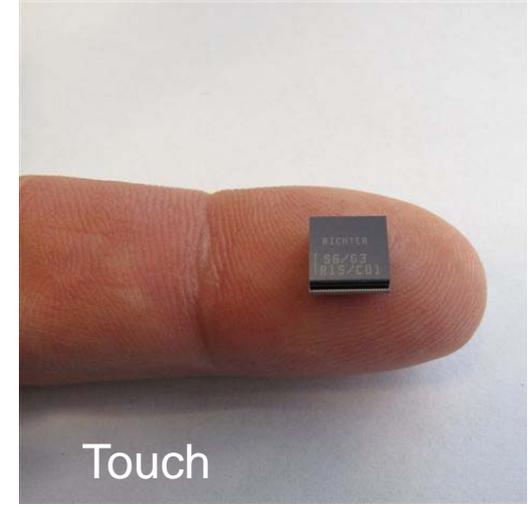
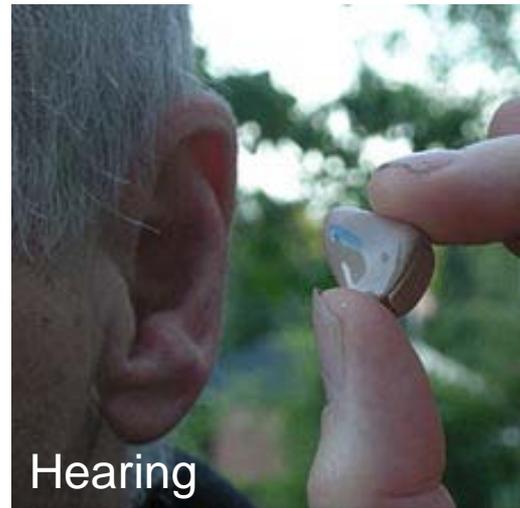


# Implement taste and smell with nanosensors

**Zhiyong Li**  
**HP Labs, Palo Alto, CA, USA**  
**[zhiyong.li@hp.com](mailto:zhiyong.li@hp.com)**



# Microtechnology and semiconductor industry have revolutionalized modern life



Smell



Taste



## San Bruno Fire



## Milk adulteration with melamine



## Pesticide residue?

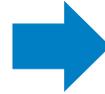
# Analysis of food contaminants in Lab



Extraction



Sample concentrator



Analysis (GCLC-MS)

Time-consuming: several hours (exclude sample shipping)

Expensive tools: hundreds of thousands dollar

Complicated: need professional operator (labor cost)

# Safe, secure, sustainable world and people's well-being demand more sensors



Nanosensor is the solution to implement smell and taste (chemical sensing or chemosensation)



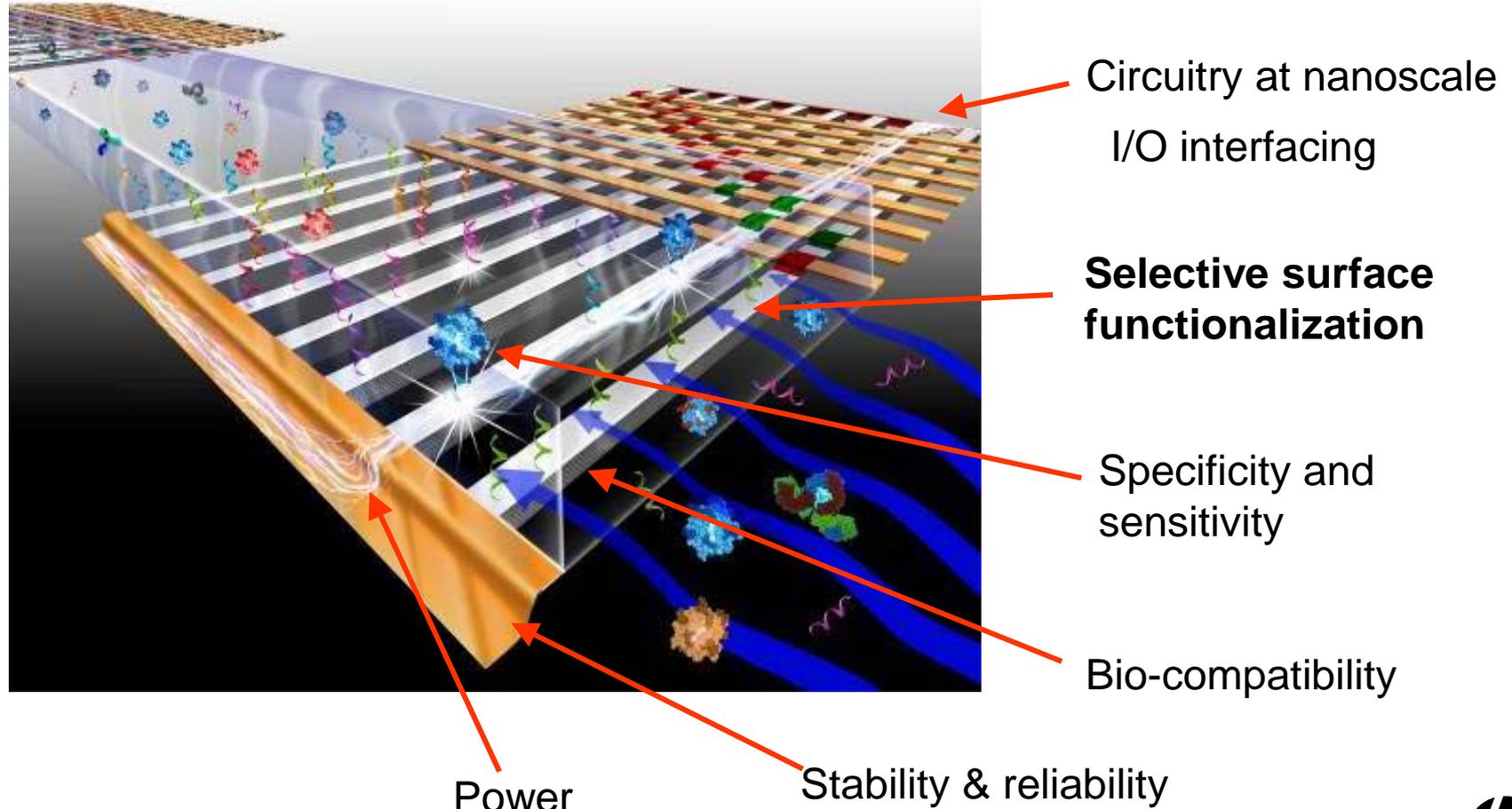
# Potential application of smell and taste nanosensors

- ❑ Food and agriculture: food contaminant test and monitoring, **\$1.6billion** market
- ❑ Healthcare: Disease diagnostic, patient monitoring, multi-function test strips **\$53billion** IVD market
- ❑ Drug regulations: supply monitoring, anti-counterfeiting, 5-10% of WW pharmaceutical annual sales of **\$800billion** is believed to be counterfeit
- ❑ Chemical industry: industrial chemical monitoring
- ❑ Government: environmental monitoring, security and defense applications, food, agriculture and drug regulations
- ❑ R&D organizations: developing new apps



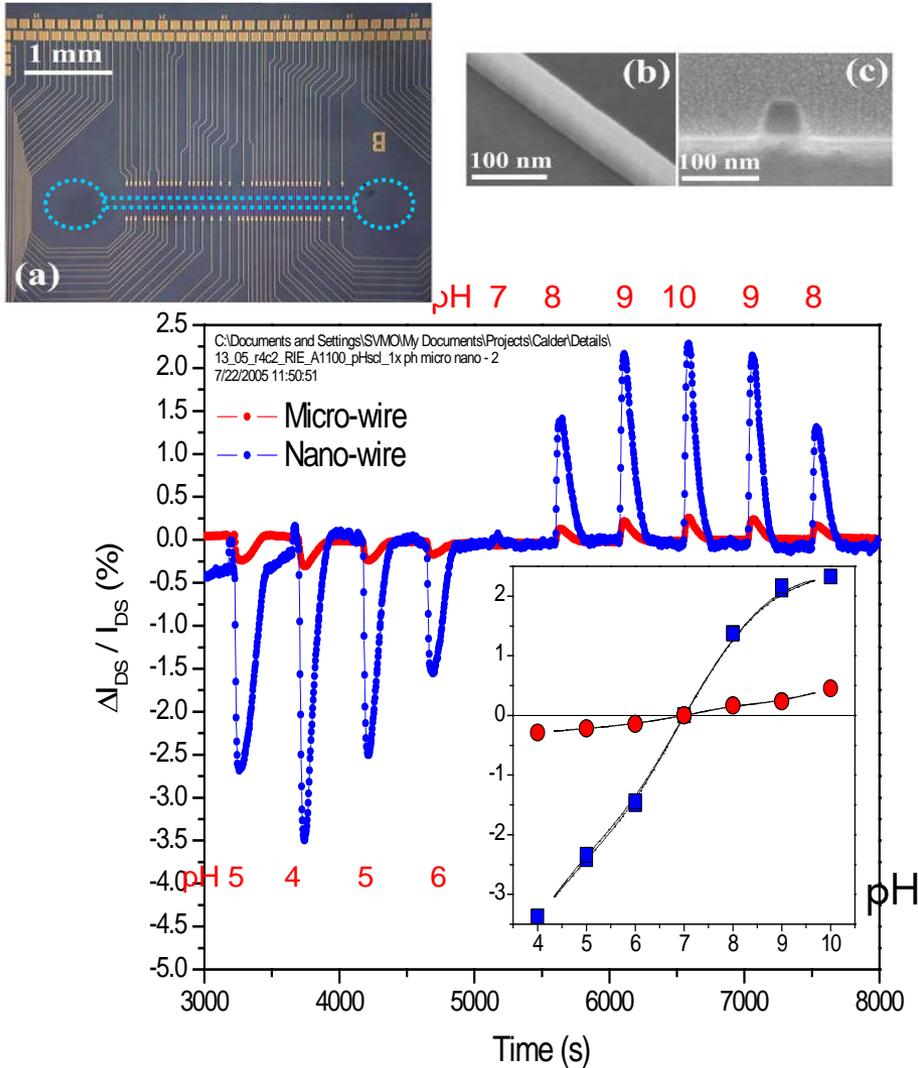
# Silicon ChemFET Nanosensor

Low-cost high-value sensor technology for parallel detection of 100s – 1000s of bio-molecular species.

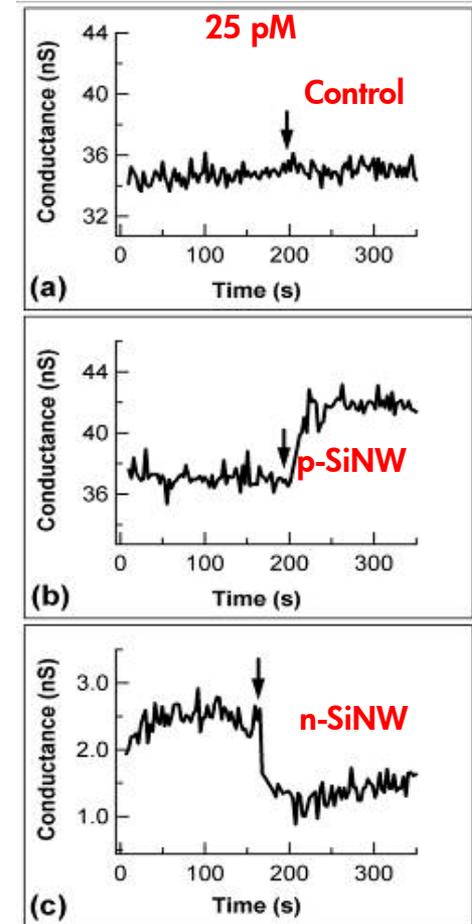
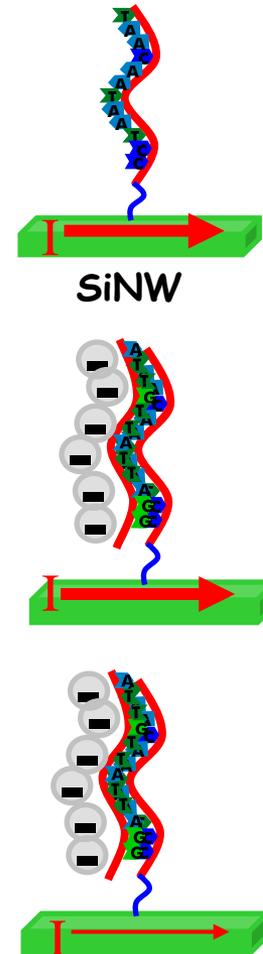


# Sensing proton to DNA

pH sensing

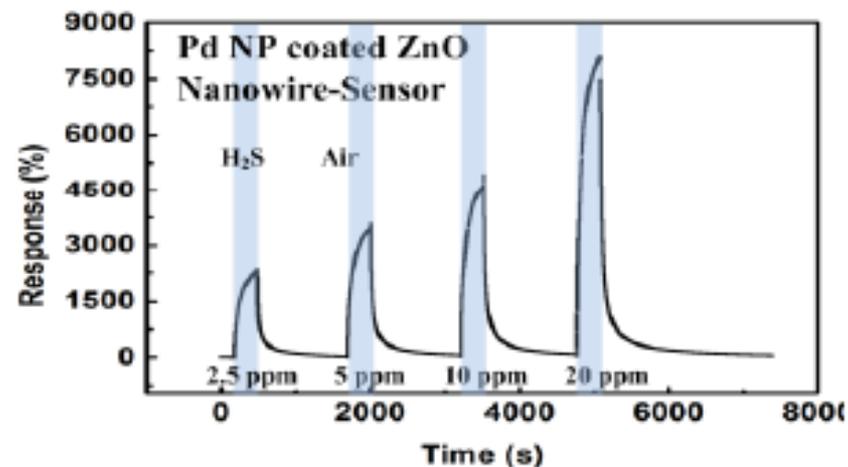
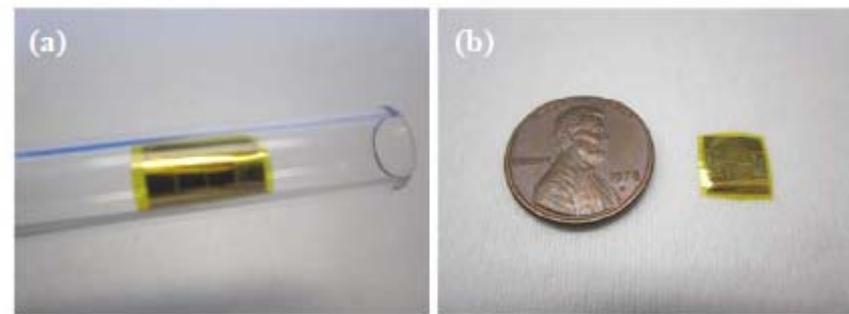
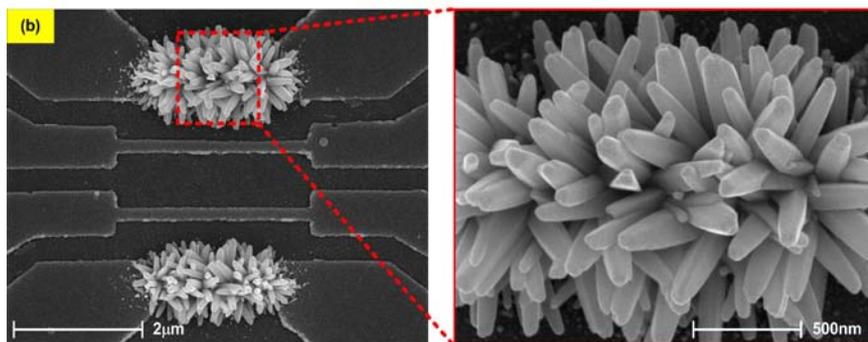
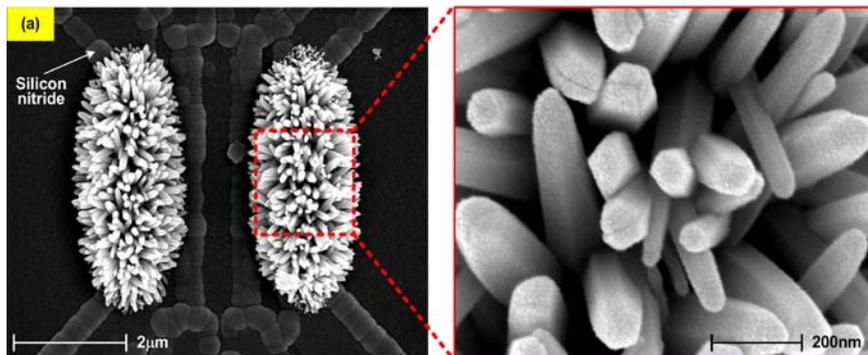


DNA sensing



Z. Li, et al, Nanoletter, 2004, 4, 245

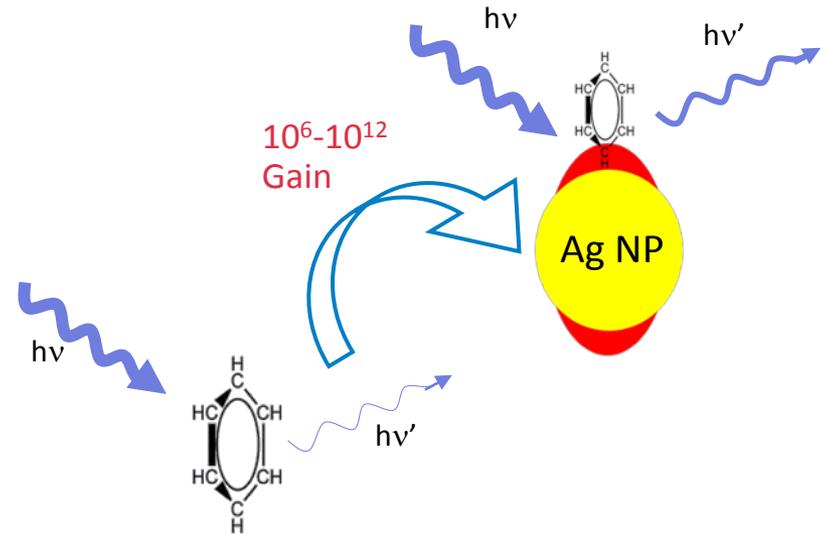
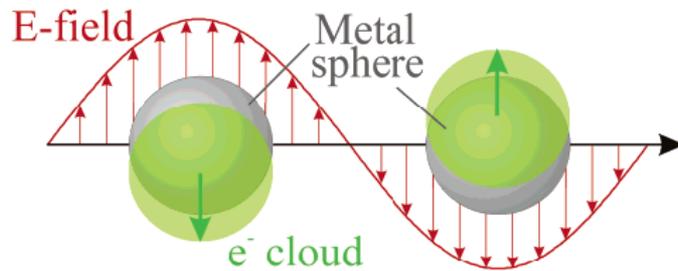
# Smelling the hydrosulfide gas



I. Park, Z. Li et al, Nano Letters, 2007 and 2011

# Surface Enhanced Raman Spectroscopy (SERS) – enabling “molecular fingerprinting”

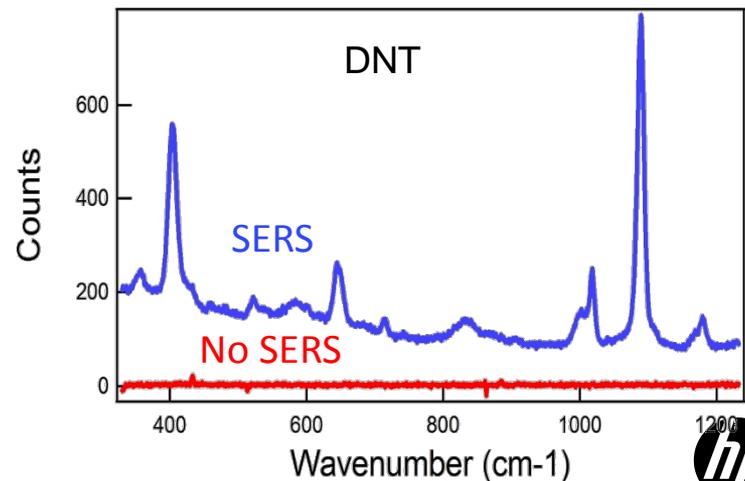
Localized surface plasmon on nanostructure can enhance the Raman scattering process -- SERS



SERS Enhancement Factor  $\propto |E(\omega)|^2 |E(\omega')|^2$

also approx. to  $\sim |E|^4$

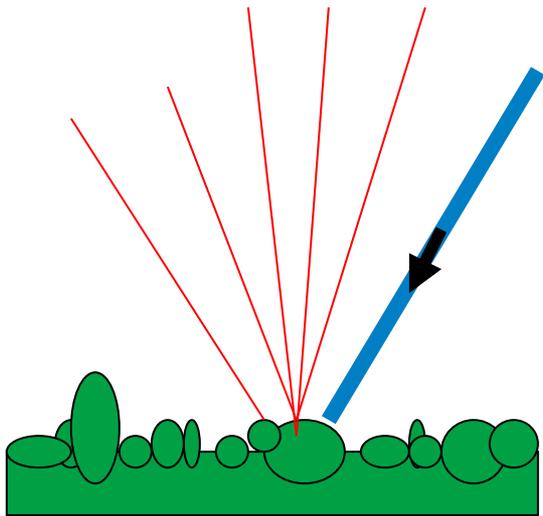
Electromagnetic field induced EF:  $10^6 - 10^{12}$



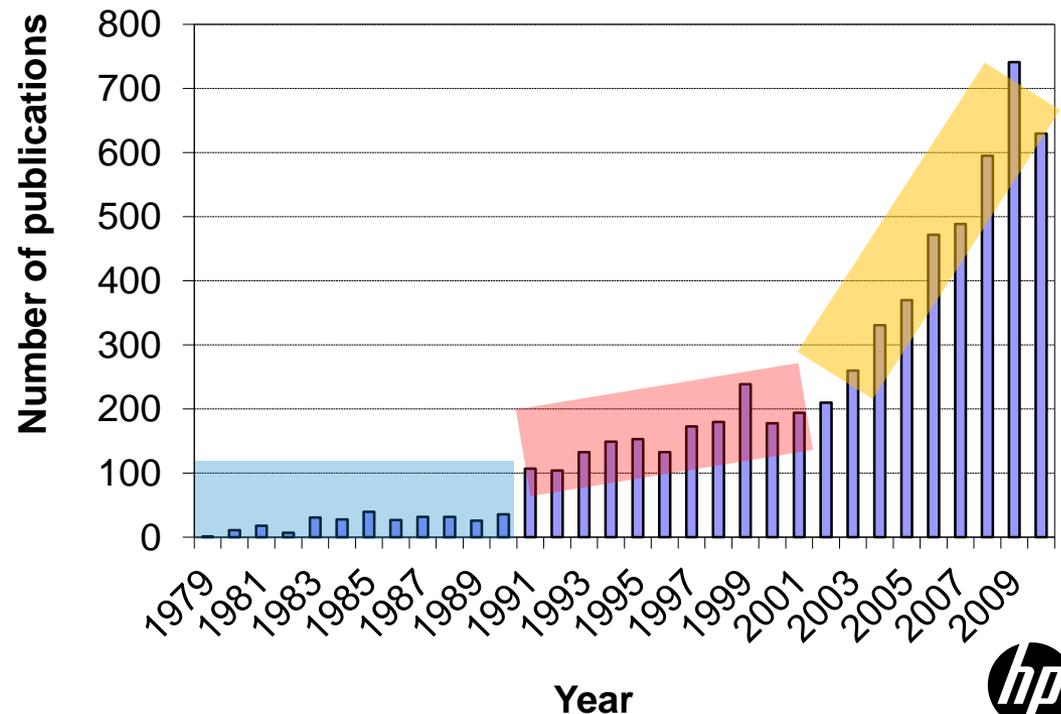
# Surface Enhanced Raman Scattering (SERS)

1974 – M. Fleischman studied pyridine on roughened silver with increased surface area.

1977 – Rick Van Duyne and Alan Creighton reported enhancement of  $\sim 10^5 - 10^6$  -- much too large to account for, by the increased surface area alone.

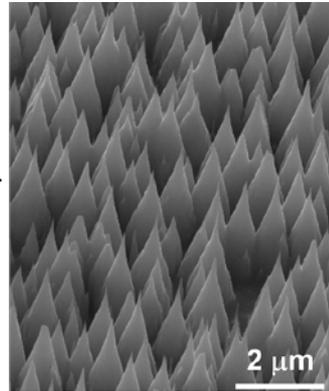


Publications in SERS area



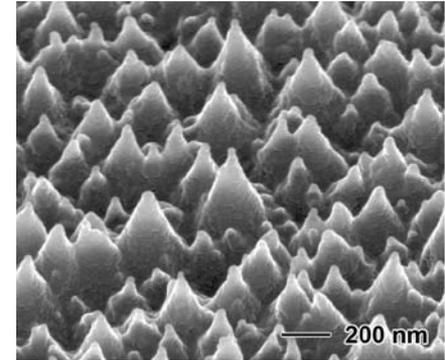
# HP's SERS Technology Evolution

Black Silicon  
(Etched Silicon Cones)



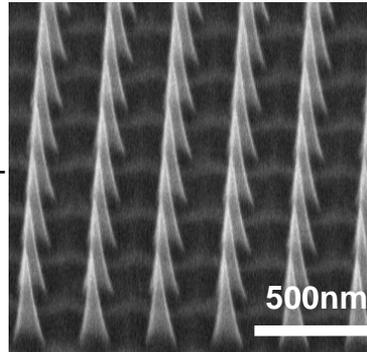
2008

Polymer Cones  
(nanoimprinted)



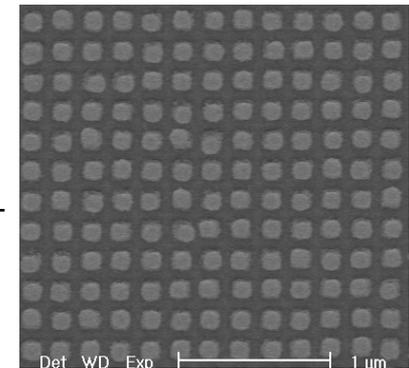
2009

Periodic Cones  
(nanoimprinted)



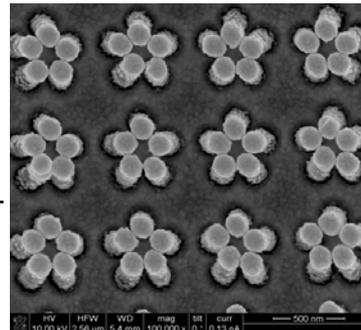
2010

Periodic  
Gold Fingers  
(nanoimprinted)



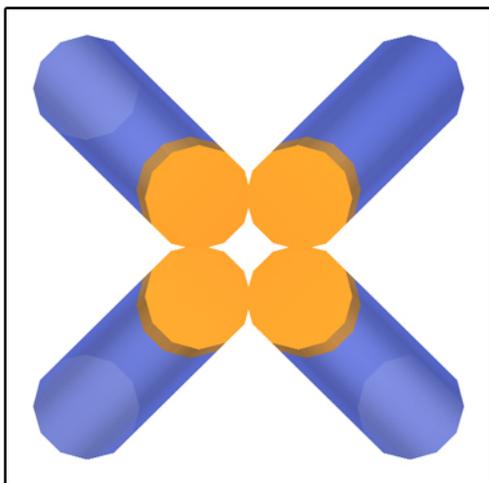
2011

Deterministic  
Gold Fingers  
(nanoimprinted)

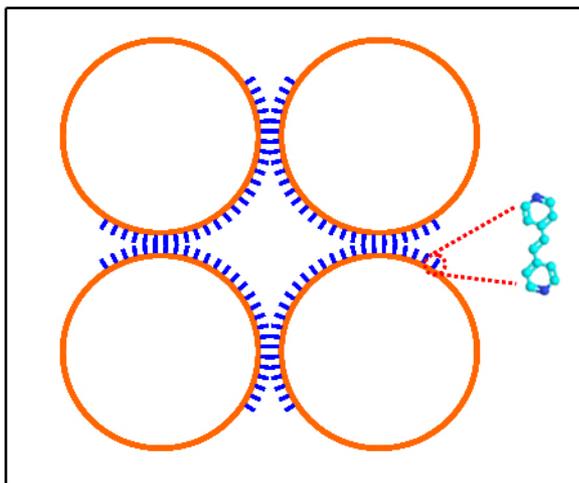


# Molecular Trapped in SERS “hot-spots”

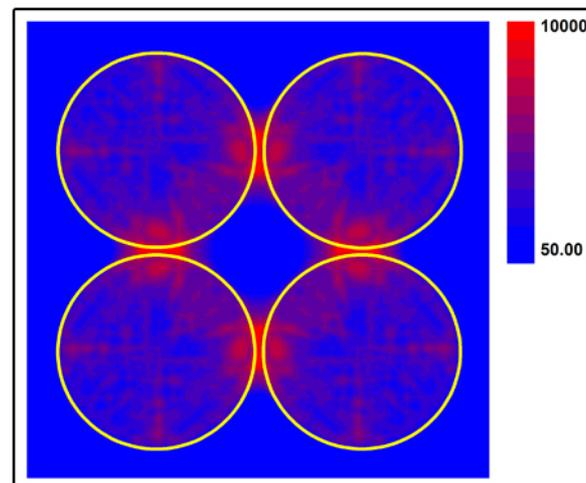
Top view of nanofingers



Cartoon of molecular Trapping



Field map of closed nanofingers



Hu, M. et. al. *J. Am. Chem. Soc.* **2010**, 132, 12820.

The background of the slide is a scanning electron micrograph (SEM) showing a highly ordered, periodic array of nanostructures. Each structure is a small, three-dimensional, conical or cylindrical shape, arranged in a regular grid pattern. The structures are interconnected at their bases, forming a porous, lattice-like structure. The overall appearance is that of a self-assembled or top-down fabricated photonic crystal or SERS substrate.

# **Top-down meets self-assembly**

**— the leap from stochastic to deterministic SERS structures**

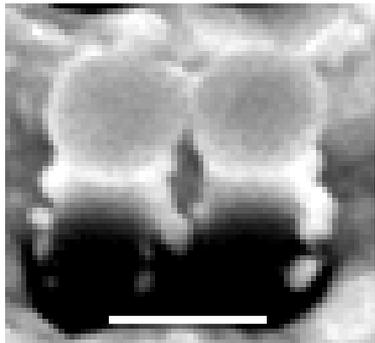
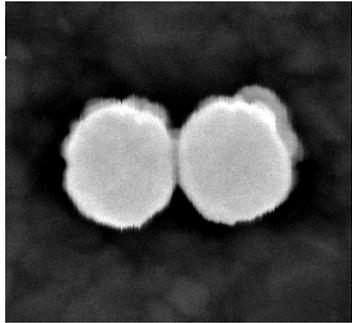
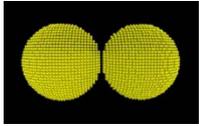
# Advantages of nanofinger structures

- Leverage advantages from both top-down and bottom-up approaches – No need of costly critical dimension control.
- Easy scale-up for large area uniformity and reliable hot spots – Roll-to-roll plastic fab.
- Micro-capillary driven “finger” closing – Easy for fluidic interface, no power nor complicated controls needed.
- Molecule self-limiting of the gap sizes, as small as sub-nm – Physical limit of the smallest separation manufacturable, hence strongest coupling effect.
- Active molecule trapping by the fingers – Molecular tweezer with build-in sensing functionality.

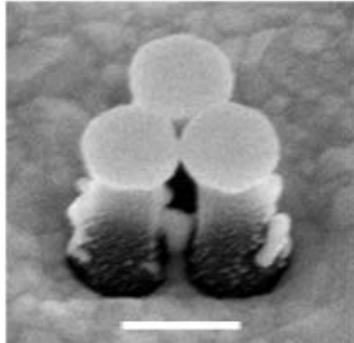
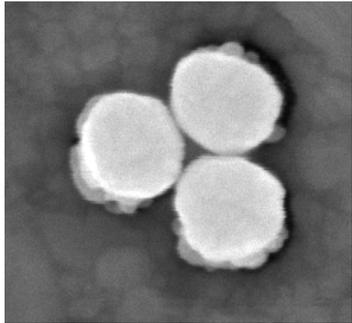
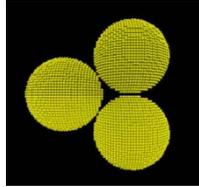


# CAN WE DESIGN FINGER SYMMETRY?

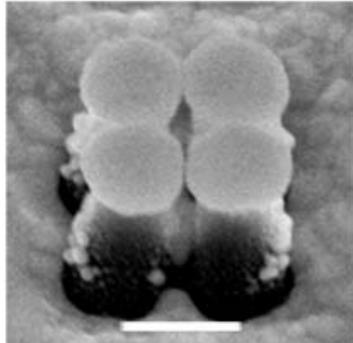
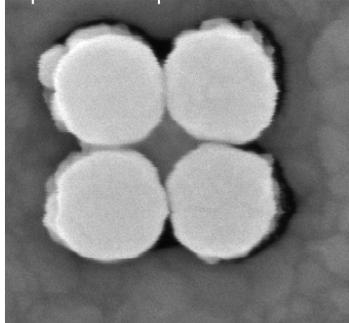
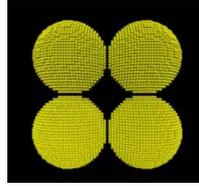
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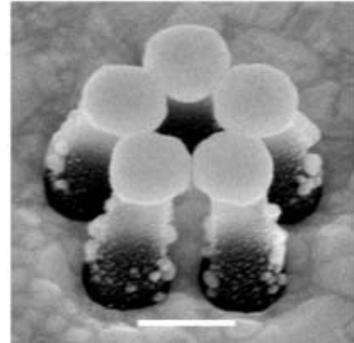
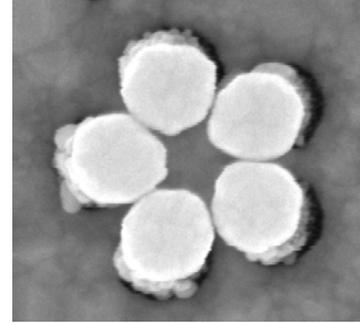
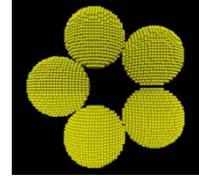
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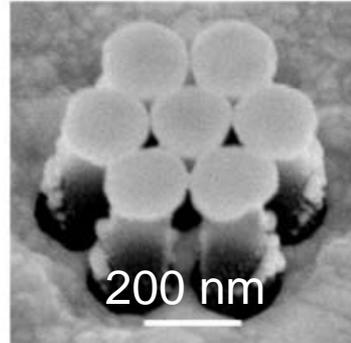
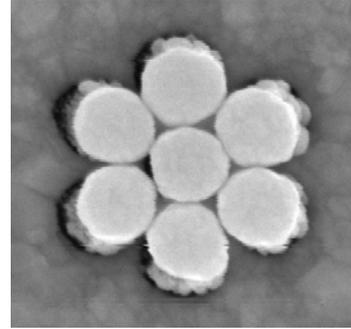
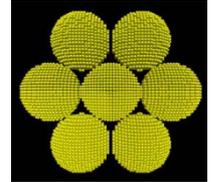
4



5

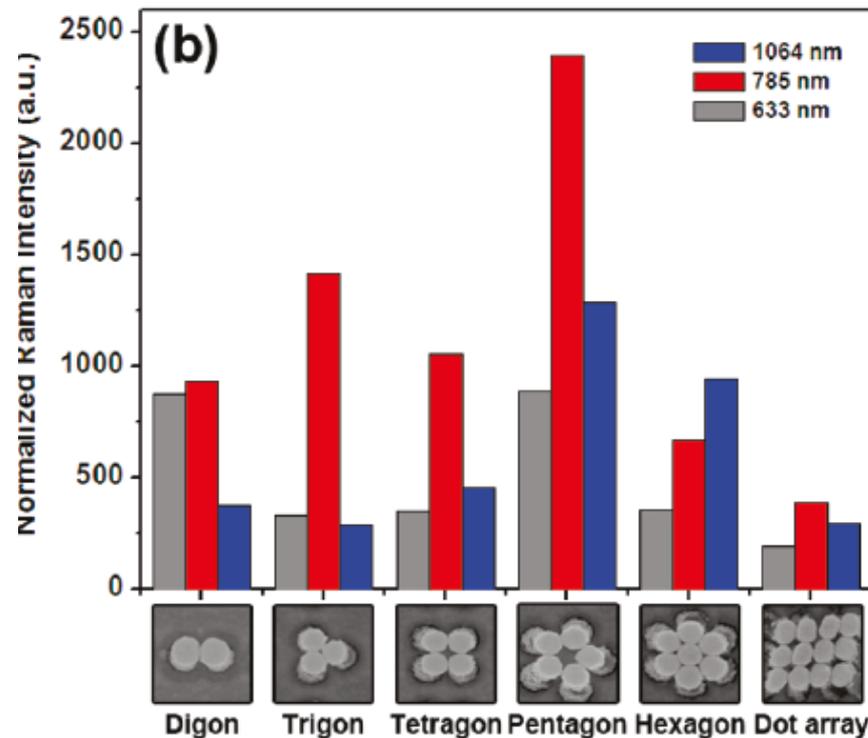
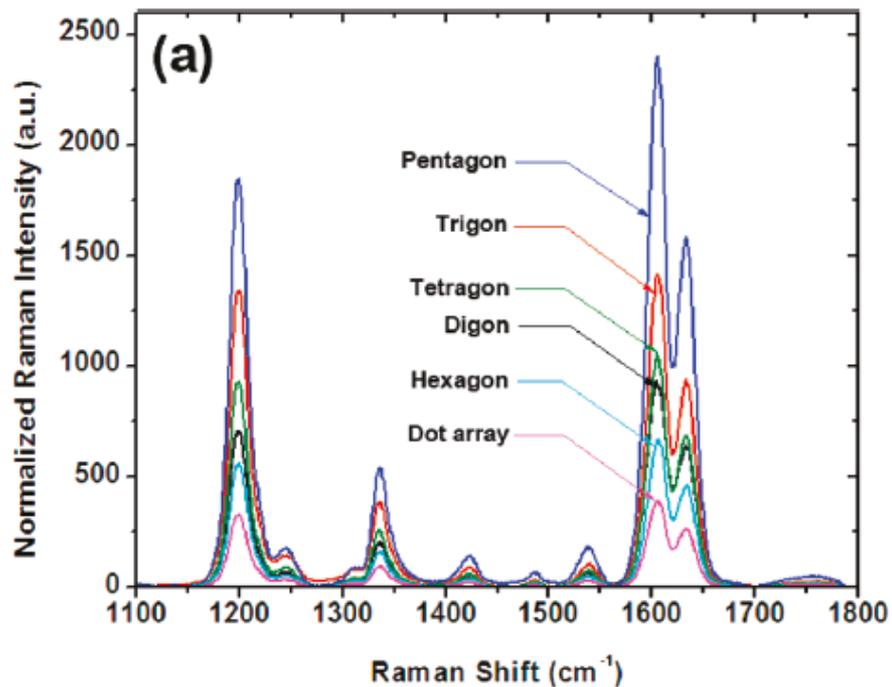


7



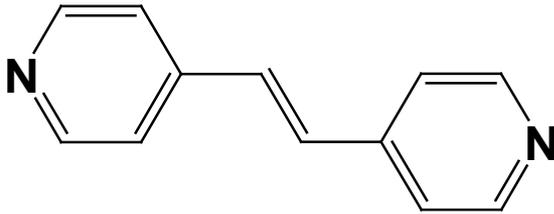
# SERS of nanofinger of different symmetry

BPE

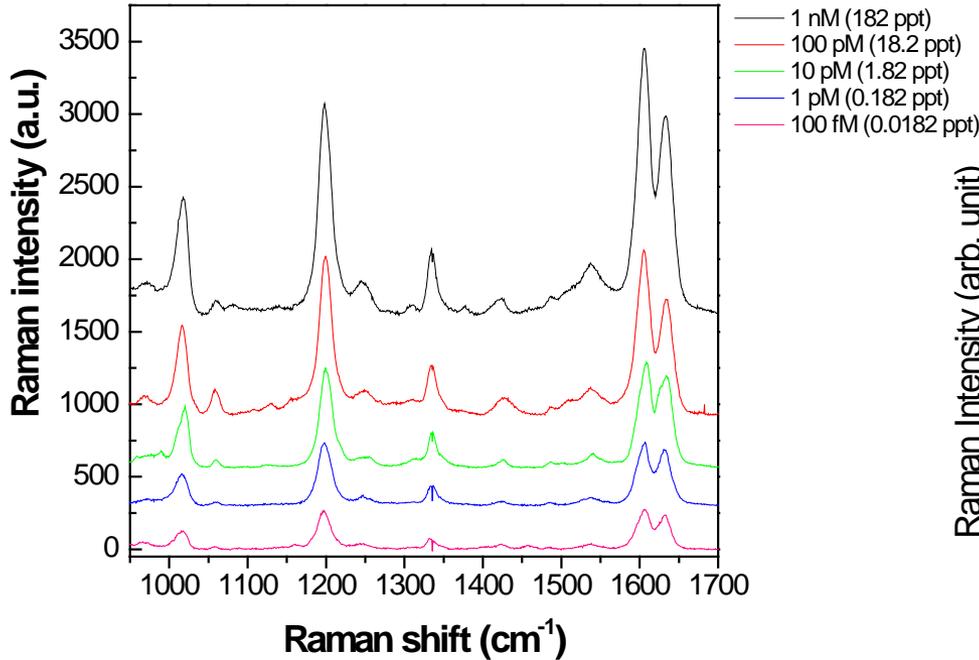


Ou, F. S. et. al. Nano Letters, 2011, 11, 2538-2542.

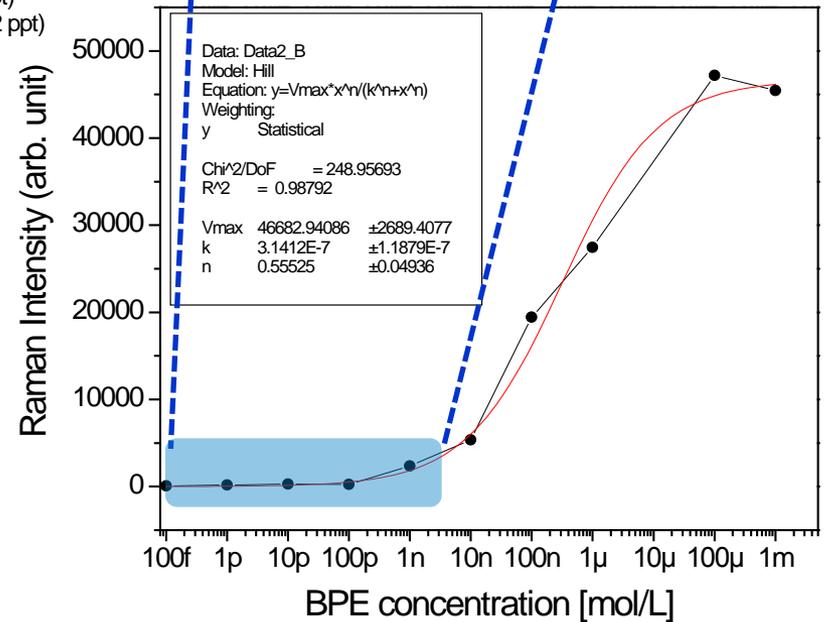
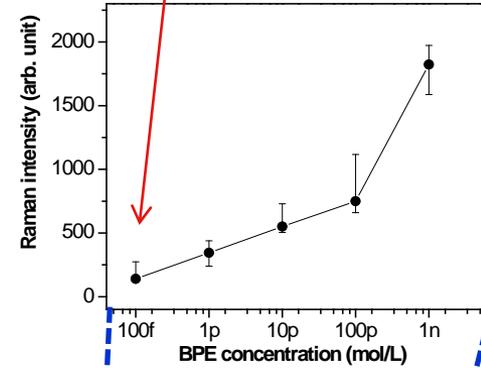
# BPE sensing



Ethanol solution



Detection limit of  
0.02 parts per trillion

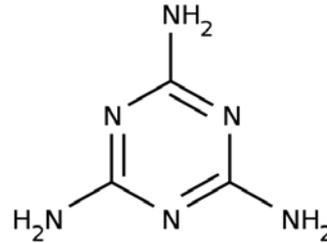


# Demonstration A:

Melamine sensing with HP nanofinger SERS: >10,000× better than competitors

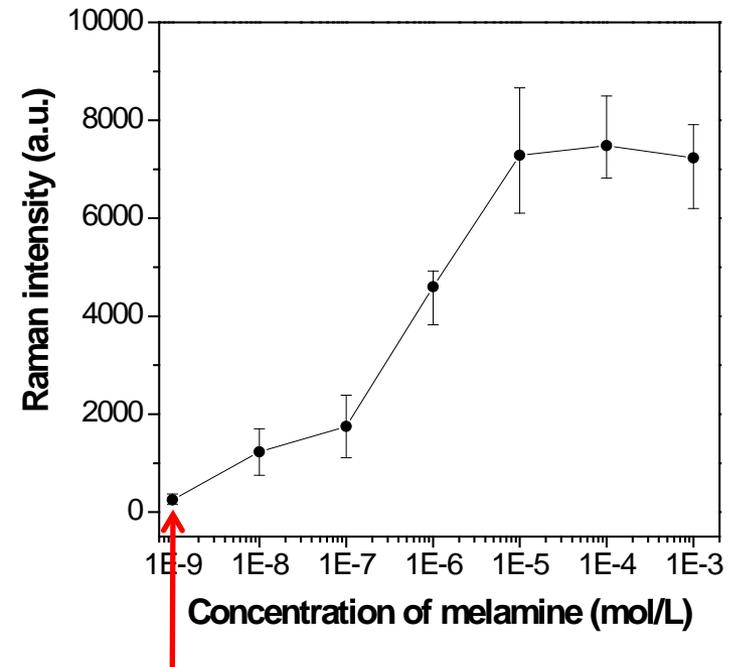
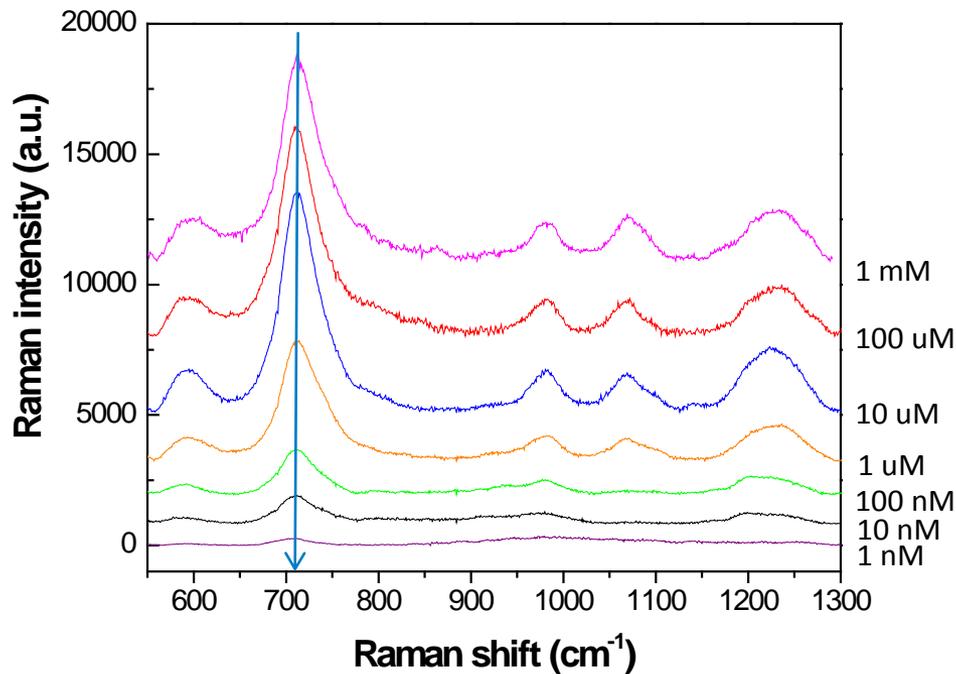


Melamine contamination in milk, 300,000 victims in China 2008



max. amount in infant formula (FDA):

1 mg/kg (1 part per million)



Detection limit of 100 parts per trillion

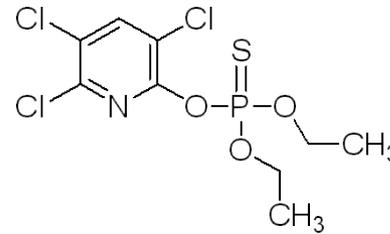


# Demonstration B:

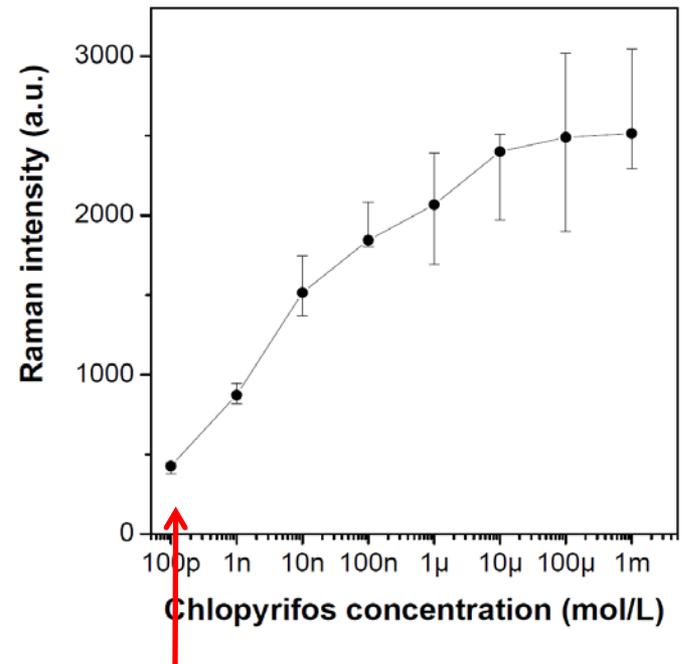
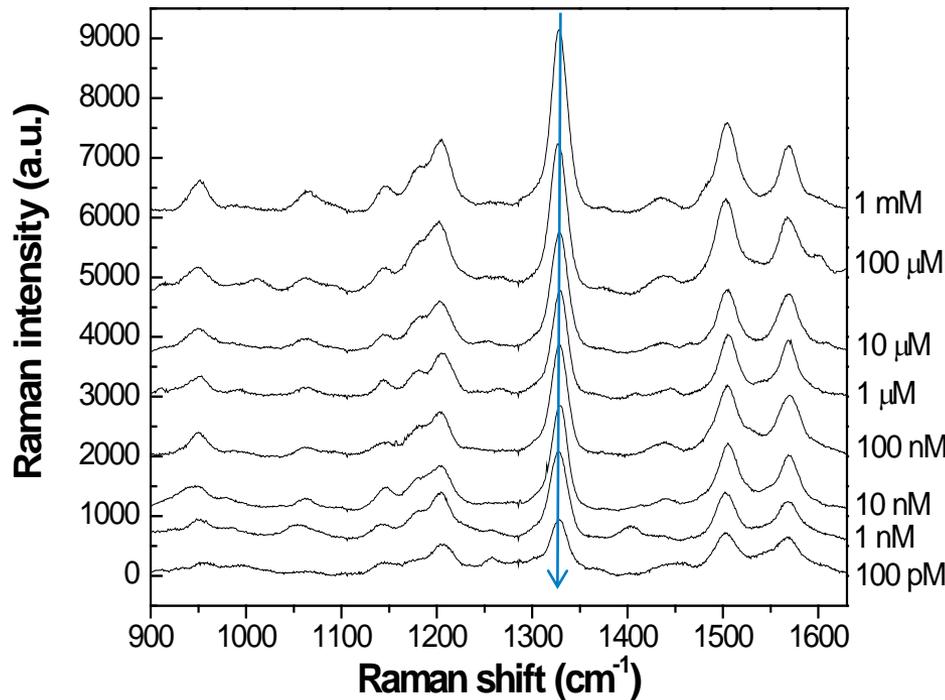
Chlorpyrifos sensing with HP nanofinger SERS:  $>1,000\times$  lower than EPA regulation



Chlorpyrifos, is a **neurotoxin**, **carcinogen**, once popular pesticide used worldwide, and the residue can be found in vegetables, fruits, etc.



EPA regulation:  
0.1 parts per million  
on citrus fruits



Detection limit of  
35 parts per trillion

