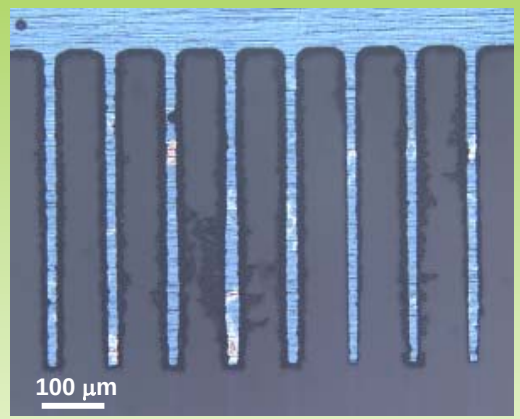
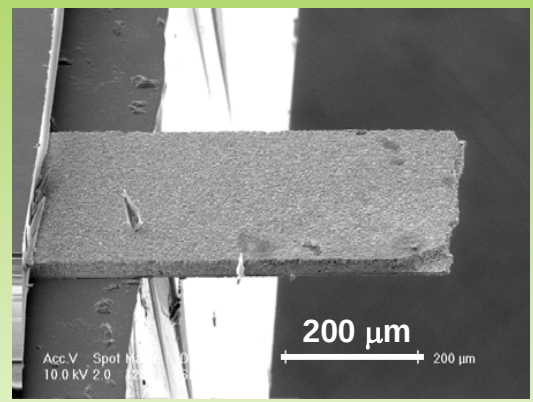
U.S. EPA 2004 Nanotechnology Science To Achieve Results (Star)
Progress Review Workshop-Nanotechnology and the Environment II

Ultrasensitive Pathogen Quantification in Drinking Water Using High Piezoelectric PMN-PT Microcantilevers





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U.S. EPA - Science To Achieve Results (STAR) Program
Grant # R829604

E.coli 0157:H7

- E.coli 0157:H7 is the main cause of :
  - Foodborne illness
    - Contaminated meat – improperly cooked beef
    - Lettuce
    - Unpasteurized milk and juice
    - Salami
    - Sprouts
  - Waterborne illness
    - Creeks, rivers, streams, lakes, ground water, portable water and swimming pools

E coli alone killed some 240 people in 2001!

Current pathogen detection technology

Disadvantages:

- Slow
- Not real-time, in-situ
- Not quantitative

Need: a sensor that is

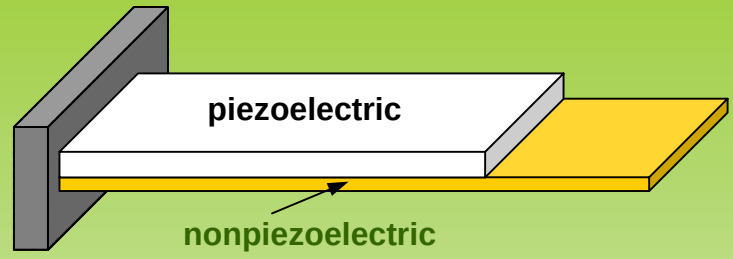
direct, sensitive, rapid, real-time, and in-situ

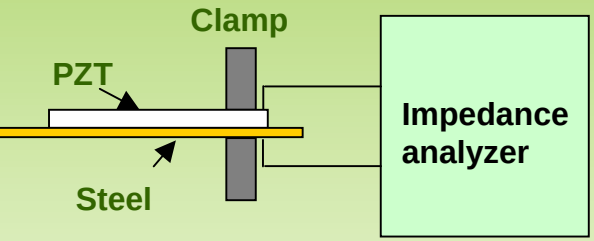
Dynamic Applications: Biosensors

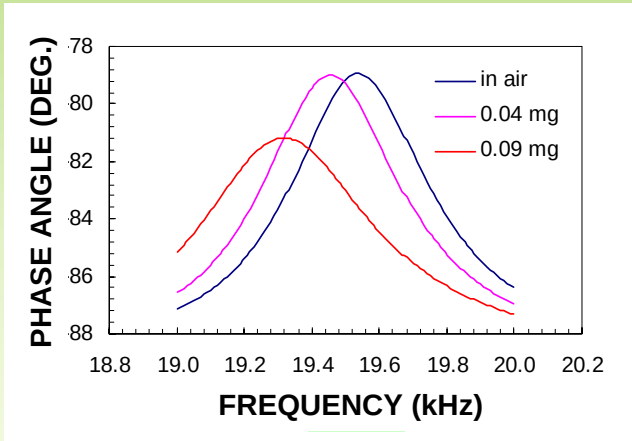
DESIGN

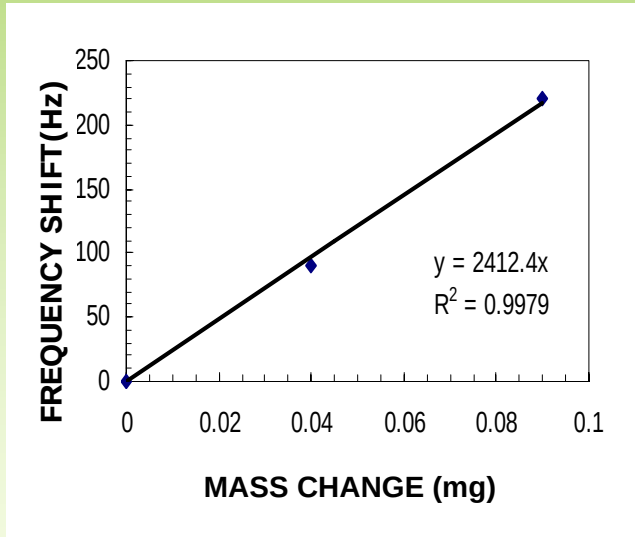
Detection: DETECT MASS CHANGE
BY RESONANCE FREQUENCY SHIFT

Measurement: ELECTRICAL





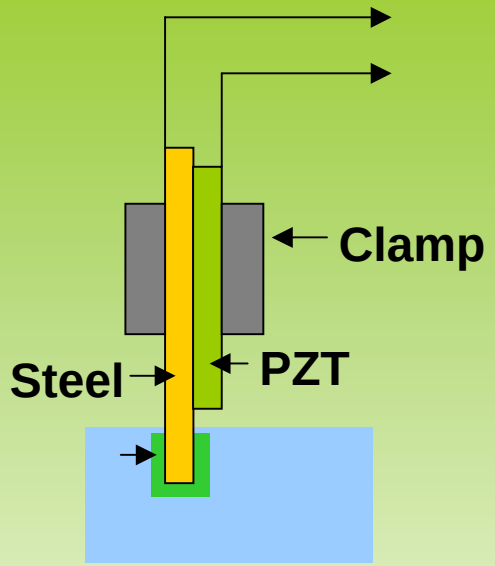


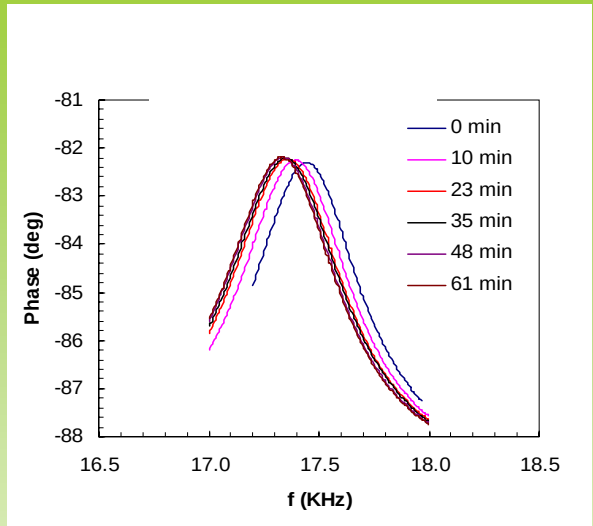


Advantages:

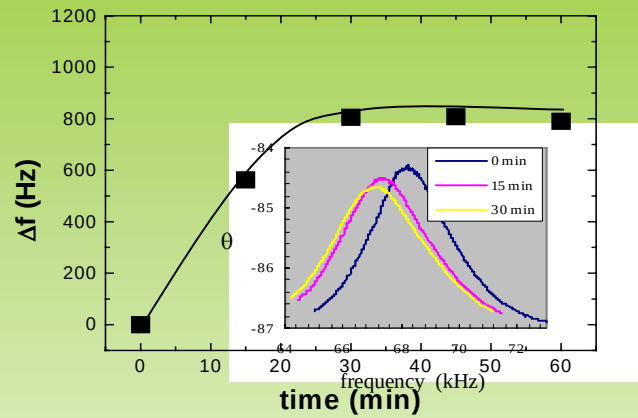
- Label free
- Portable
- Rapid real-time detection
- Airborne and in-liquid

Piezoelectric Microcantilever Biosensing

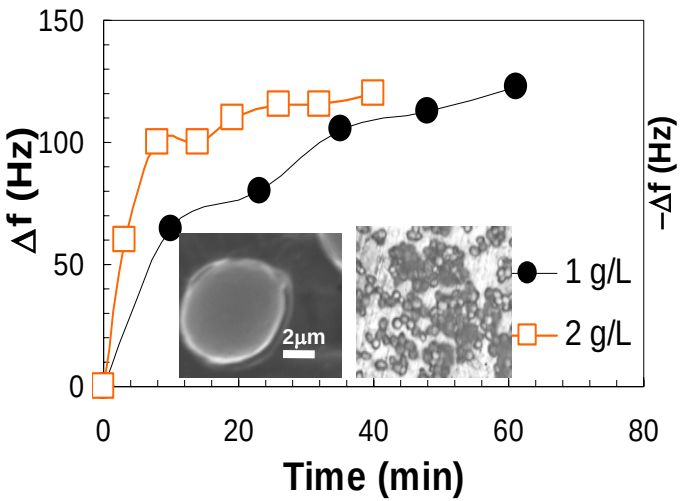




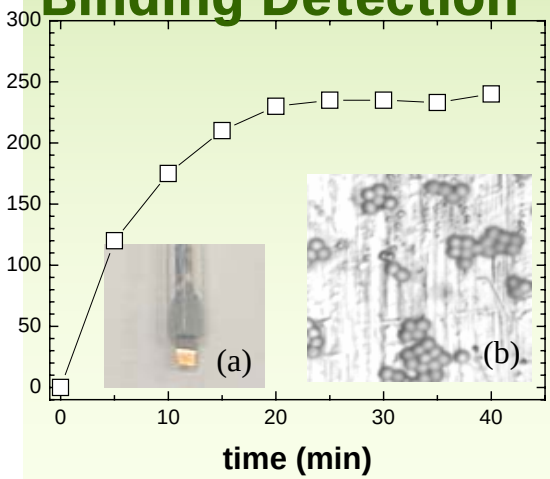
Protein Detection: Avidin



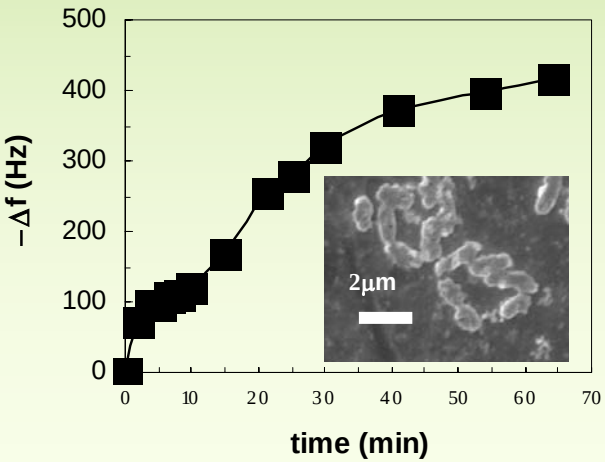
Yeast Quantification



Biotin-Avidin Binding Detection

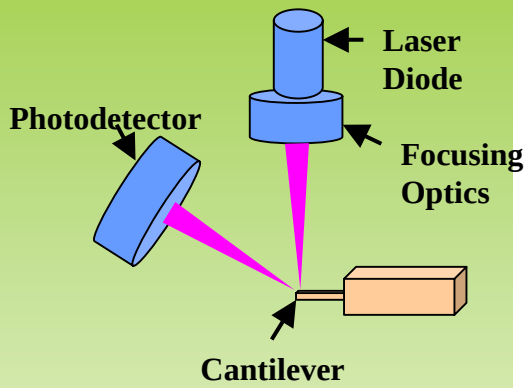


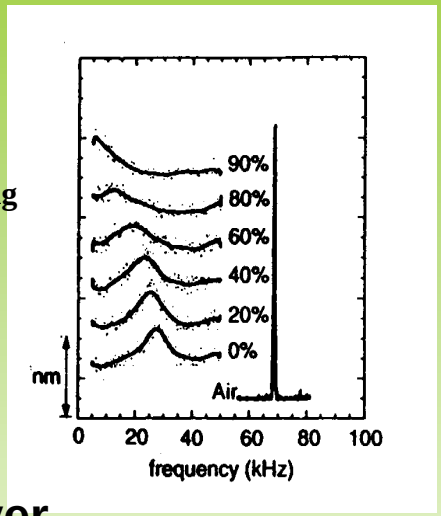
E coli Detection



Comparisons

Silicon microcantilever





Silicon microcantilever

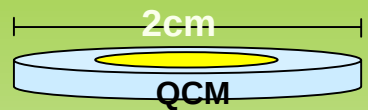
Disadvantages:

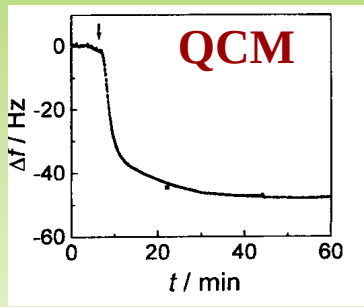
- need a driver for actuation
- Need optical system for detection
- Q factor ≈1 in water,
- in-water detection difficult
- Difficult for multiplexing

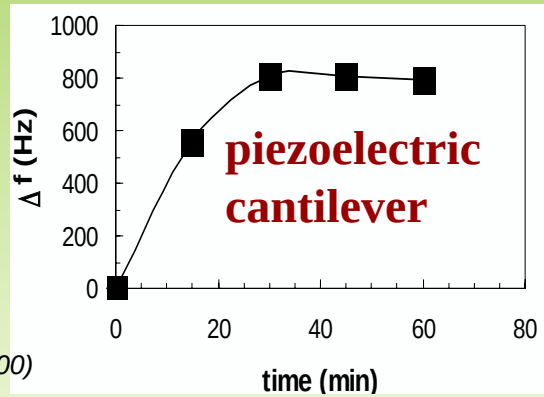
T. Thundat, E. A. Wachter, S. L. Sharp, and R. J. Warmack, Appl. Phys. Lett., ***66***, *1695 (1995).*
B. Ilic, D. Czaplewsli, H. G. Craighead, P. Neuzil, C. Campagnolo, and C. Batt, Appl. Phys. Lett., ***77***, *450 (2000).*

Quartz Crystal Microbalance(QCM)

Avidin binding on 3-mercatopropionic acid





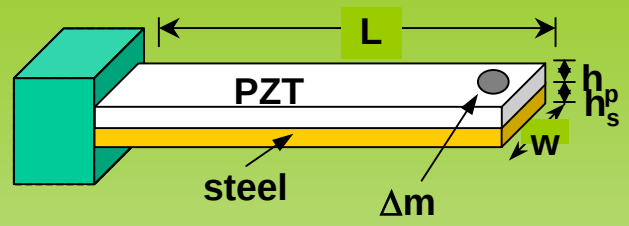


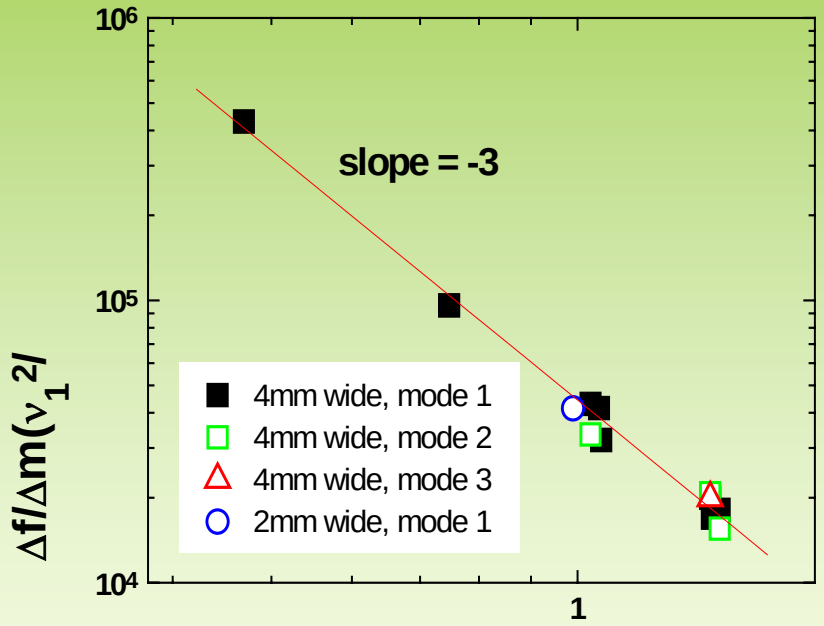
Biophysical Journal, ***78****, 487 (2000)*

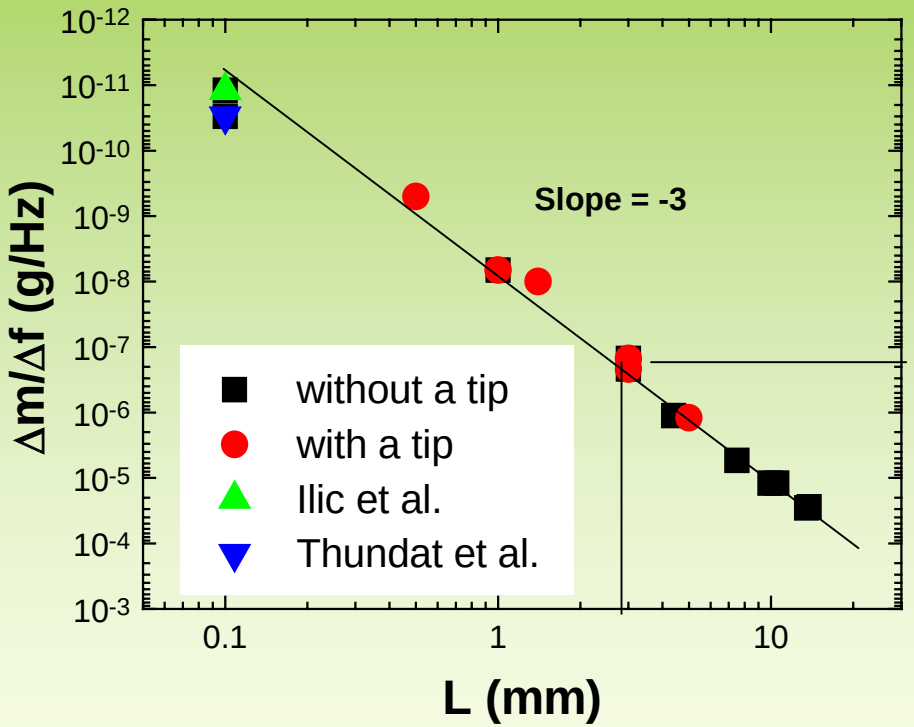
- Cantilever of 0.7 mm long PZT with a 2.5 mm tip is already 16 times more sensitive in Δf than the most common 5MHz QCM
- Also difficult for multiplexing

Mass Detection sensitivity

$$\frac{\Delta f}{\Delta m} \cong \frac{1}{2}\frac{f}{M} = \frac{\nu^2}{4\pi}\frac{1}{L^3 w}\left(\frac{1}{0.236\sqrt{12}\,\tilde{\rho}}\sqrt{\frac{\tilde{E}}{\tilde{\rho}}}\right)$$







At 100μm length, Δm/Δf will approach 10^{-16} g/Hz !

J. W. Yi, W. Y. Shih, W. –H. Shih, *J. Appl. Phys.*, 91(3), 1680-1686 (2002).

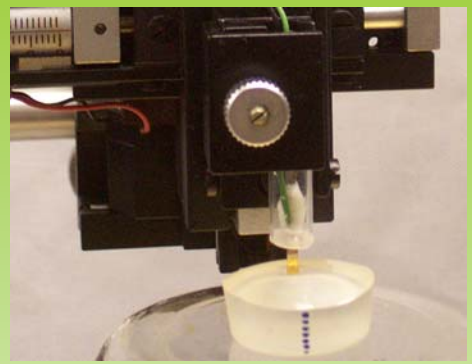
Objectives

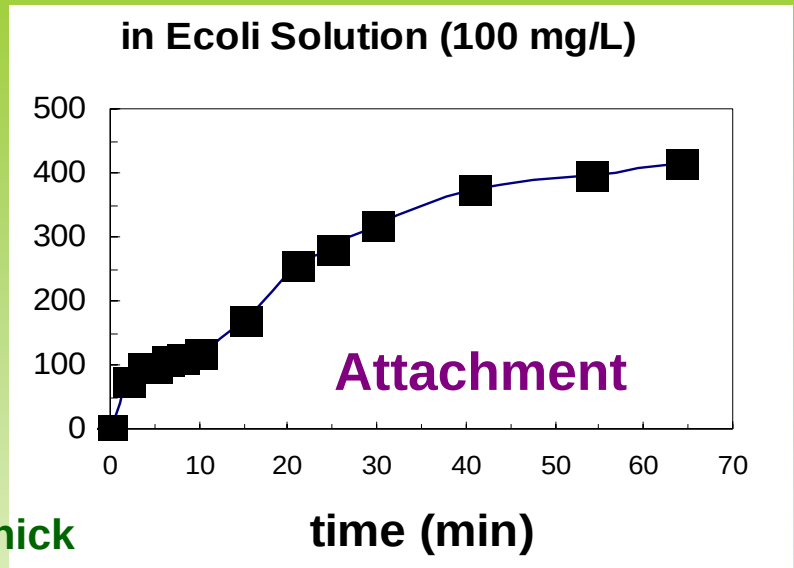
To develop high piezoelectric microcantilever sensors for real-time, in situ ultrasensitive pathogen pathogen detection in water

Tasks:

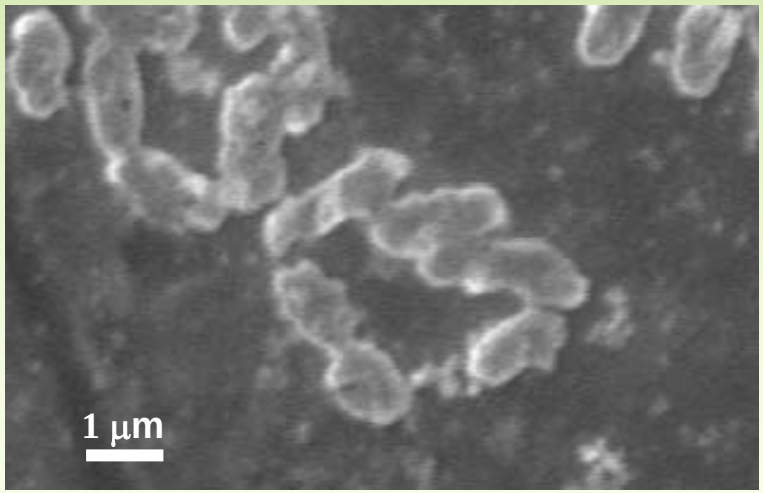
- **To develop highly piezoelectric lead magnesium niobate-lead titante (PMN-PT) films for microcantilever miniaturization**
- **To fabricate and characterize highly PMN-PT microcantilever sensors**
- **To use sub-millimeter PZT cantilevers for immediate pathogen detection development**

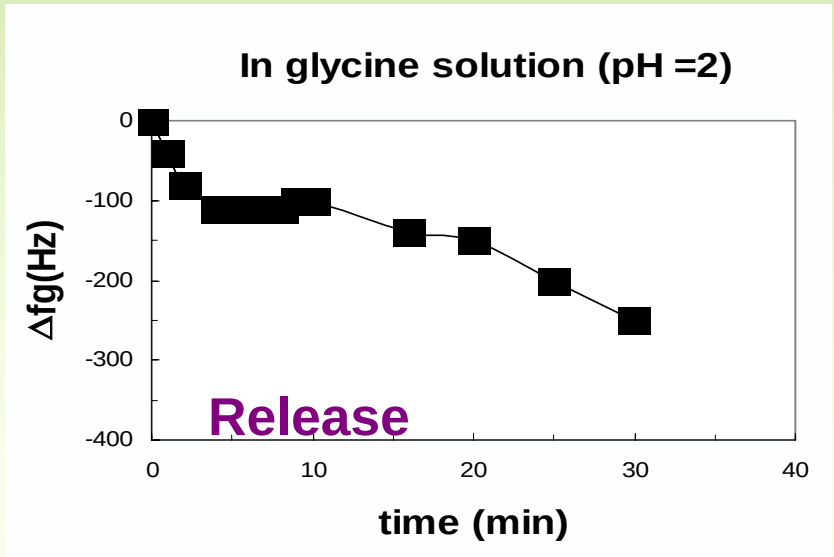
Ecoli 057:H7 Detection and Release



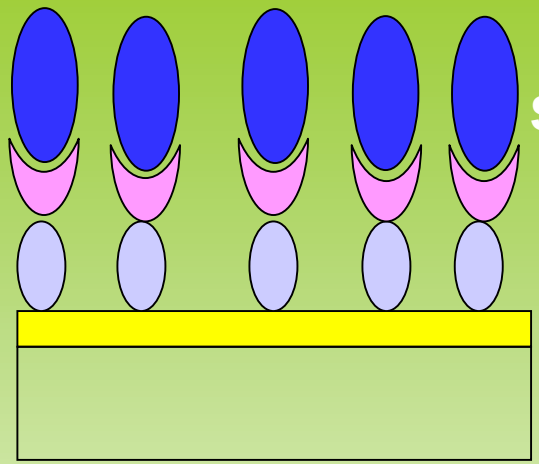


PZT: 0.6 mm long, 2 mm wide, 127 μm thick
stainless steel tip: 4 mm long, 2 mm wide, 50 μm thick





Immobilization on glass, Ti, and Au



Salmonella T.

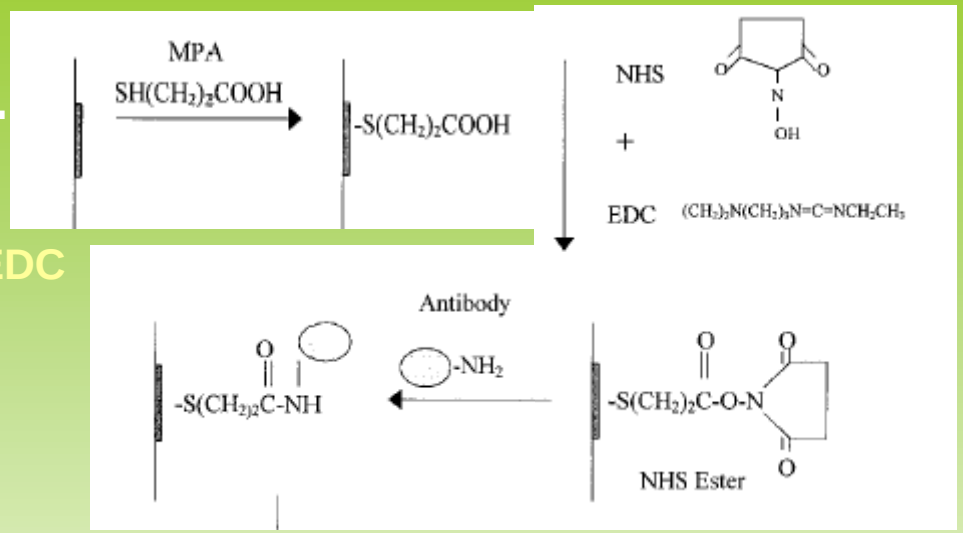
Antibody

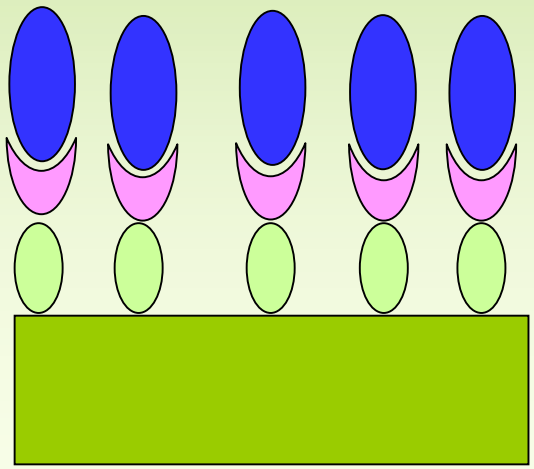
MPA in NHS+EDC

Gold

Glass

PZT/Au-coated glass cantilever



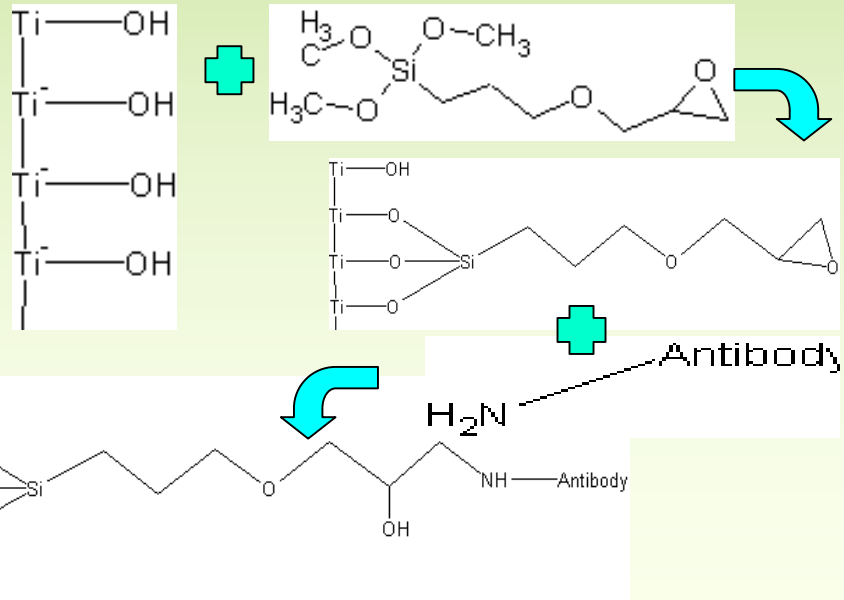


Salmonella T.

Antibody

GOPTS

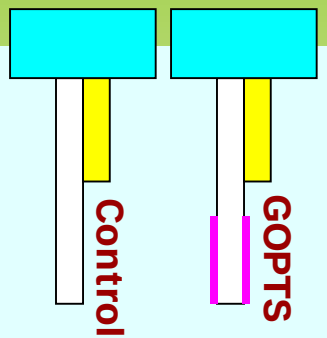
Titanium



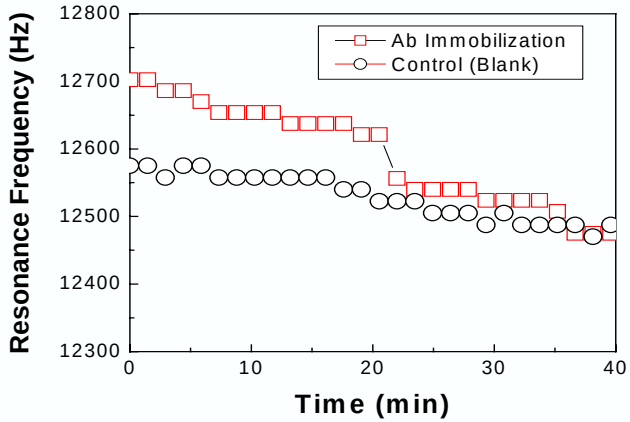
PZT/Ti cantilever

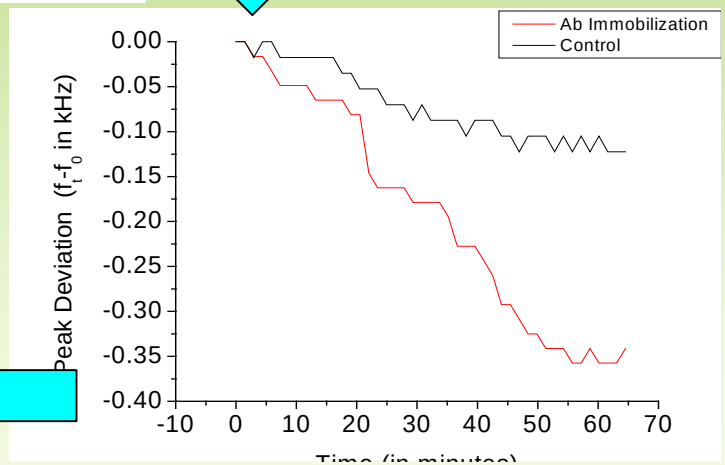
Multiplexing

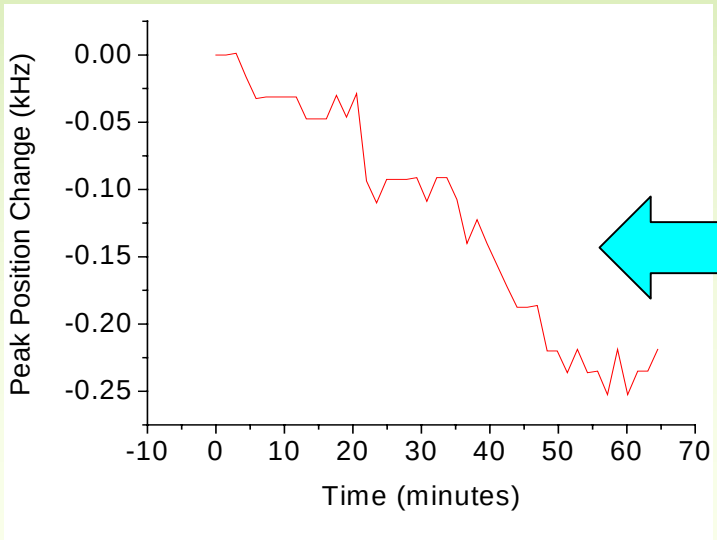
Detection with a Control



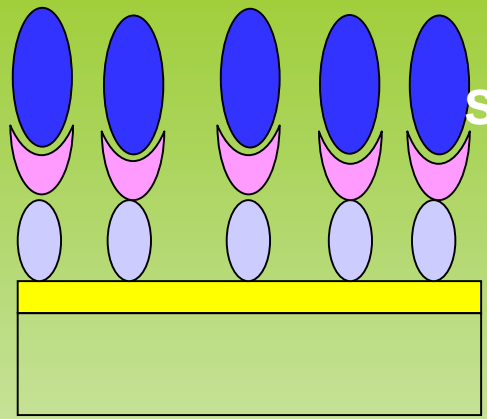
Antibody solution





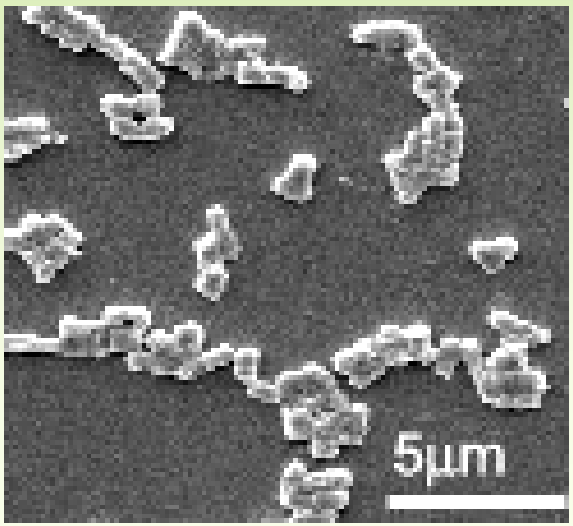


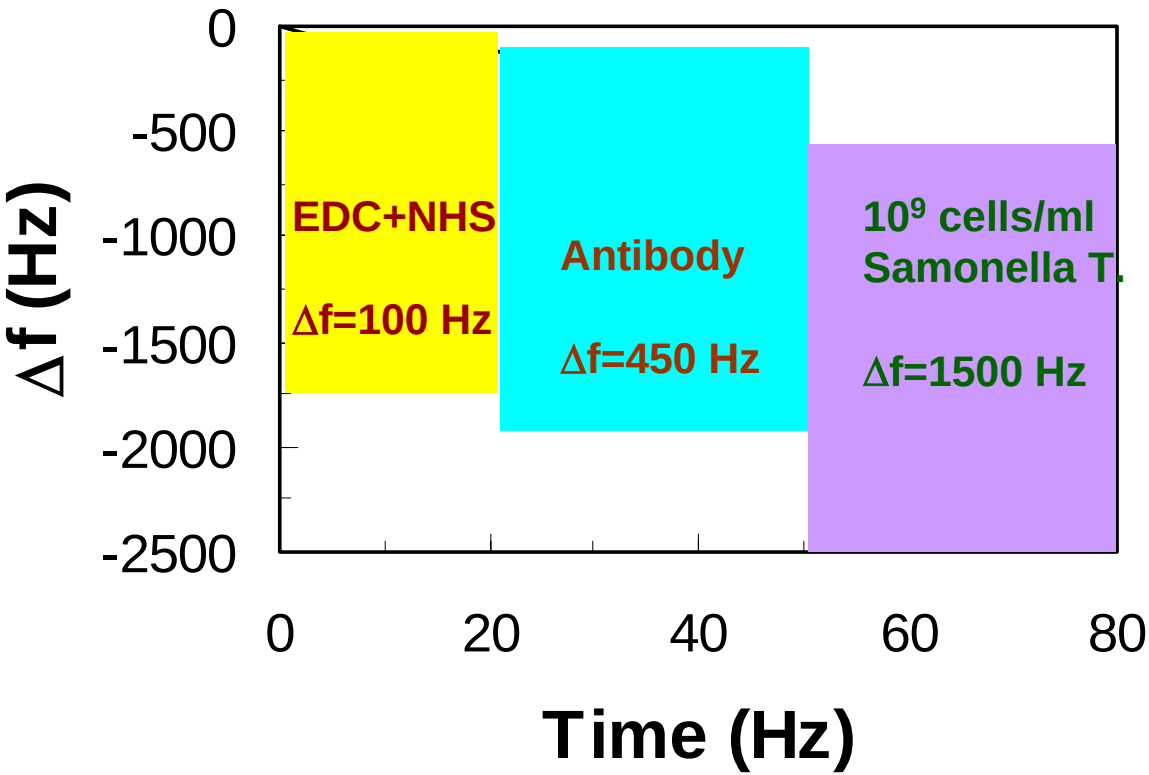
Salmonella detection on gold coated PZT/glass cantilever



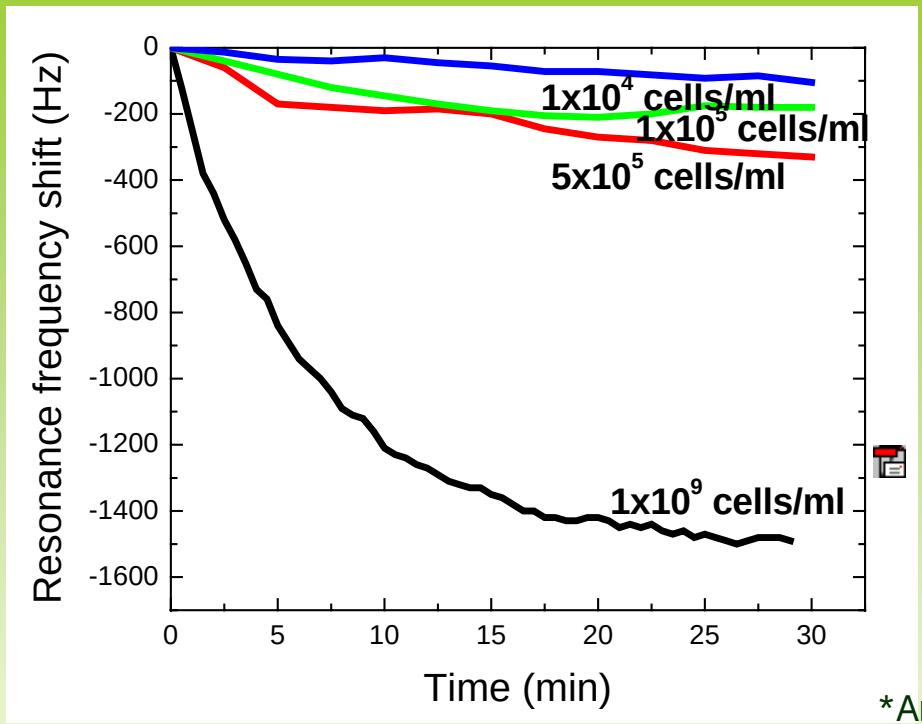
PZT/Au-coated glass cantilever

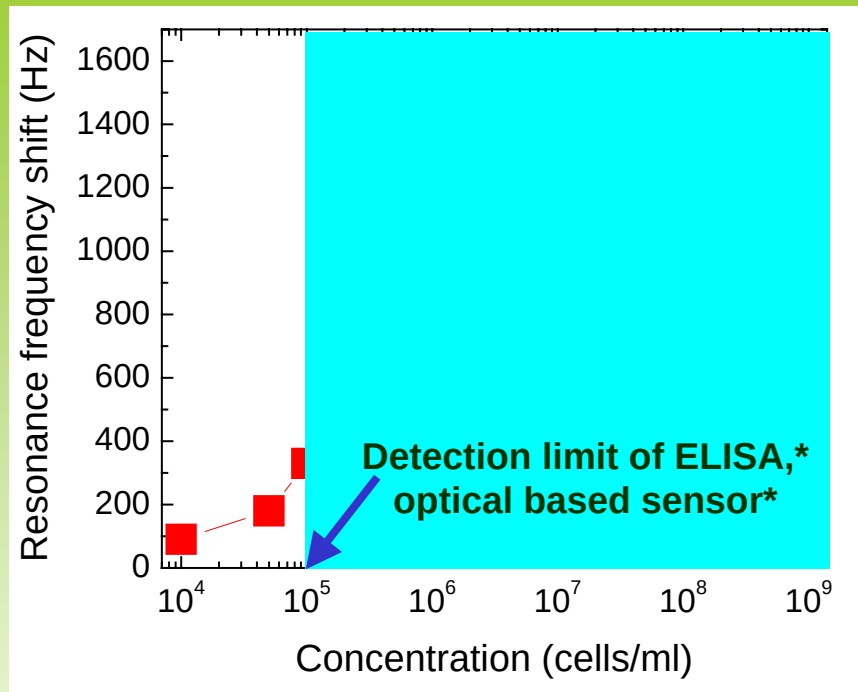
Salmonella T



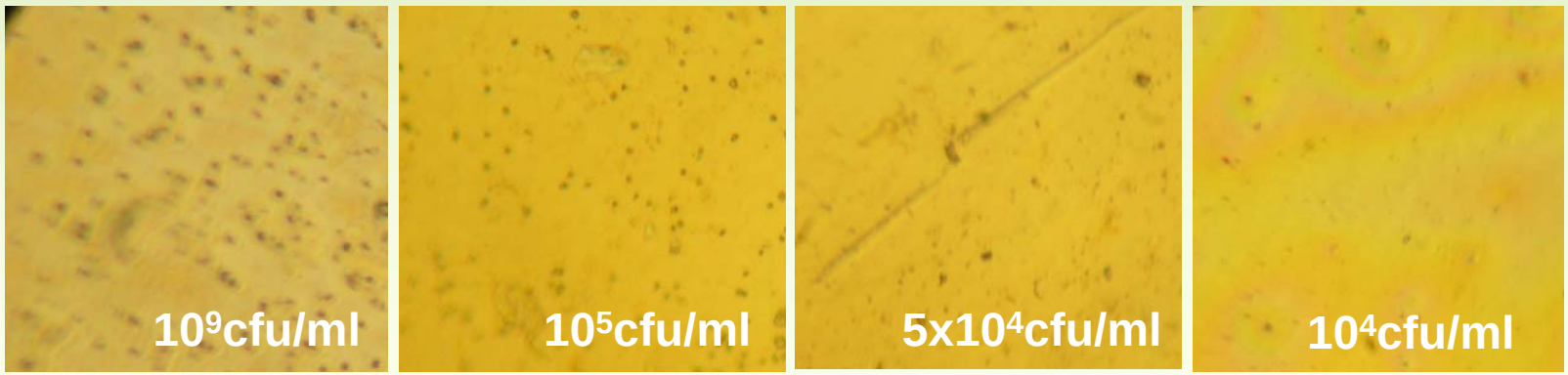


Salmonella detection on gold coated PZT / glass cantilever

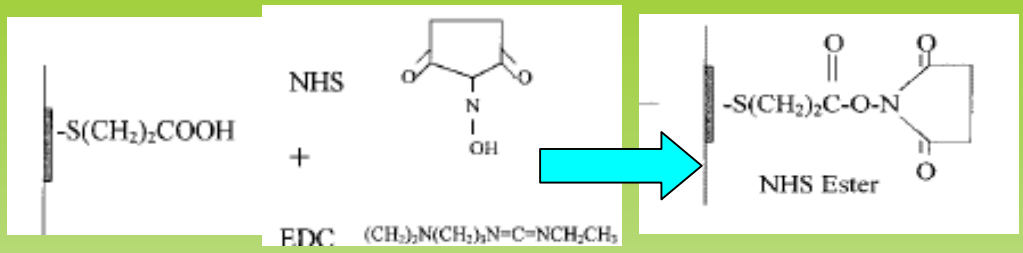


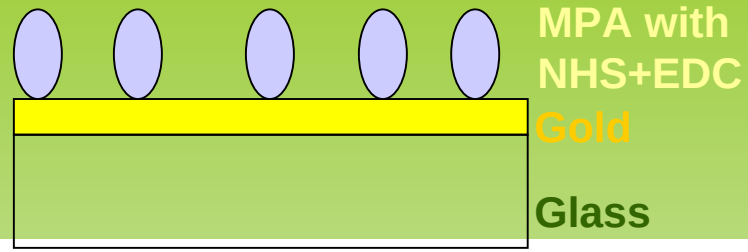


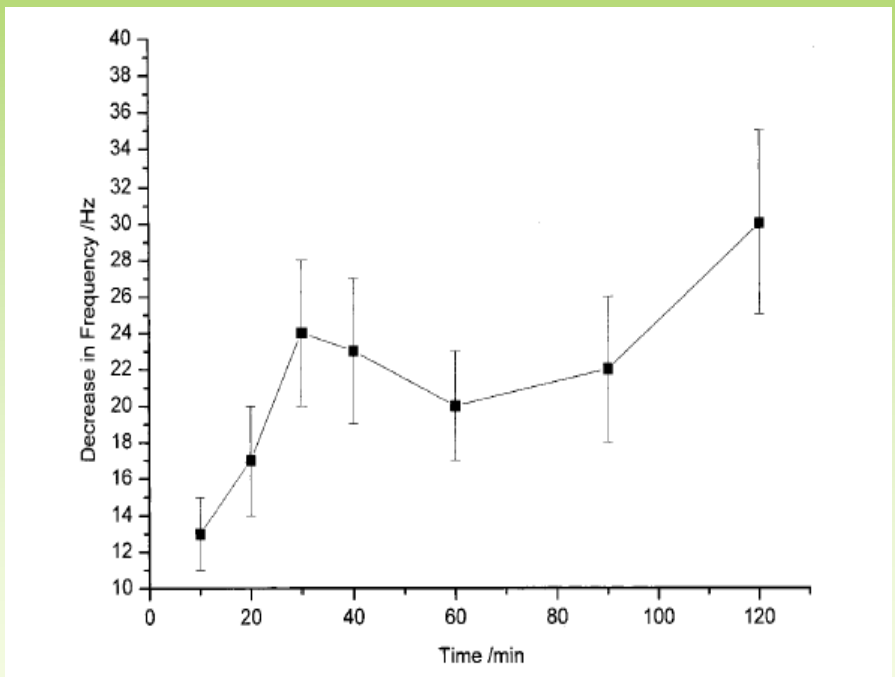
*Anal. Chem. 71, 3846 (1999), Anal Chem. 75, 5293 (2003)

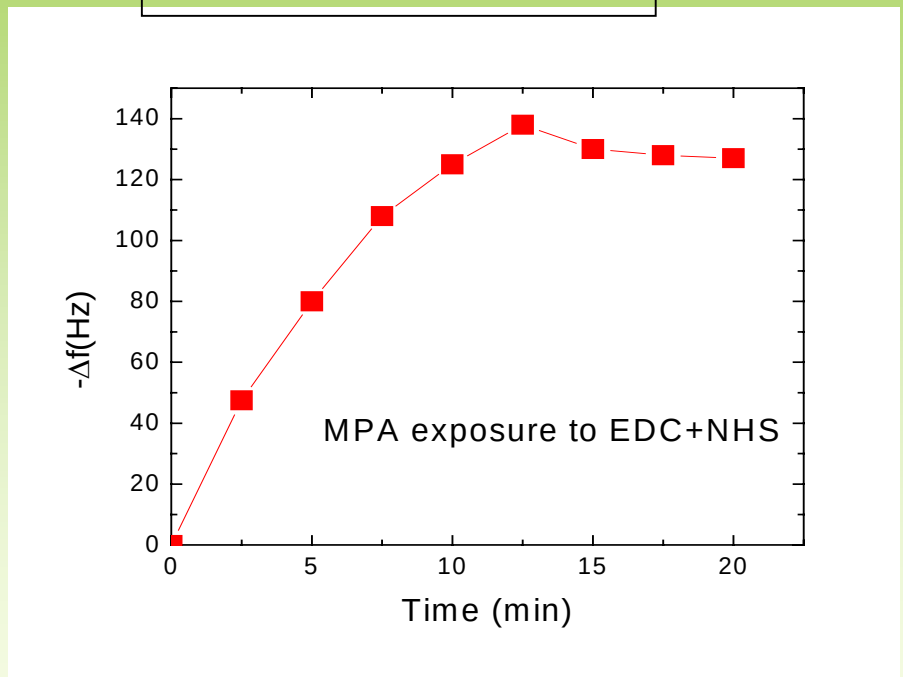


MPA exposure to EDC +NHS







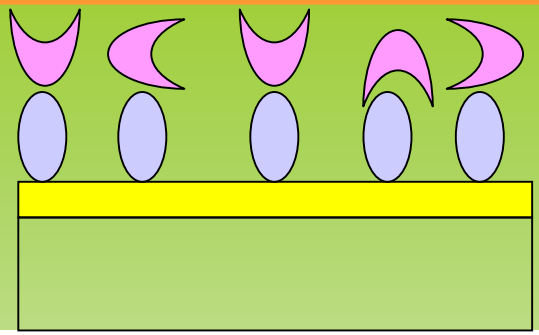


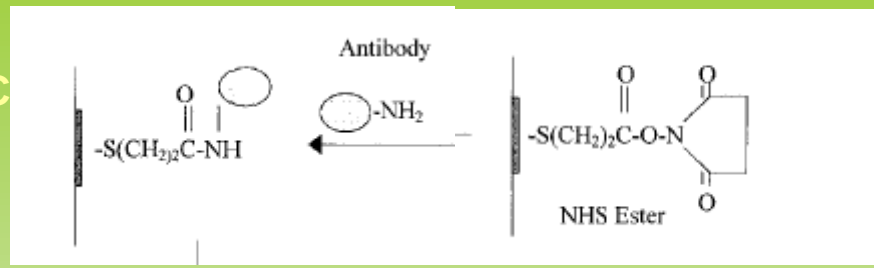
10 MHz QCM*
Δf=30 Hz

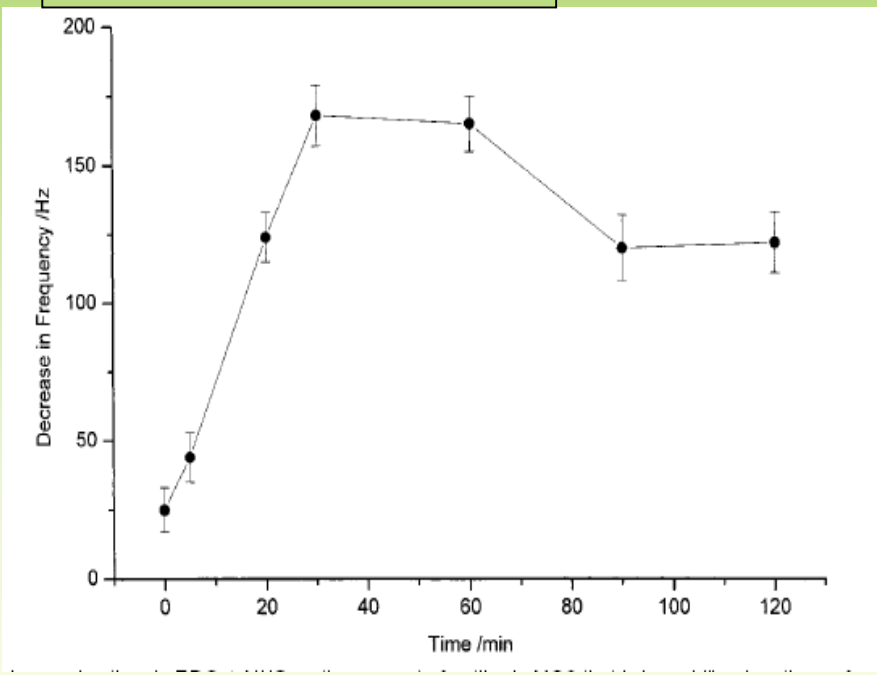
PZT/glass cantilever
Δf=100 Hz

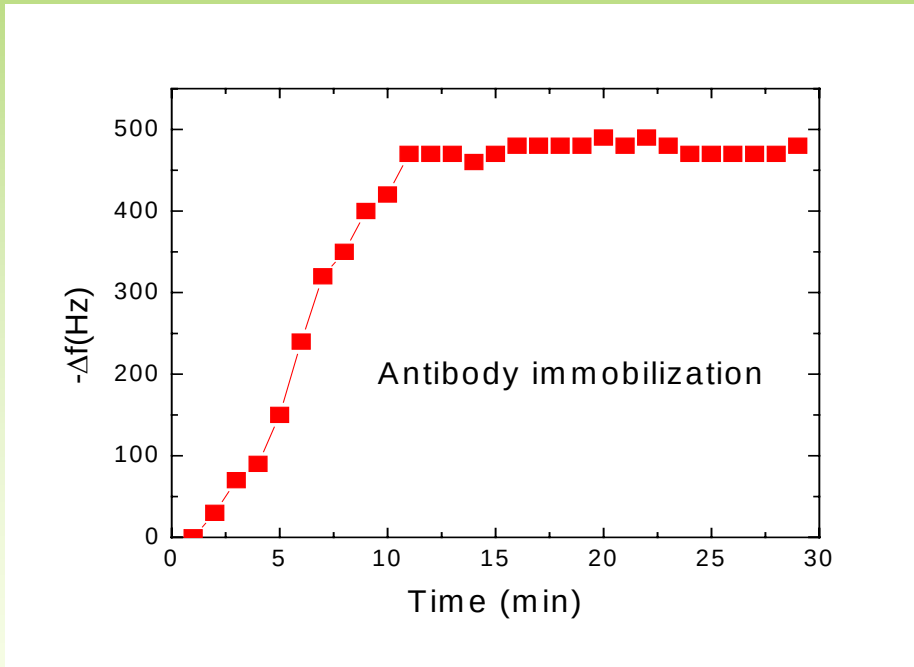
***Y. S. Fung* and Y. Y. Wong,** Anal. Chem.**2001,** 73,5302-5309

Antibody immobilization detection







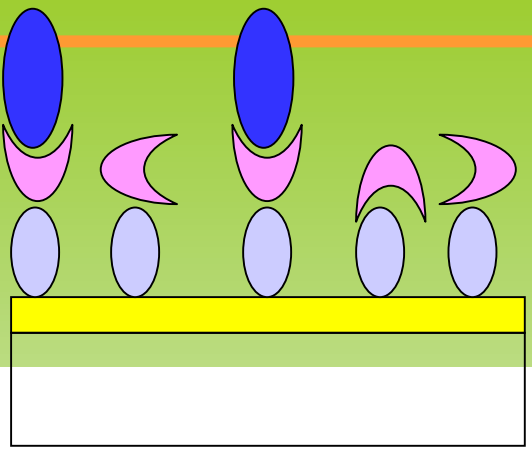


10 MHz QCM*
Δf=150 Hz

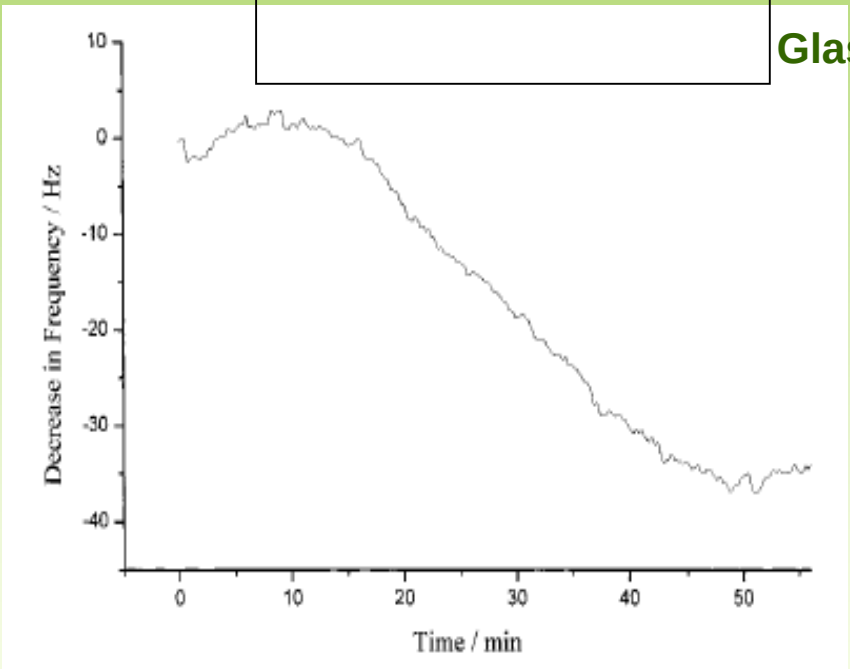
PZT/glass cantilever
Δf=450 Hz

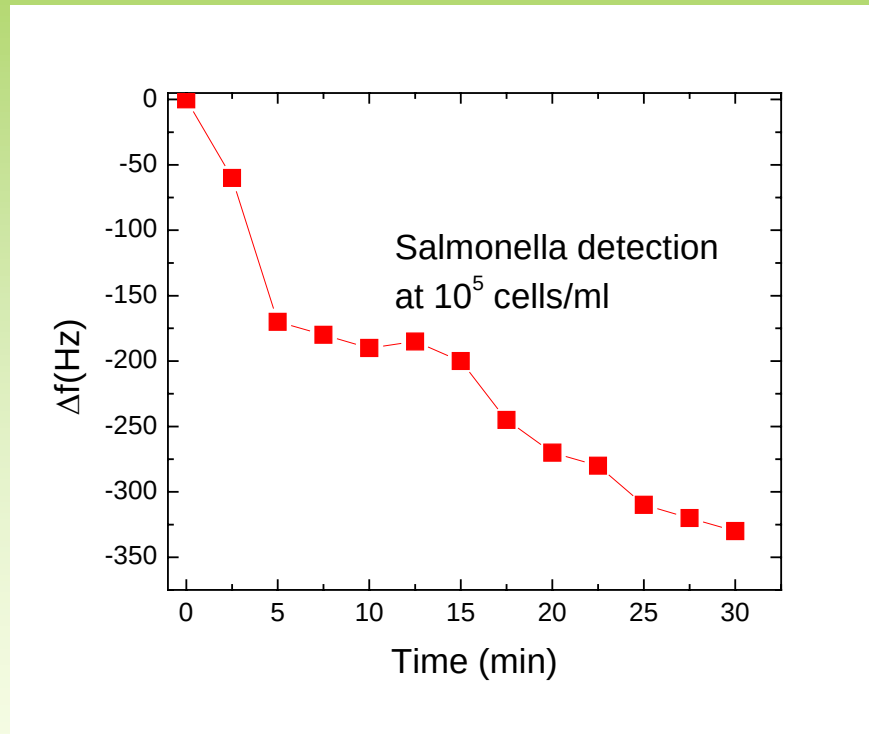
***Y. S. Fung* and Y. Y. Wong,** Anal. Chem.**2001,** 73,5302-5309

Salmonella detection at 10^5 cells/ml



Salmonella T. at 10^5 cfu/ml





10 MHz QCM*
Δf=40 Hz

PZT/glass cantilever
Δf=300 Hz

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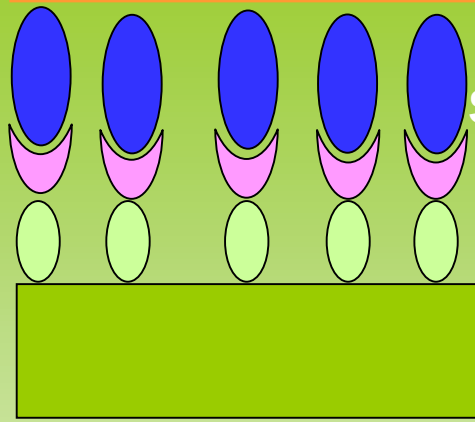
Summary for 0.4 mm long PZT/glass cantilever

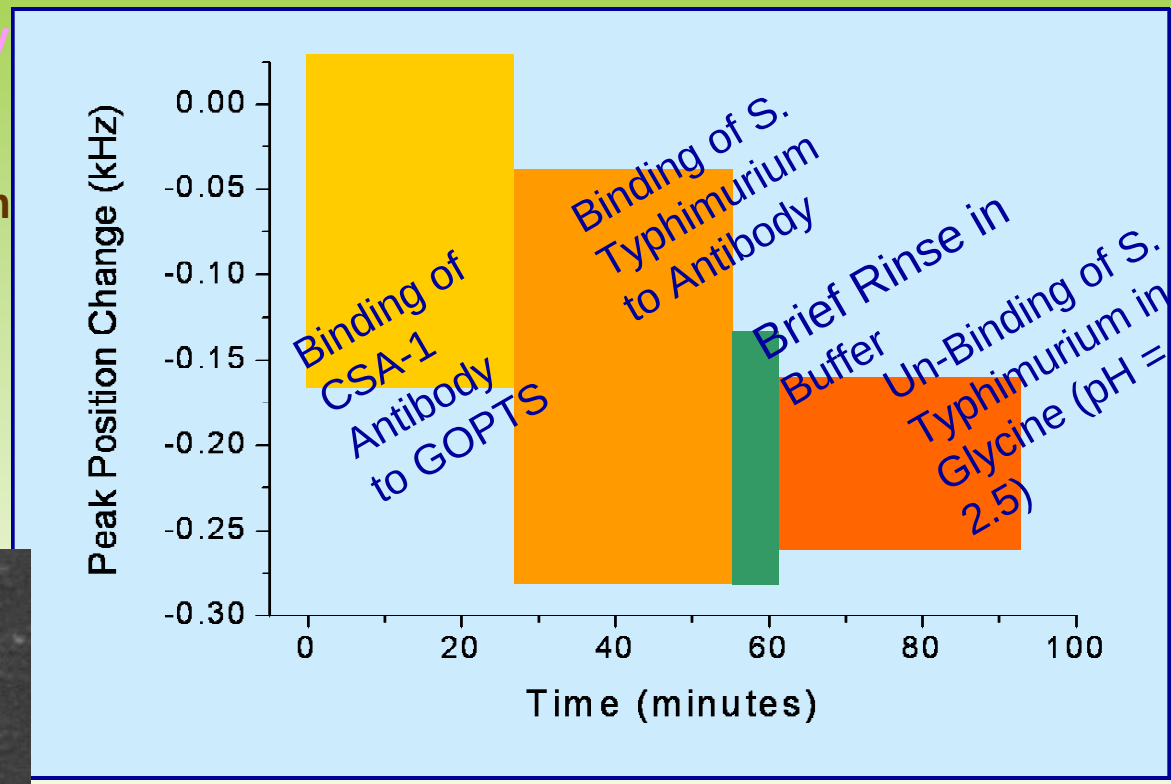
Detection sensitivity: 3x10-11 g/Hz

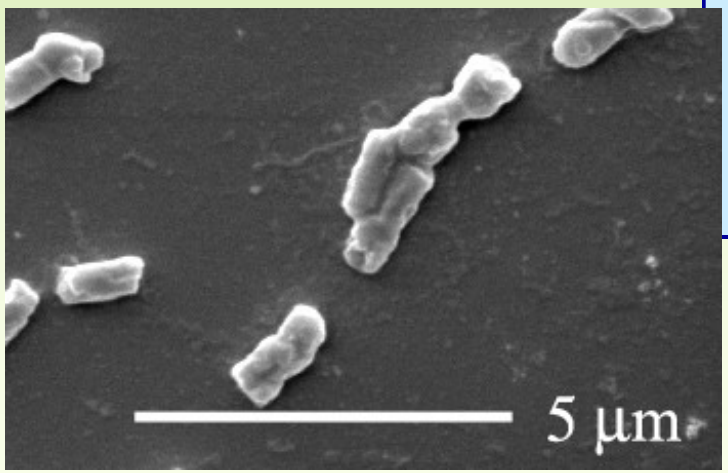
C (cells/ml)	$1x10^9$	$1x10^5$	$5x10^4$	$1x10^4$
Δf	1400 Hz	300 Hz	180 Hz	90 Hz
Δm	42 ng	10 ng	6 ng	3 ng
Cells needed	$3x10^5$	4000	3000	1500
Vol. needed	4 μl	50 μl	70 μl	170 μl
Diffusion type	Linear	3-d	3-d	3-d

1.5 mm long PZT/Ti cantilever

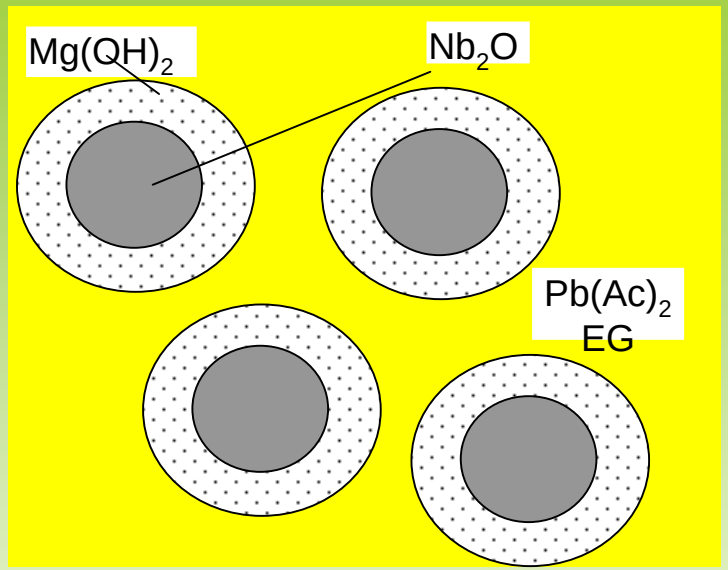


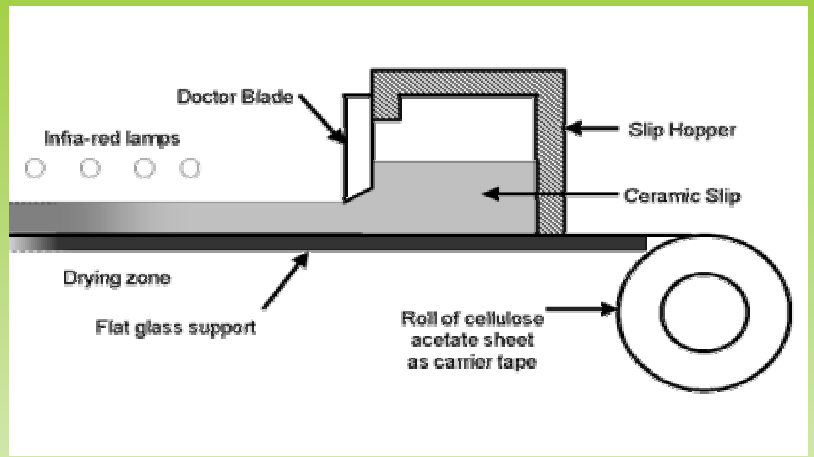
PZT/Ti cantilever

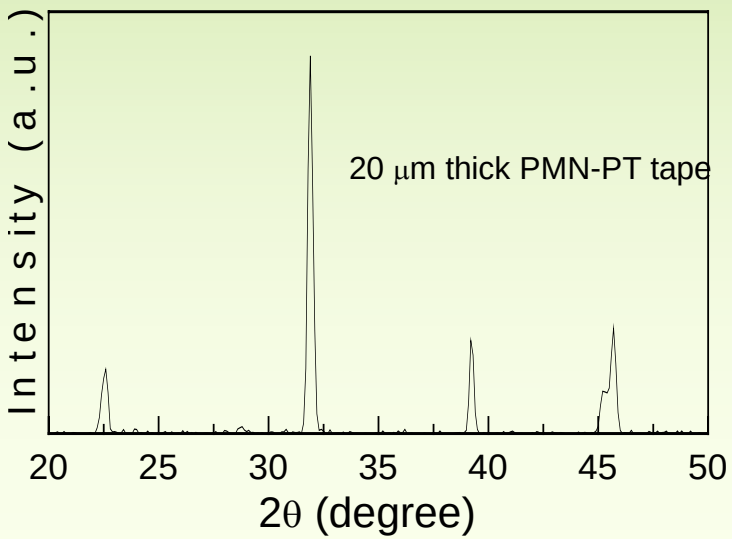


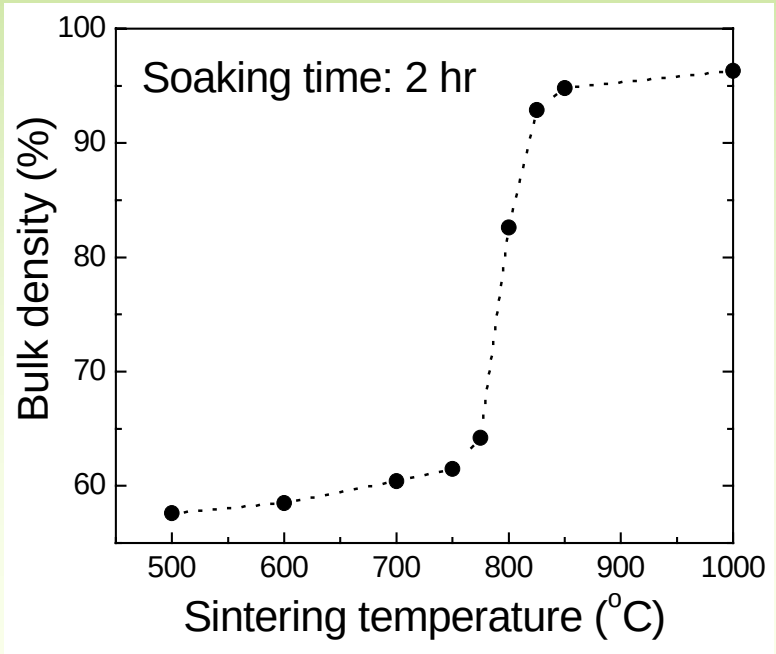


Novel Coating Process for PMN-PT



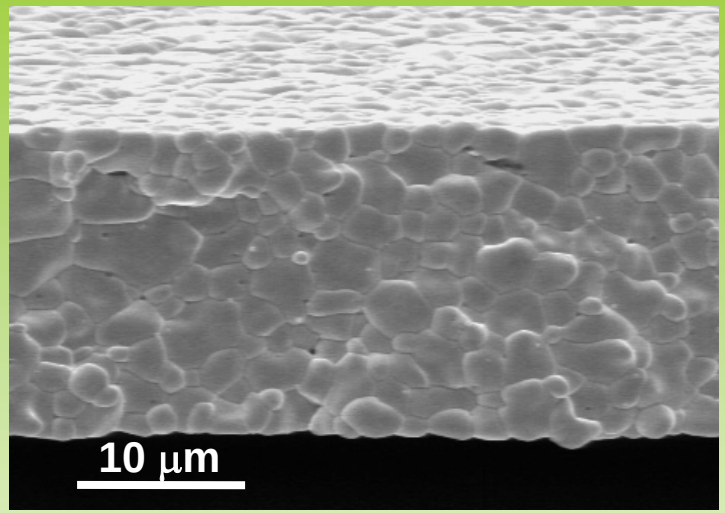


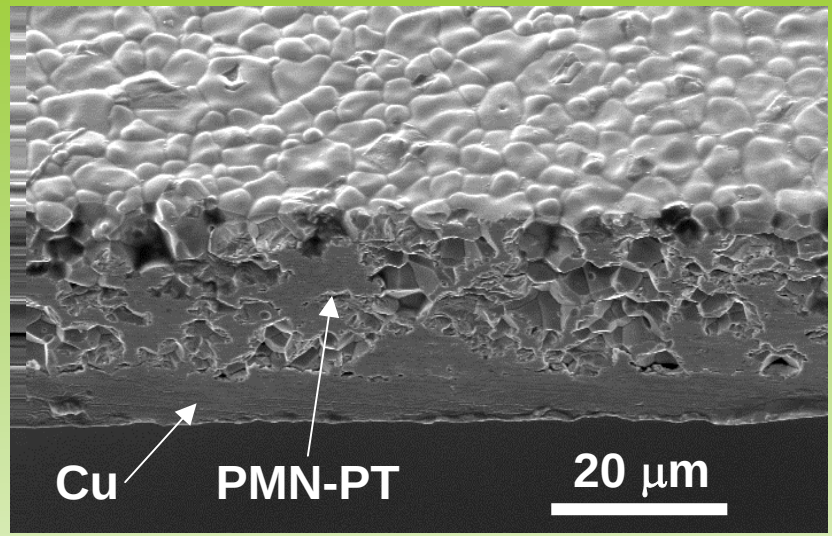


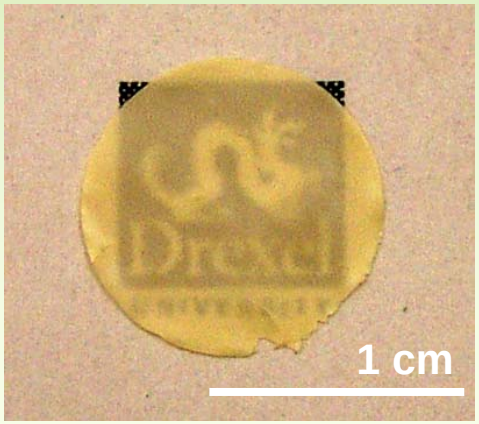


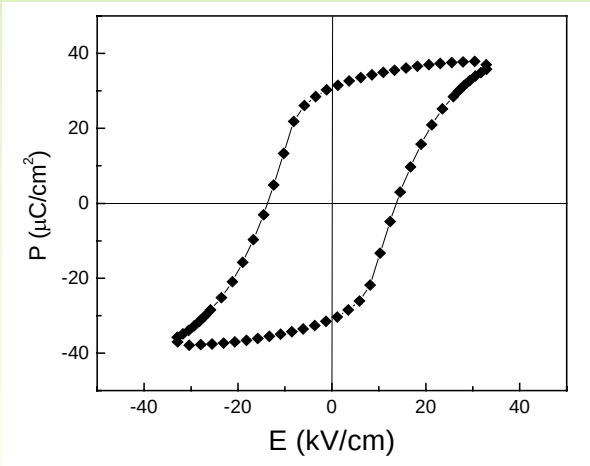
PMN-PT / Cu Microcantilevers

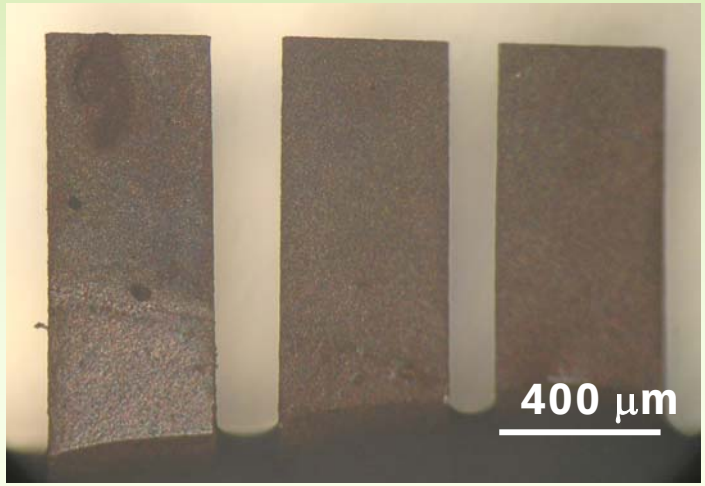
Freestanding PMN-PT film



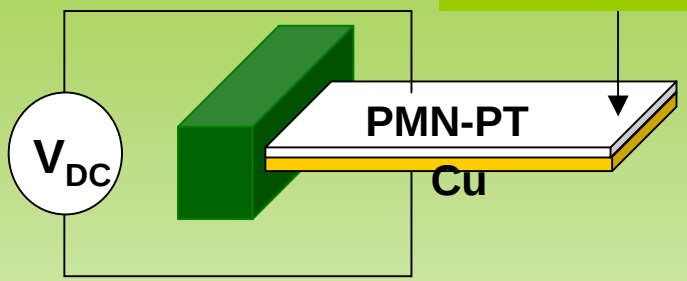




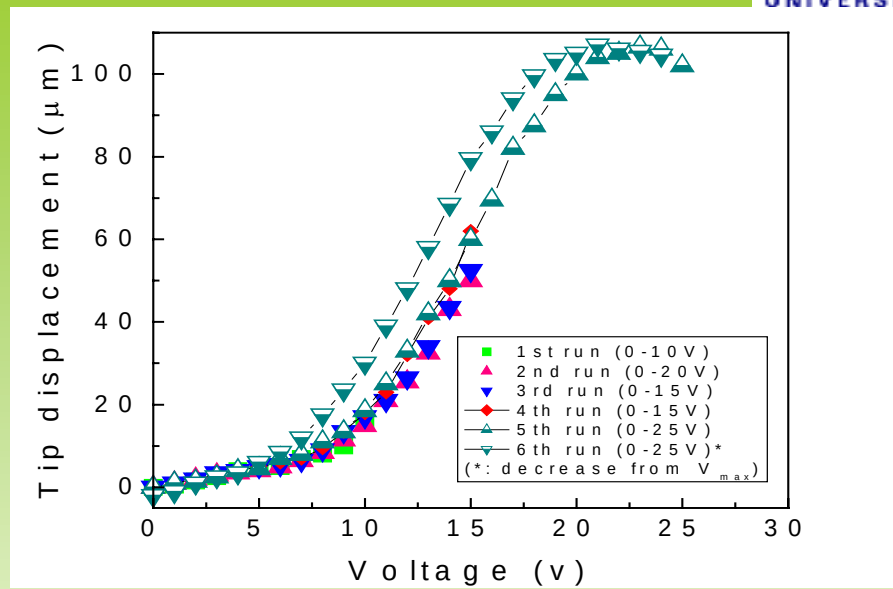


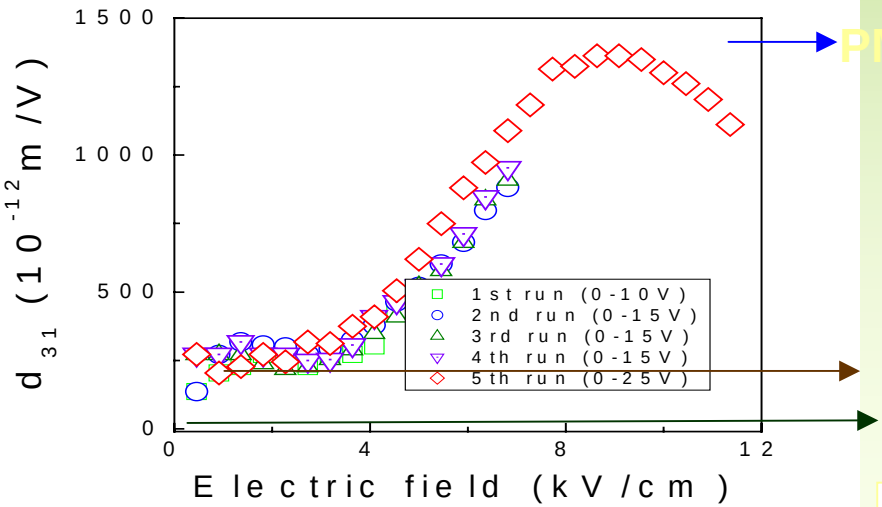


PMN-PT/Cu Microcantilevers

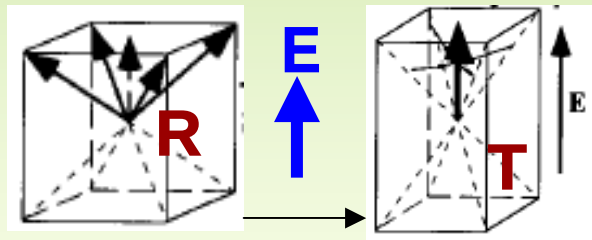


2 mm long PMN-PT/Cu cantilever





PMN-PT single crystal cut in (100) d_{31} ~ 1500

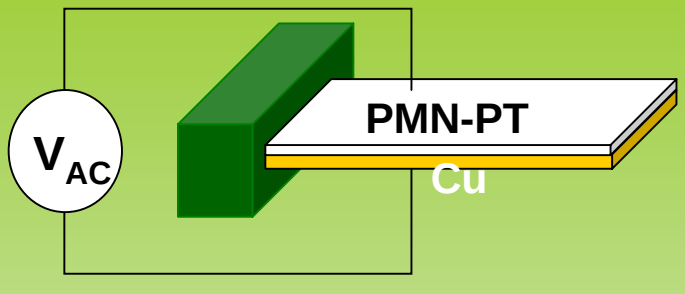


Bulk PMN-PT d_{31} ~ 250

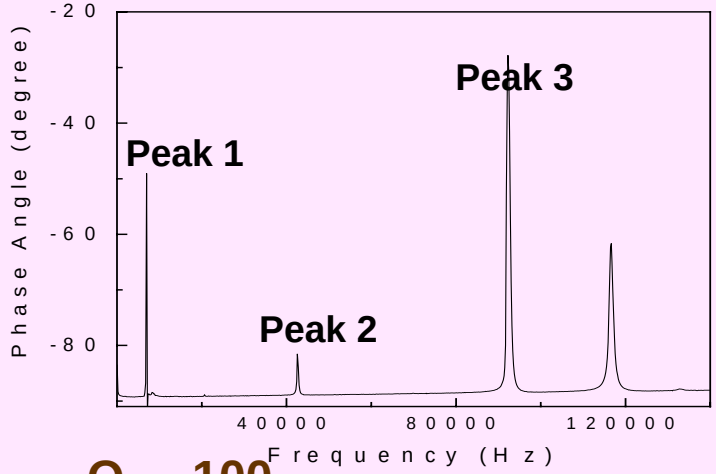
ZnO_2 d_{31} < 10

$$d_{31} = \frac{h}{3VL^2} \cdot \frac{E_1^2 t_1^4 + E_2^2 t_2^4 + 2E_1 t_1 E_2 t_2 (2t_1^2 + 2t_2^2 + 3t_1 t_2)}{E_1 E_2 t_1 (t_1 + t_2)}$$

PMN-PT/Cu Microcantilevers

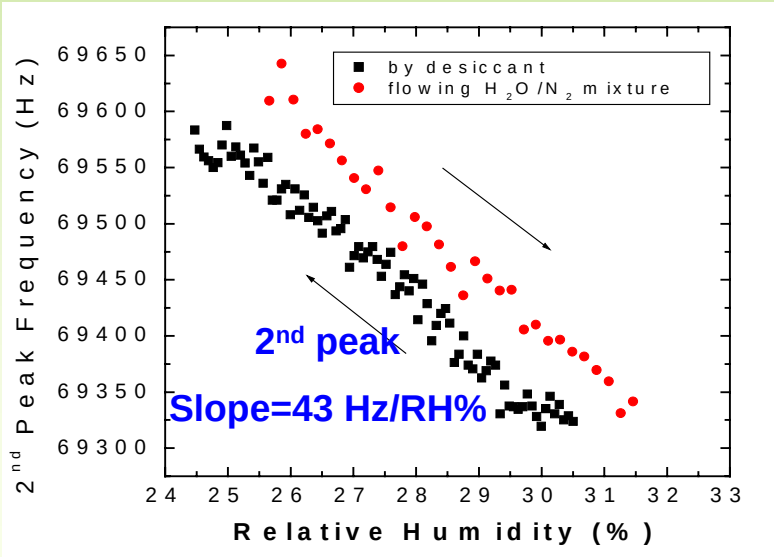


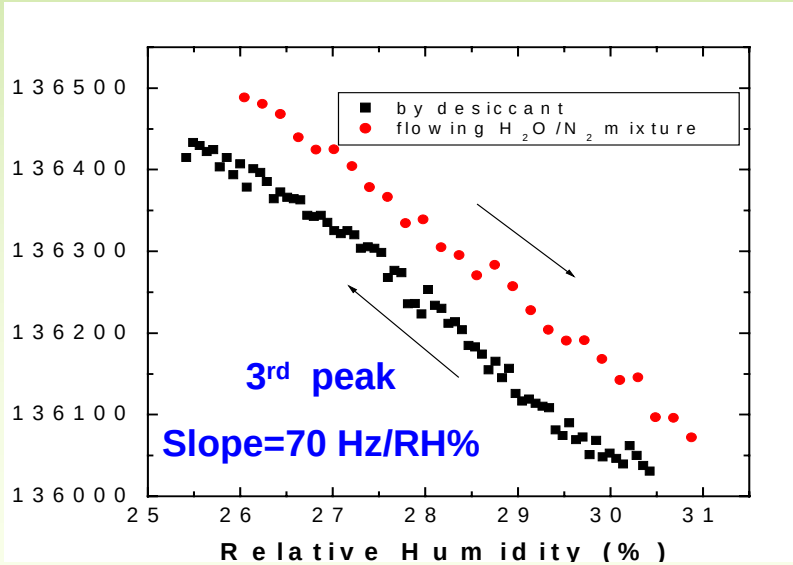
0.6 mm long PMN-PT/Cu cantilever
PMN-PT 20 μm thick, Cu 5 μm thick



Q ~ 100

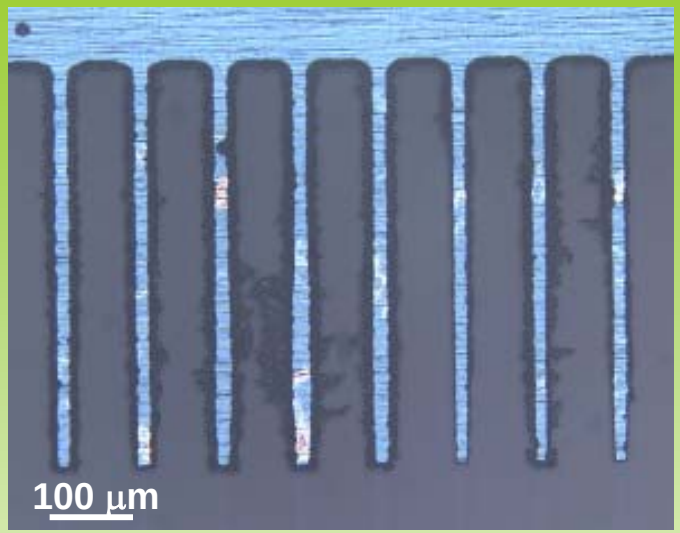
Humidity Sensing



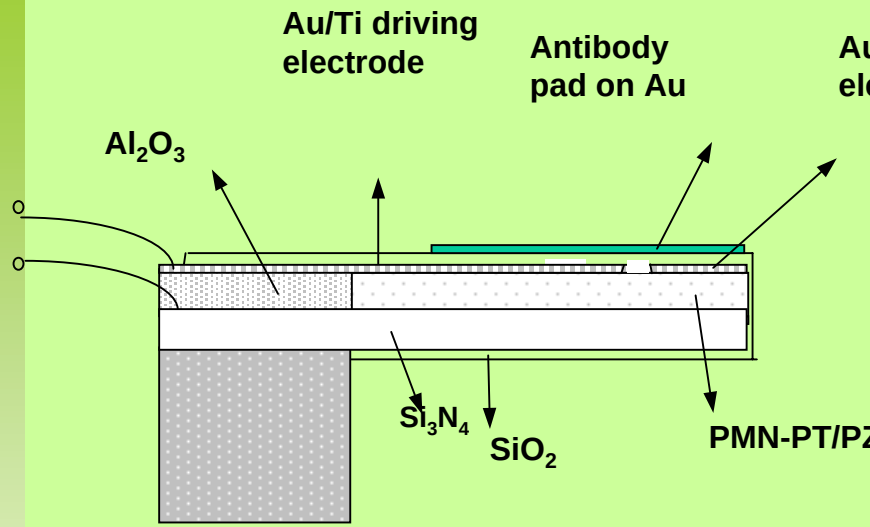


$\Delta m/\Delta f \sim 10^{-12}$ g/Hz

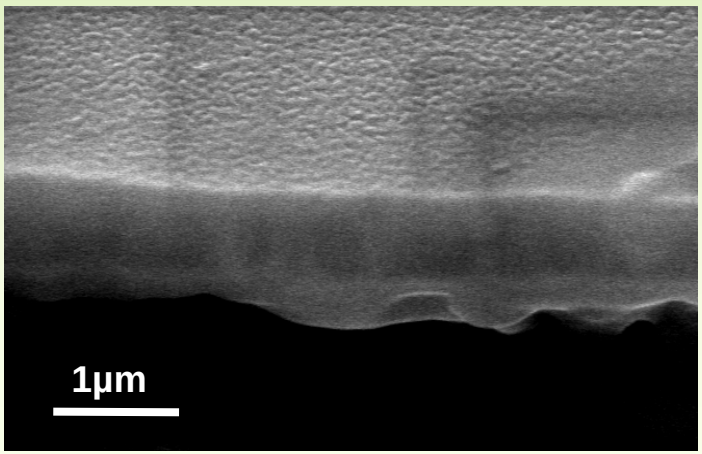
Piezoelectric Microcantilever Fabrication

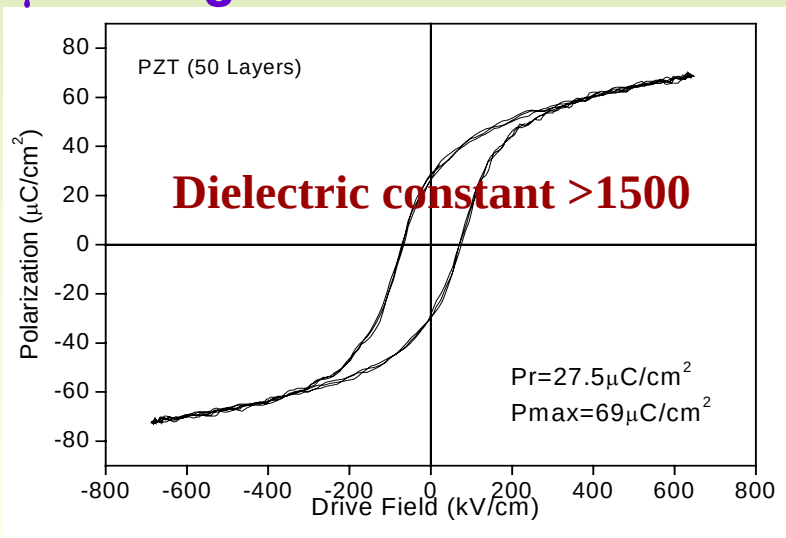


PZT/Mo microcantilevers



$\Delta m/\Delta f = 10^{-15}$ g/Hz for 50 μm long cantilever





Conclusions

- High piezoelectric PMN-PT films have been successfully made with better than specially cut single-crystal piezoelectric properties
- Array PMN-PT/Cu microcantilevers 500 μm long were made showing better than 10^{-12} g/Hz
- we demonstrated in-situ real time detection of Salmonella in standing water with PZT/glass and PZT/Ti cantilevers with various immobilization schemes
- 0.4 mm long PZT/glass cantilevers of 3x10-11 g/Hz sensitivity 3-4 times more sensitive than 10MHz QCM in protein/molecular detection, 6-7 times more sensitive than 10MHz QCM's planar detection in cell detection
- The better than 10^4 cfu/ml detection sensitivity comparable to a 10 MHz QCM, better than commercial ELISA, and tapered optical fiber sensors
- Further sensitivity improvement includes using PMN-PT/Cu microcantilevers, using a flow cells

Ceramic Processing and Sensor Group

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