# Electrochemically Synthesized Multi-block Nanorods

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Electrochemical Vibrational Characterization of Metal Nanoelectrodes

Surface Chemistry
Electrochemistry
Nanoparticle electrocatalysis

PURDUE UNIVERSITY

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*J. Am. Chem. Soc.* 2006, ASAP
*J. Phys. Chem. B* 2006, 110, 2150-2154
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*Science*, 2004, 303, 348-351

Nanoparticle Synthesis and Applications

Nanorods
Core-Shell nanoparticles
DPN,
Nano-Bio Chemistry

INSTITUTE FOR NANOTECHNOLOGY
Northwestern University

# Nanotechnology: What is it?

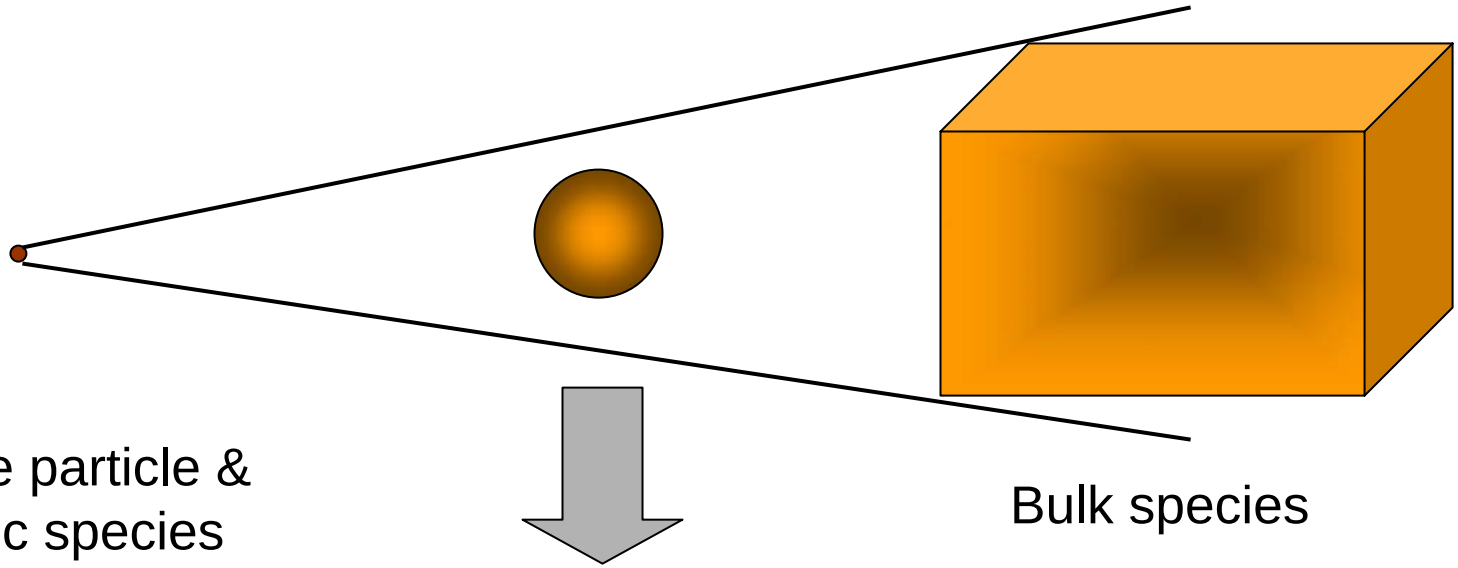
1. Developing synthetic and analytical tools for characterizing and manipulating materials on the nanometer (nm) length scale.

2. Determining the chemical and physical consequences of miniaturization.

3. Exploiting the ability to miniaturize and its consequences in the development of new technology.

# Nanometer Scale Materials

Why are we interested in small particles?

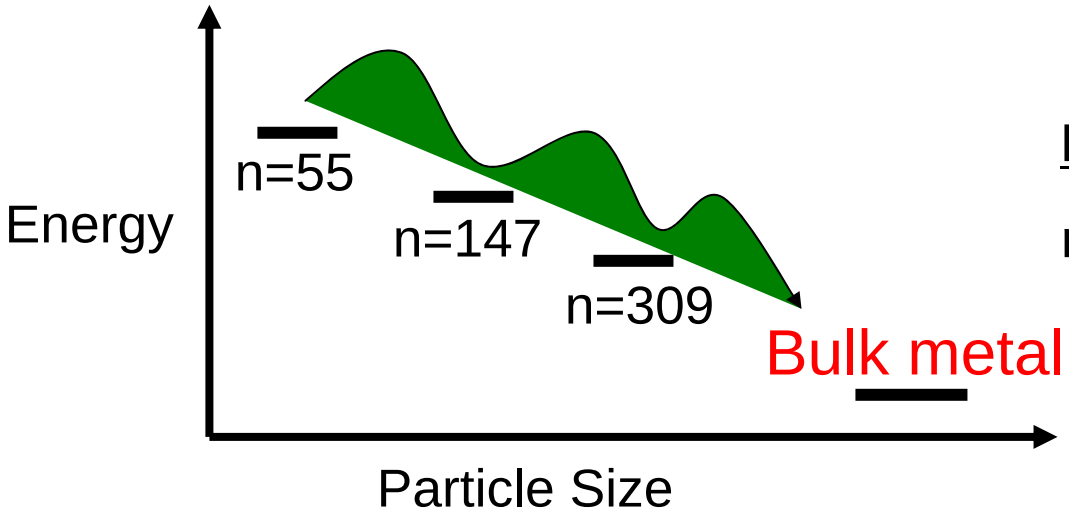


Single particle &
Atomic species

Bulk species

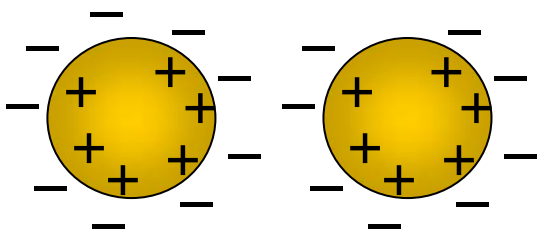
Many fascinating potential uses: quantum dots or quantum computers and devices, chemical sensor, light-emitting diodes, industrial lithography and so on ……Electrochemical catalysts, SERS

# Stability of Particles?

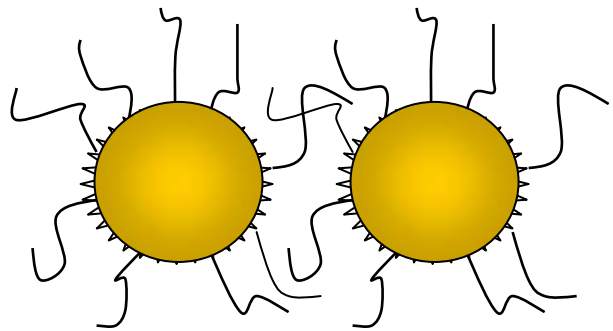



**Kinetically stable**,

not thermodynamically

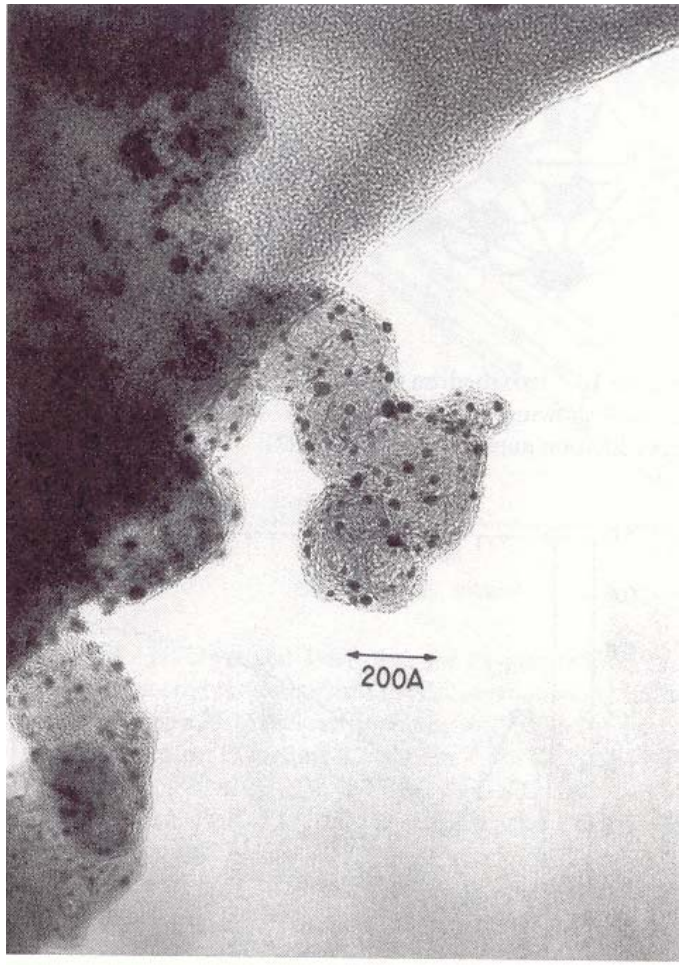


(a)



(b)

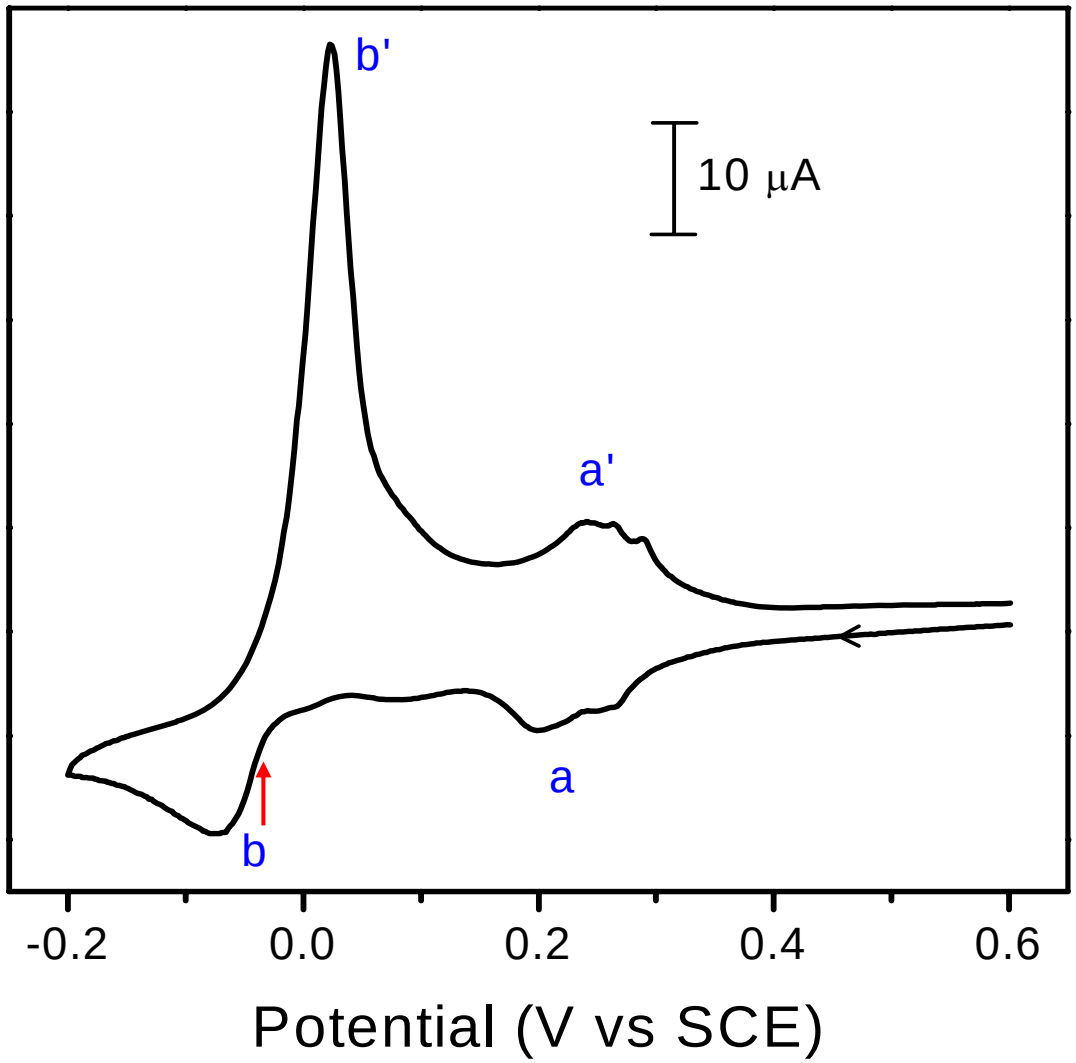
# Carbon Supported Nanoparticles



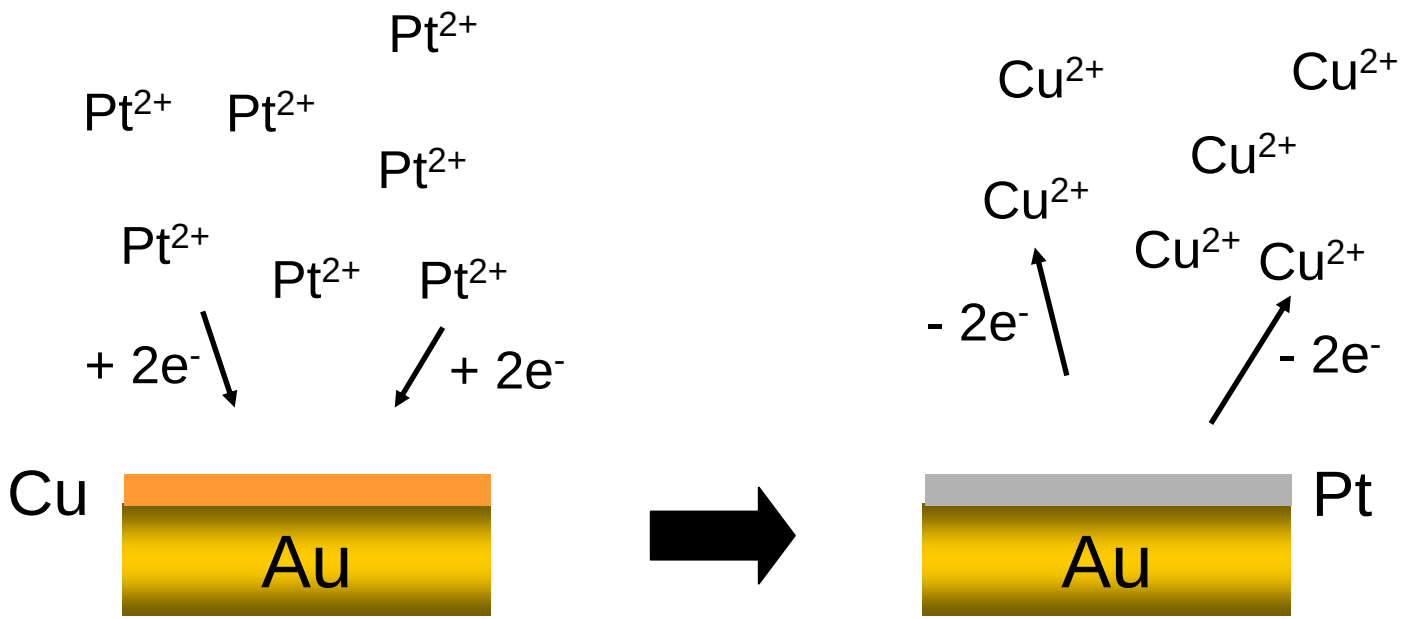

(by K. Kinoshita)

# Underpotential Deposition of Copper Monolayer

$$Cu^{2+} + 2e^-_{substrate} \rightleftharpoons Cu^0_{UPD}$$



# Replacement of $Cu_{UPD}$ Adlayer with Pt

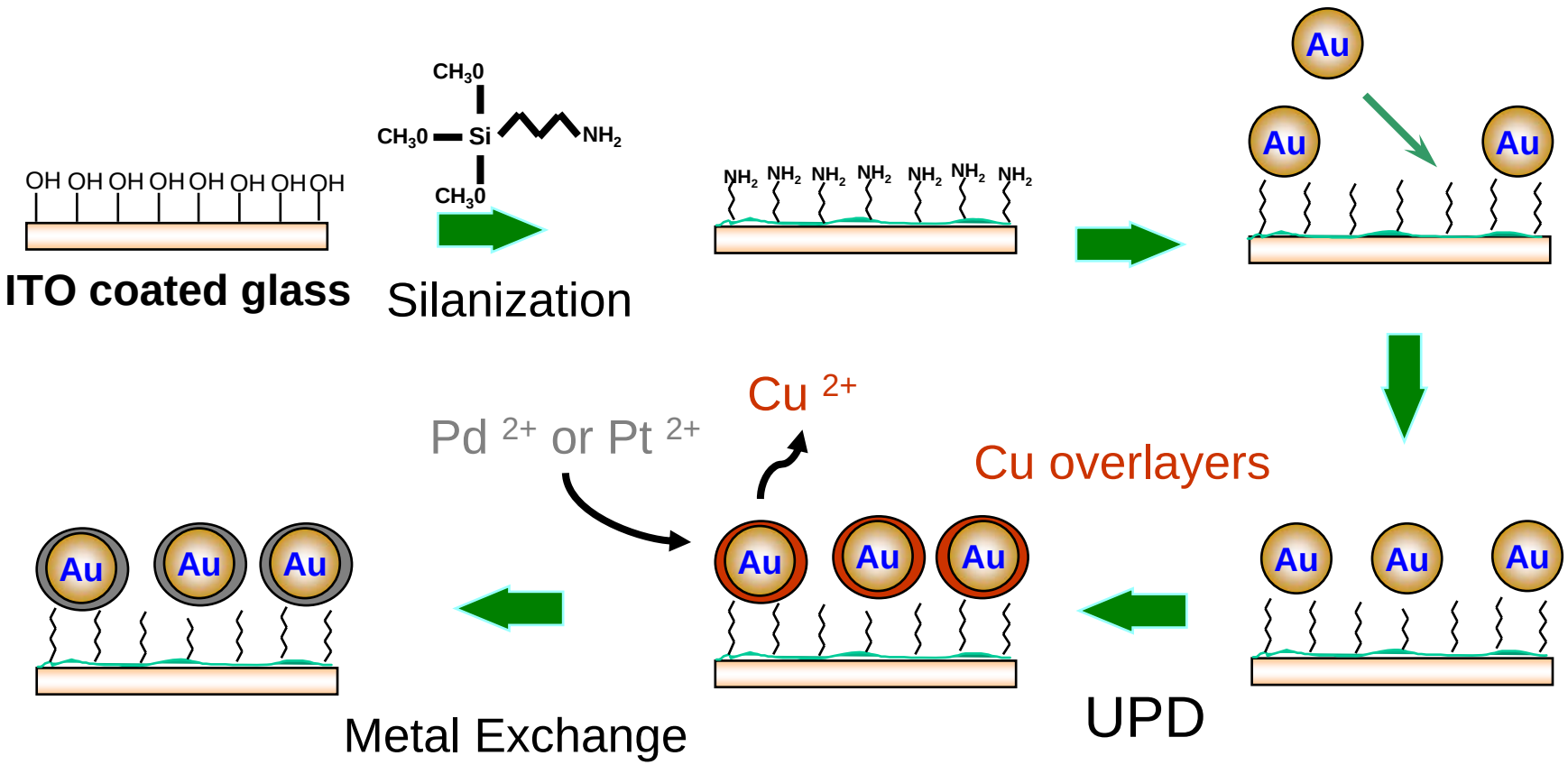



$Cu^0 + Pt^{2+} \rightarrow Cu^{2+} + Pt^0$

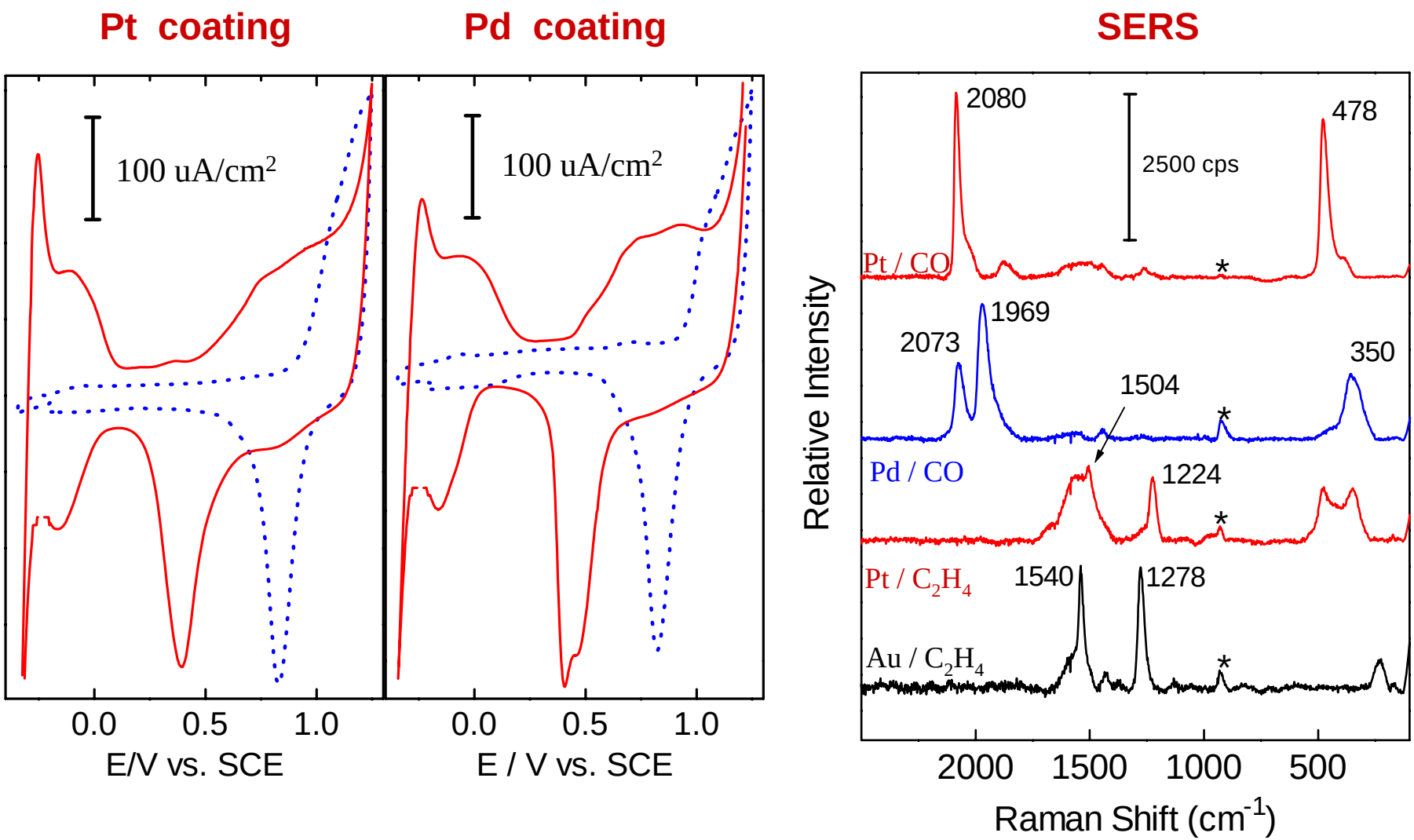
$PtCl_4^{2-}/Pt$ $E^0 = 0.48$ V

$Cu^{2+}/Cu_{upd}$ $E^0 = 0.2$ V

# Pt-group metal coated gold nanoparticles



# SERS of Pt-group modified gold nanoparticles

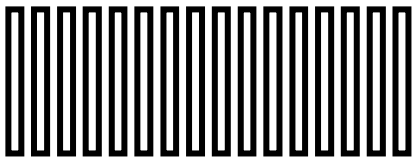





*J. Phy. Chem. B* **2002**, 106, 8667

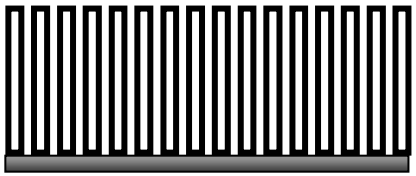
*JACS.* **2002**, 124(11), 2428

# Nanorod Synthesis

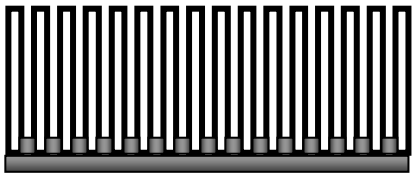


Alumina membrane

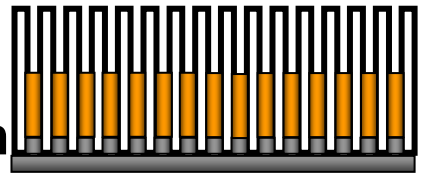
150 ~200 nm
Ag evaporation



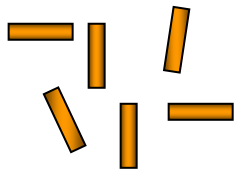
Ag deposition
(EC)



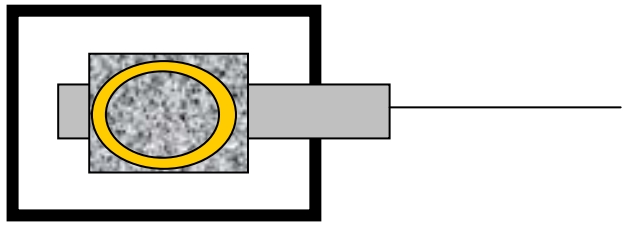
Au deposition
(EC)



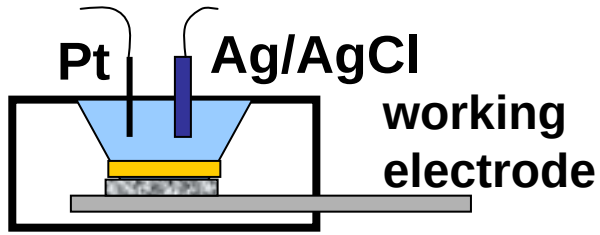
1. $HNO_3$
2. NaOH



Top view



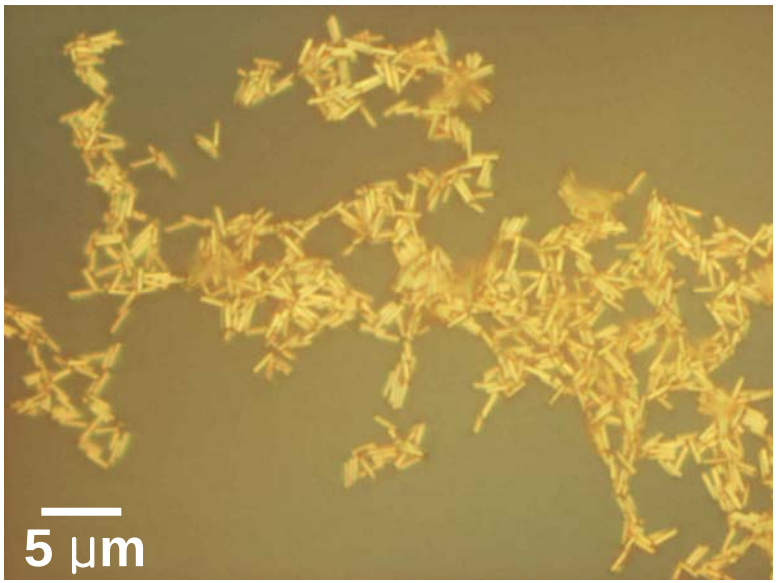
Side view

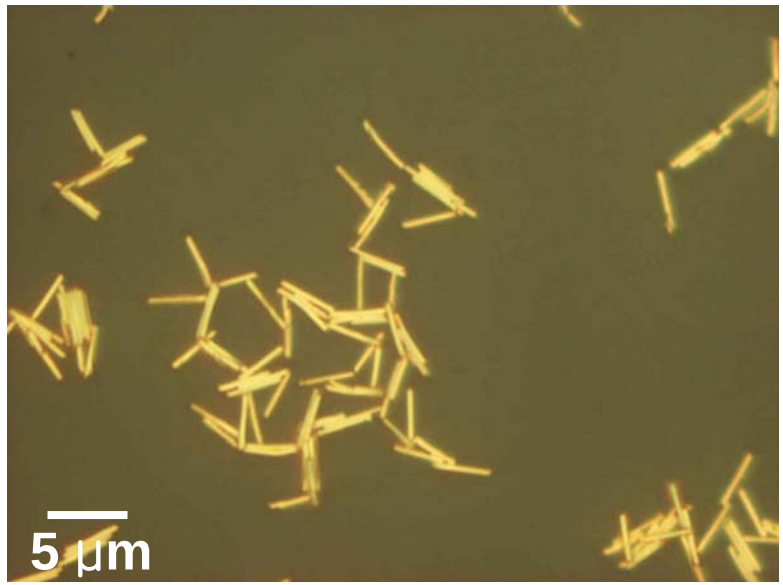



Pioneered by Prof. Martin and Prof. Moskovits

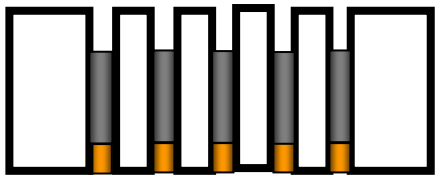
# Gold Nanorods

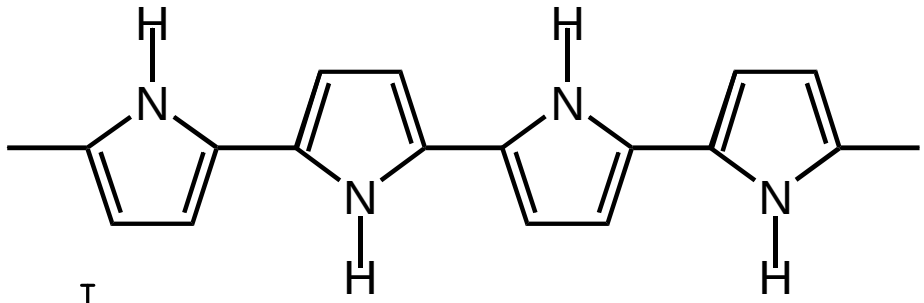
## Optical Microscope Images

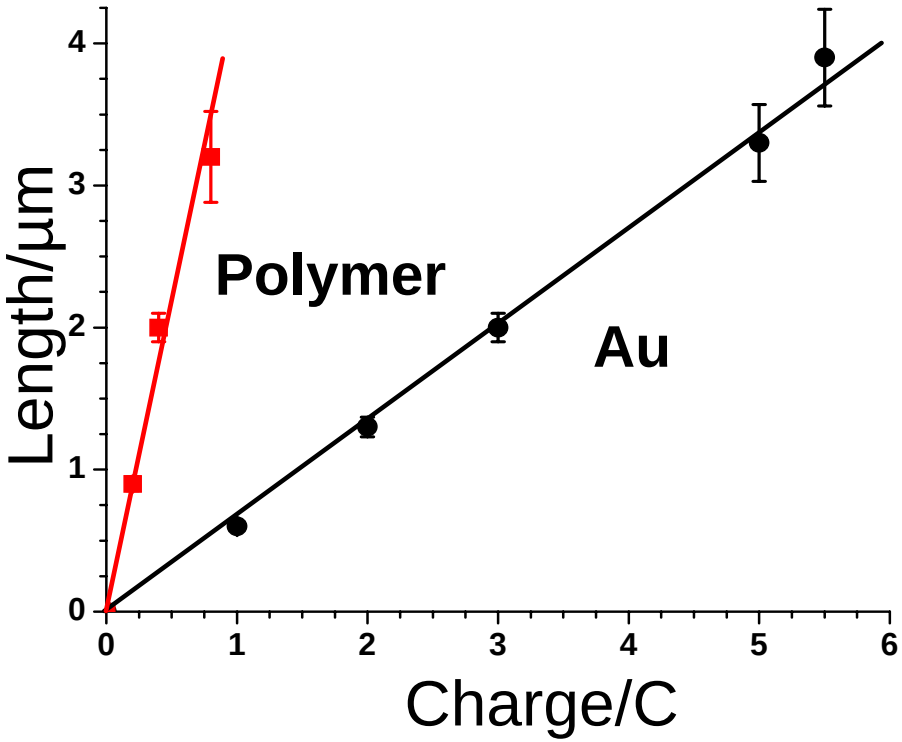


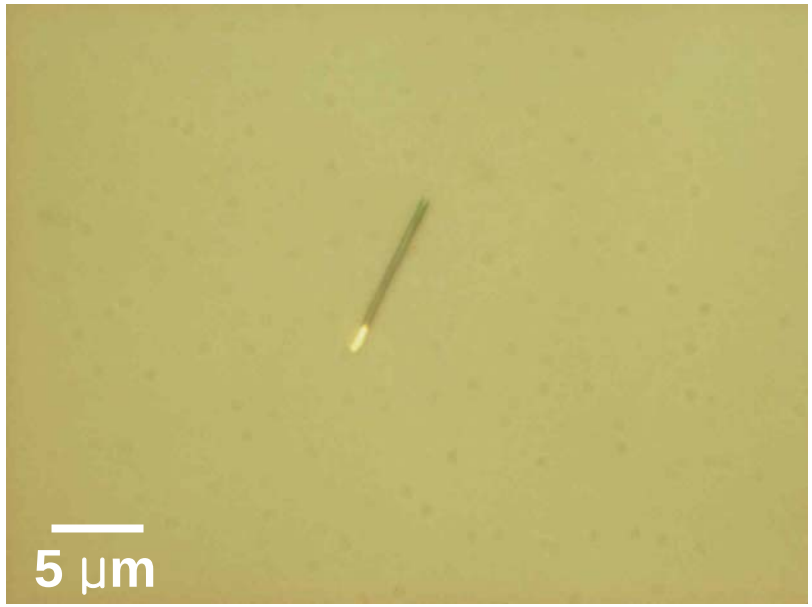



# Rods made from Conducting Polymers

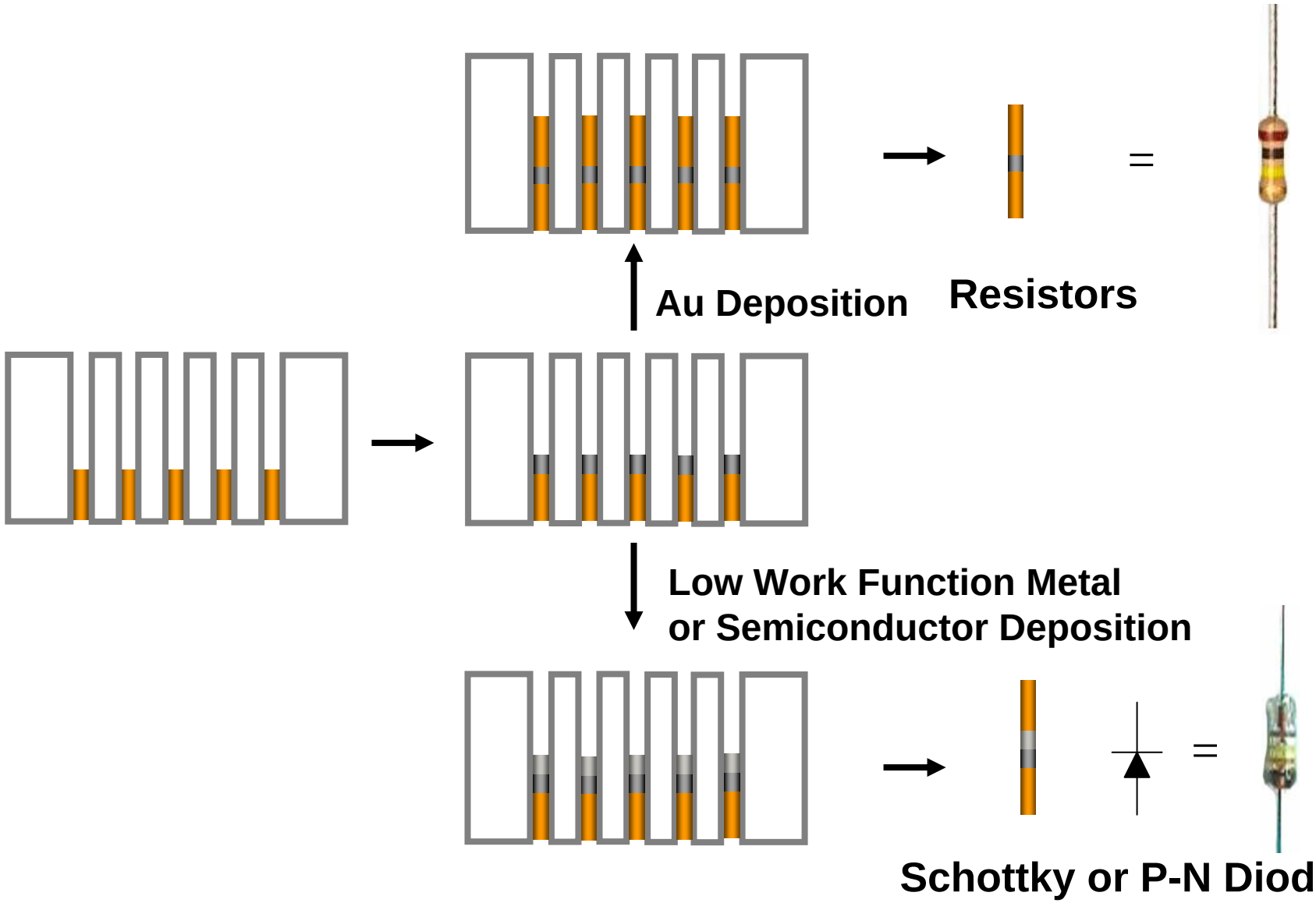




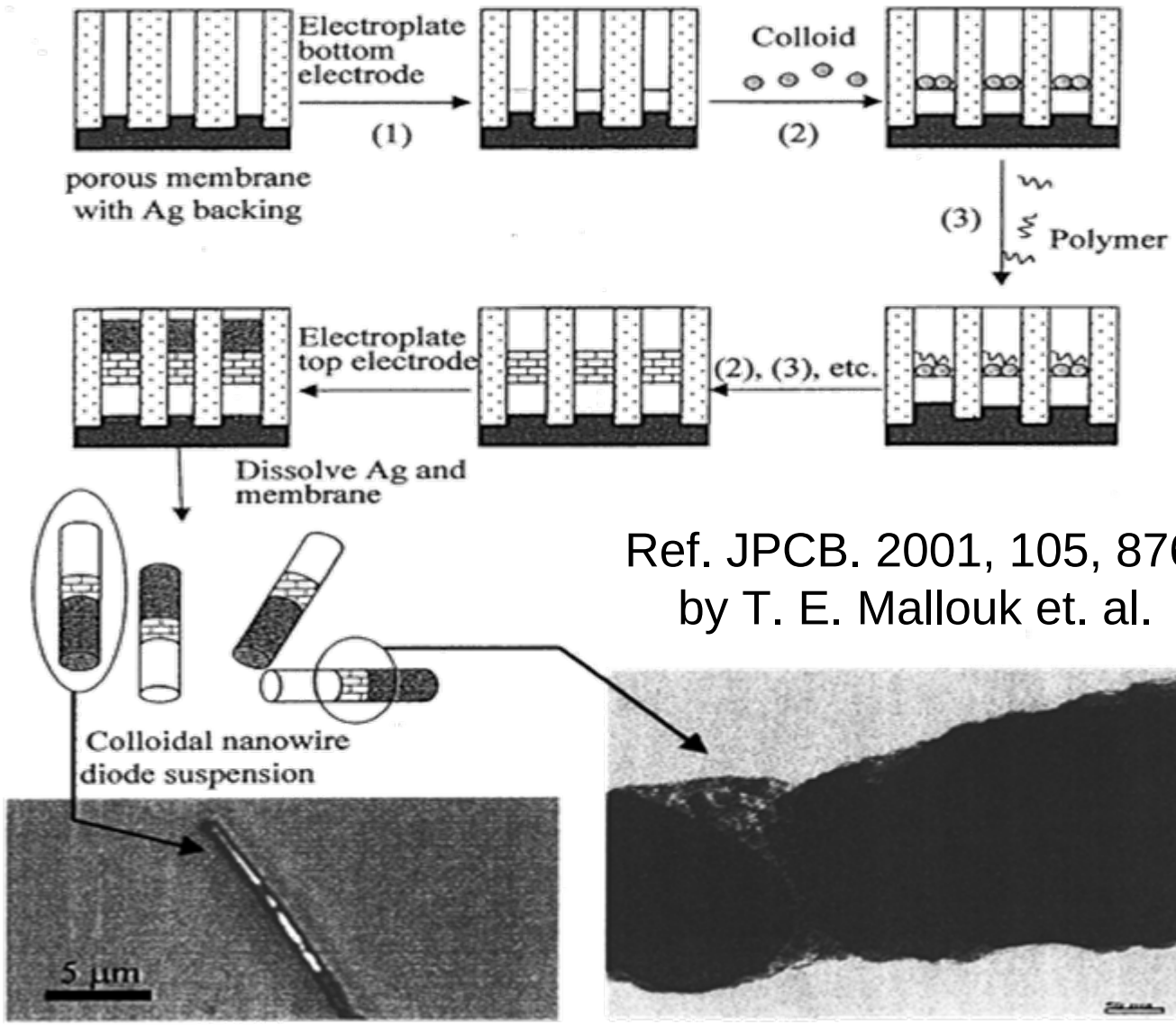



# Nanoresistors & Nanodiodes

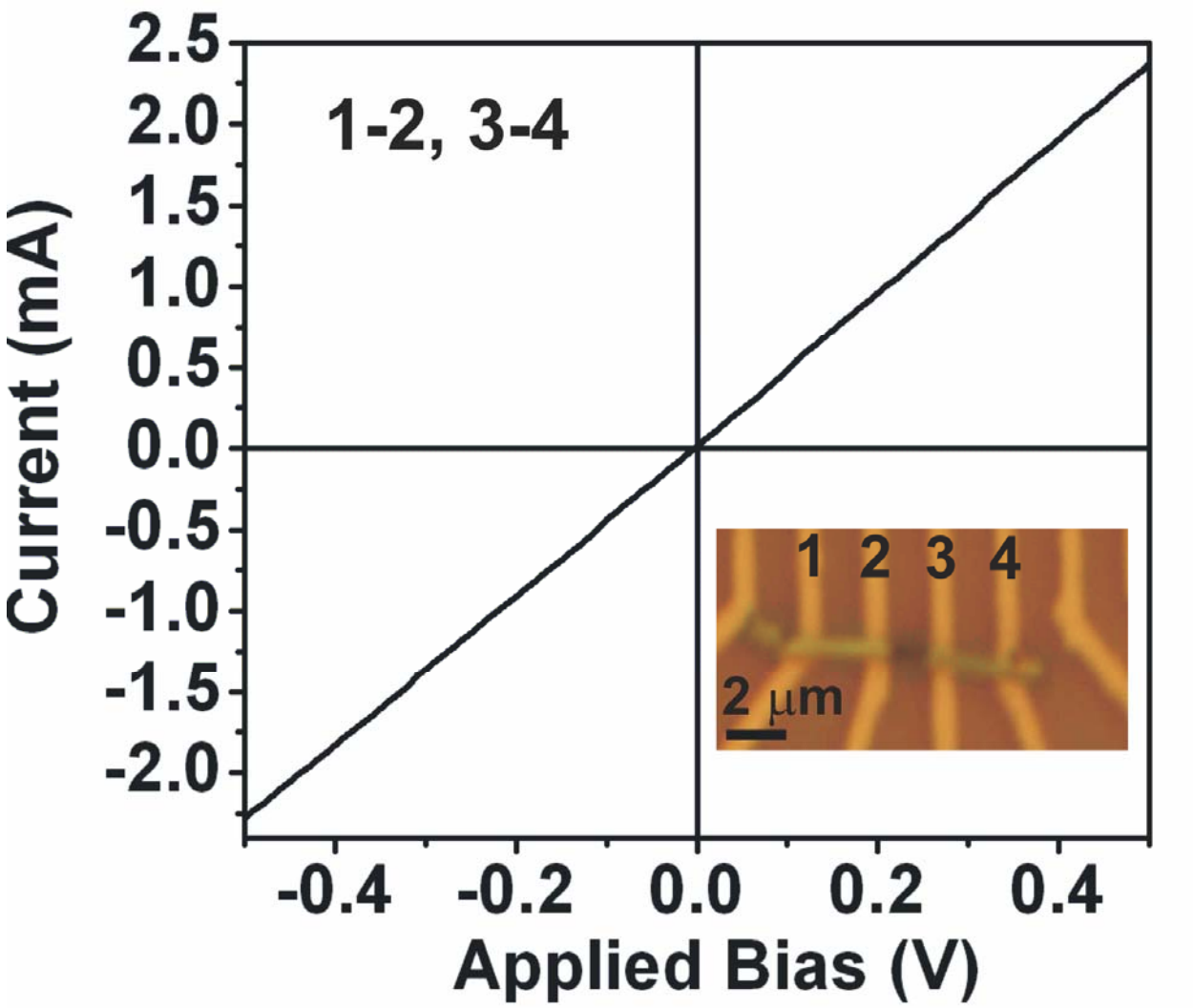


# Layer by Layer Assembly

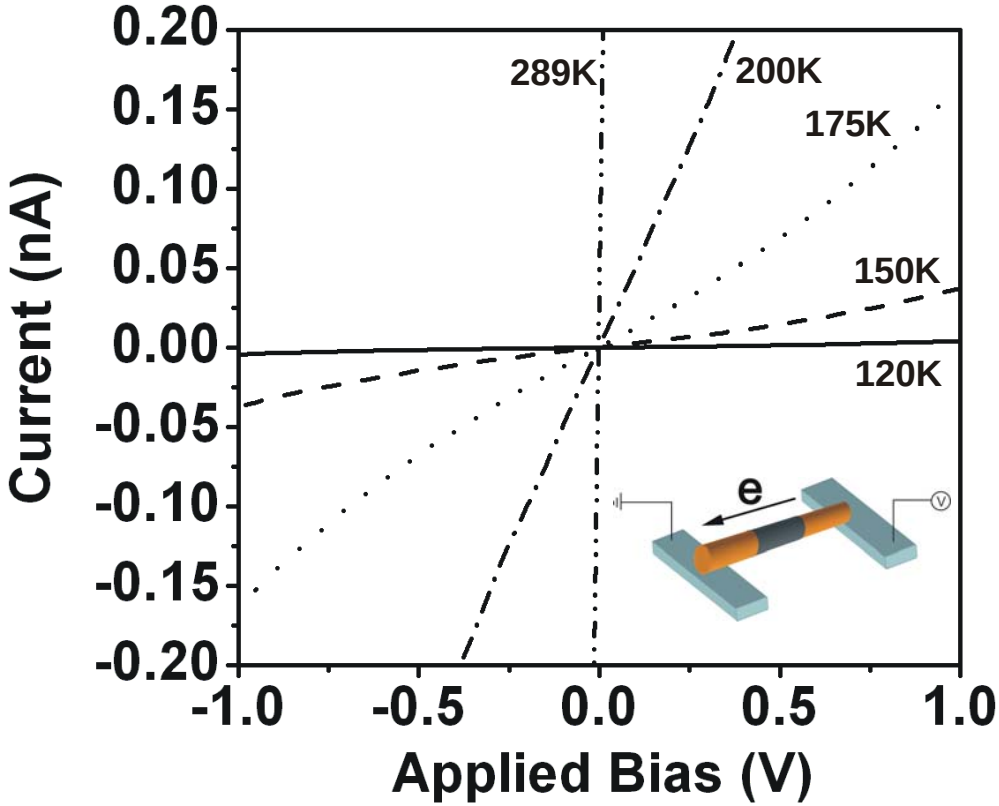


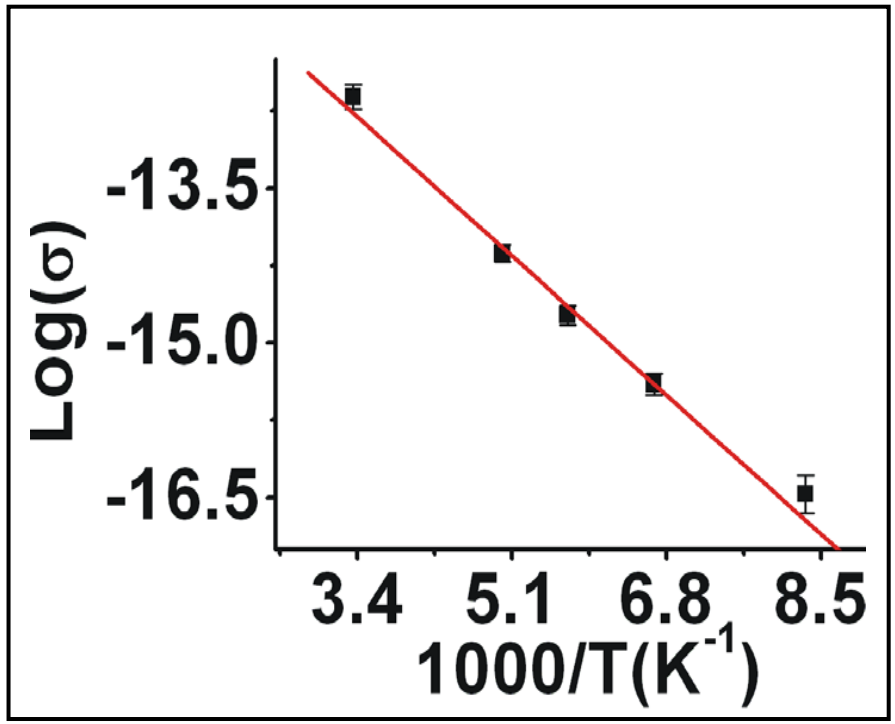

Ref. JPCB. 2001, 105, 8762
by T. E. Mallouk et. al.

# Electrical Transport Measurement



# Electrical Transport Measurement

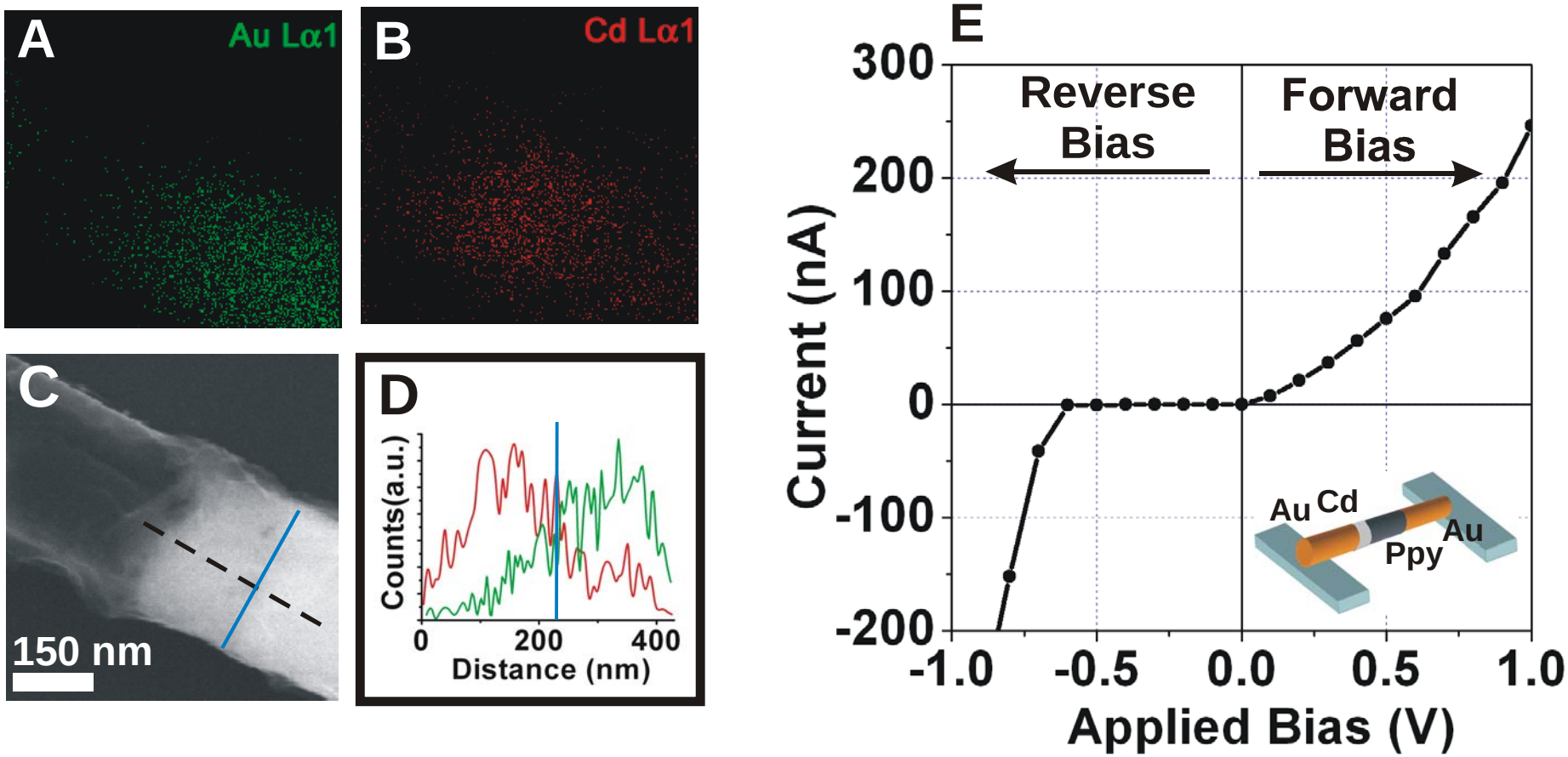



At Room Temperature,
conductivity ~ 3 mS $cm^{-1}$

log σ(T) vs 1/T, showing a linear response
($\sigma = \sigma_0 \exp(-E_a/kT)$,
σ: conductivity, T: temperature)
the activation energy $E_a$ ~ 0.07 eV.

# Au-Ppy-Cd-Au, Schottky Diodes

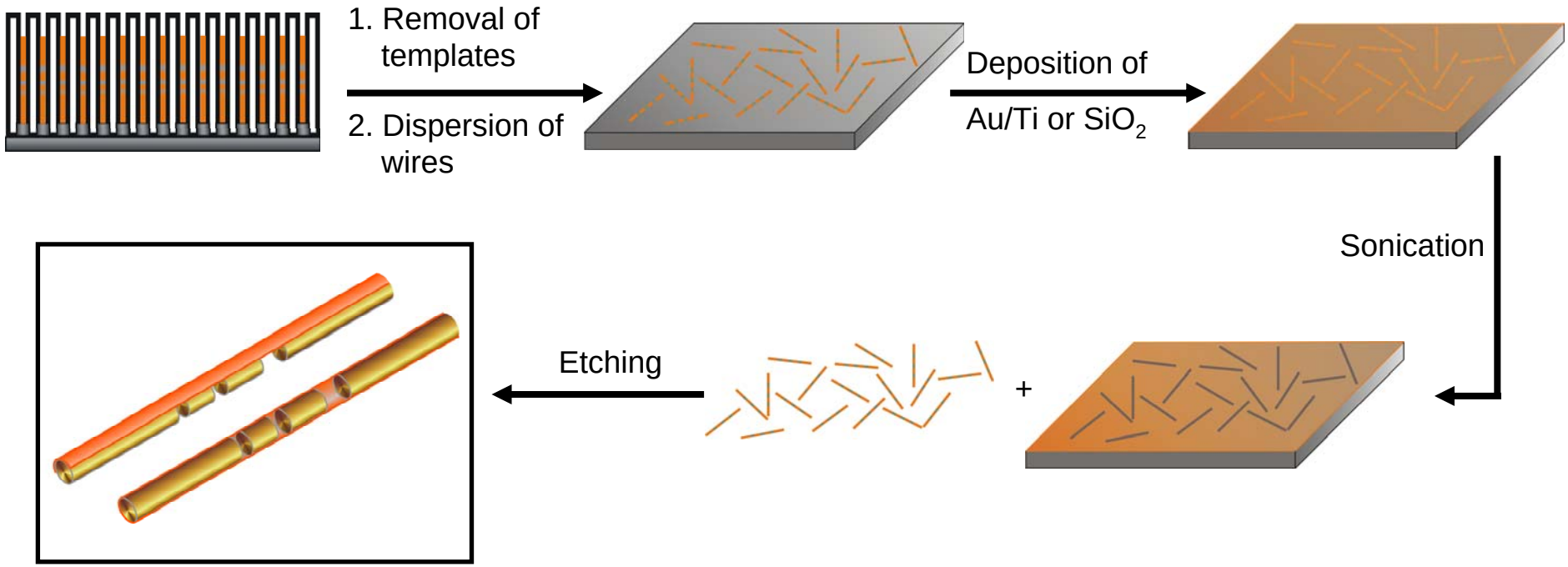


# Conclusions (Part 2)

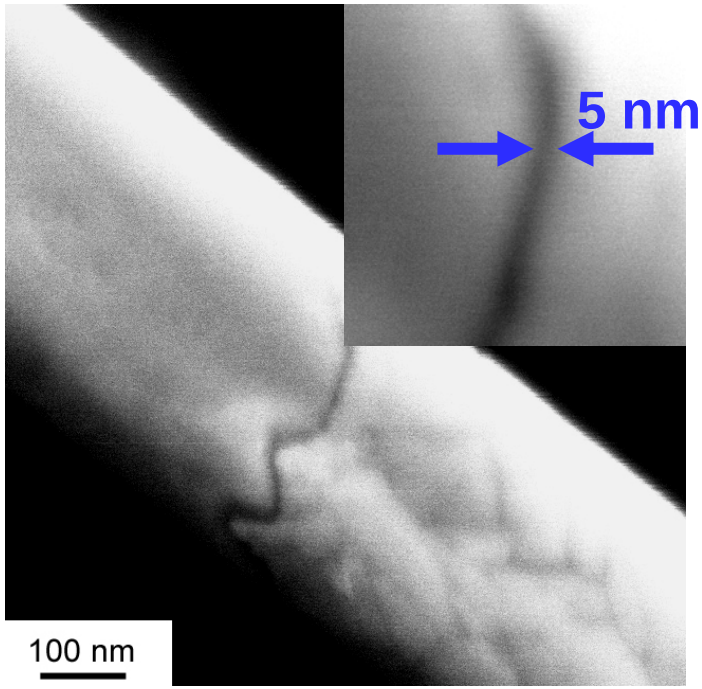
- **The electrochemical deposition provides excellent control over the block length of the metal and organic regions of nanorods.**

- **They show either resistor or diode properties depending on their compositions and spatial distribution of the different compositional blocks.**

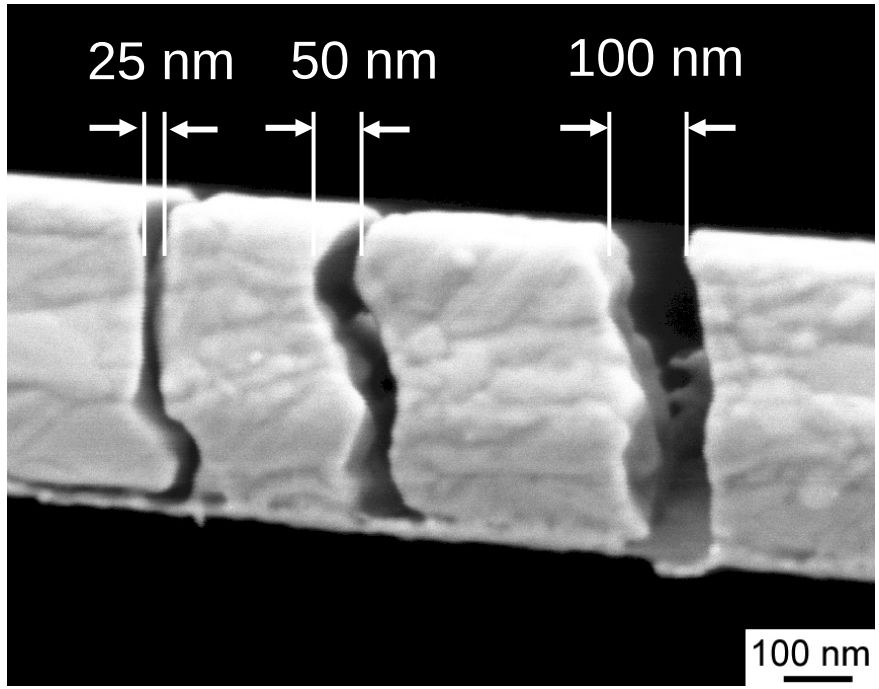
# Nano-Gap Fabrication
# On-Wire Lithography (OWL)



# Zoomed-in SEM Images of Wires

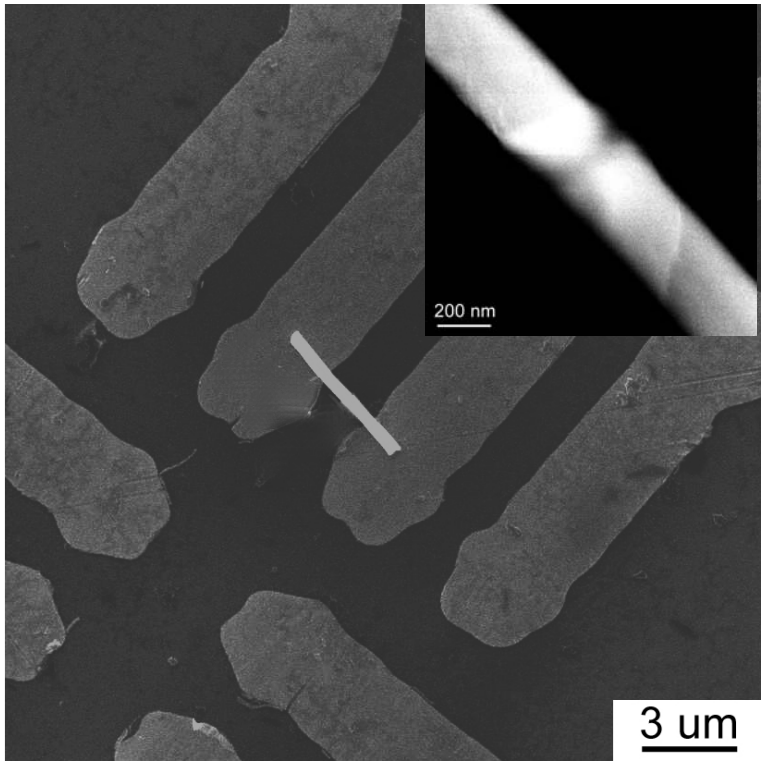



Lowest limit ~ 5 nm
(at current stage)

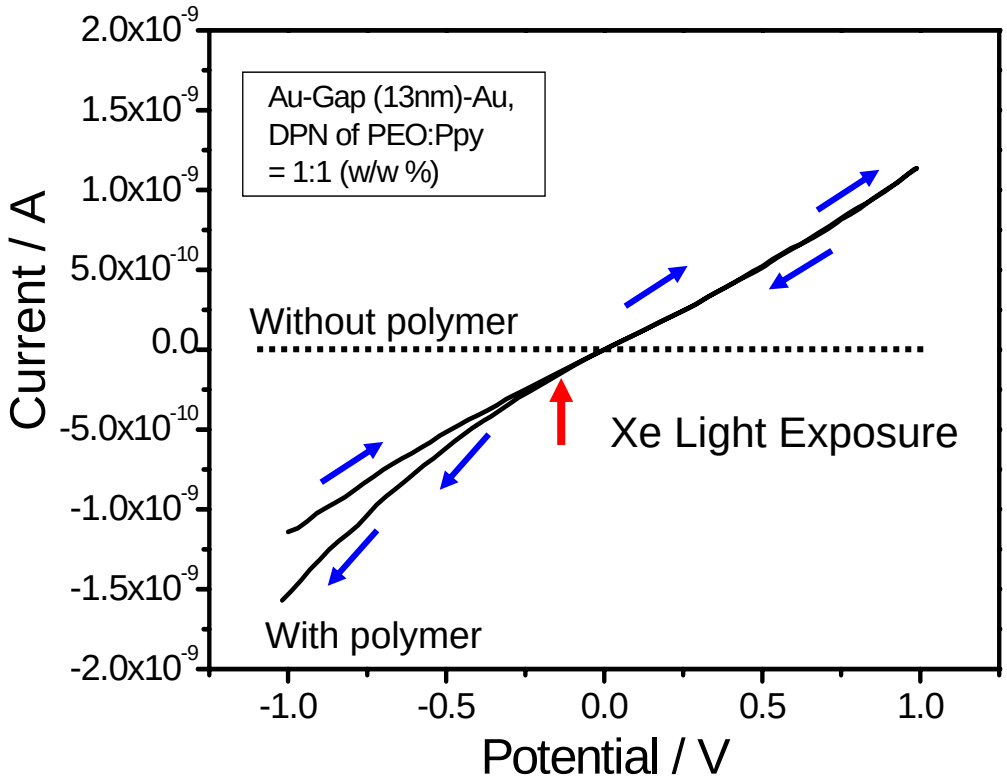



Zoomed-in Image with Au/Ti coating, after chemical etching of Ag blocks.

# Photo-Sensitive DPN Patterns at the Gap

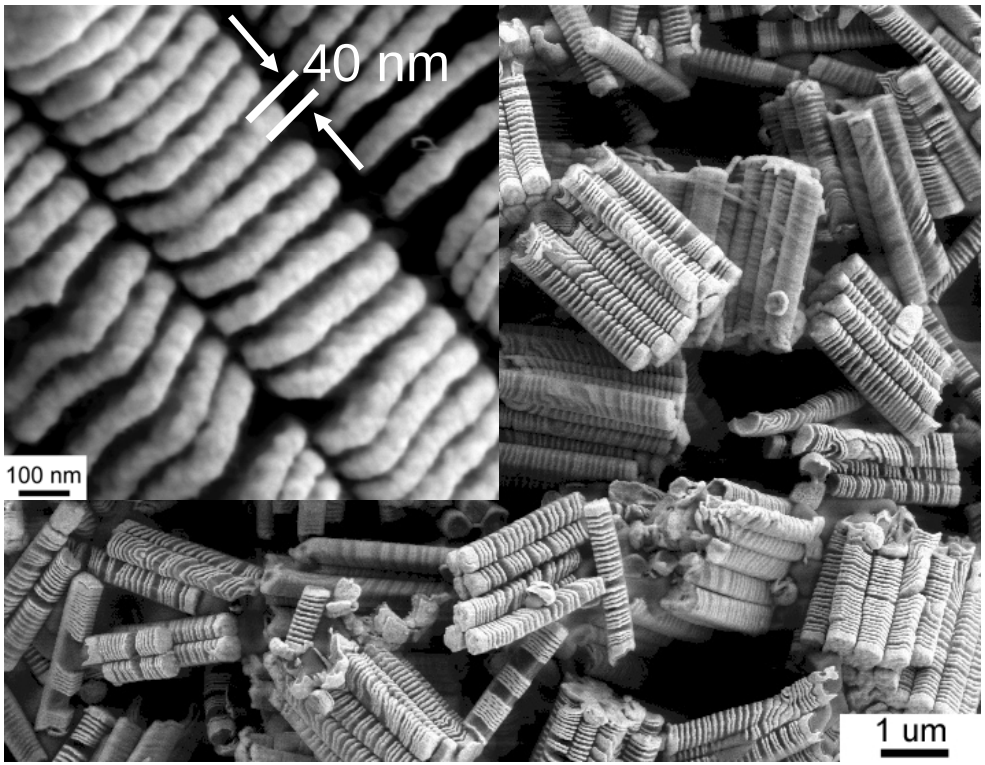



SEM Image of wire on micorelectrodes after DPN of a mixture of PEO & Ppy

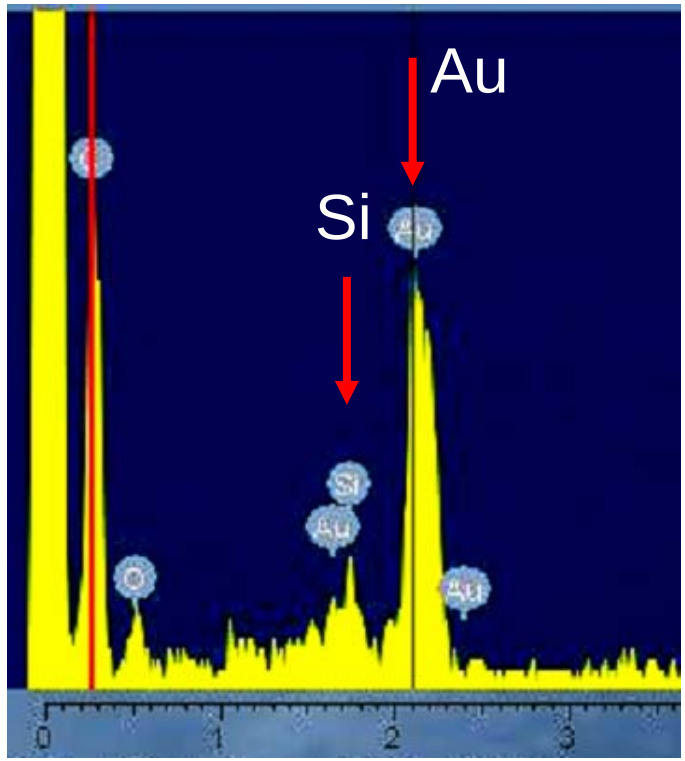



Scanned starting from –1.0 V to +1.0 V, Xe Light was shined on the gap at –0.1 V on the way back

# SEM Image and EDS of Disk Arrays




SEM Images of Nano-Disk Arrays
after Si Deposition



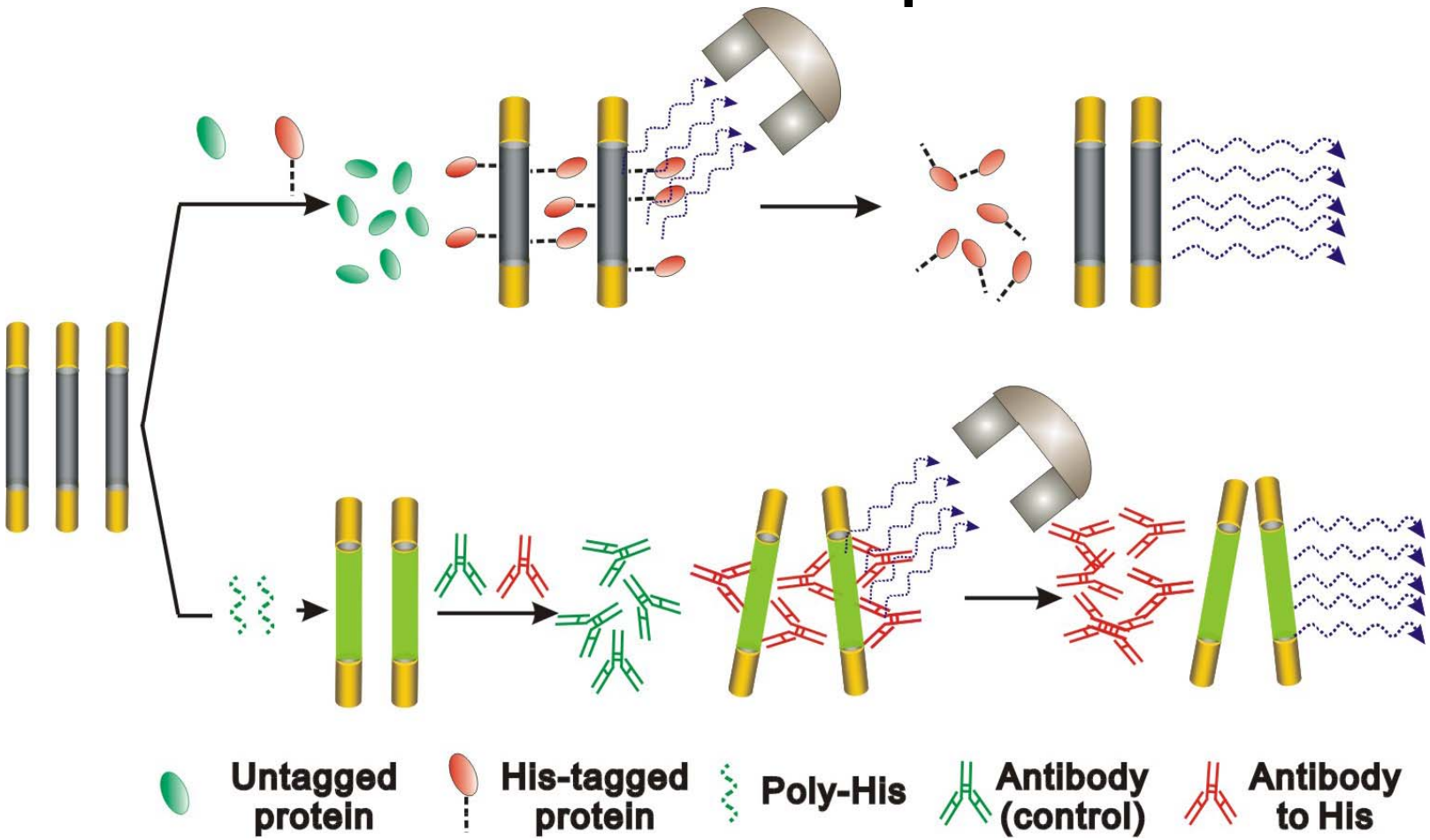

EDS of Nano-Disk Arrays
after Si Deposition and Ag Etching

# Conclusions (Part 3)

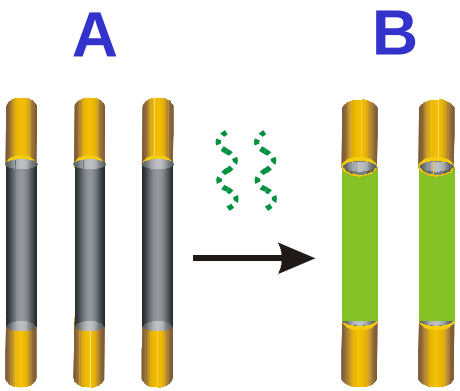
- **The electrochemical deposition and selective etching provide excellent control over metal block length and nano gap distance in nanorods.**

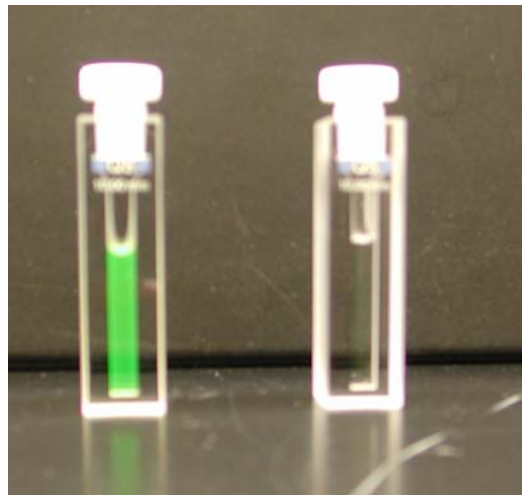
- **They show potential application in molecular electronics and we demonstated “proof-of-concenpt” experiment with and without conducting polymer at the gap.**

# Multicomponent Magnetic Nanorods for Biomolecular Separations



# Affinity of Poly-His to Ni Blocks of Au-Ni-Au Nanorods



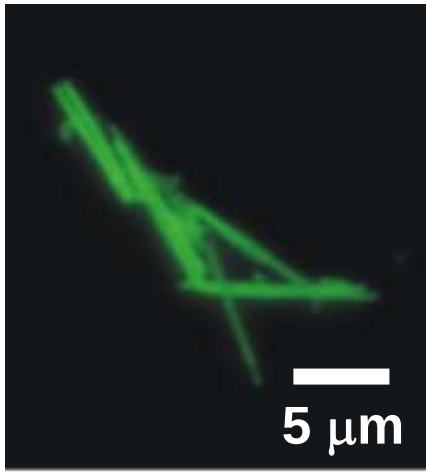



A B

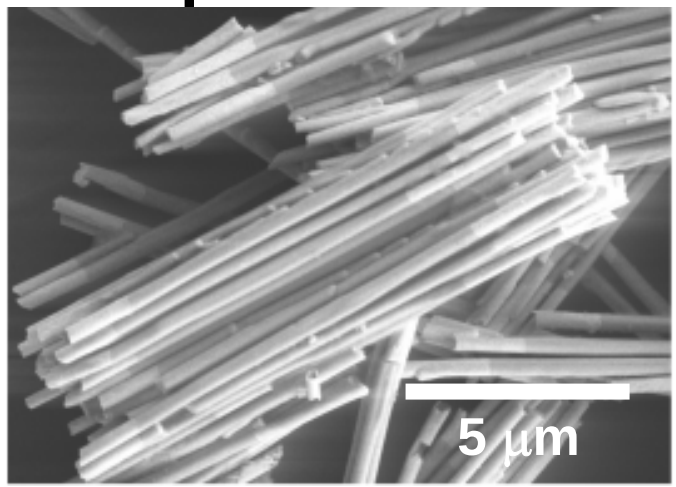
~ $4 \times 10^9$ Nanorods

# Multicomponent Magnetic Nanorods for Biomolecular Separations

A

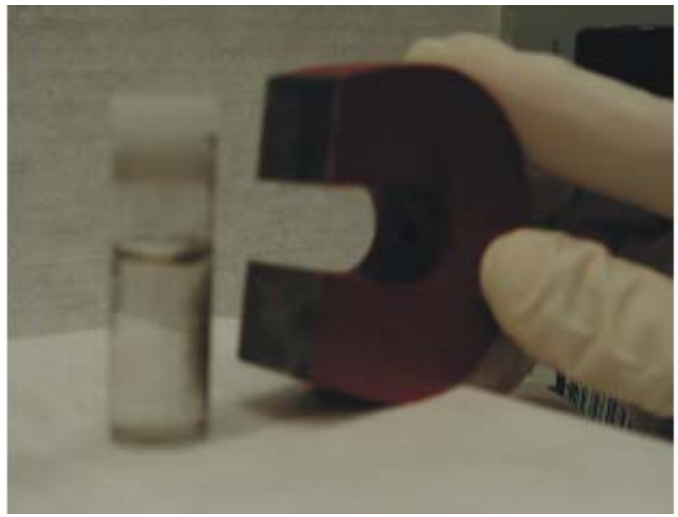



B

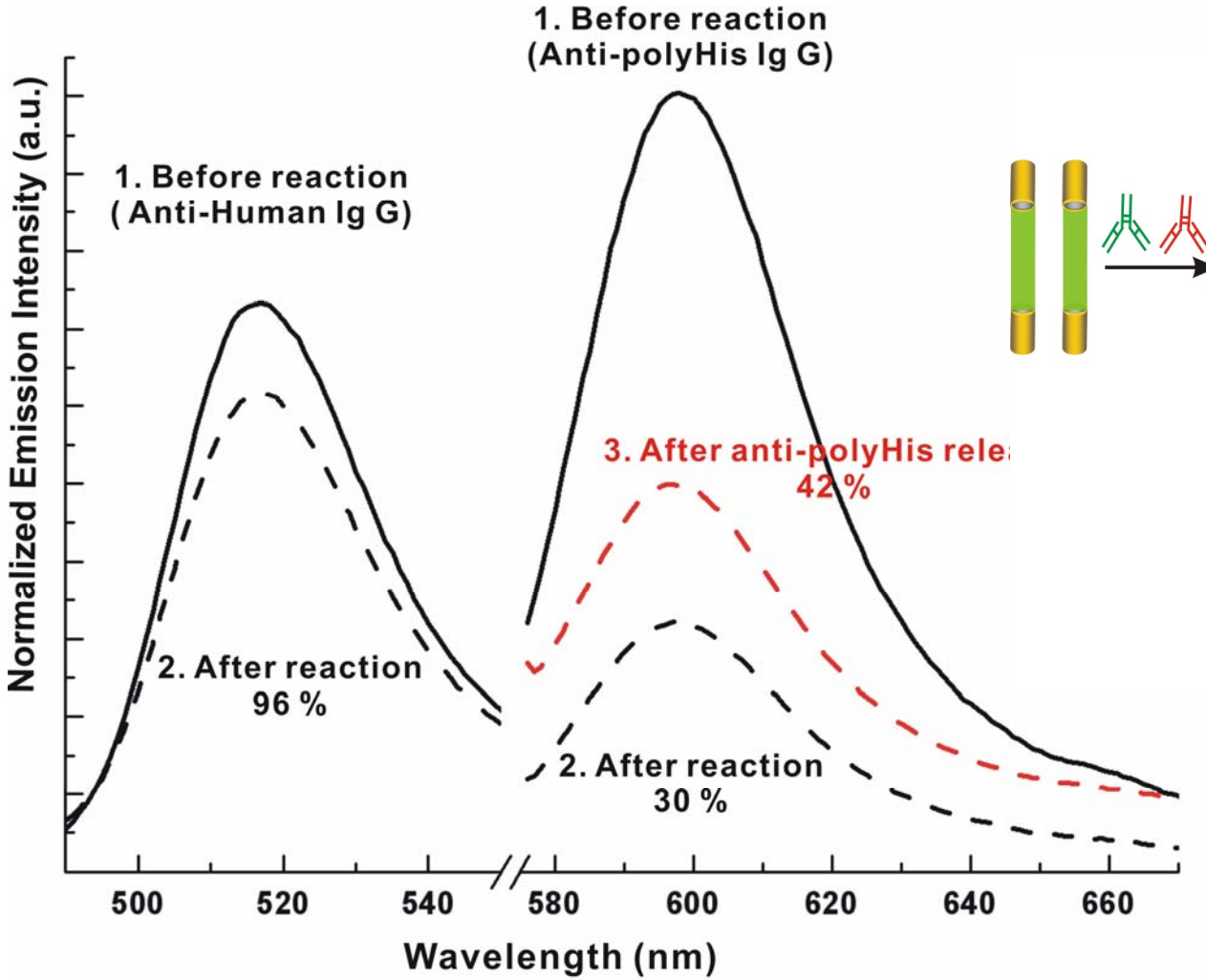


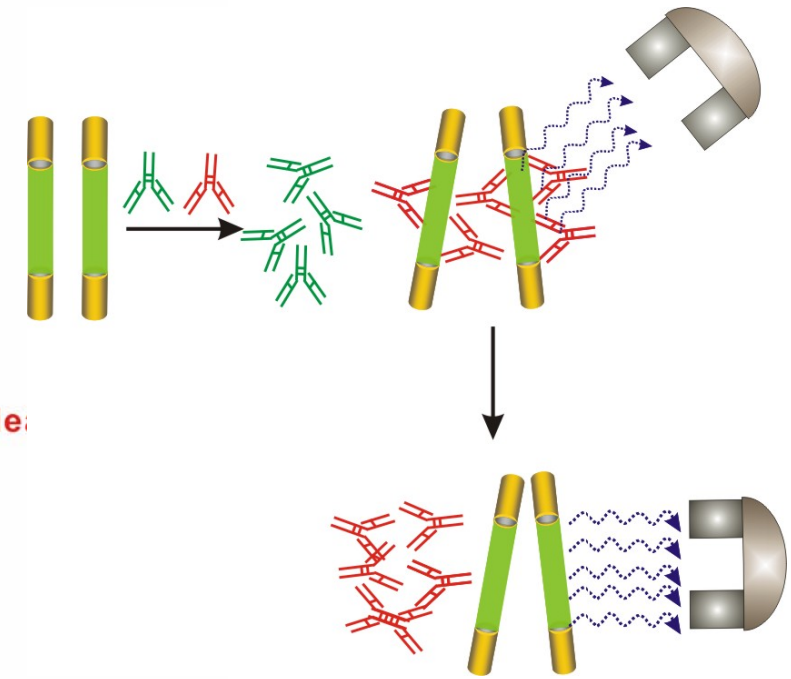

C

D

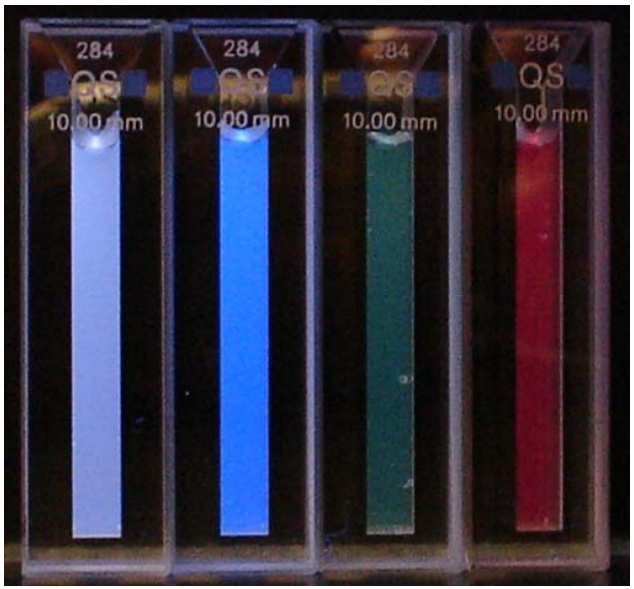


# Anti-PolyHis Ig G Antibody Separation by Au-Ni-Au Nanorods



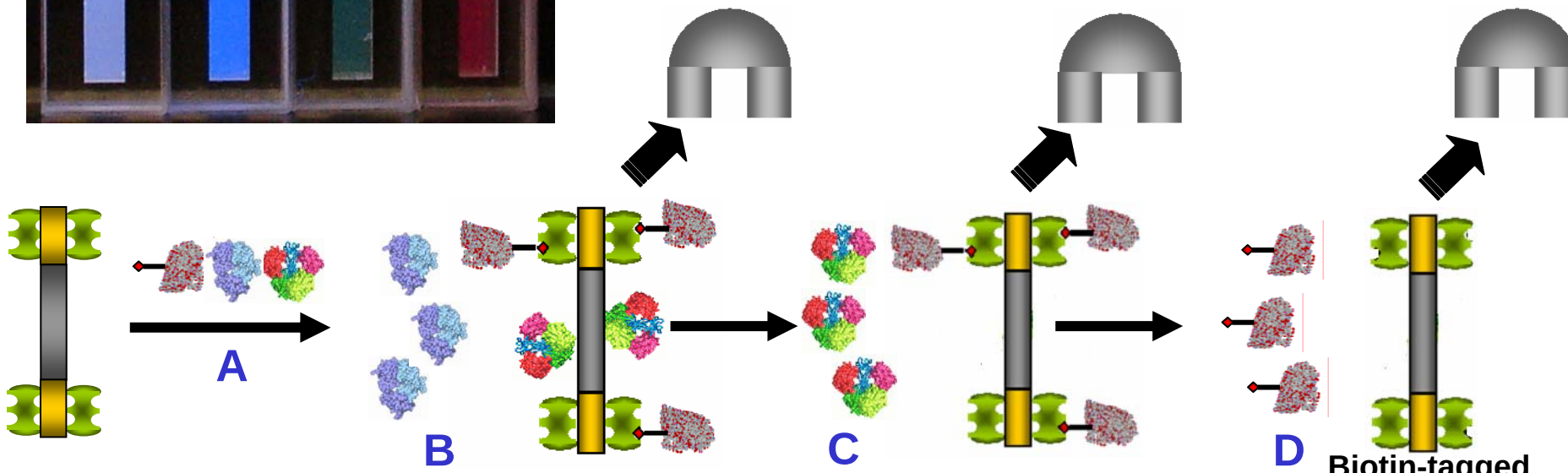



# Multi-Component Separation




Dye color

- Nitrostreptavidin
- nontagged protein (protein A)
- Histidine tagged protein (ubiquitin)
- Biotin tagged protein (BSA)



# Conclusions (Part 4)

- Multicomponent metal nanorods have several advantages (e.g. stability and modification).
- Multiblock nanorods can be used for separation of various proteins by exploiting the chemical and physical properties of these nanostructures.
- The nanorods provide increased surface area and are a pseudo-homogeneous system, increasing the efficiency of the target binding and separation process.

# Acknowledgements

Purdue University (West Lafayette), Prof. Michael J. Weaver

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