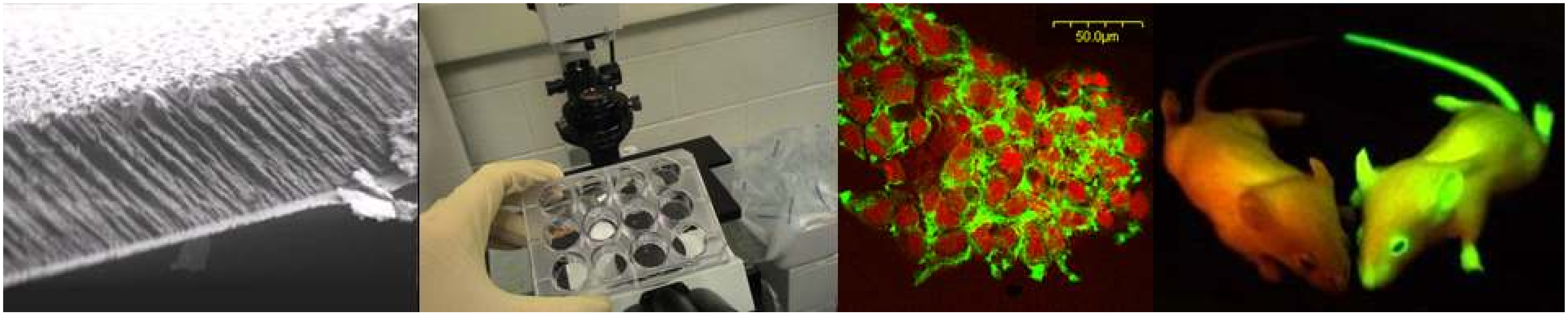


FUNCTIONAL NANOSTRUCTURED POLYMER-METAL INTERFACES

Melik C. Demirel, PhD

Pearce Assistant Professor of Engineering
Materials Research Institute & Huck Life Institute of Sciences
Pennsylvania State University

July 23, 2008

Acknowledgement

Funding

- Young Investigator Award, Department of Defense
- Office of Naval Research
- Penn State University
- Institute for Complex Adaptive Matter (ICAM)
- Johnson and Johnson (USA)
- Kisco International (Japan)
- BD International (USA)

Polymer / Boeing

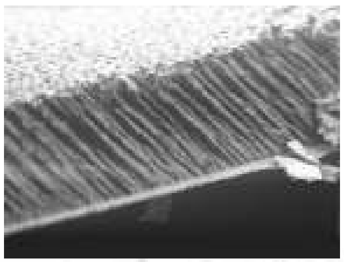
Polymers are needed in energy, sustainability, clean water, health care, informatics, defense and security.

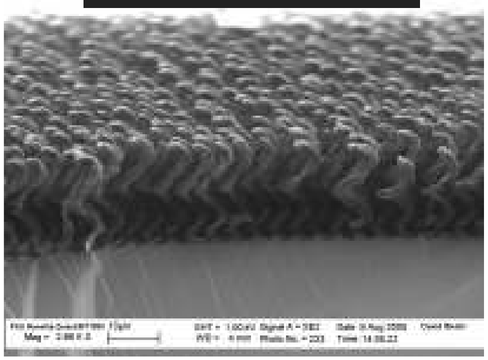
Boeing 787:
This new plane is 50% by weight and 80% by volume polymer-based composite

Boeing 787

Nanofiber Polymers

OBLIQUE ANGLE POLYMERIZATION

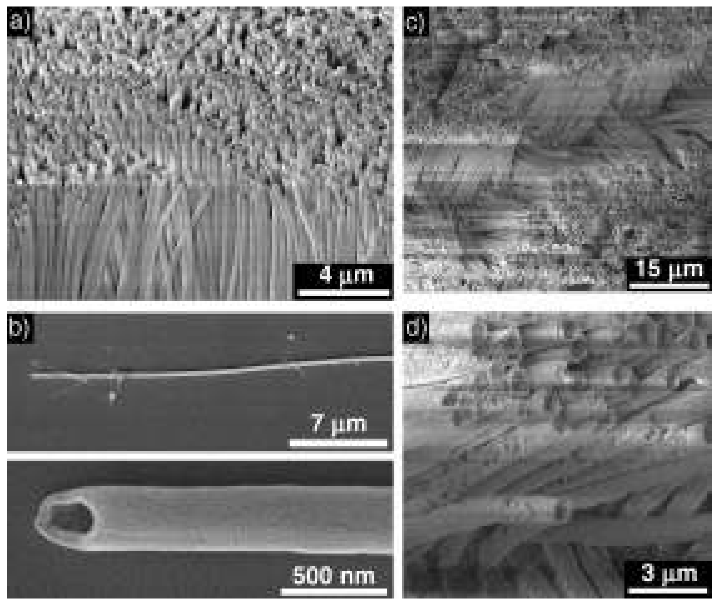




Demirel *et al*, Langmuir, 2007

Bottom-up

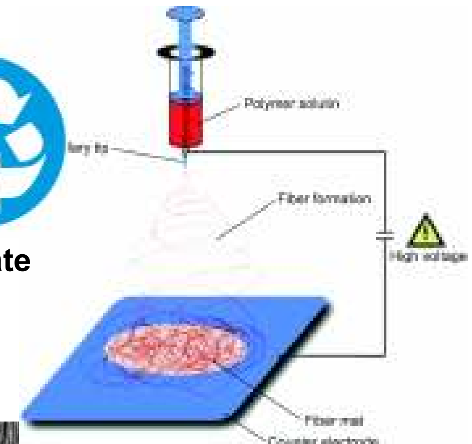
TEMPLATE BASED WETTING

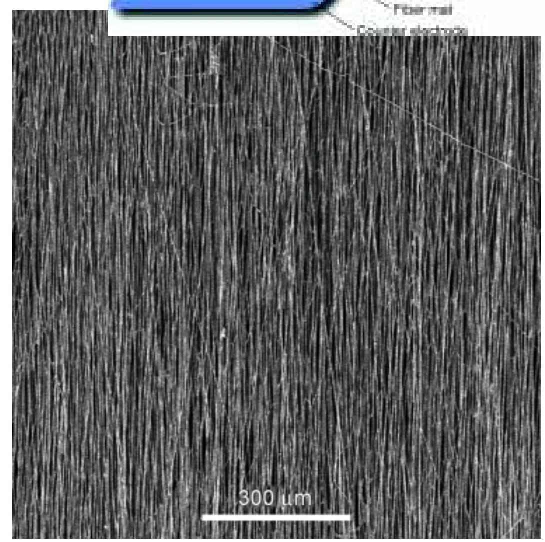


M. Steinhart,et al., Adv. Mater. 2003, 15, 706.

Top-Down

rotate





ELECTROSPINNING

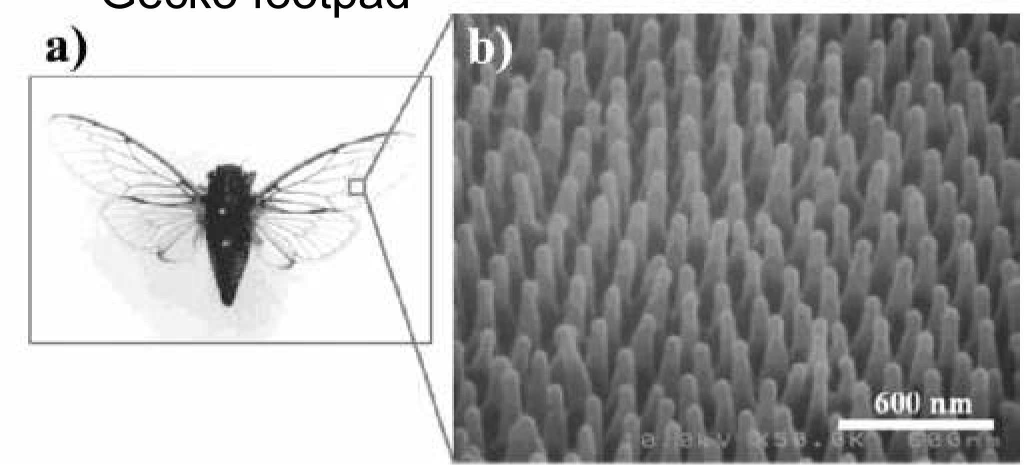
J. A. Matthews, et al. Biomacromolecules 2002, 3, 232 – 238.

Demirel Lab 2008

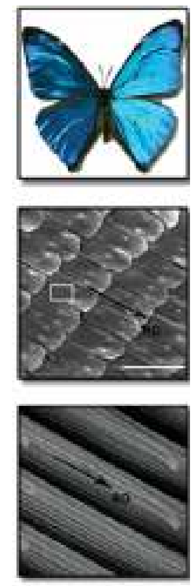
Similar Architectures in Nature

100-200nm structures with high aspect ratio (micron scale length)

Gecko footpad



Duck Feather

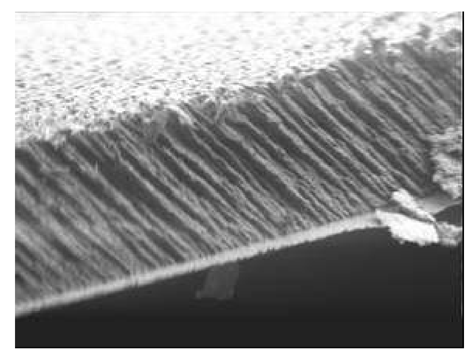


Butterfly wings

Demirel Lab 2008

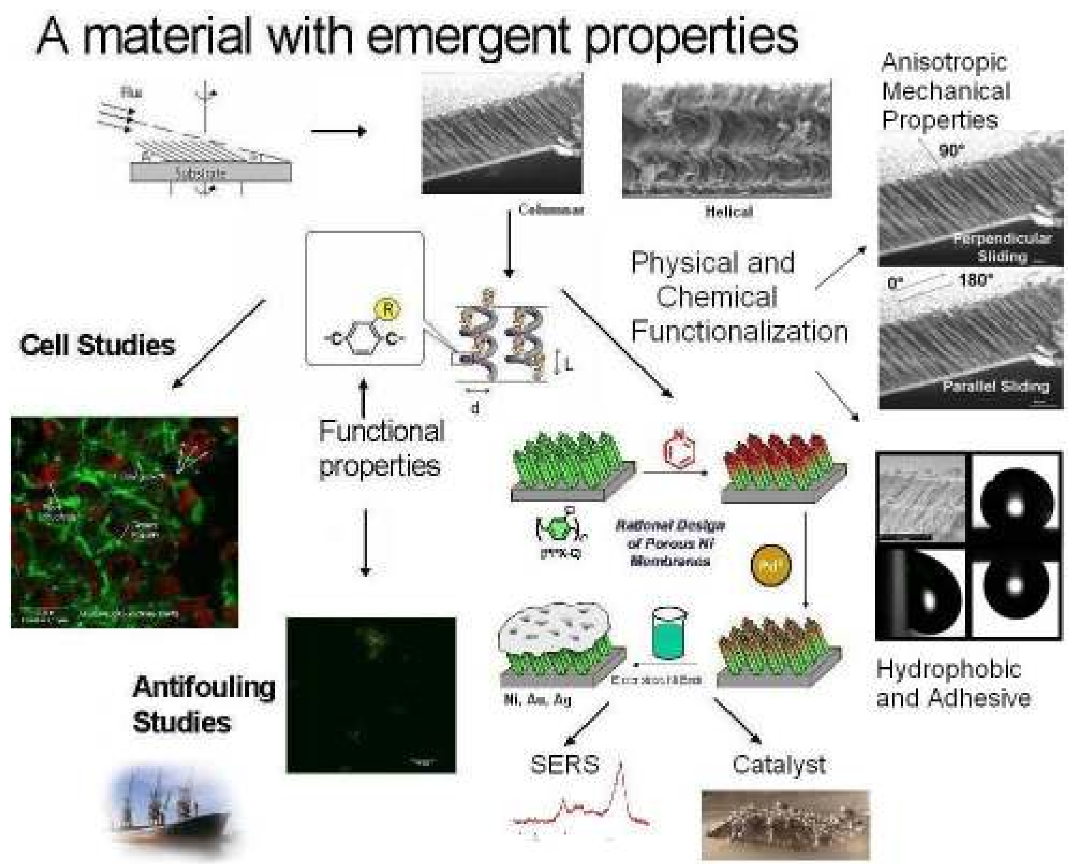
Cicada orni wings

Structured Polymers



OBJECTIVE

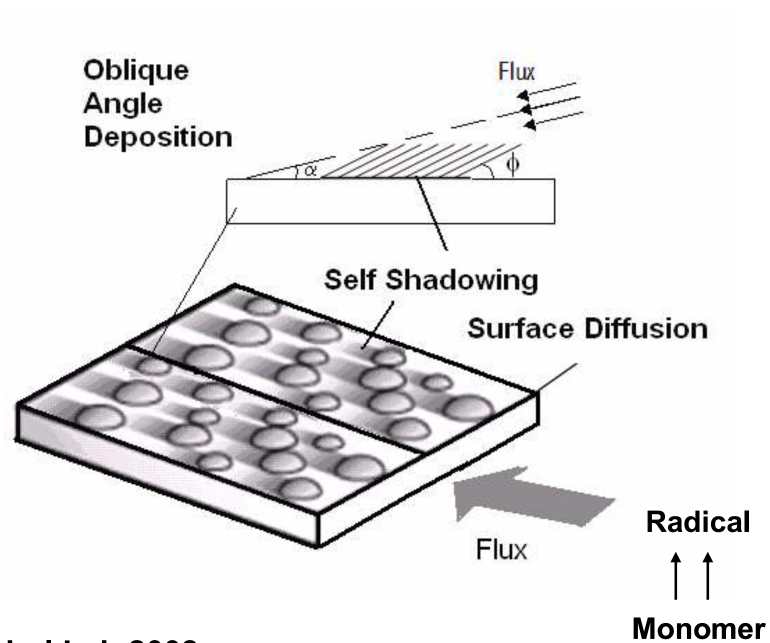
We are creating nanostructured polymers with controlled physicochemical properties, such as ***mechanical properties, structure (morphology) and chemistry*** for applications in the area of nanostructured surface coatings



TECHNICAL APPROACH

Our method is a bottom-up process based on oblique angle polymerization developed by our group.

In this process, monomer vapors produced by pyrolysis of chemically functionalized precurcors are directed at an oblique angle towards a surface to initiate structured polymer growth.



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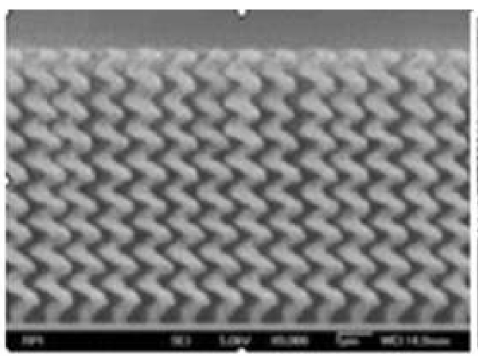
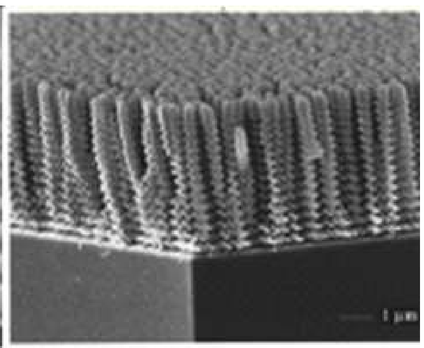
Metallic, ceramic, and organic nanostructured films

Short history of oblique angle deposition
Kundt 1876—first columnar film
Hansma 1950—first study of morphology
Messier, Lu, Brett ~1990—metallic / ceramic films
Demirel 2005—polymeric films

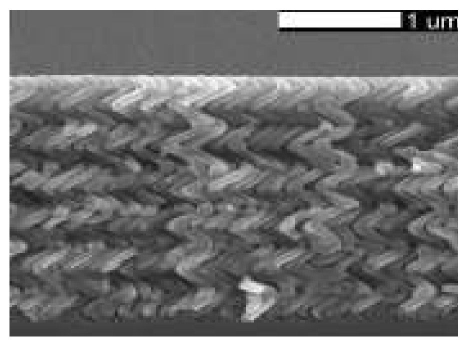
Helical Si
Lu, RPI



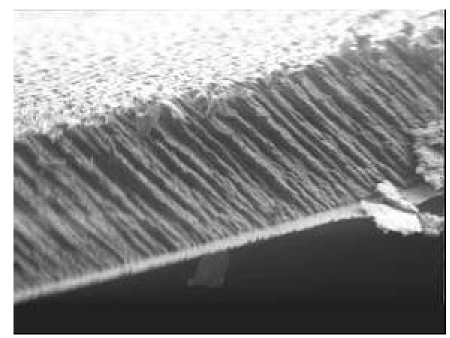
helical Au
Zhao, U. Georgia



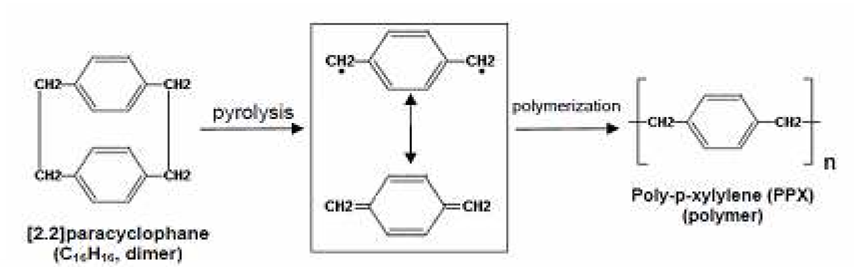
helical Alq3
Brett, U. Alberta



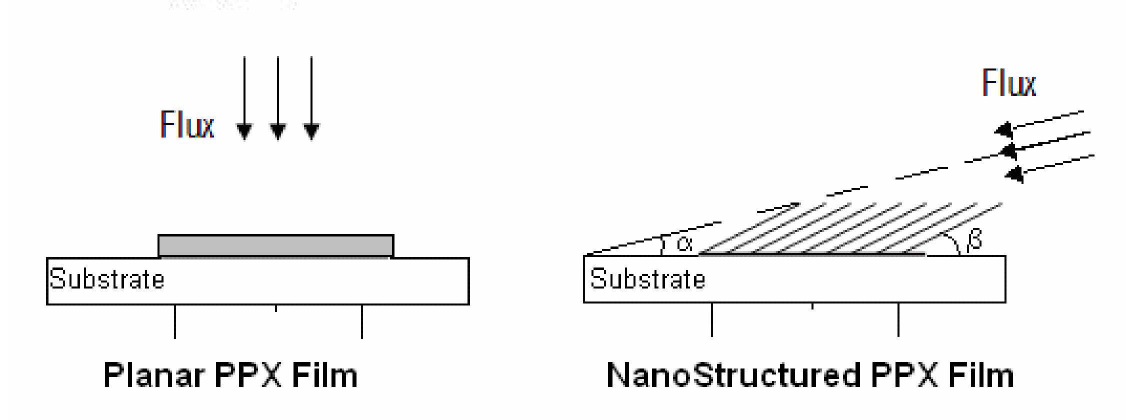
parylene-PPX
Demirel, Penn State



Parylene (PPX) deposition

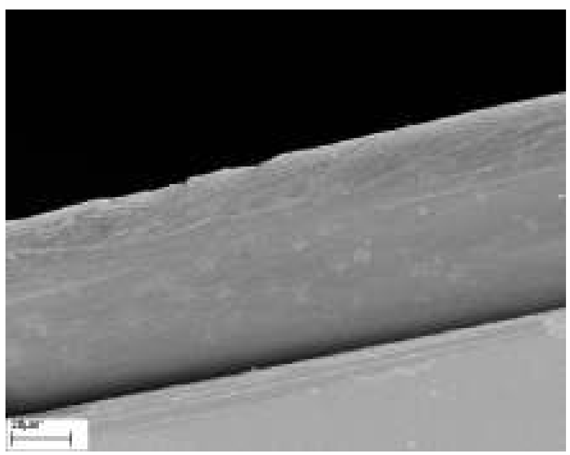


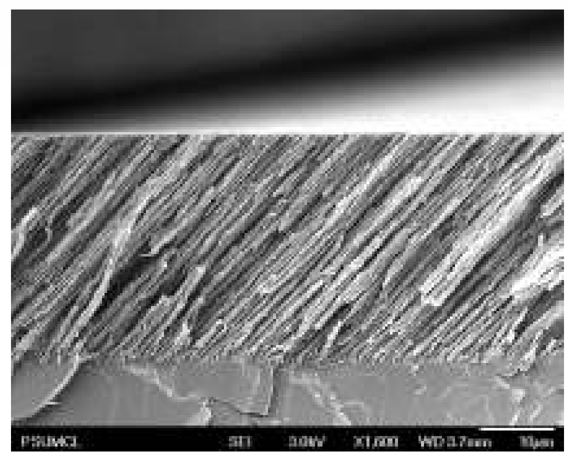
Gorham 1960



Demirel 2007

Gorham WF. *J Polym Sci Part A-1,* 4(1966), 3027.



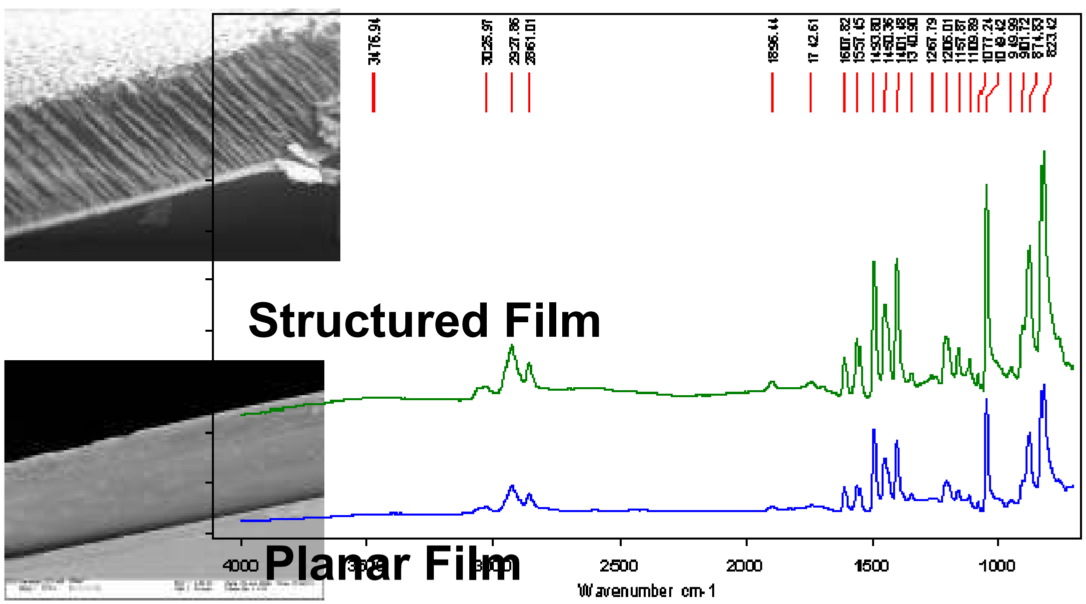


Langmuir, **23** (11), 5861 - 5863, 2007

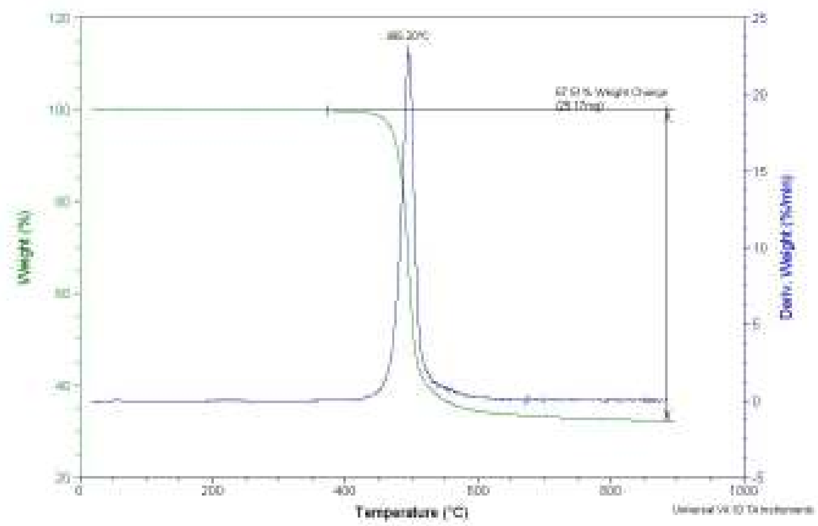
Demirel Lab 2008

Polymer composition doesn’t change

FTIR



TGA

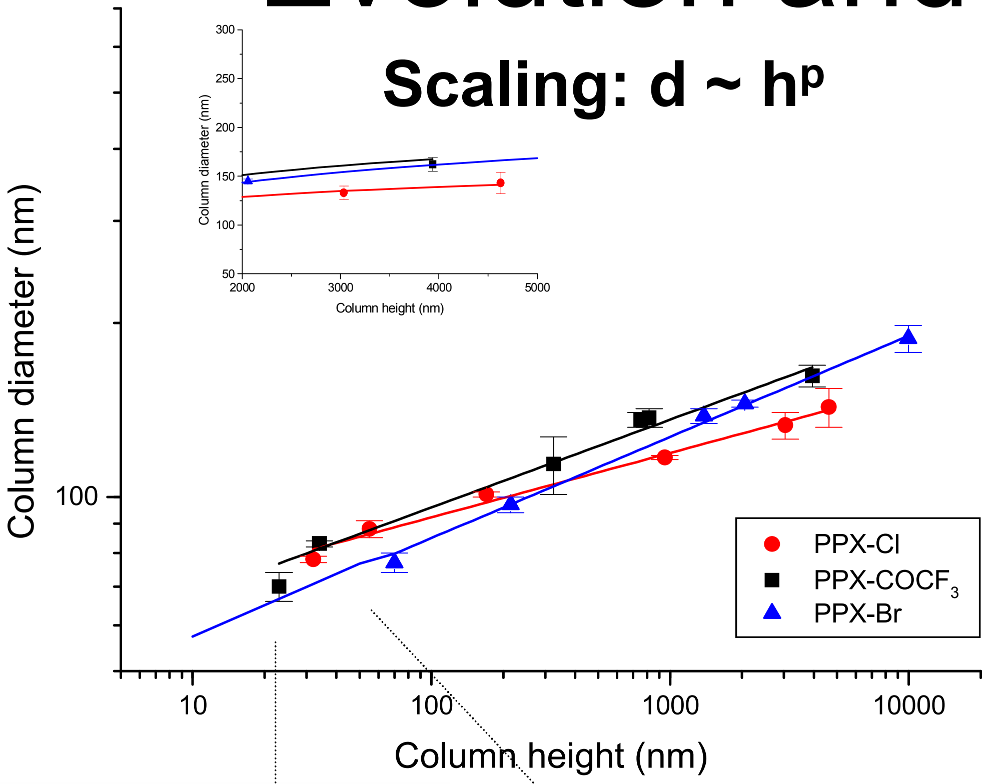


Structured Film

Demirel, M.C., et al. *Langmuir,* **23** (11), 5861 -5863, 2007

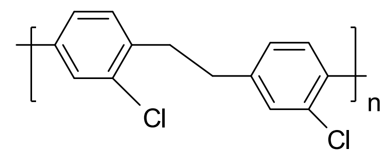
Evolution and Growth

Scaling: d ~ h^p

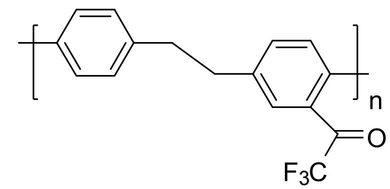


0<p<0.3 high diffusion

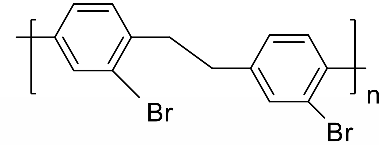
PPX-C ----- p= 0.12

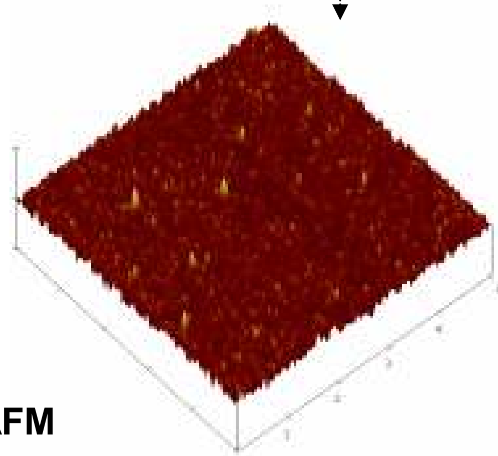


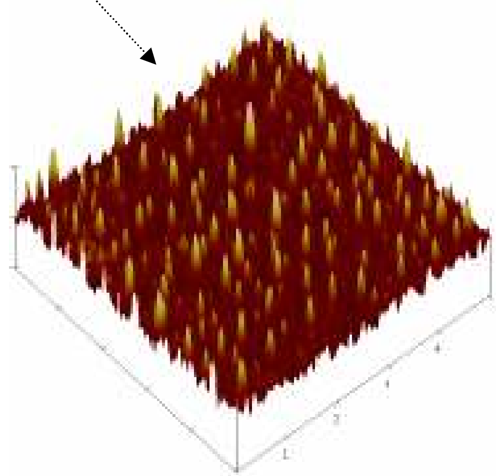
PPX-Br ----- p= 0.17



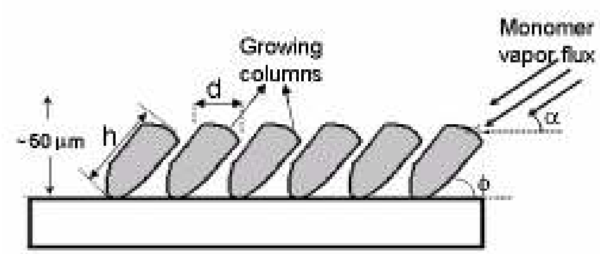
PPX-COCF3 ---- p= 0.20





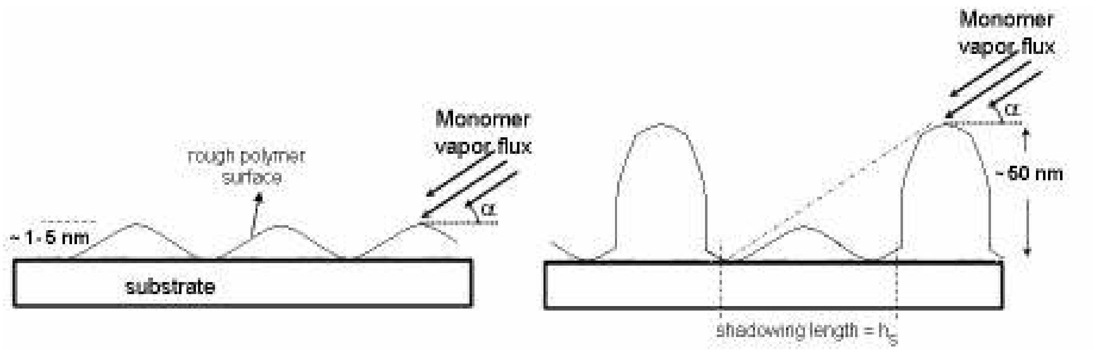


AFM

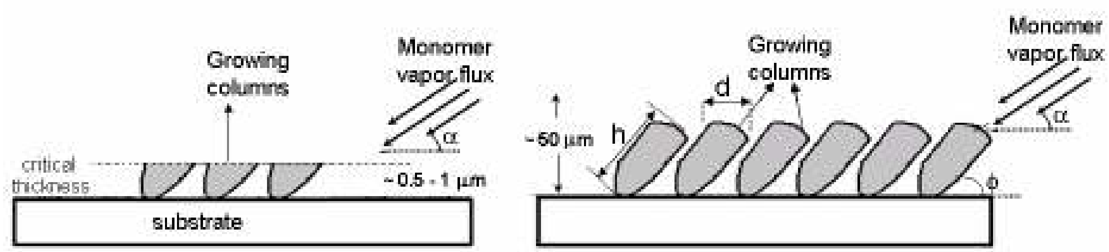


Cetinkaya, M., et al., Journal of Polymer Science, in press, 2007

Growth Model



Roughness is destabilized due to oblique angle

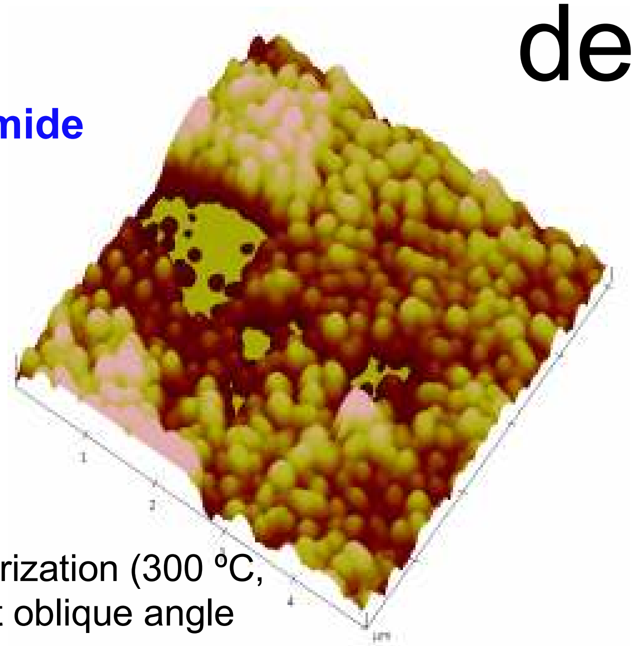


Ballistic Monte Carlo Method

Cetinkaya, M., Malvadkar, N., Demirel, M.C., JOURNAL OF POLYMER SCIENCE PART B: POLYMER PHYSICS, Vol. 46, pg 640-648, 2008.

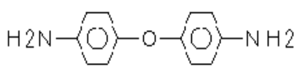
Chemistry: Polyimide and PPV deposition

Polyimide

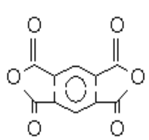


Co-polymerization (300 ºC, 0.1 Torr) at oblique angle

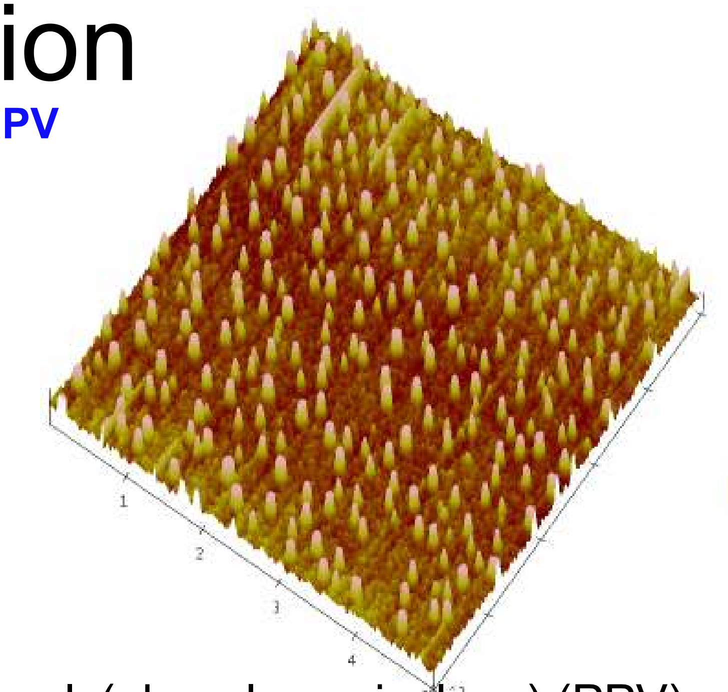
4,4'-DIAMINODIPHENYL ETHER



PYROMELLITIC DIANHYDRIDE

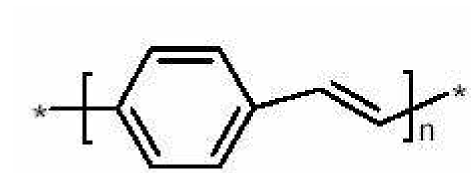


PPV



poly(phenylene vinylene) (PPV)

Polymerization (60 ºC, 0.1 Torr) at oblique angle



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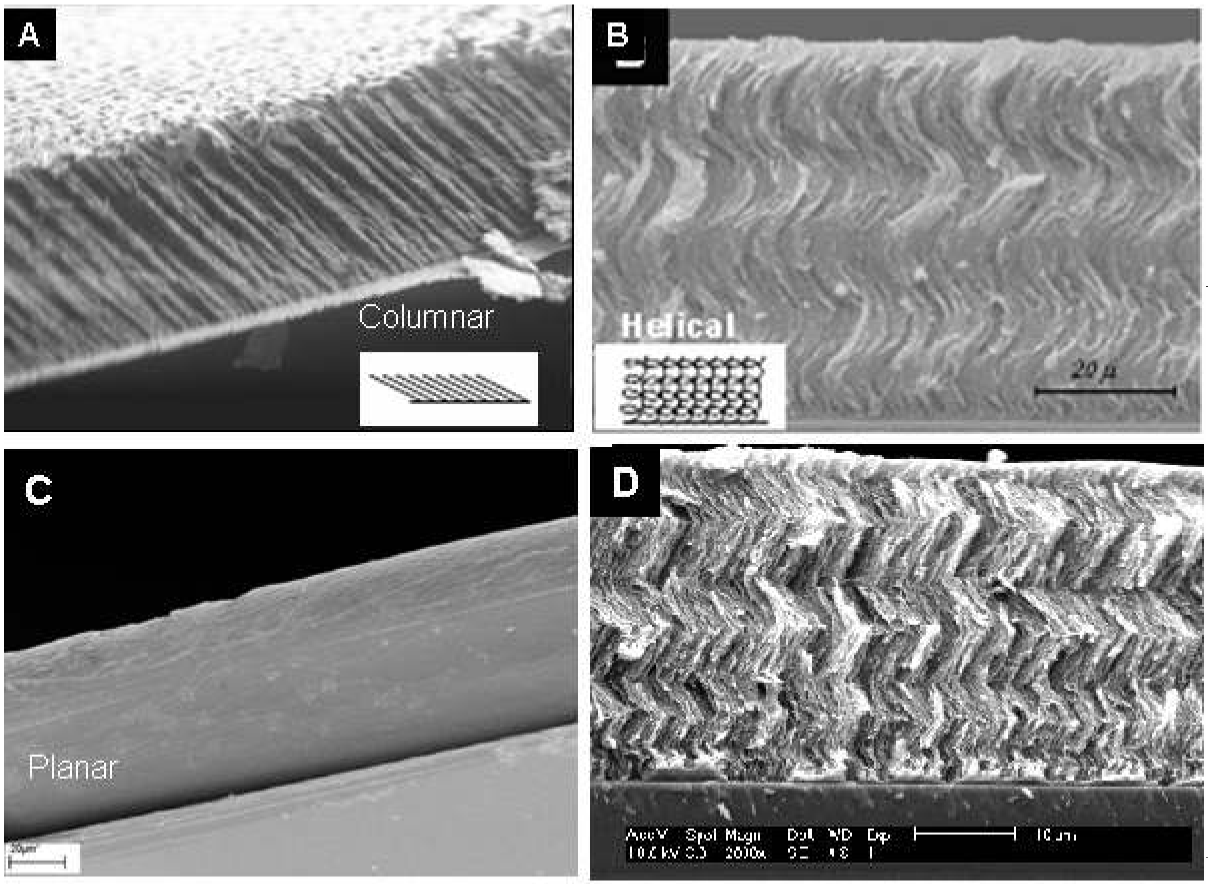
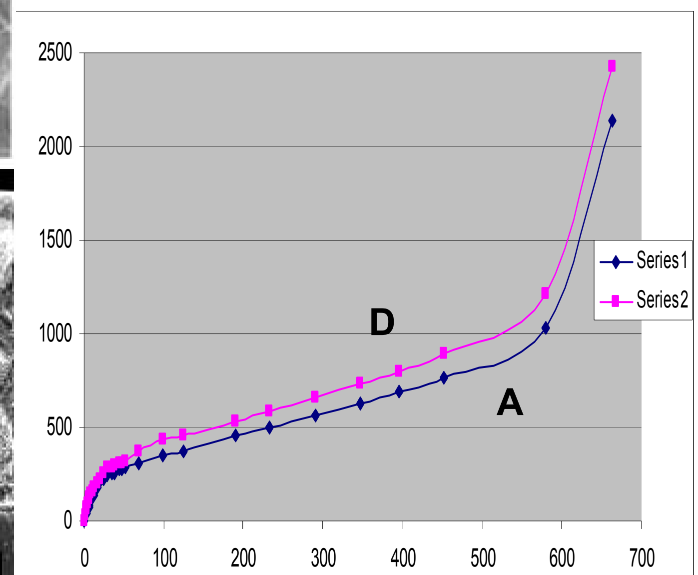
Morphology Control



Porosity is measured by BET/QCM

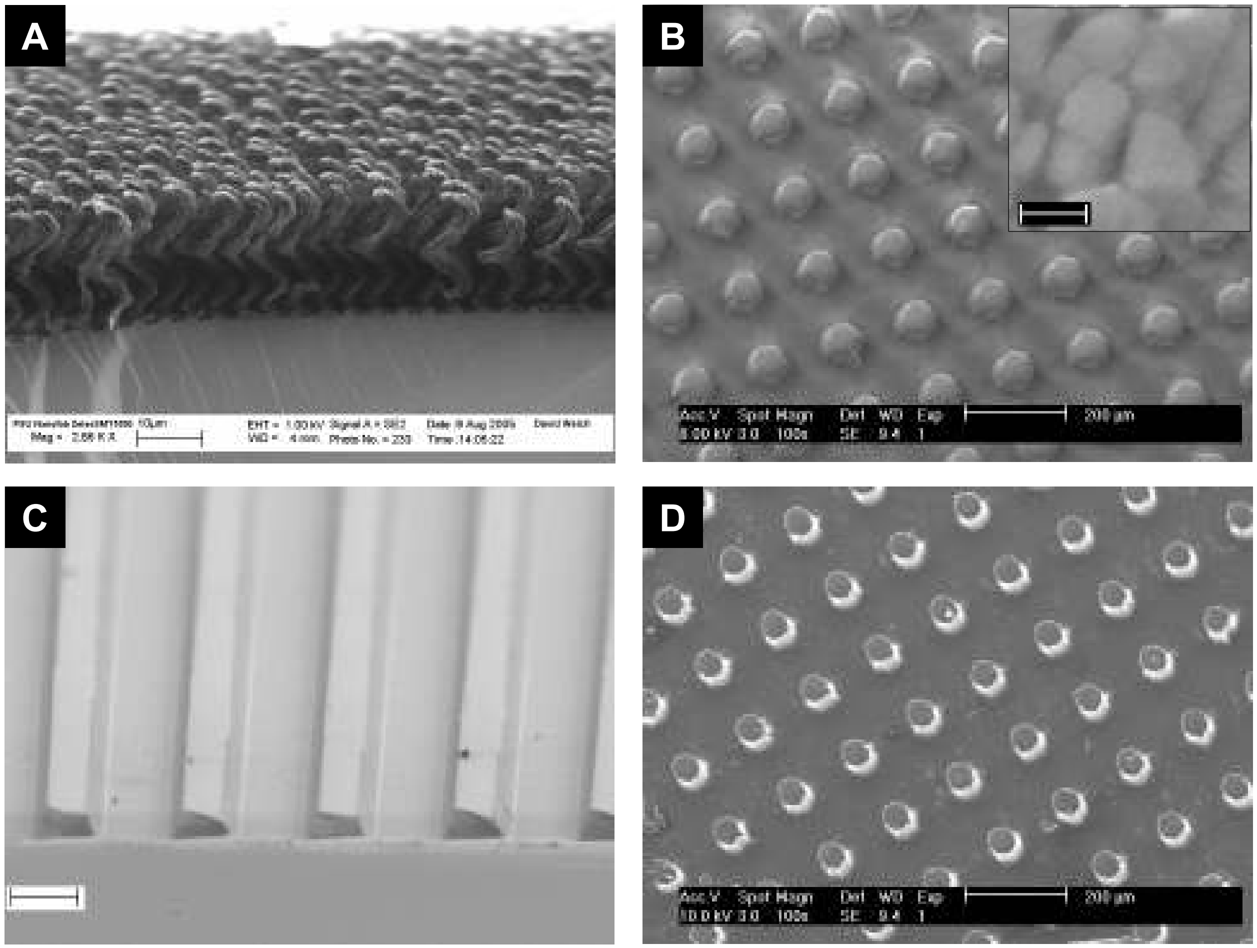


Demirel, M.C., et al. *Langmuir,* **23** (11), 5861 -5863, 2007

Controlling: Topology

After deposition

Before deposition



Si Substrate

PDMS Substrate

Functional Polymer-Metal Interfaces

Ions→metal nano-clusters

OBLIQUE ANGLE POLYMERIZED FILMS (developed by Prof. Demirel)

Vapor→metal nano-clusters

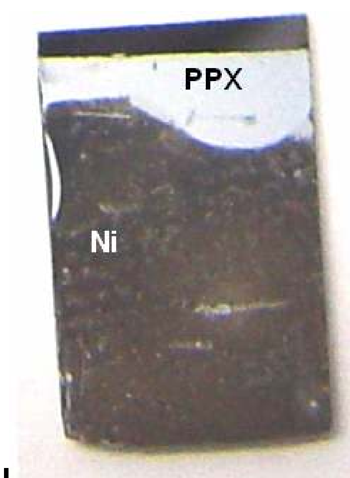
1. Liquid Phase Electroless Metallization

2. Vapor Phase Metallization

Parameters
- Surface crystal structure
- Surface area
- Ligand and colloid binding

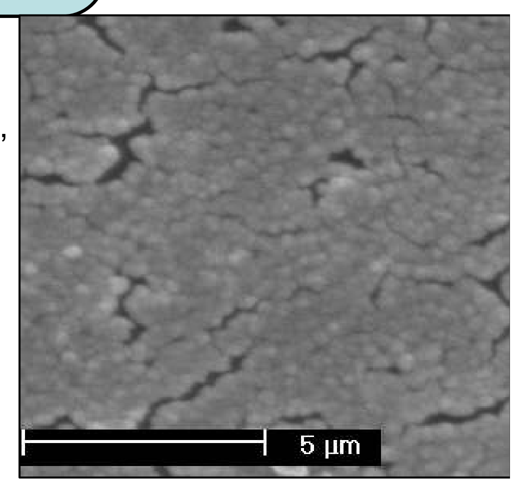
Applications: Catalyst, nanoparticle assembly, Biosensors, thermal barriers, neural interfaces

Parameters
- Confinement
- Surface crystallinity

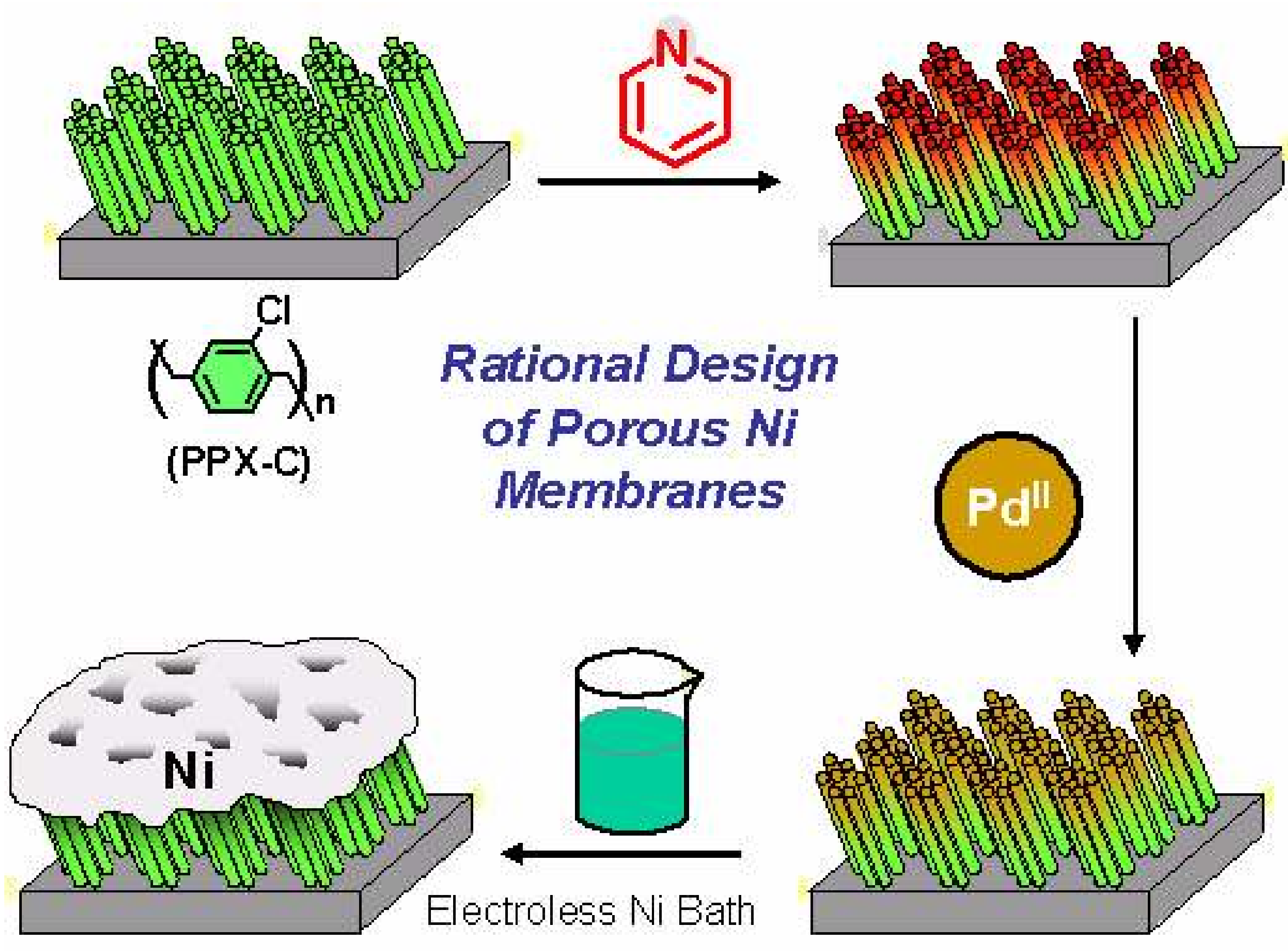


Demirel

Surface enhancement: increasing surface area, introducing porosity, controlled dispersity
Controlled chemical and physical properties: different monomer chemistry, different film morphology.
Industrial scale production: relatively inexpensive, no clean rooms, no lithography or masks.

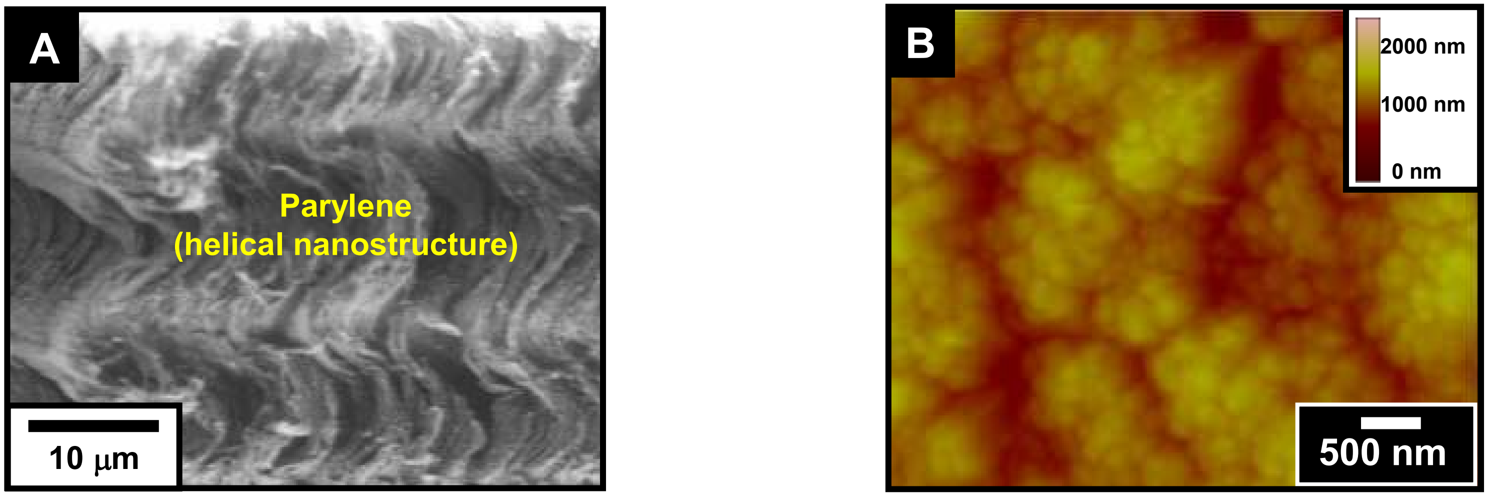


Liquid Phase: Metal Membranes

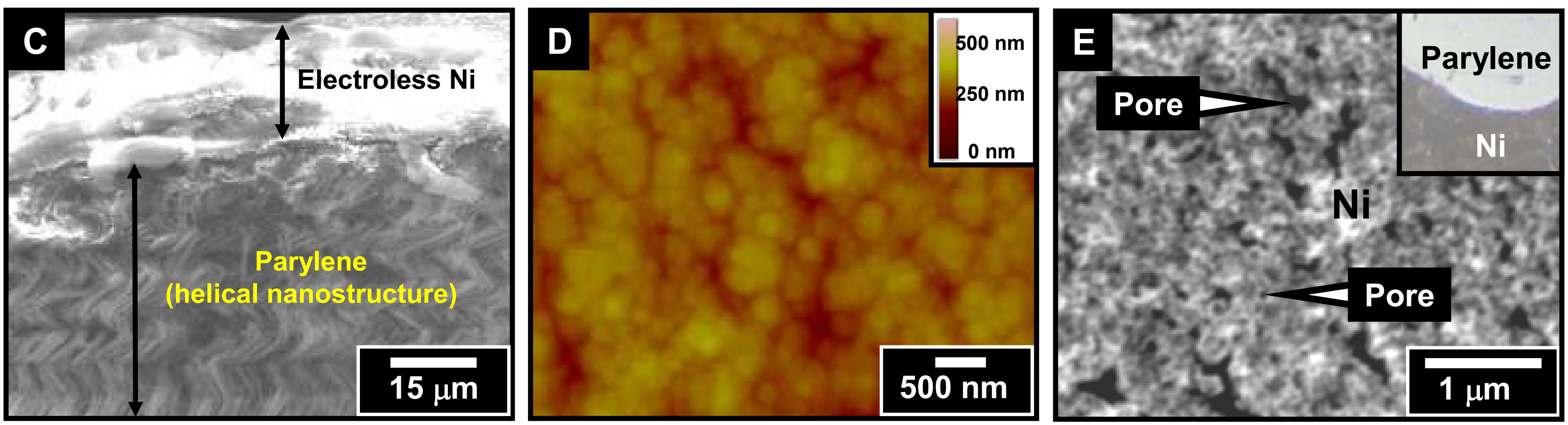


Demirel, *et al.* Advanced Materials, 2007

Reduction to Practice



Nanostructured parylene films before metallization: (A) SEM (cross-section); (B) AFM (film top)

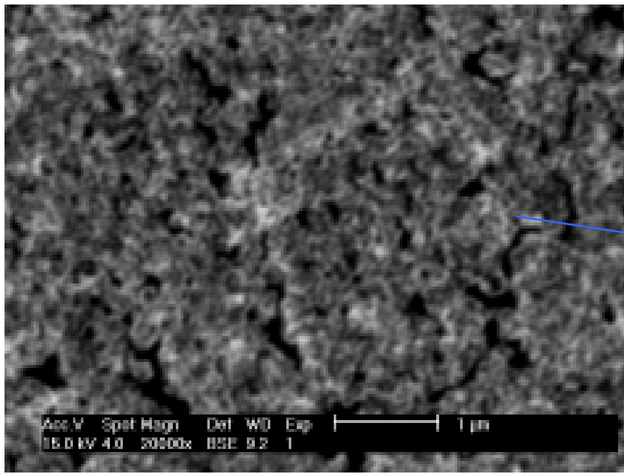


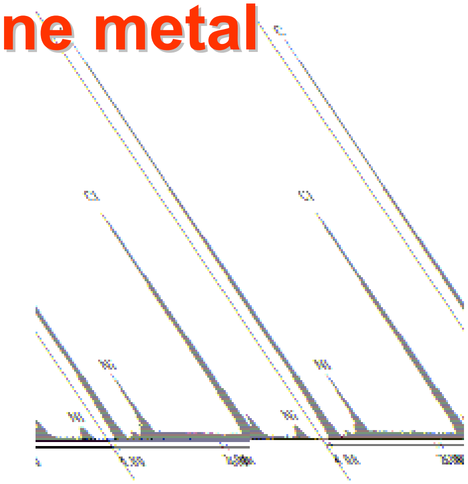
Nanostructured parylene films after Ni metallization: (C) SEM (cross-section); (D) AFM (Ni film top); (E) SEM (Ni film top). Film regions shown in parts (A) and (B) are not the same as those shown in parts (C), (D), and (E).

Characterization

30-50nm thin porous membrane metal

Porous
Nickel
Top surface
(SEM)

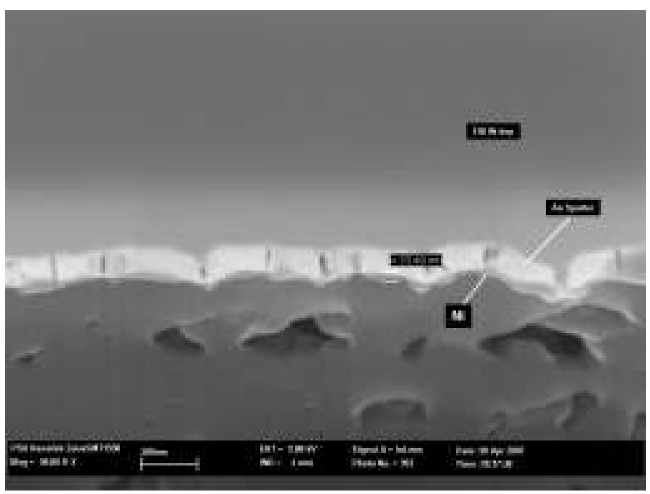




EDX spectra

Cross Section

(FIB)



Demirel, *et al.* Advanced Materials, 2007

Selective, covalent binding of Sn-free Pd(II) nanoparticles at the adsorbed ligand sites on the nanostructured PPX surface.

Treatment of the Pd(II)-catalyzed surface with an electroless Ni bath, leading to reduction of Pd(II) to Pd(0) and catalysis of electroless Ni deposition templated by the nanostructured PPX surface.

Functional Polymer-Metal Interfaces

OBLIQUE ANGLE POLYMERIZED FILMS (developed by Prof. Demirel)

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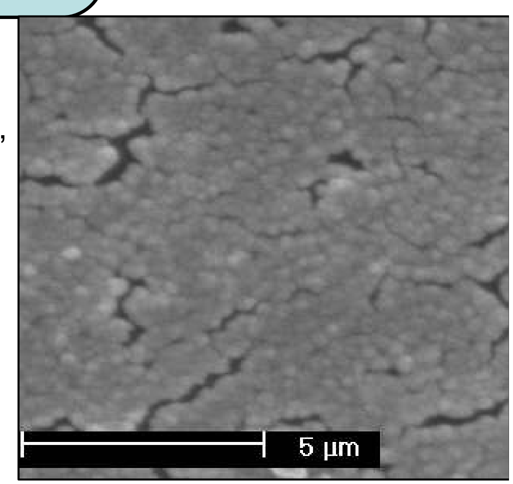

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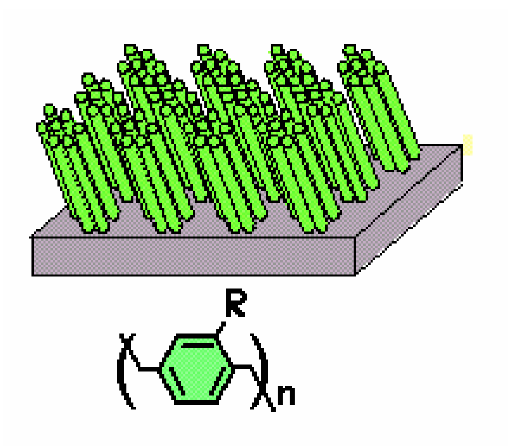
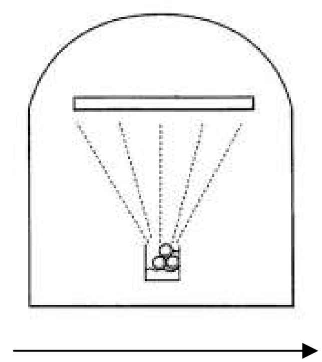
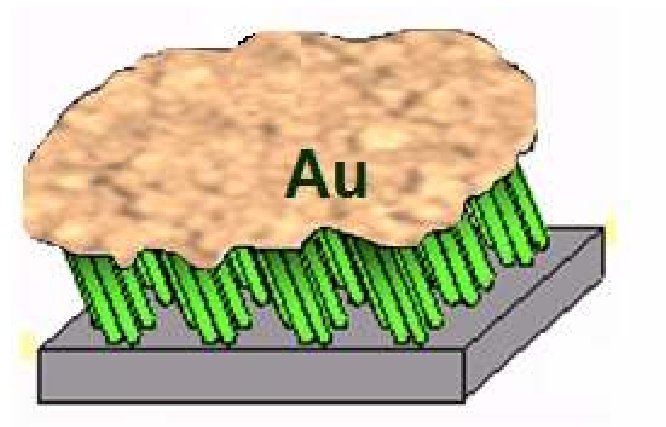
Vapor Phase: Metal Membranes





metalized

Au, Ag, Co, Cu, etc…



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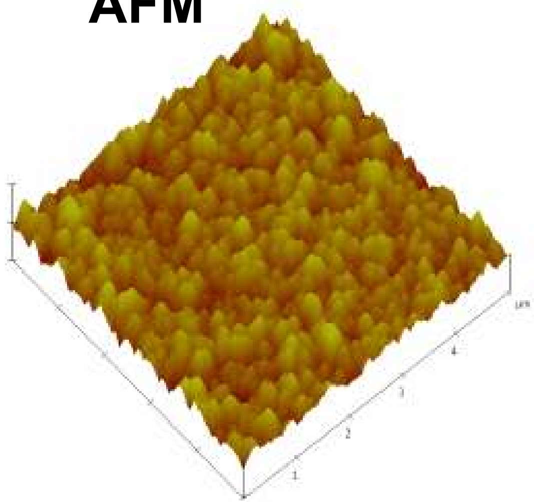
Vapor Phase: Metal Membranes

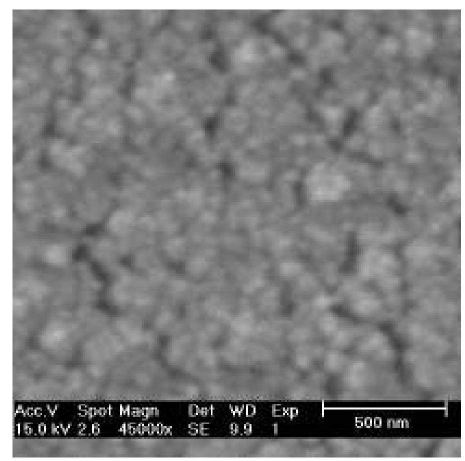
QCM / BET Results

Sample	Surface area	Multiple of electrode area (0.1964cm2)
Only polymer film	76.98 cm^2	391.96
Deposit Ag on top	48.72 cm^2	248.07

AFM



SEM



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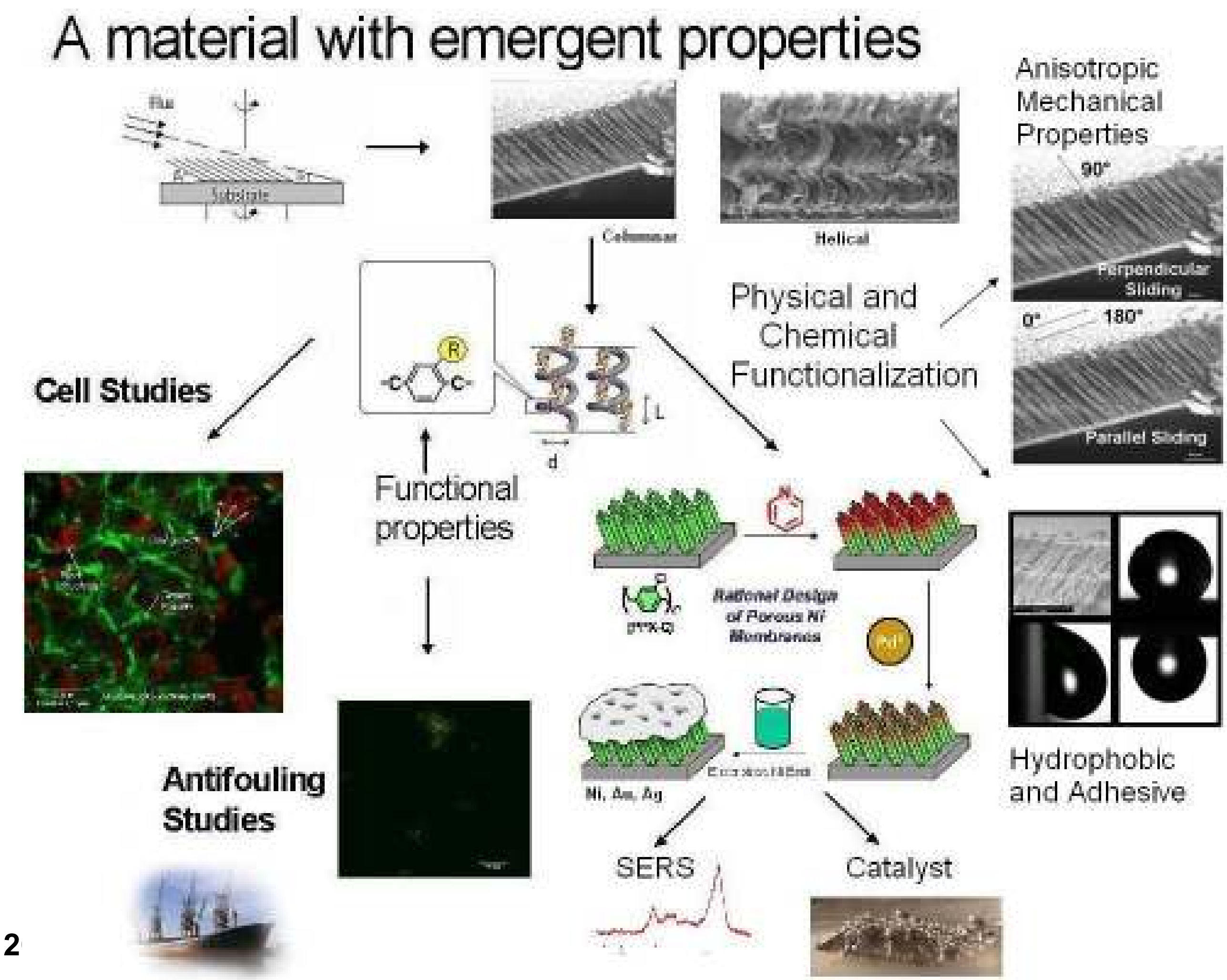
Why do we need these type of nanostructured polymer surfaces?

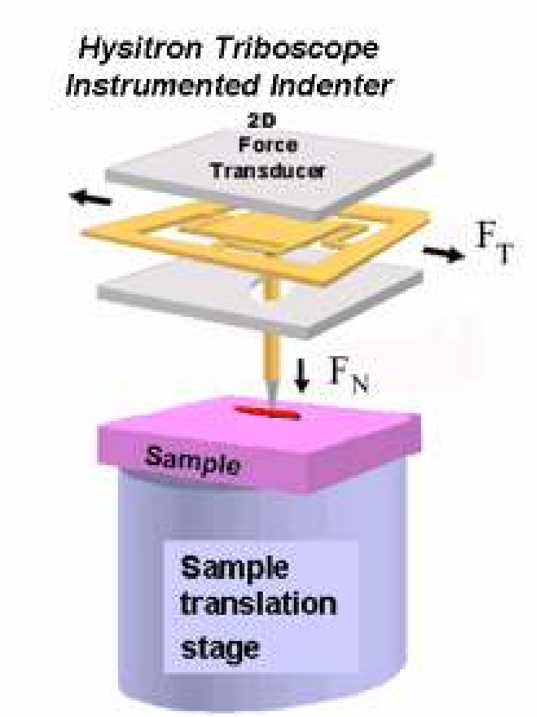


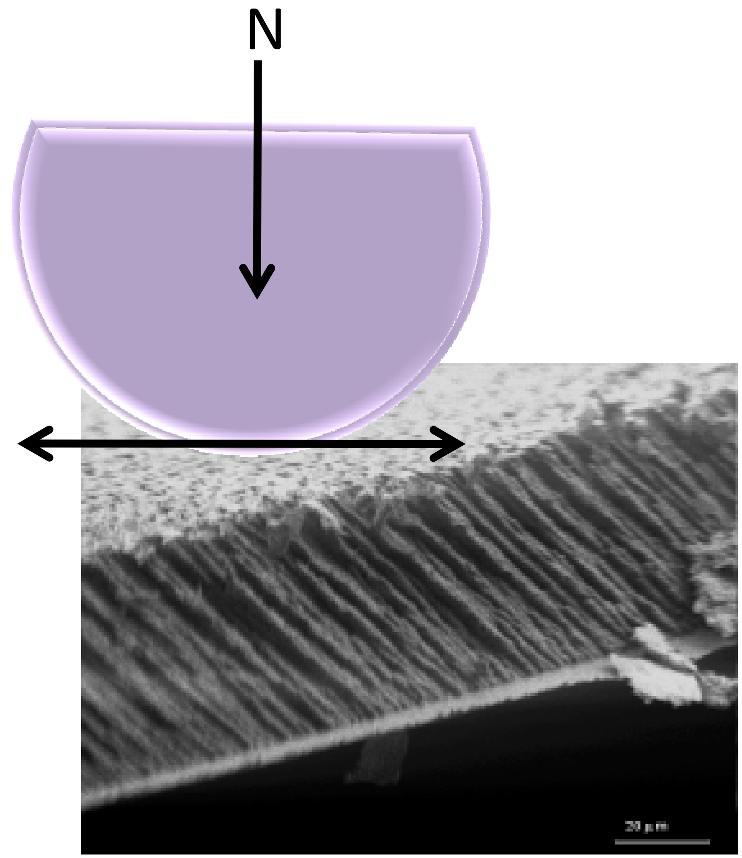
Demirel Lab 2

Applications

- Mechanical Properties
- Self cleaning
- Biosensor
- Energy / Catalyst

Microtribology of Nanostructured Materials





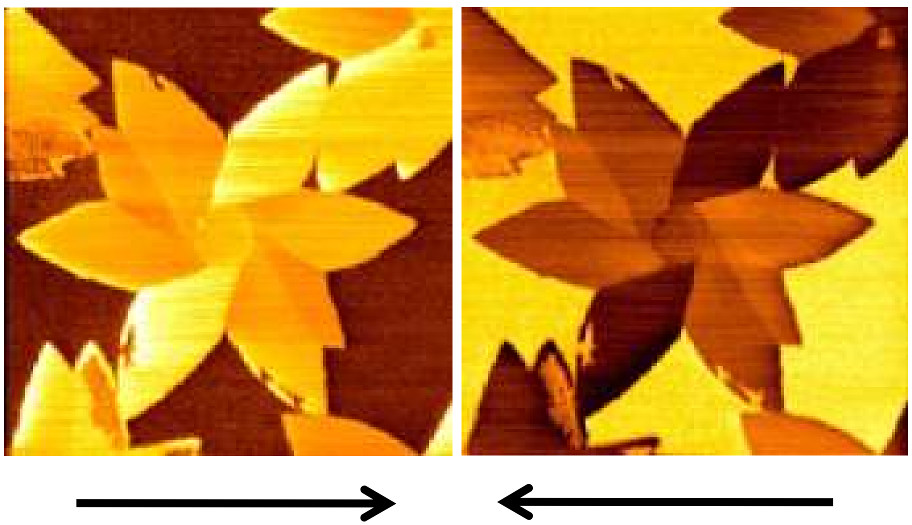
Do material anisotropies influence friction, deformation processes?

Demirel Lab 2008

Tribology of Nanostructured Materials
- Films of Molecules or Fibers

Friction Anisotropy

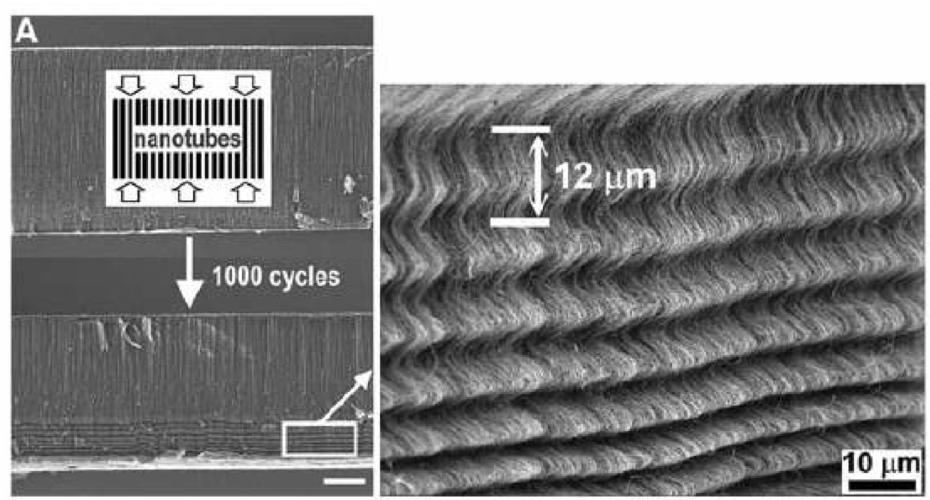
Thiolipid monolayer on mica



Sliding direction

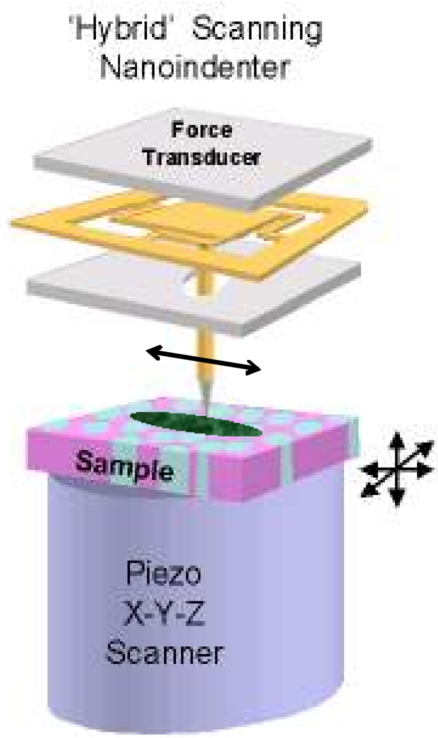
Liley et al., *Science* 280 (1998) 273-275

Collective Buckling



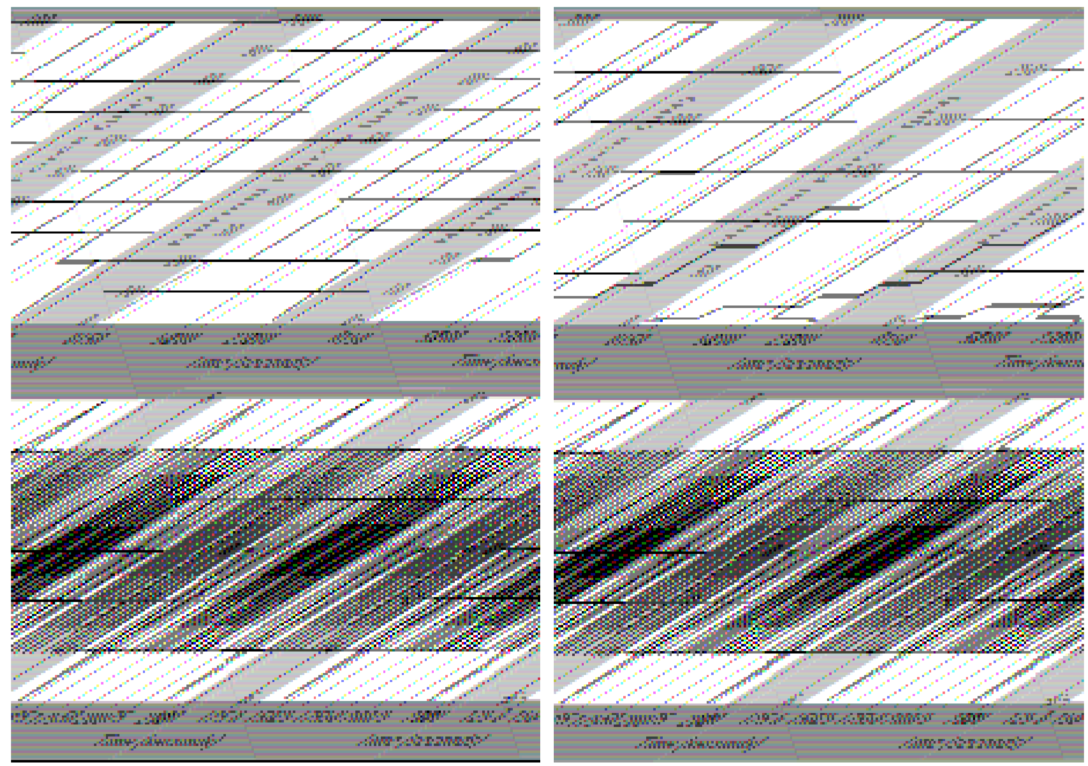
Cao et al., *Science* 310 (2005) 1307

Microtribometry Protocol



- •17 ± 4 µm Conospherical Diamond Tip
- •8 µm Wear Track
- •40 Sliding Cycles

Constant Load Test **Increasing Load Test**

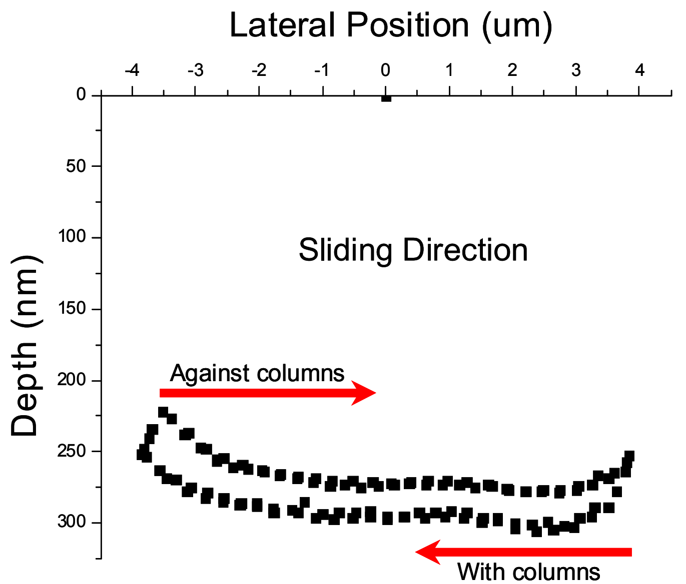


Load and displacement profiles

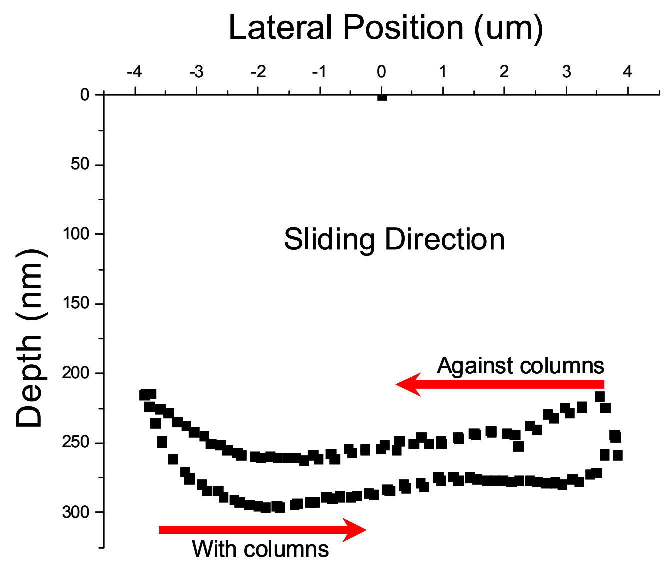
- 100 µN Constant Load
- 300 µN Ramped Load

K. Wahl, E. So, M. Demirel

Contact Depths During Sliding



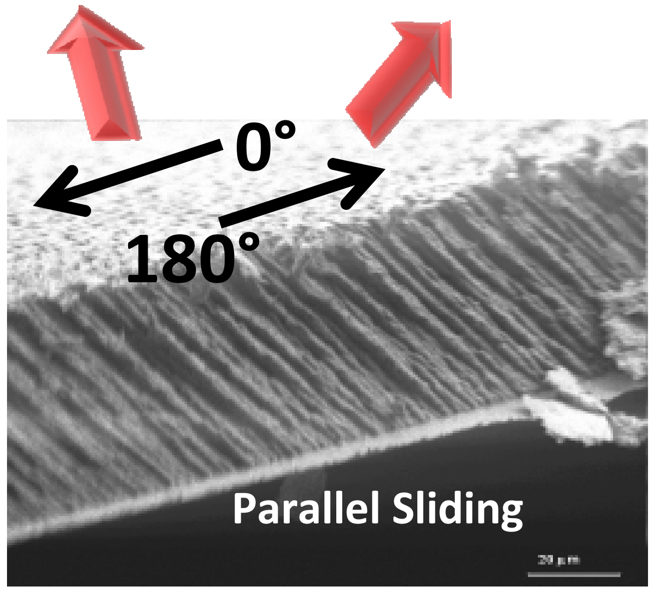
100 uN load, 0-degree orientation



100 uN load, 180-degree orientation

Anisotropy? YES

Tip penetrates deeper into film when sliding with column tilt



Arrows indicate the sliding direction

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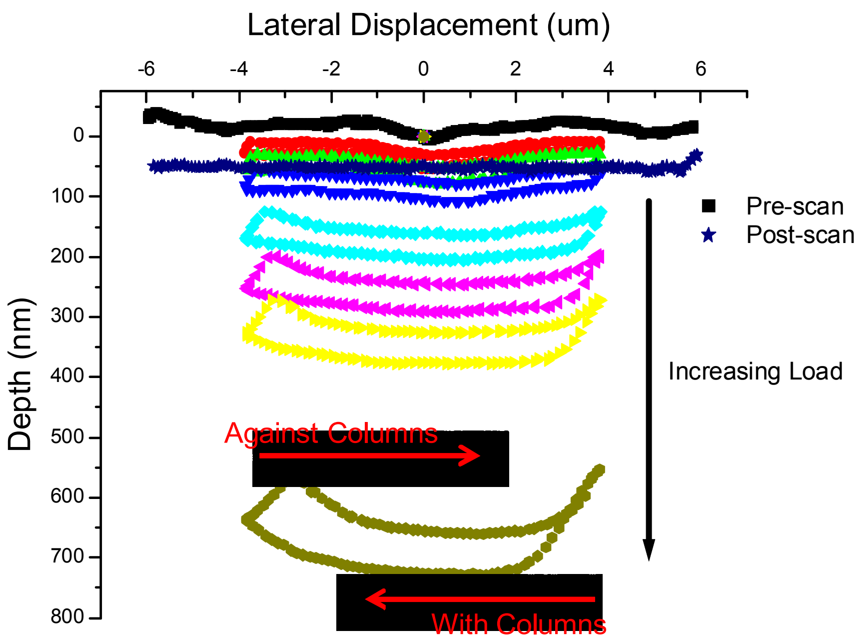
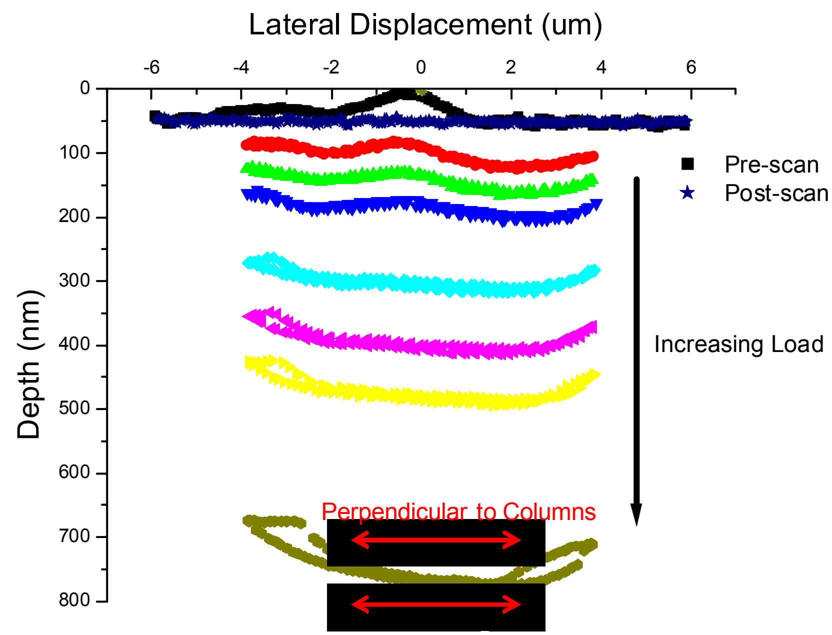
K. Wahl, E. So, M. Demirel

Depth Response w/ Load

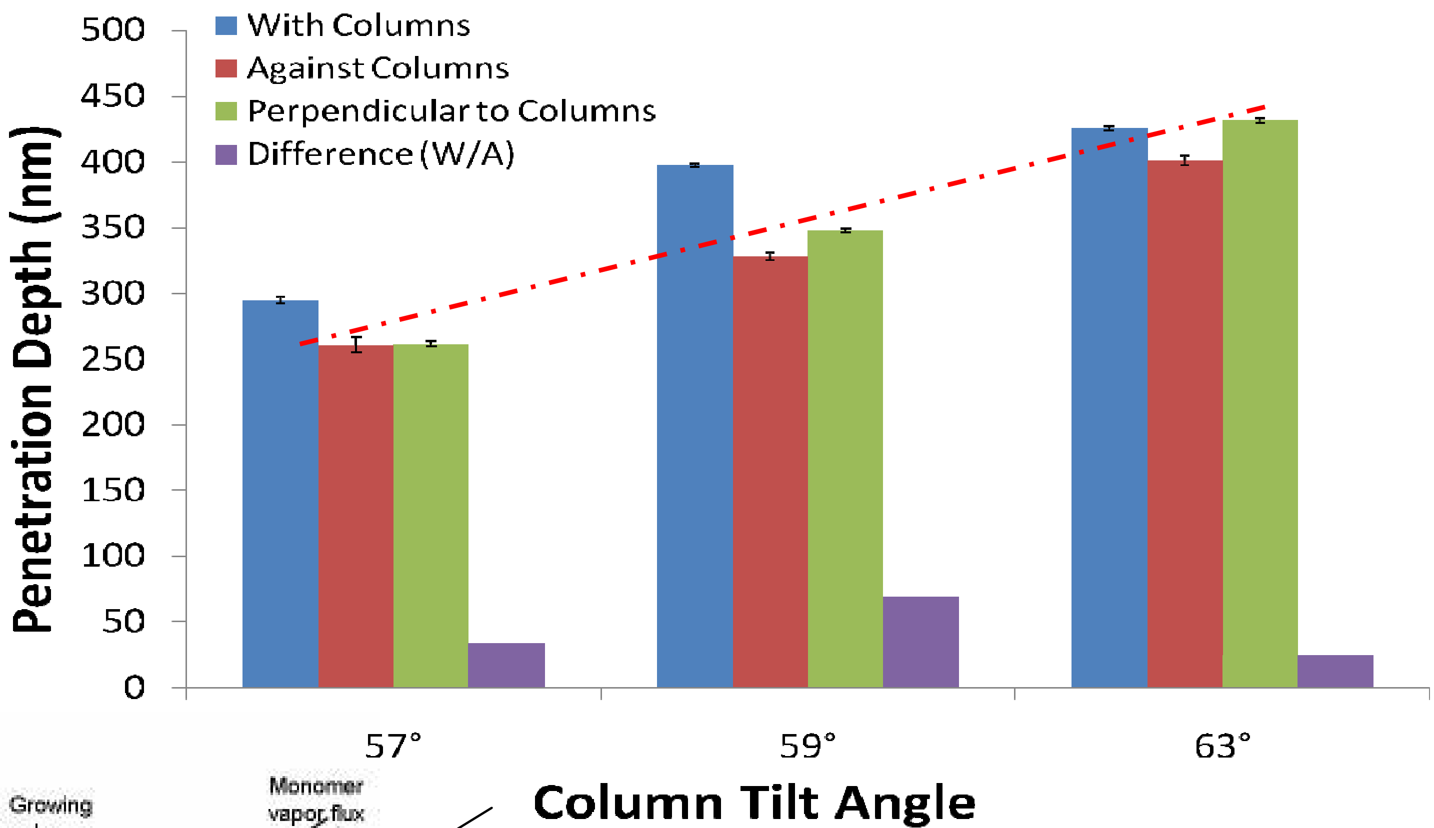


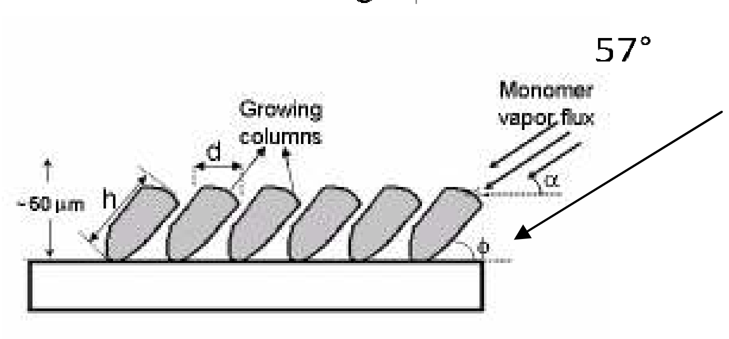


Depth anisotropy observed for all ordered films over a wide range of conditions

K. Wahl, E. So, M. Demirel

Penetration Depth vs. Load





Highly confident statistics demonstrating depth anisotropy

K. Wahl, E. So, M. Demirel

Mechanical Deformation Hysteresis

Beam Equation

$$\frac{\partial^2}{\partial x^2}\left(EI\frac{\partial^2 u}{\partial x^2}\right)=\omega$$

Solution

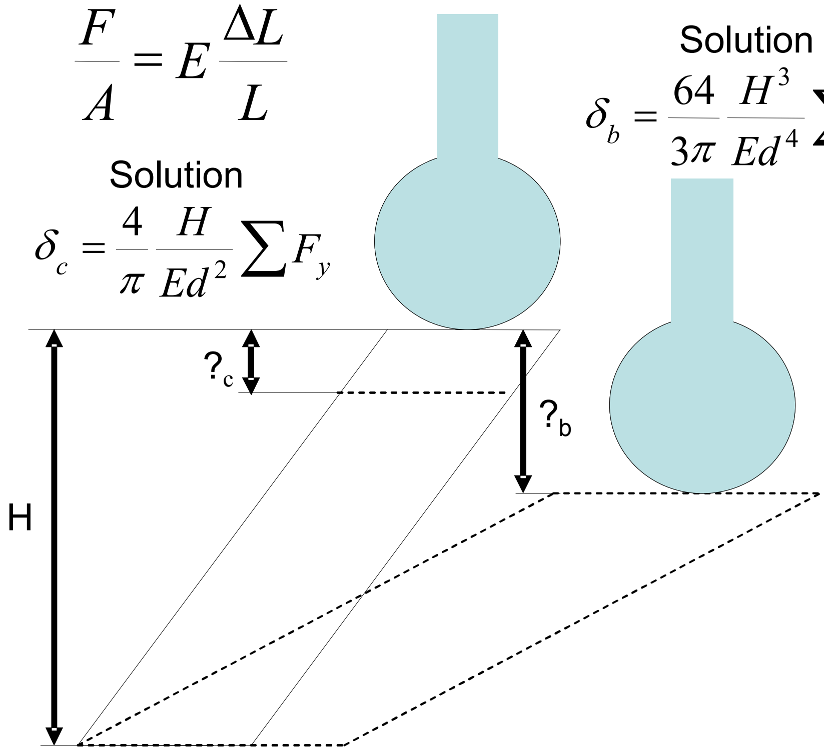
$$\delta_b = \frac{64}{3\pi}\frac{H^3}{Ed^4}\sum F$$

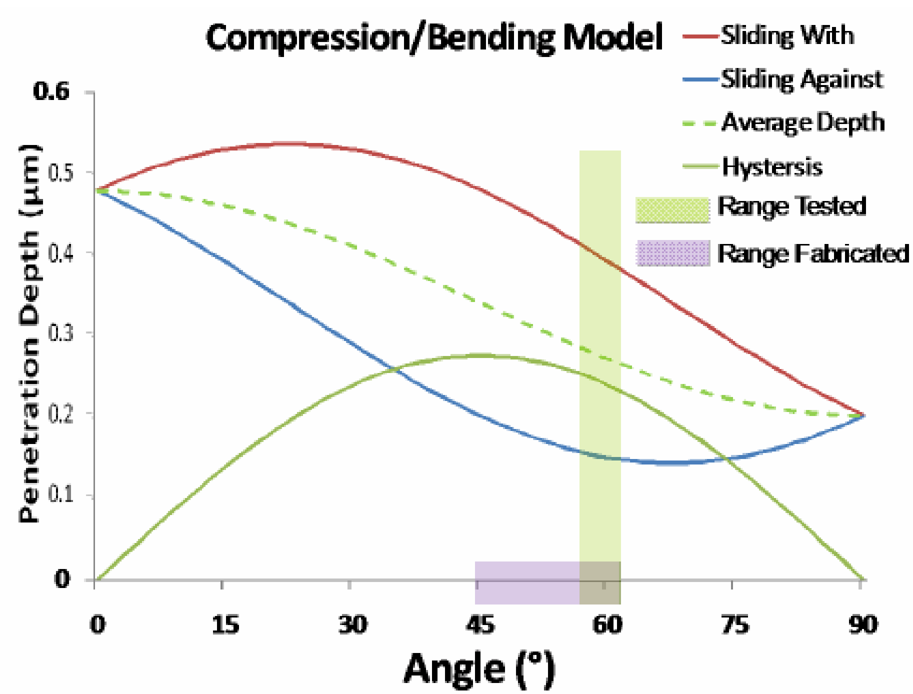
Hooke's Law

$$\frac{F}{A} = E\frac{\Delta L}{L}$$

Solution

$$\delta_c = \frac{4}{\pi}\frac{H}{Ed^2}\sum F_y$$





- Variations in total penetration depth may be more strongly correlated to film density, modulus
- Model does not include density, inter-column contact or friction

$$Depth = \delta_b\cos(\alpha) + \delta_c\sin(\alpha) = \frac{4H}{\pi Ed^2}\left[\frac{16H^2}{3d^2}\sum F_x\cos(\alpha) + \sum F_y\sin(\alpha)\right]$$

Sliding perpendicular to film results in no hysteresis, predicted depths between with/against

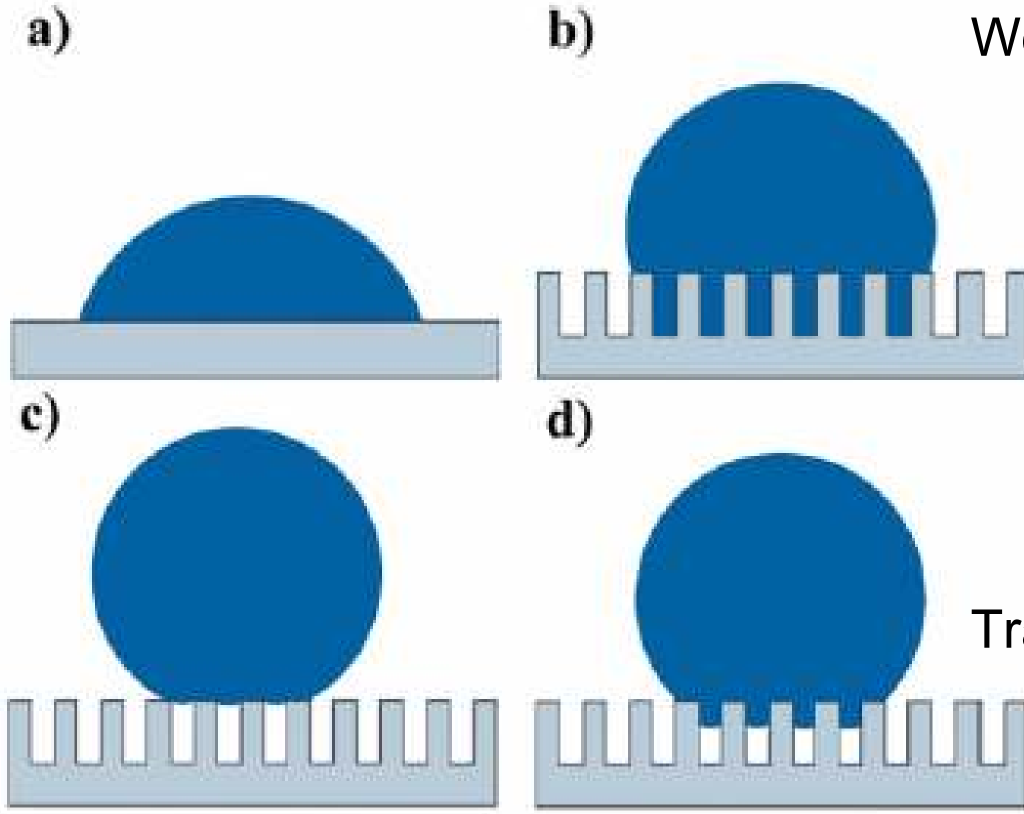
Applications

- Mechanical Properties
- Self cleaning
- Biosensor
- Energy / Catalyst

Wetting Behavior

Wenzel's Mode

Young's Model



Cassie's Model

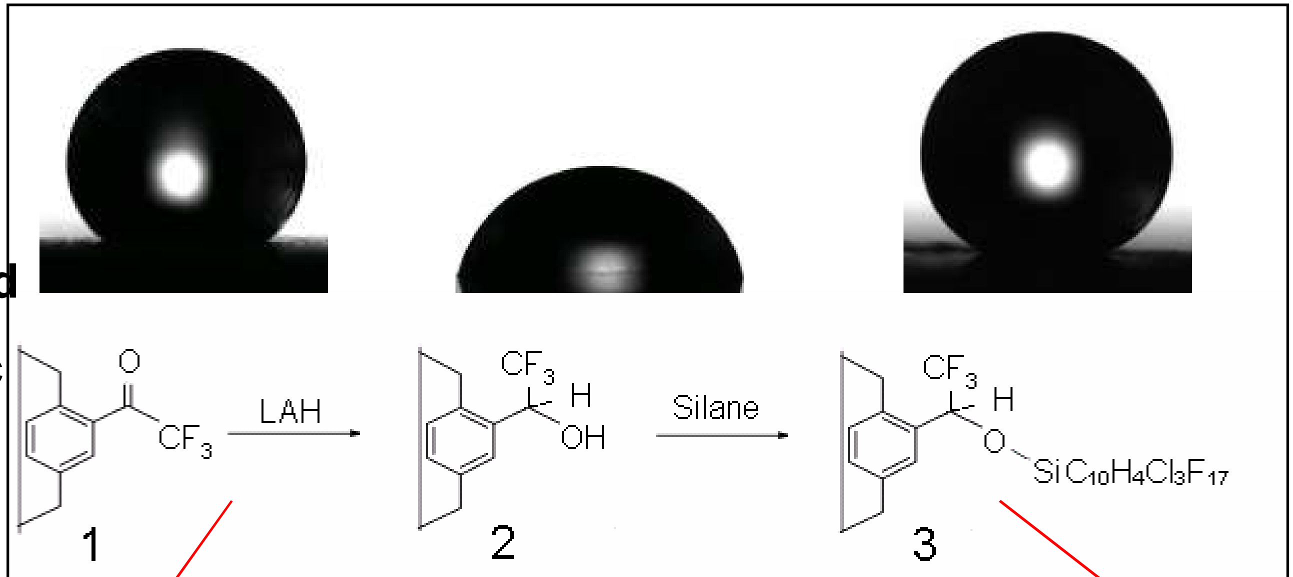
Transition Model

+ Gecko State ??? (adhesive + hydrophobic)

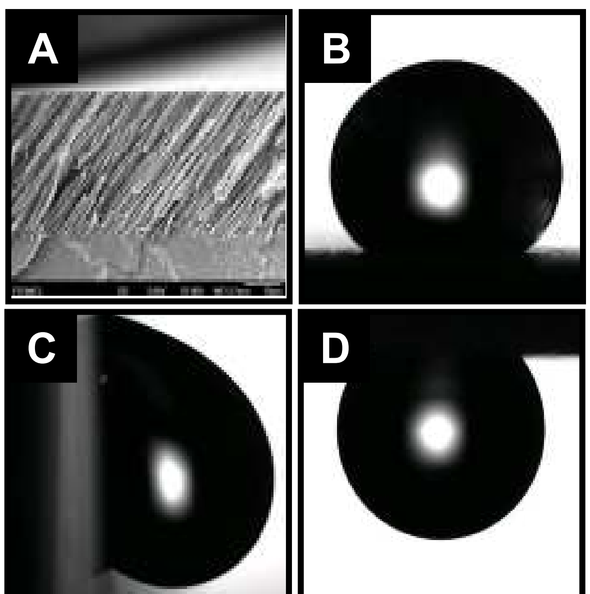
J. Liang, et al., Adv. Mat, 2007

Surface Wetting

Adhesive and Hydrophobic



Non-Adhesive and Hydrophobic Roll off angle < 5 degrees



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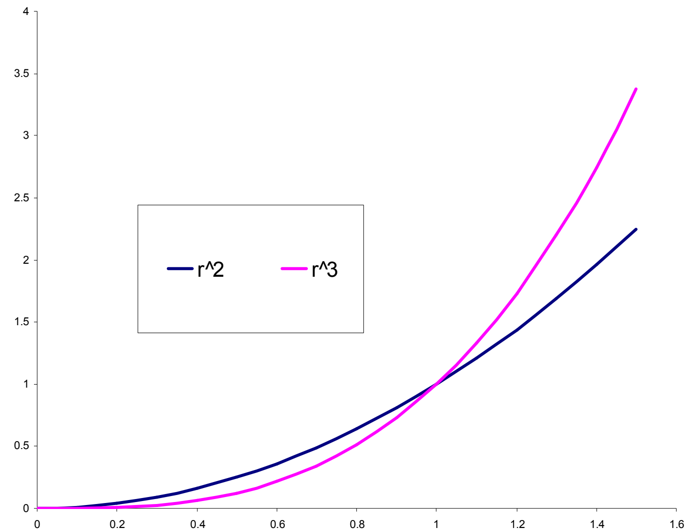
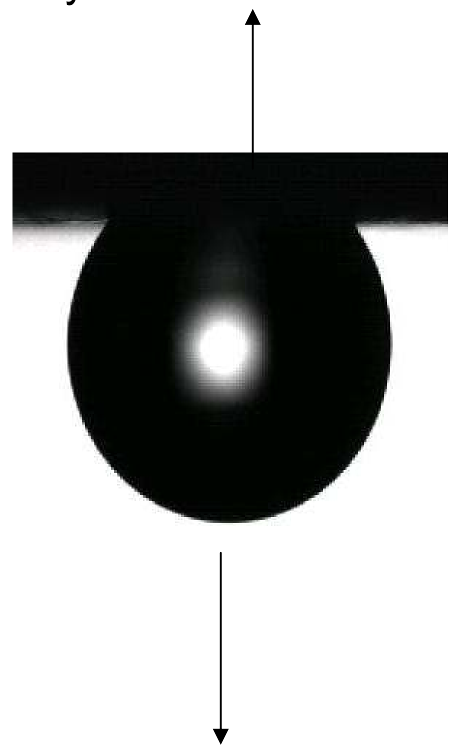
Boduroglu et al, Langmuir, 2007

Possible explanation!!!



Force Balance

Capillary ~ Surface Area ~ r^2



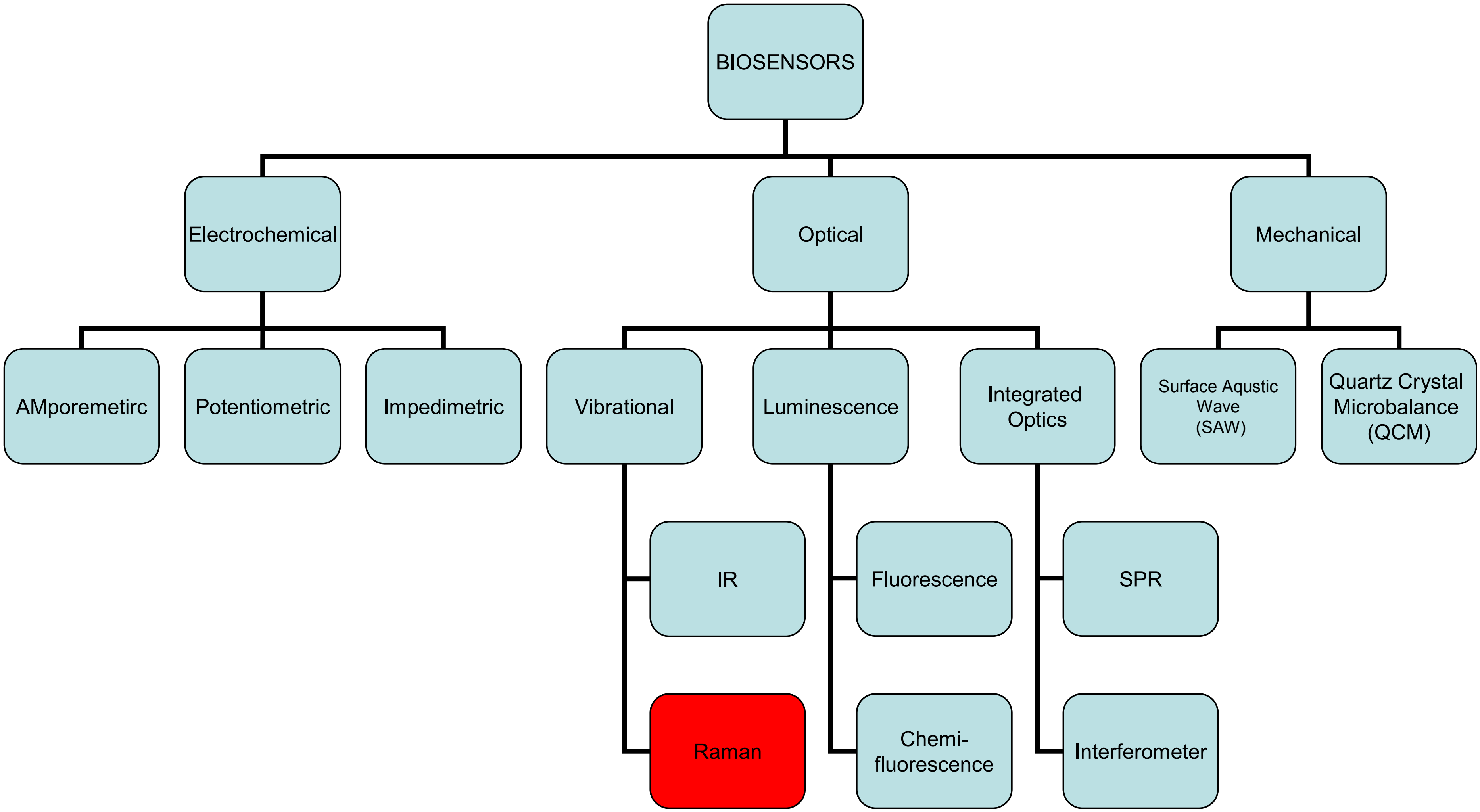
Gravity ~ mg ~ Vg ~ r^3

Note: Water drop is stable up to 40 microliter.

Applications

- Mechanical Properties
- Self cleaning
- Biosensor
- Energy / Catalyst

The Biosensor Tree



T. Cass, C. Toumazou, Biosensors and Biomarkers, Foresight Project Review

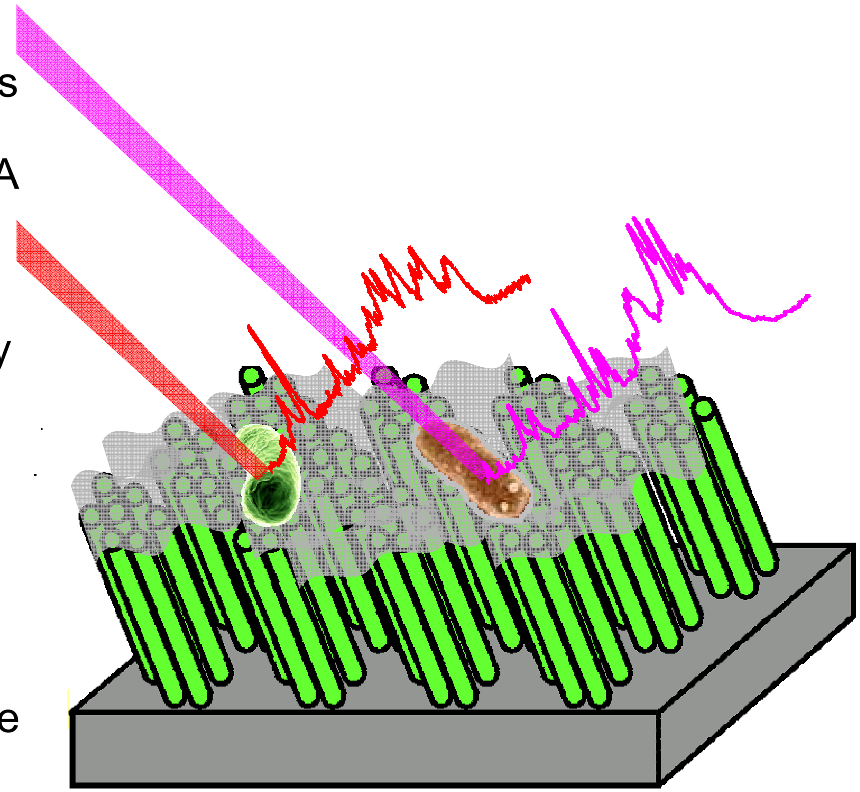
Raman for Biological Detection

ADVANTAGES

- Reagentless method: No reagent but provides chemical structure information (specificity)
- Single Cell Detection: No amplification of DNA (PRC) or Laboratory growth techniques.
- Applications includes identification of characteristic spectra from viruses, bacteria, or protozoa for biomedical, homeland security (CBW agents), aerospace (aerosols) areas.
- Substrate Preparation: High-throughput technique (advantage of vapor deposition), relatively inexpensive

PITFALLS

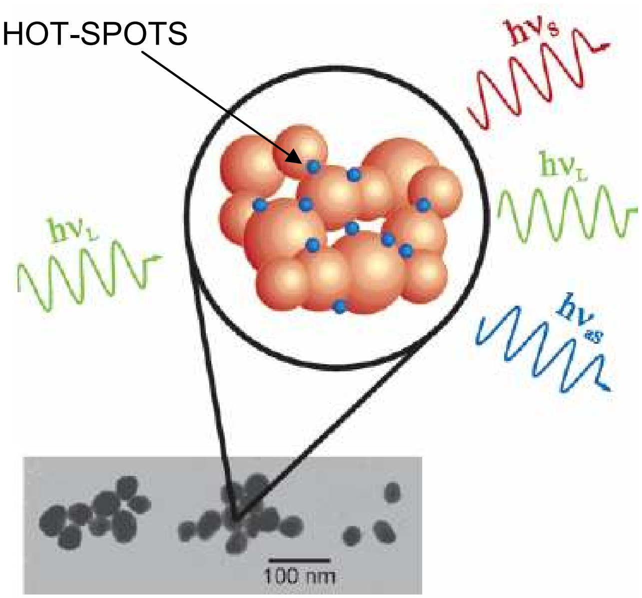
- Requires creation of database for infectious agents (Raman database)
- Requires bioinformatics tools for analyzing the database (deconvolution and pattern detection)



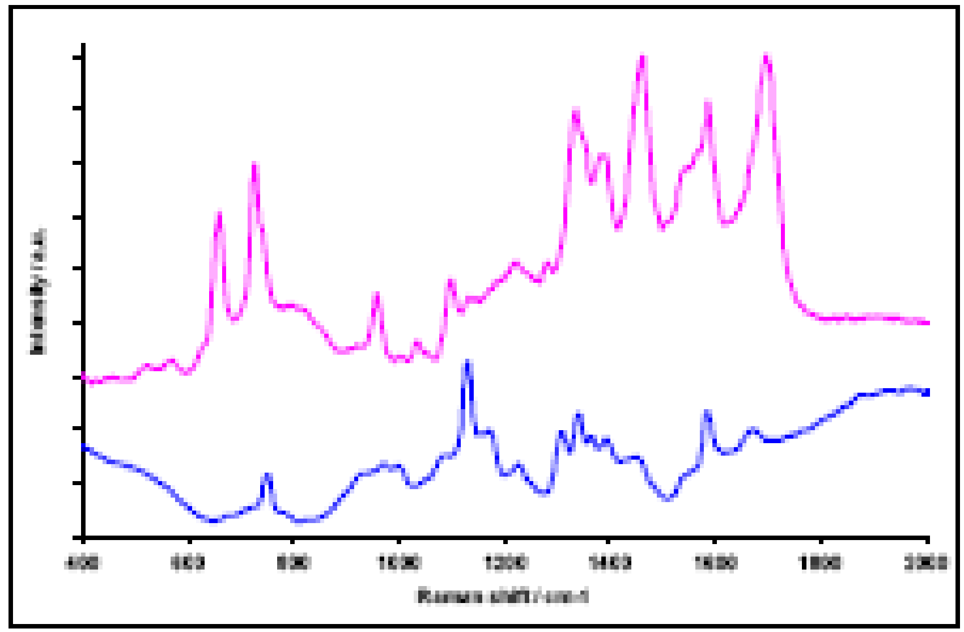
Demirel et al, Adv. Materials, 2008, in press

Raman v.s. SERS

--Raman, 1920 (Nobel Prize--1930)
--SERS (1977), Van Duyne and Jeanmaire and, independently, Albrecht and Creighton



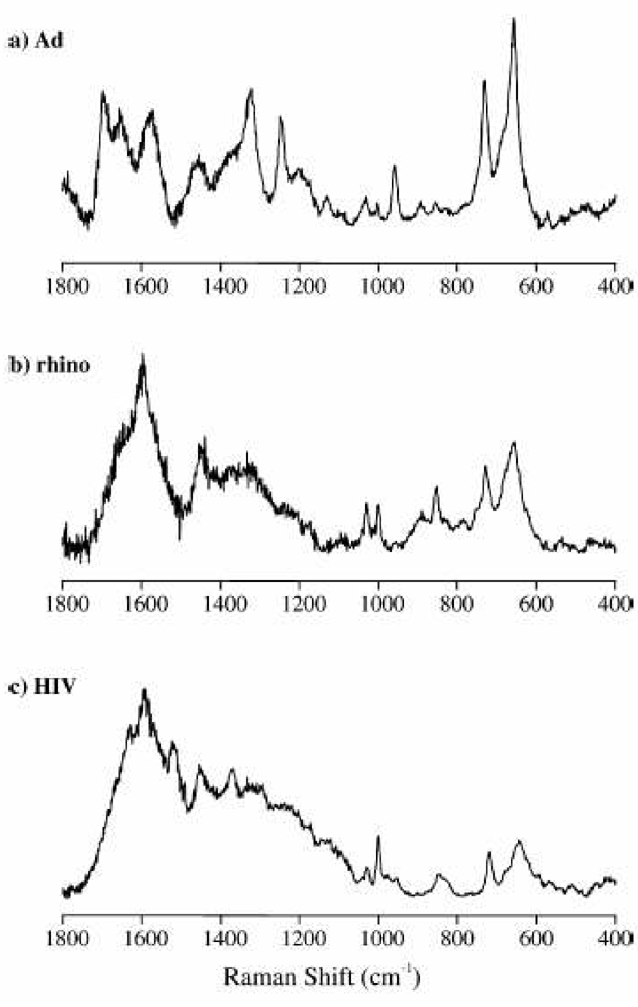
SERS phenomena of silver nanoparticles



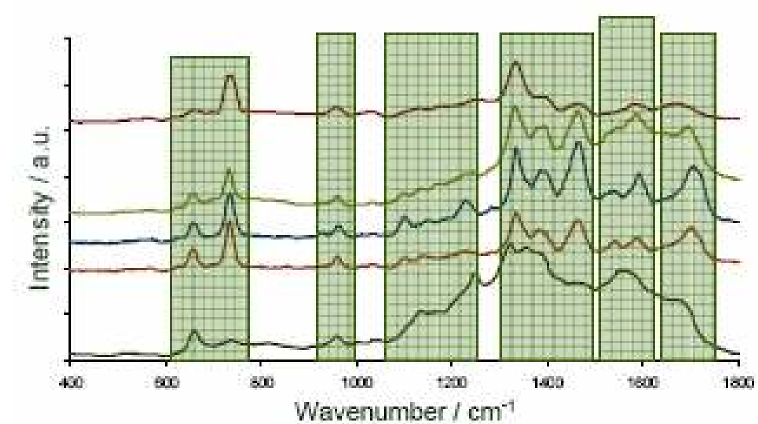
Escherichia coli Raman spectrum and the SERS spectrum

Kneipp, Acc. Chem. Res. **2006,** 39, 443-450

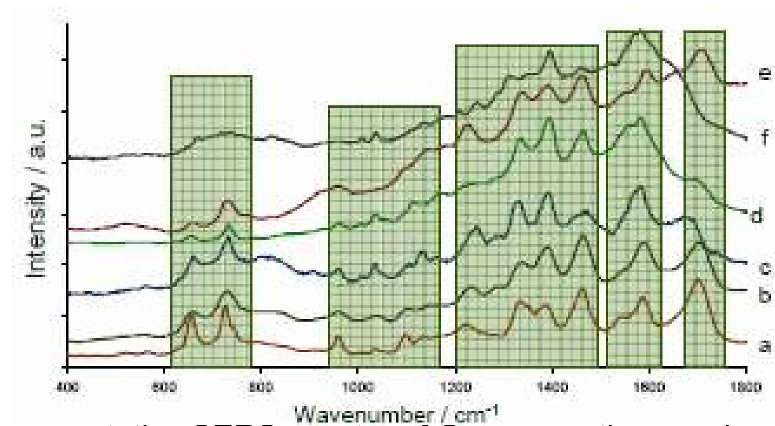
SERS: Viral and Bacterial Detection



Representative SERS spectra of a) Adenovirus, b)Rhinovirus, c) HIV *Zhao, Nano Lett., Vol. 6, No. 11,* ***2006***



Representative SERS spectra of Gram-positive species: a)*B. subtilis*; b) *B. cereus*; c) *B. thuringiensis*; d) *S. epidermidis*; and e) *S. aureus*.



Representative SERS spectra of Gram-negative species: a) *E. coli;* b) *S. Tennessee;* c) *K. pneumoniae;* d) *E. aerogenes;*, e) *P. mirabilis;* f) *P. aeruginosa.*
T. Pineda, M.S. Thesis, University of Puerto Rico, ***2006***

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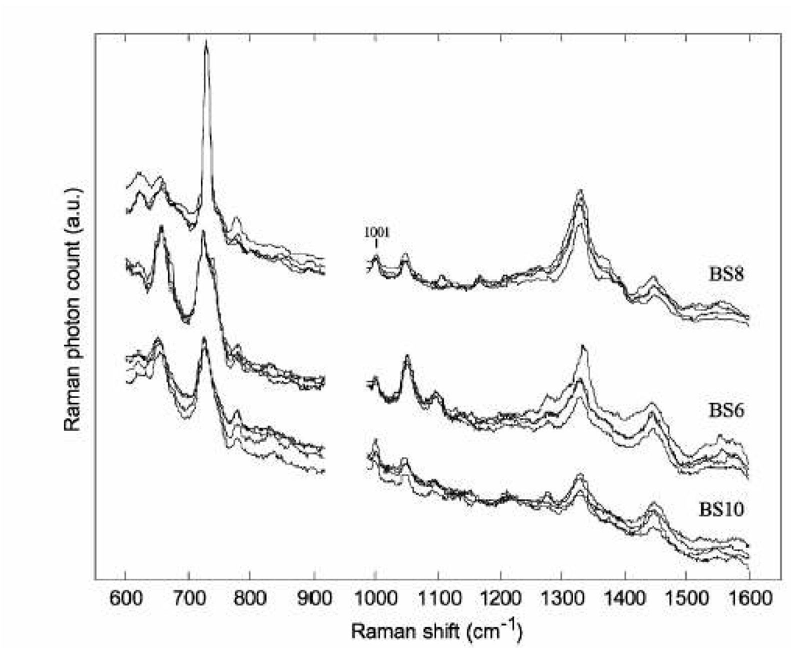
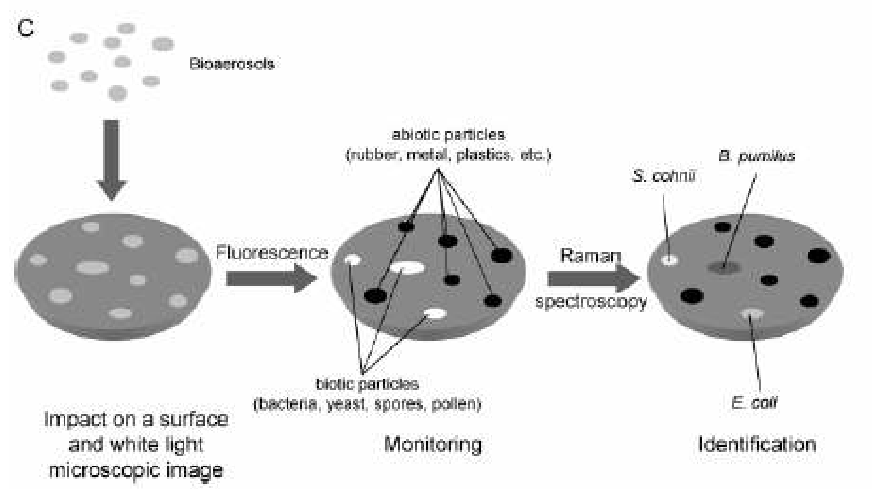
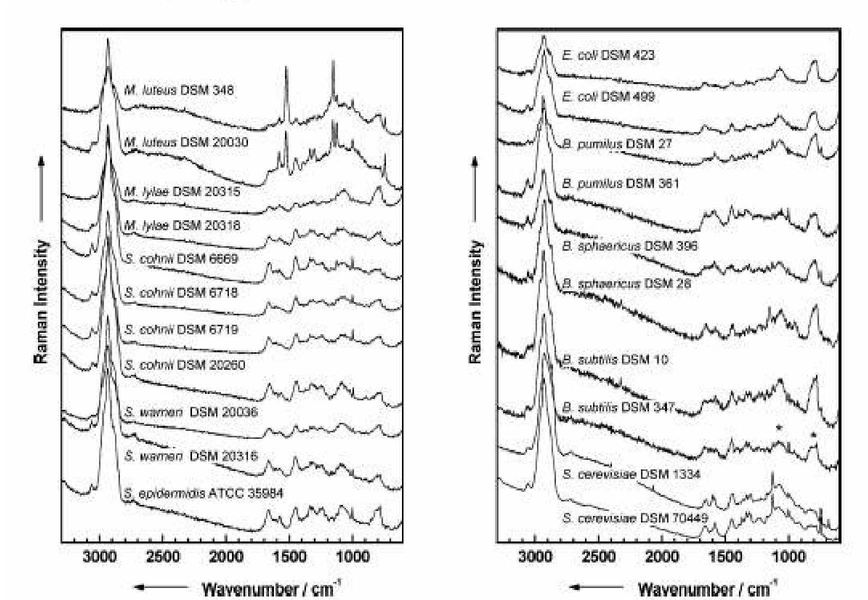
SERS: Strain Identification



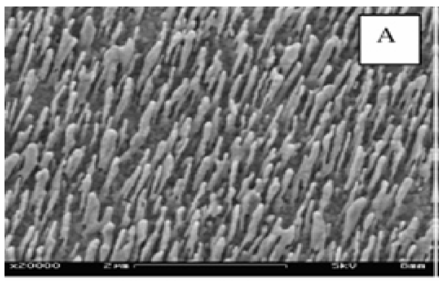




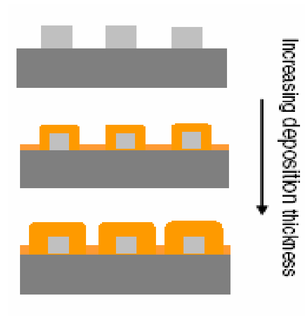
Rosch et al. , Analytical Chemistry, Vol. 78, No. 7, April 1, 2006

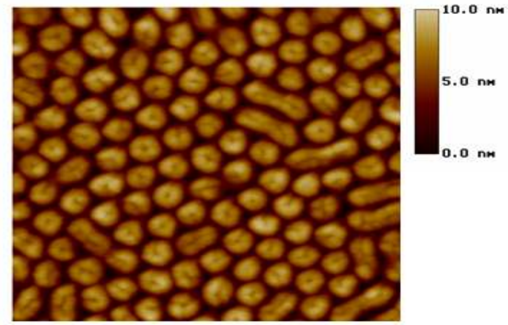
SERS Substrates

- Several methods have been implemented for microorganism detection using SERS such as gold nanoparticle coated SiO2, electrochemically roughened metal surfaces, and colloidal metal particles.

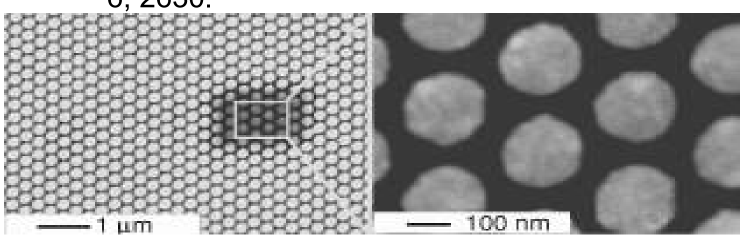


Shanmukh et. al. Nano Letters 2006, 6, 2630.

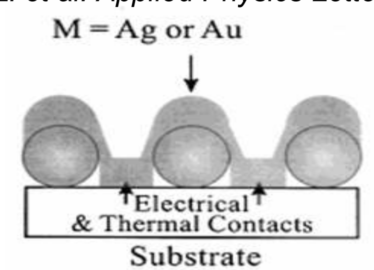




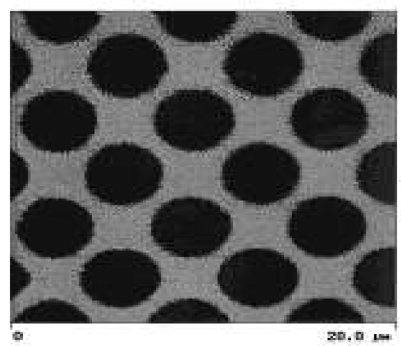
Lu.J et.al. Nanotechnology 17 (2006) 5792–5797

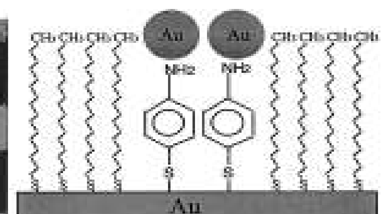


Gunnarsson, L. et al. Applied Physics Letters **78**, 802-804 (2001).



Dick. L et. al. *J. Phys. Chem. B* **2002,** *106,* 853-860

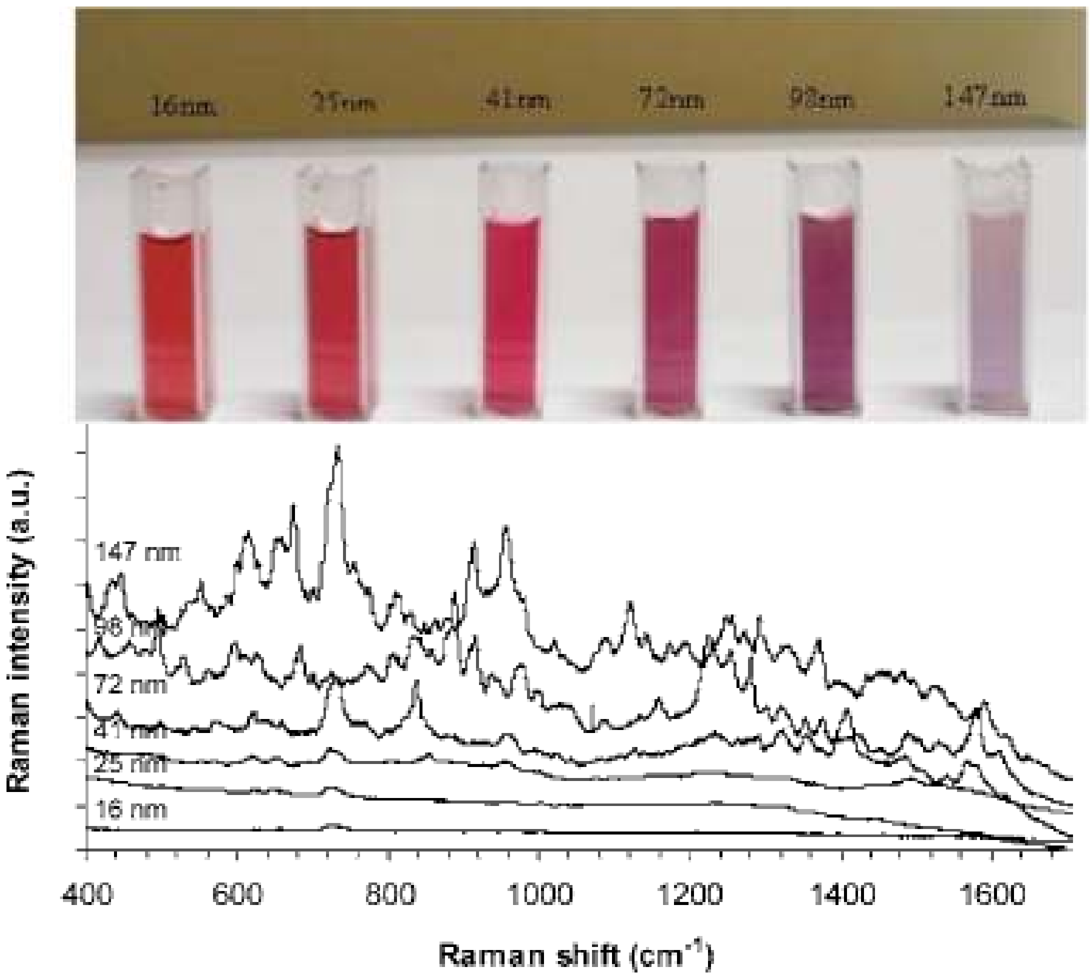




He H. et. al. *Langmuir* **16**, 3846-3851 (2000).

SERS Detection

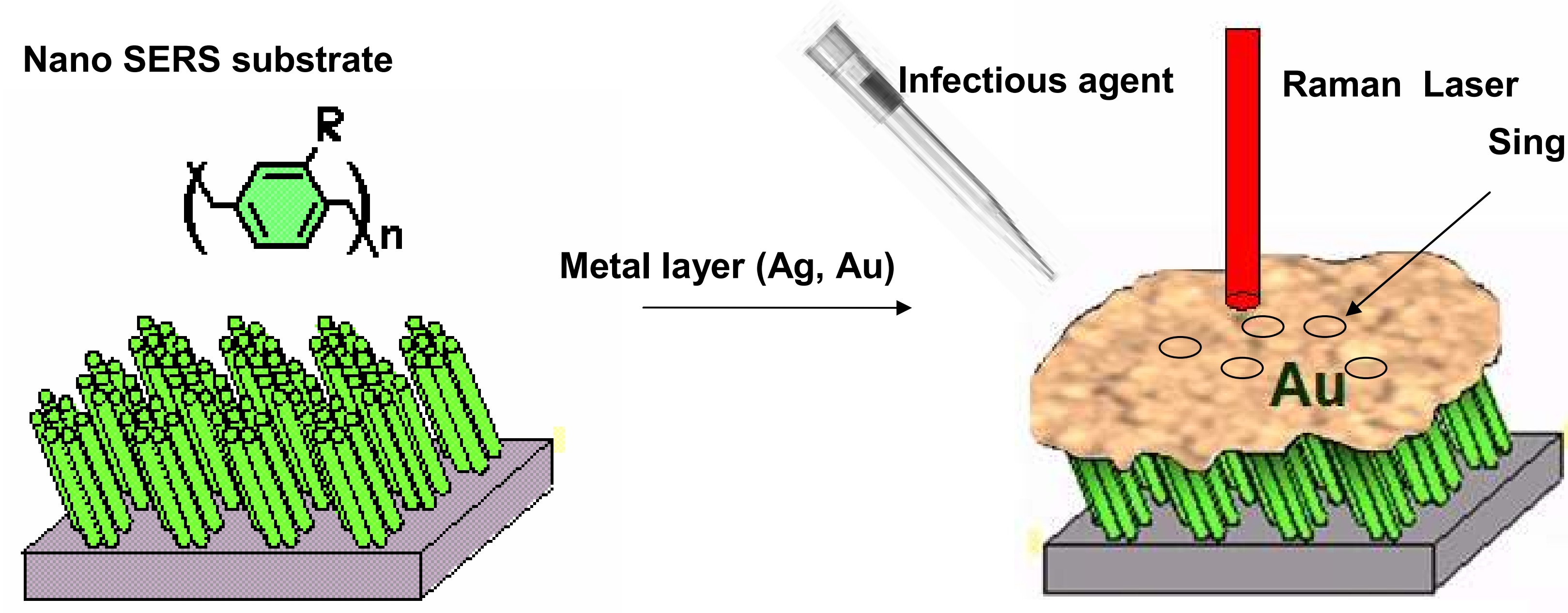
The lack of reproducibility of these techniques and uniform signal detection make it difficult to get consistent SERS results.

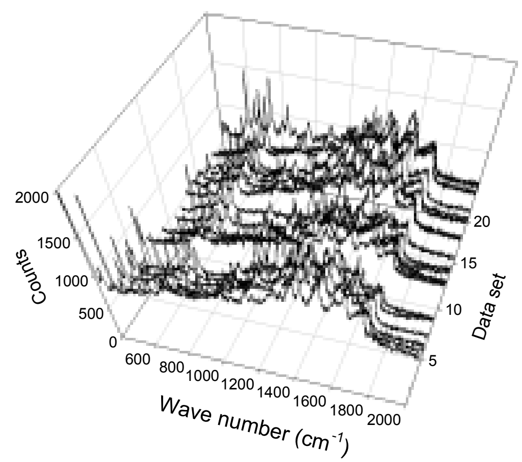


Example: Influence of gold nanoparticle size on SERS spectrum of *B.megaterium*.

Culha et al., Journal of Biomedical Optics 125, 054015

Non-lithography based Polymer/Metal SERS substrate





Database

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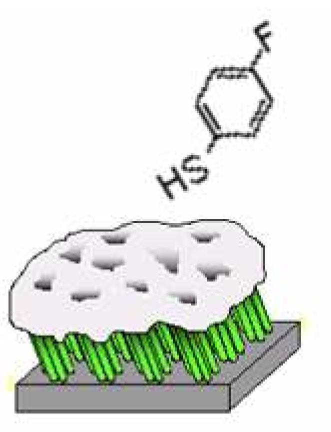
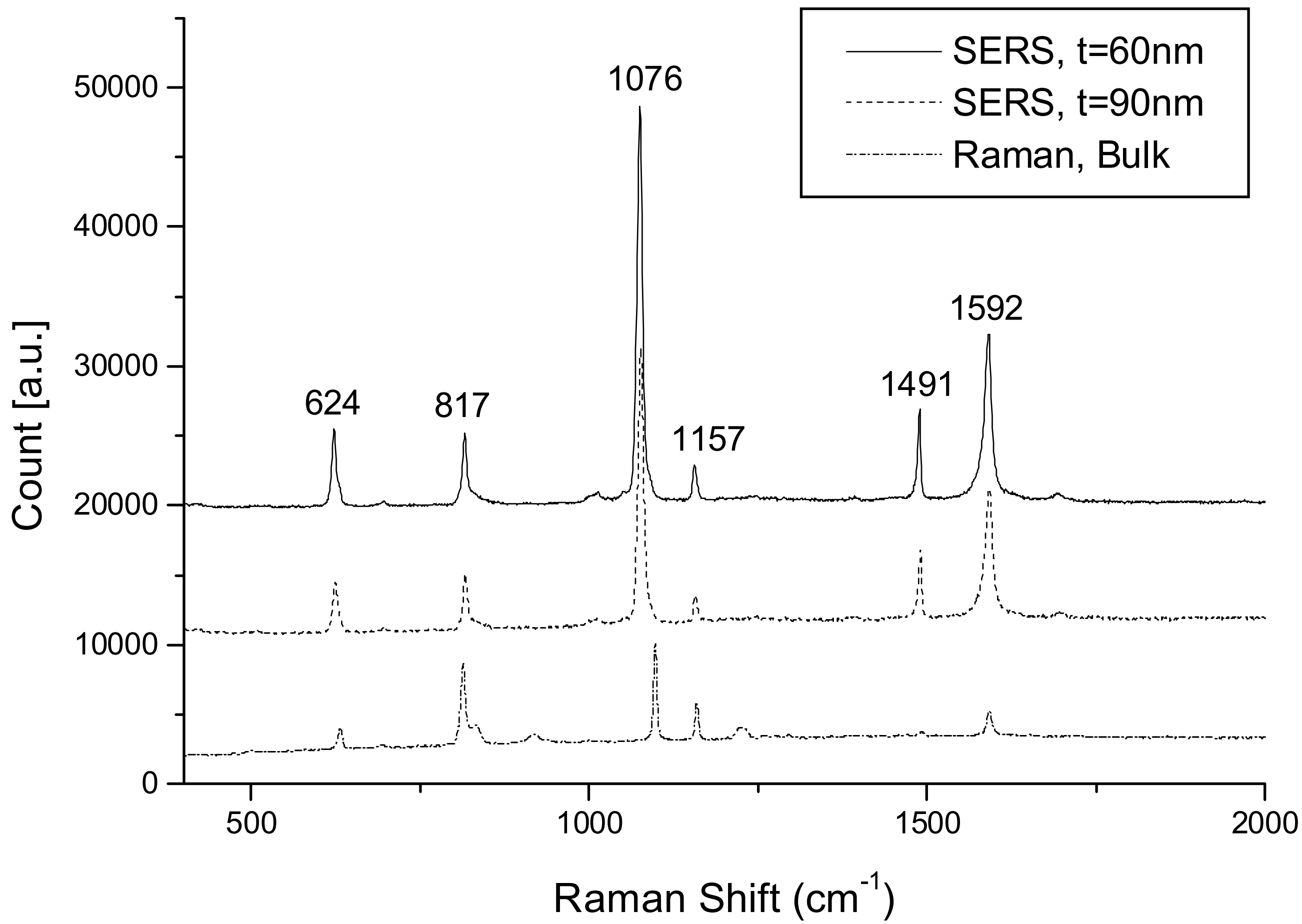
Demirel et al, Advanced Materials, in press, 2008

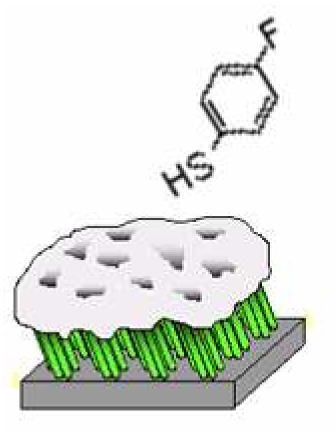
SERS: Metal Layer Thickness

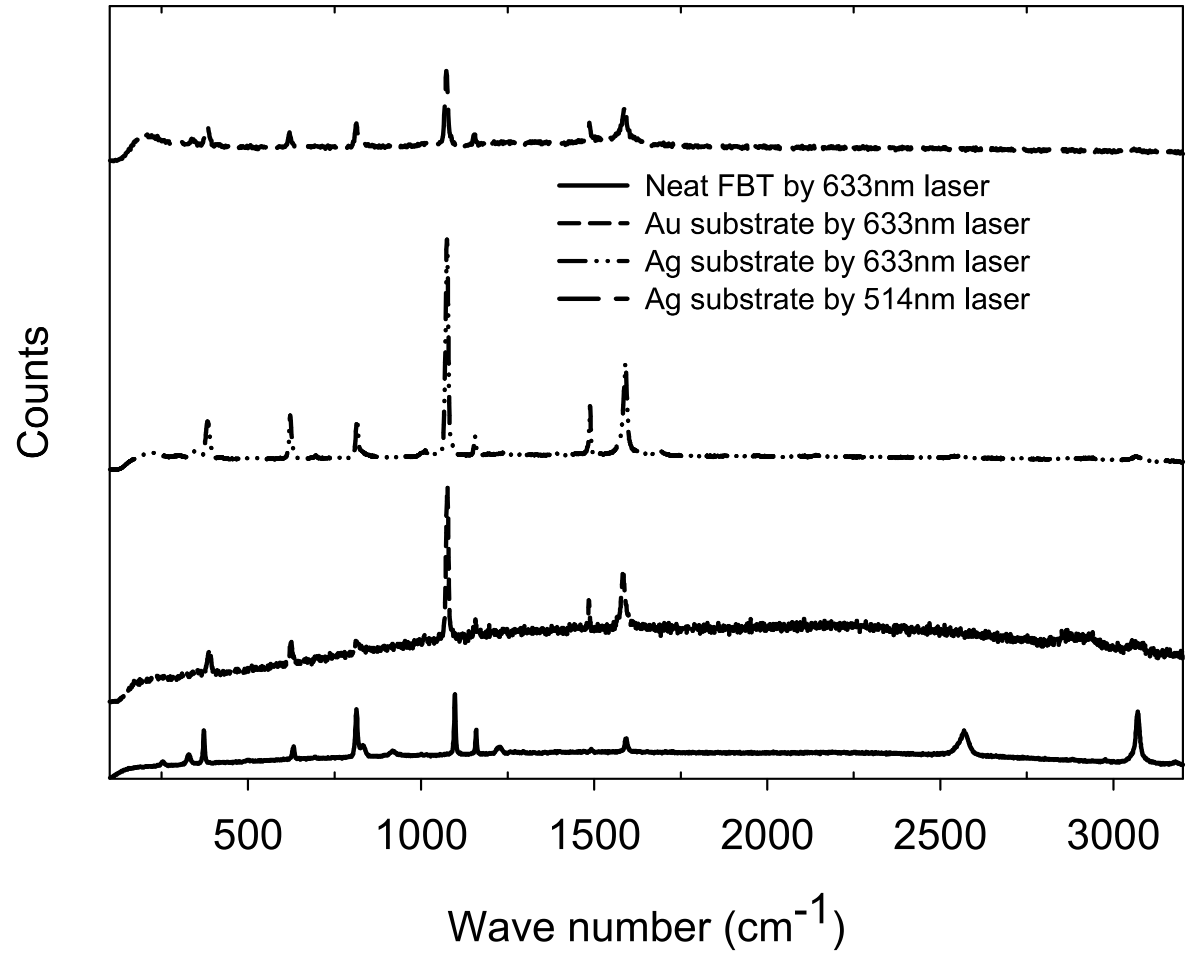




Demirel et al, Advanced Materials, in press, 2008

SERS: Laser Wavelength





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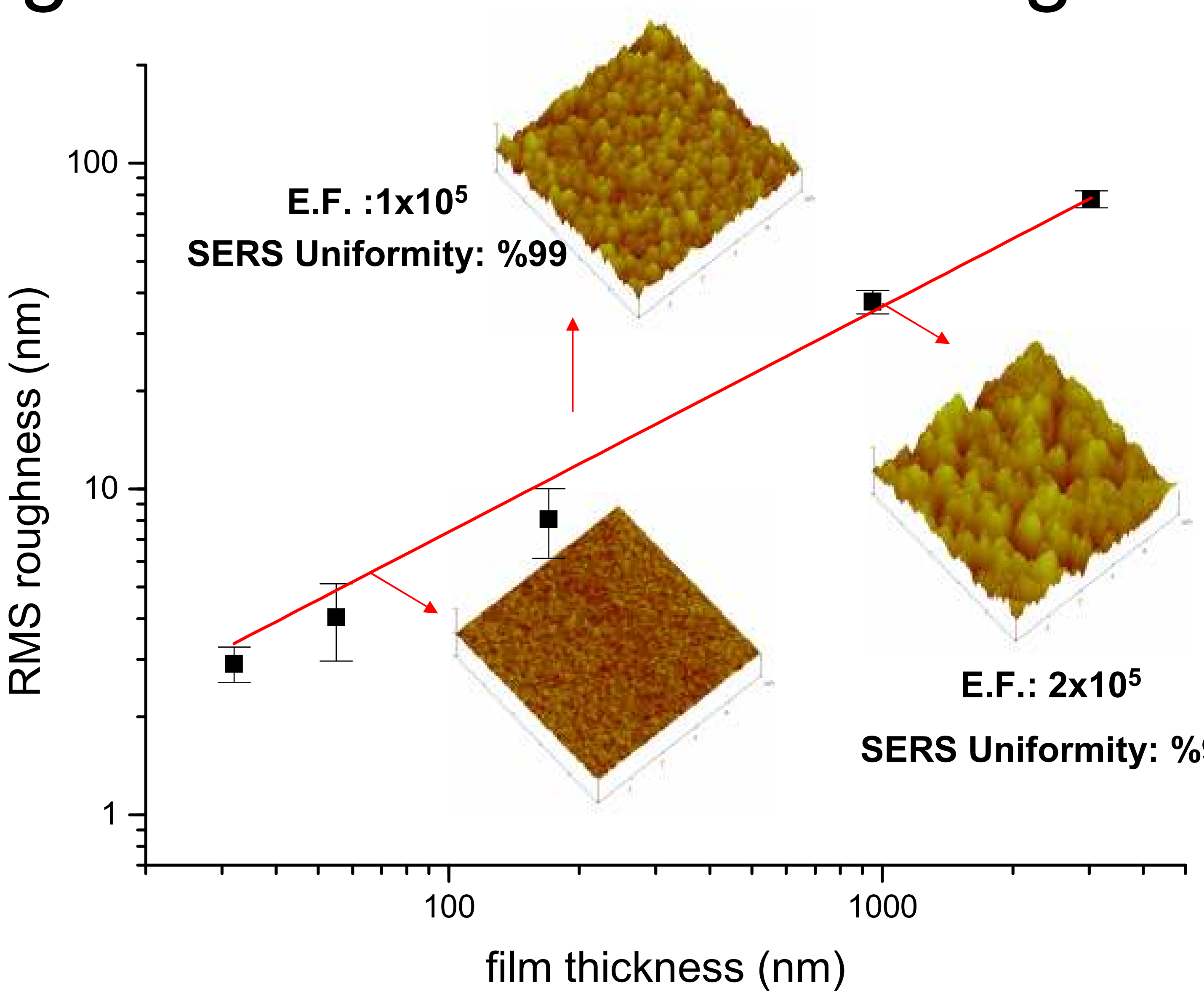
Roughness control over 2 length scale



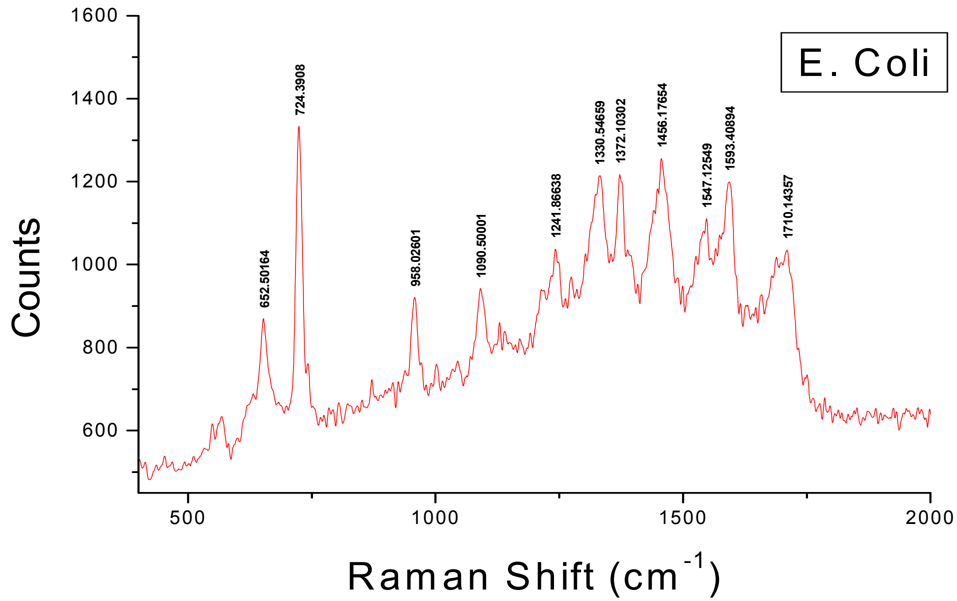
Demirel et al, Advanced Materials, in press, 2008

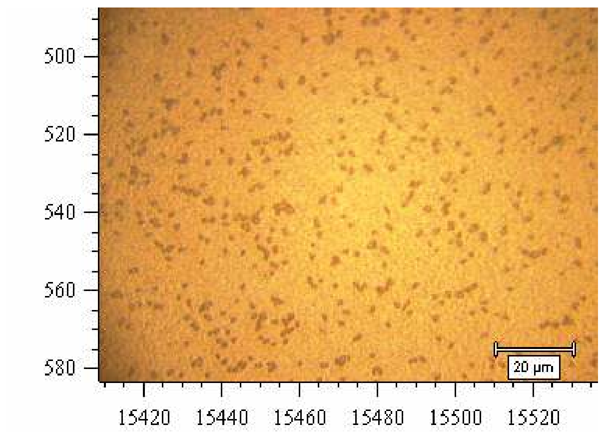
SERS: Life time measurement

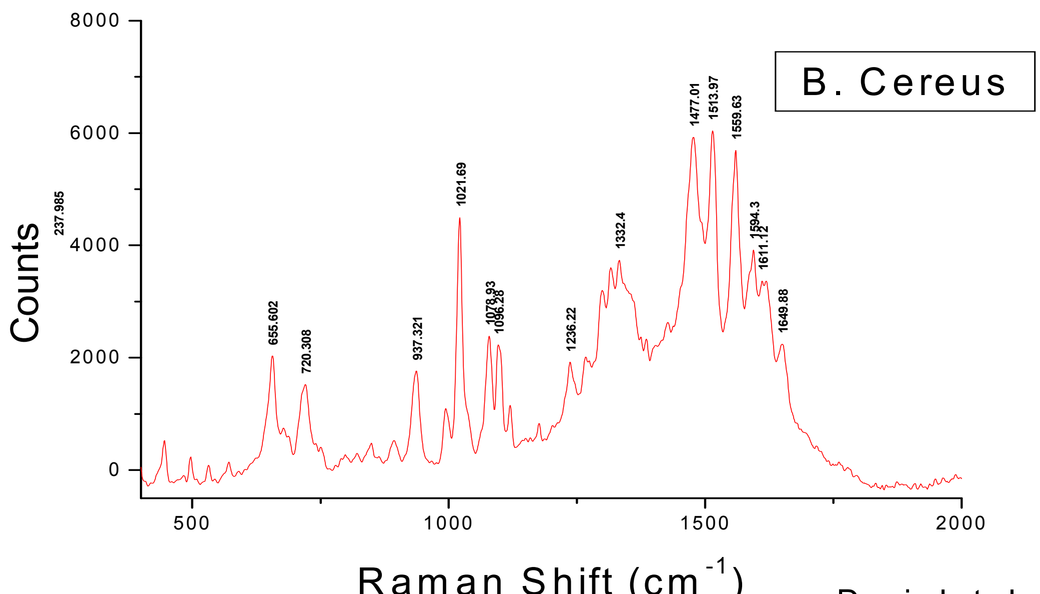
	Fresh sample	After one month	After two months
Au	4612	Not measured	2369
Ag	83437	11380	Not Measured

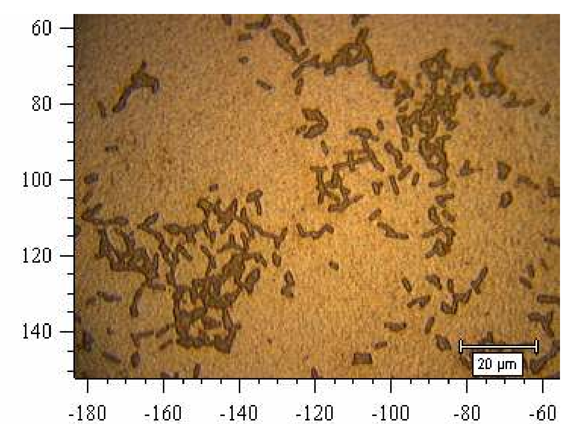
Enhancement factor for SERS substrate

Fingerprint of Bacterial Samples: Single Cell









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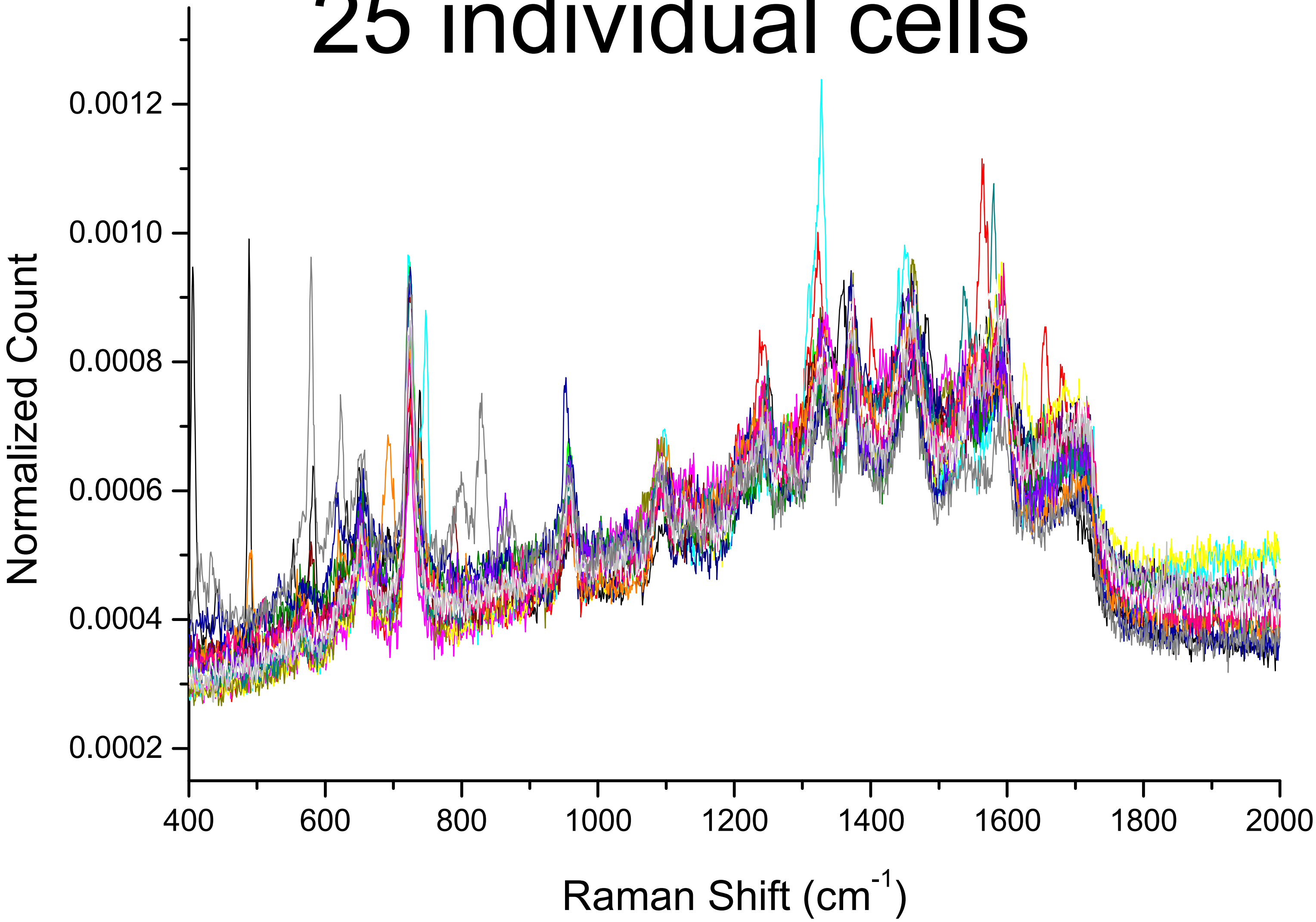
Demirel et al, Advanced Materials, in press, 2008

E.Coli SERS spectra collected from 25 individual cells



Reproducible Data: The peak at the 1372 cm-*1* shows a relative deviation of 15%.

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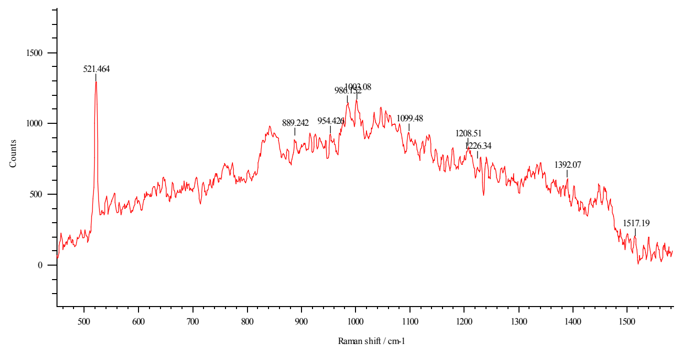
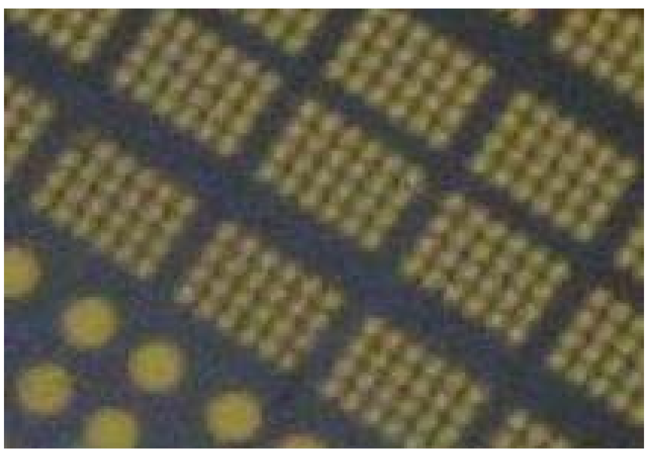
What is next: Detection of Viruses

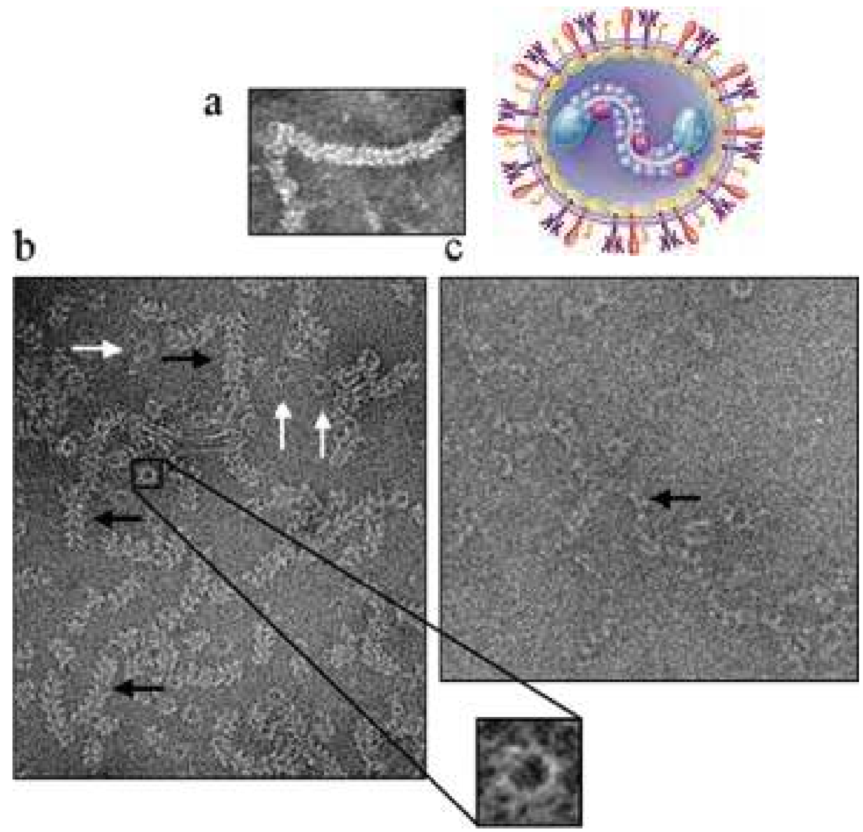


SERS Spectra of RSV



Patterned SERS Substrate (PPX-Au)

Human respiratory syncytial virus (RSV)



Cryo-negative stain images recorded at a magnification of x30,000
MacLennan, J. Virol. 2007;81:9519-9524.

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Applications

- Mechanical Properties
- Self cleaning
- Biosensor
- Energy / Catalyst

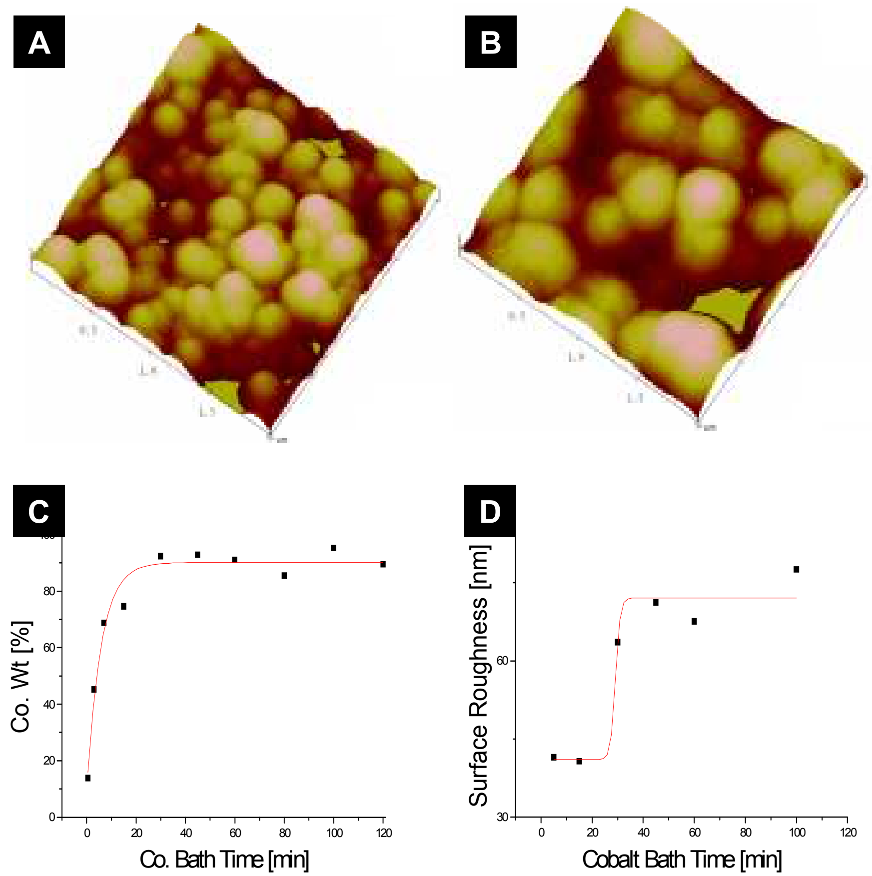
Catalysts activity of Polymer/ Metal surfaces: Cobalt for Hydrogen Release

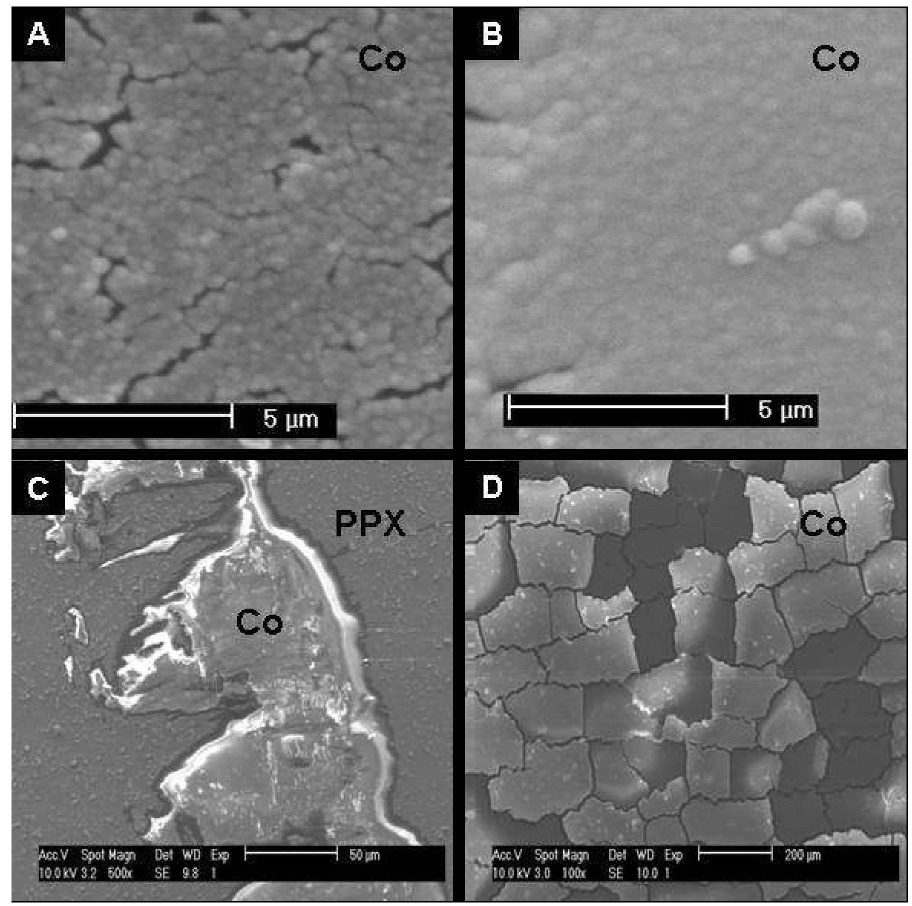
$NaBH_4 + 2H_2O \rightarrow 4H_2 + NaBO_2$

pH = 12

Catalyst	$NaBH_4$ concentration (wt. %)	NaOH concentration (wt. %)	Hydrogen release rate (mL/min-g)	Reference
A-26 (Ru based)	20	10	4032	{Amendola, 2000 #12}
IRA-400 (Ru based)	12.5	1	~9600	{Amendola, 2000 #11}
Pt/C	10	5	23,090	{Wu, 2004 #61}
Co-B	2	5	~3500	{Wu, 2005 #21}
Pt-LiCoO2	5	5	~24000	{Krishnan, 2005 #58}
Ru-C	10	10	6250	{Dong, 2003 #62}
Co-B	25	3	~7500	{Lee, 2007 #18}
Co-PPXC	2.5	10	~1500-7000	This work

Cobalt Substrate Preparation



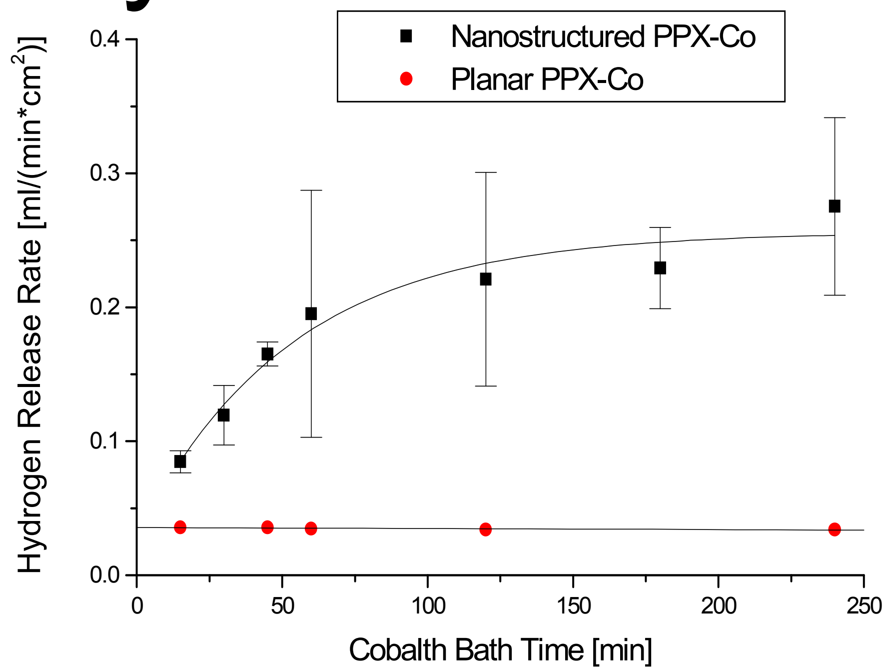


Malvadkar N., Park, S., Macdonald, M., Wang, H., Demirel, M.C., JOURNAL of POWER SOURCES, in press, 2008.

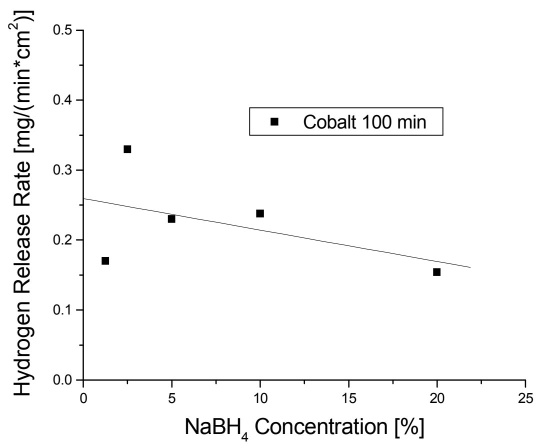
Cobalt Catalyst Results

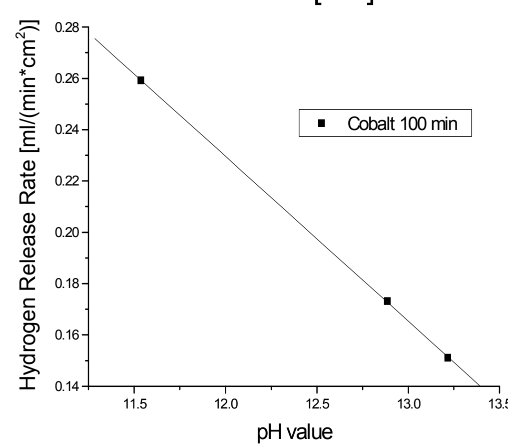
Hydrogen formation from Sodiumborohydride (Cobalt as a catalyst)

$NaBH_4 + 2H_2O \rightarrow 4H_2 + NaBO_2$
pH = 12



Concentration and pH dependence





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Malvadkar N., Park, S., Macdonald, M., Wang, H., Demirel, M.C., JOURNAL of POWER SOURCES, in press, 2008.

Conclusions

1. Structured polymers are grown, *for the first time*, by an oblique angle polymerization method. Structured Polymer growth obeys a scaling law and the growth can be modeled with a ballistic Monte Carlo method.

2. Structured Polymers offer the possibility of fabricating surfaces exhibiting tunable physical properties (i.e. modulus, hydrophobicity, toughness, porosity, etc..) by systematically varying and controlling the chemistry, morphology, and topology at the same time.

3. Structured Polymer technology is a simple and inexpensive method for the functionalization of surfaces for industrial scale applications. Applications for structured polymers: Biomedical coatings, Self Decontaminating Surfaces, Biosensors, Catalyst supports, sensor platform, Enzyme Stability, etc…

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http://www.personal.psu.edu/mcd18/

Demirel Lab:

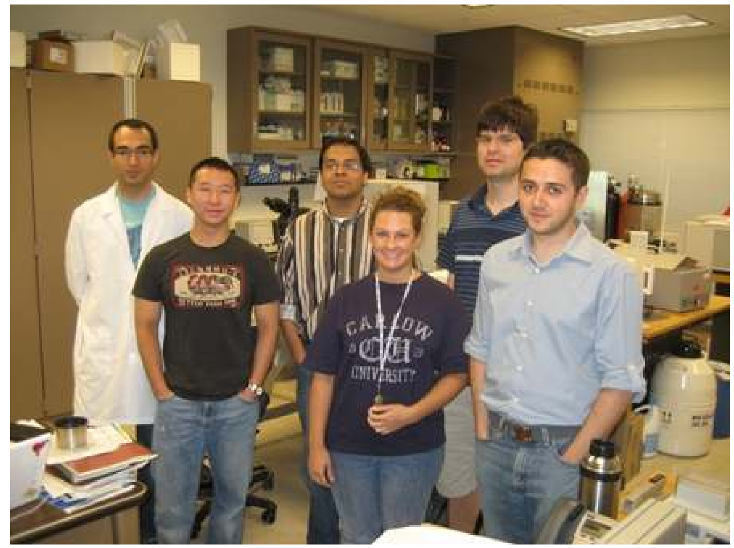
•**<u>Post-doctoral Fellows:</u>** Dr. Serhan Boduroglu, Dr. Hui Wang

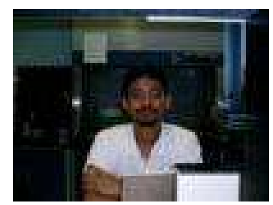
•**<u>Graduate Students:</u>** Eric So, Ping Kao, Niranjan Malvadkar, Murat Cetinkaya, Rama Gullapalli, Sunyoung Park

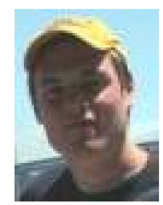
•**<u>Undergraduates:</u>** Ashlee Mangan, Tomas Marko, Brendon Purcell, Mike Anderson

Outside (Active Collaborators):

•Walter Dressick(NRL): Metallization
•David Allara(Penn State): SERS
•Kathy Wahl (NRL): Mechanical Properties
•Mary Poss (Penn State): Infectious Diseases







Thank you

More information and technical documents are available at our group web site:

http://www.personal.psu.edu/mcd18/