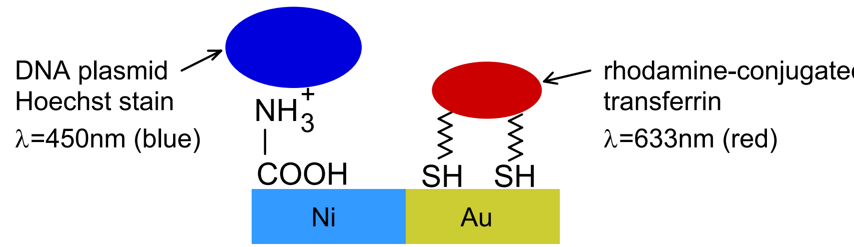
transferrin - cell targeting protein
rhodamine tag (red emission)
fraction of $-NH_2 \rightarrow -SH$

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

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

Confocal Microscopy





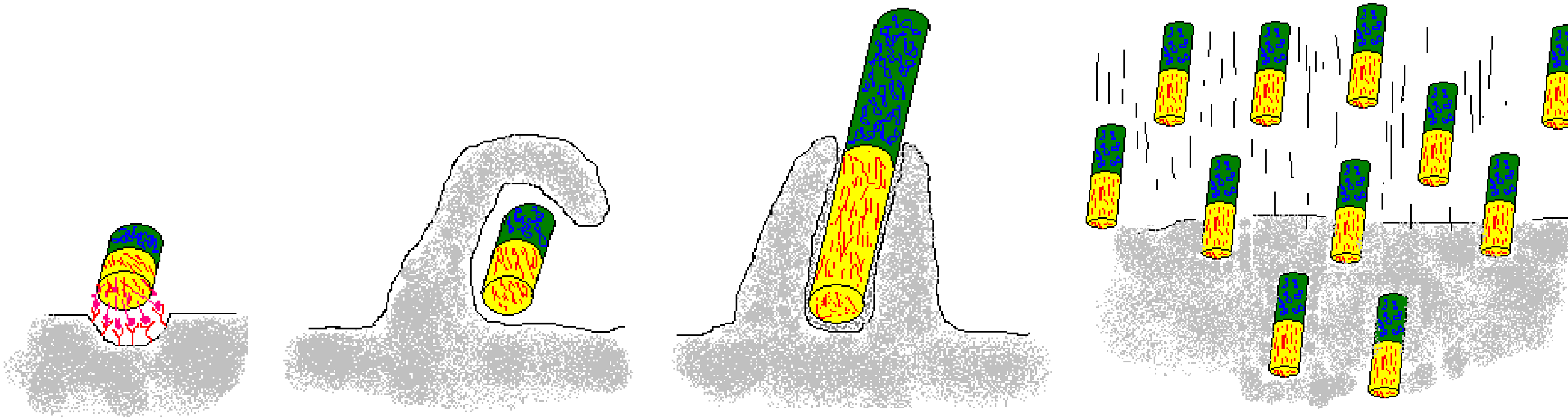
- stacked confocal microscope images of live HEK293 cells

  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

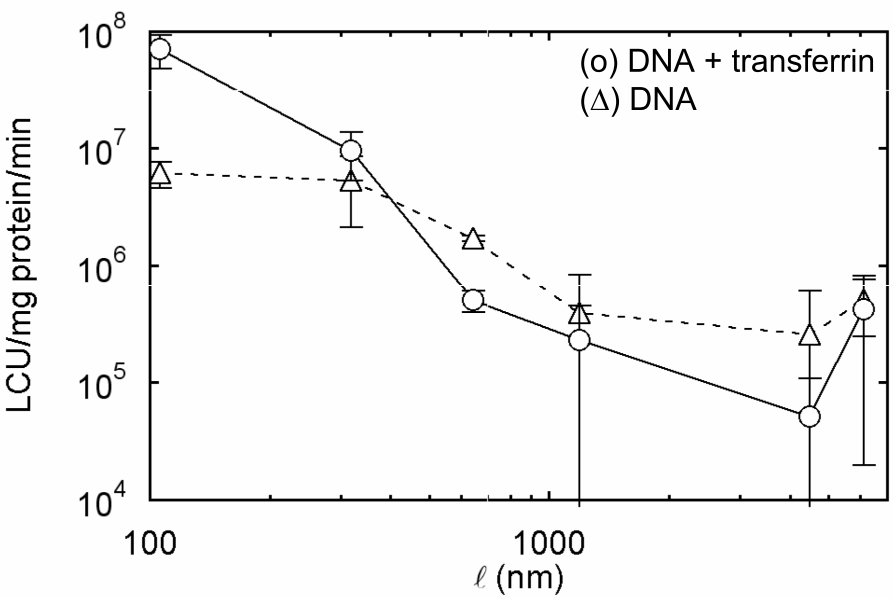


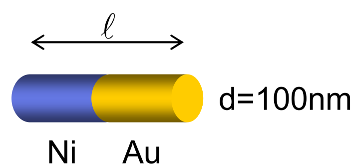
Receptor mediated endocytosis

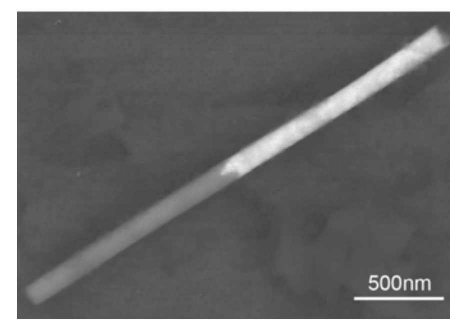
Macropinocytosis

Phagocytosis

Nanowire bombardment into cytoplasm







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

Questions and Answers