Rational Design of Nanoplasmonic Array Geometries for Biosensing

M01-2235: *(Invited, Digital Presentation)*

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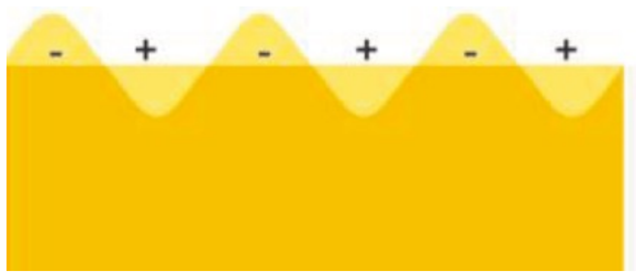
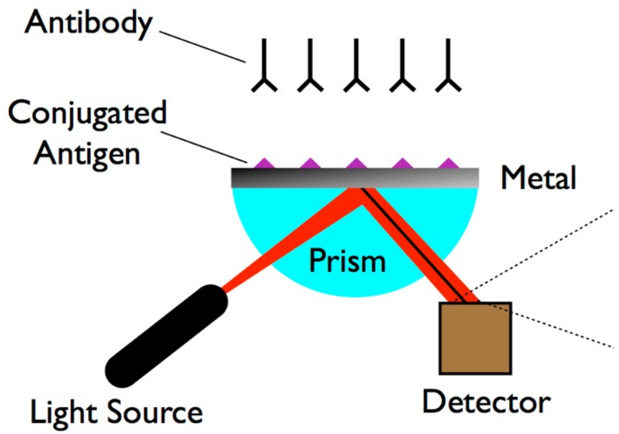
* Current: Honeywell International, Inc. Broomfield, CO. USA.

Background: Plasmonics

Fundamentals of Plasmonics

- Surface plasmons – light-induced electronic excitations
- Oscillations of electric field and polarization localized in space
- Plasmonic sensing uses change in local dielectric environment at nanoparticle surface



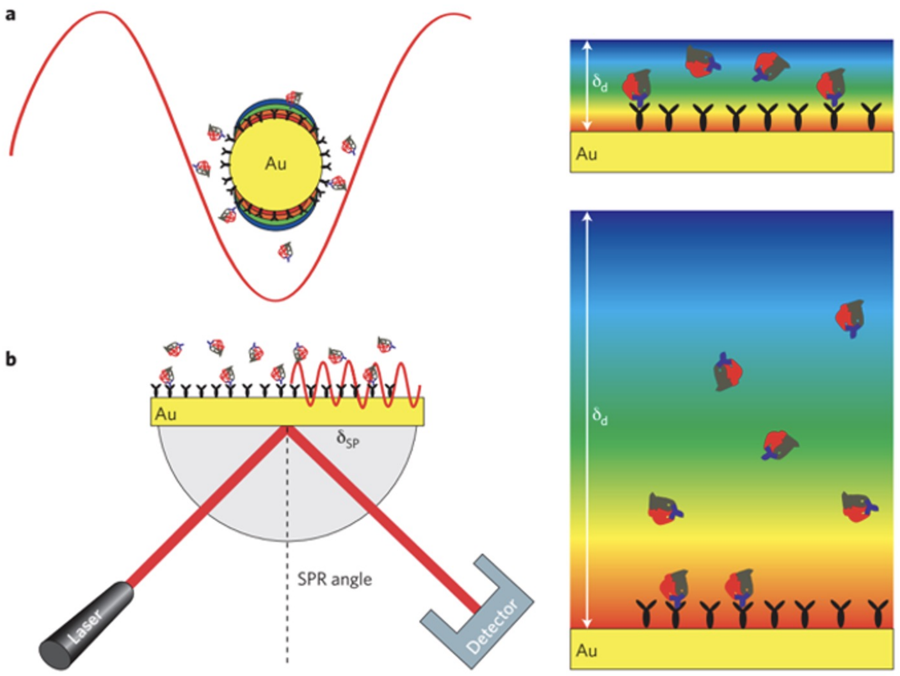


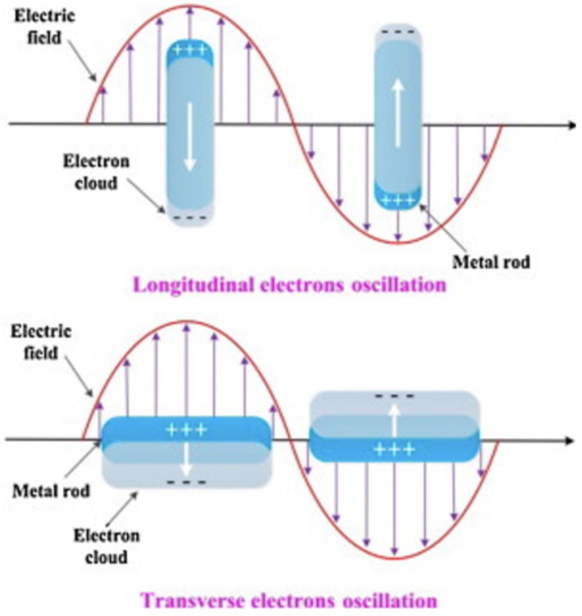
Mayer, *Chem. Rev,* 2011

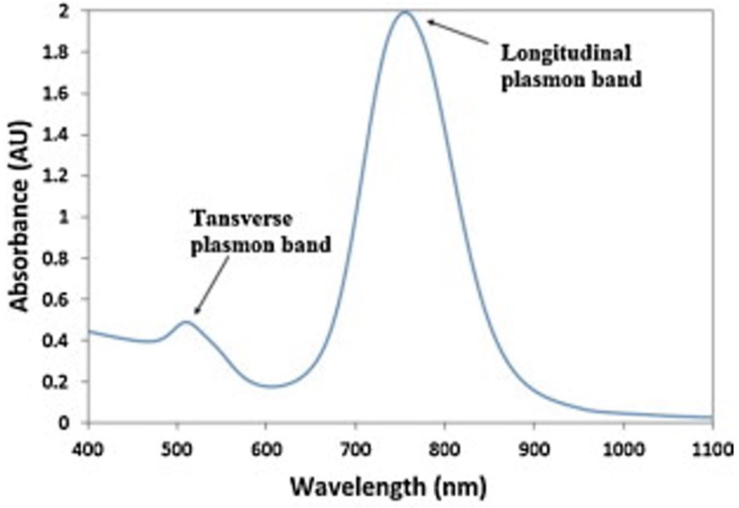
Fundamentals of Plasmonics

LSPR

SPR







Brolo, Nature Photonics 2012, 6, 709-713.
Mayer, *Chem. Rev*, 2011

Modeling Plasmonics

- Presence of plasmons is dependent on "plasma-like" permittivity of metals in the optical frequency range (Drude Model)
- Can consider a spherical nanoparticle and solve Maxwell's equations using quasi-static approximations:

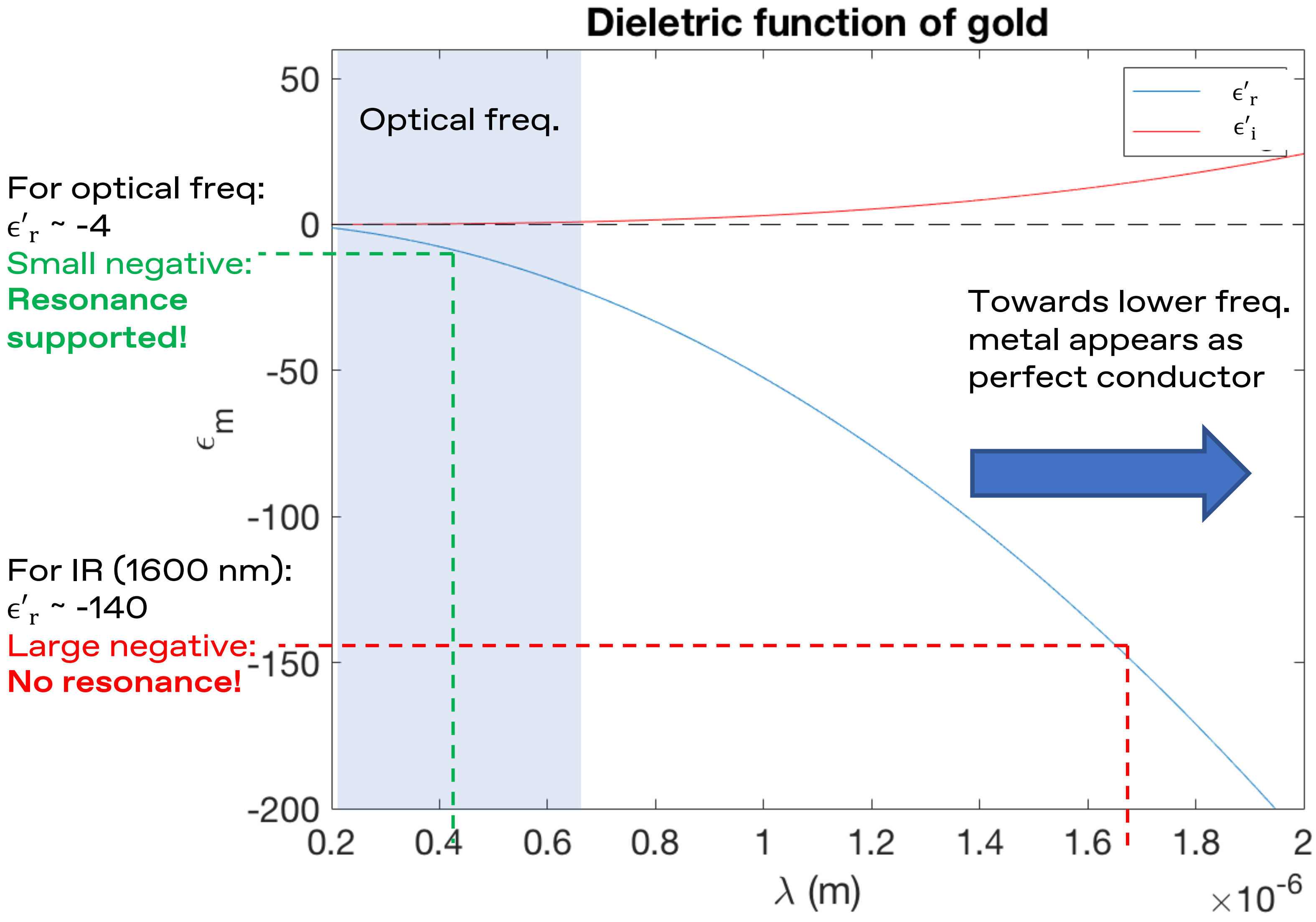
$$E_{out}(x,y,z) = E_0\hat{\mathbf{z}} - \left[\frac{\varepsilon_{in} - \varepsilon_{out}}{(\varepsilon_{in} + 2\varepsilon_{out})}\right] a^3 E_0 \left[\frac{\hat{\mathbf{z}}}{r^3} - \frac{3z}{r^5}(x\hat{\mathbf{x}} + y\hat{\mathbf{y}} + z\hat{\mathbf{z}})\right].$$

$$E(\lambda) = \frac{24\pi^2 N a^3 \varepsilon_{out}^{3/2}}{\lambda \ln(10)} \left[\frac{\varepsilon_i(\lambda)}{(\varepsilon_r(\lambda) + \chi\varepsilon_{out})^2 + \varepsilon_i(\lambda)^2}\right].$$

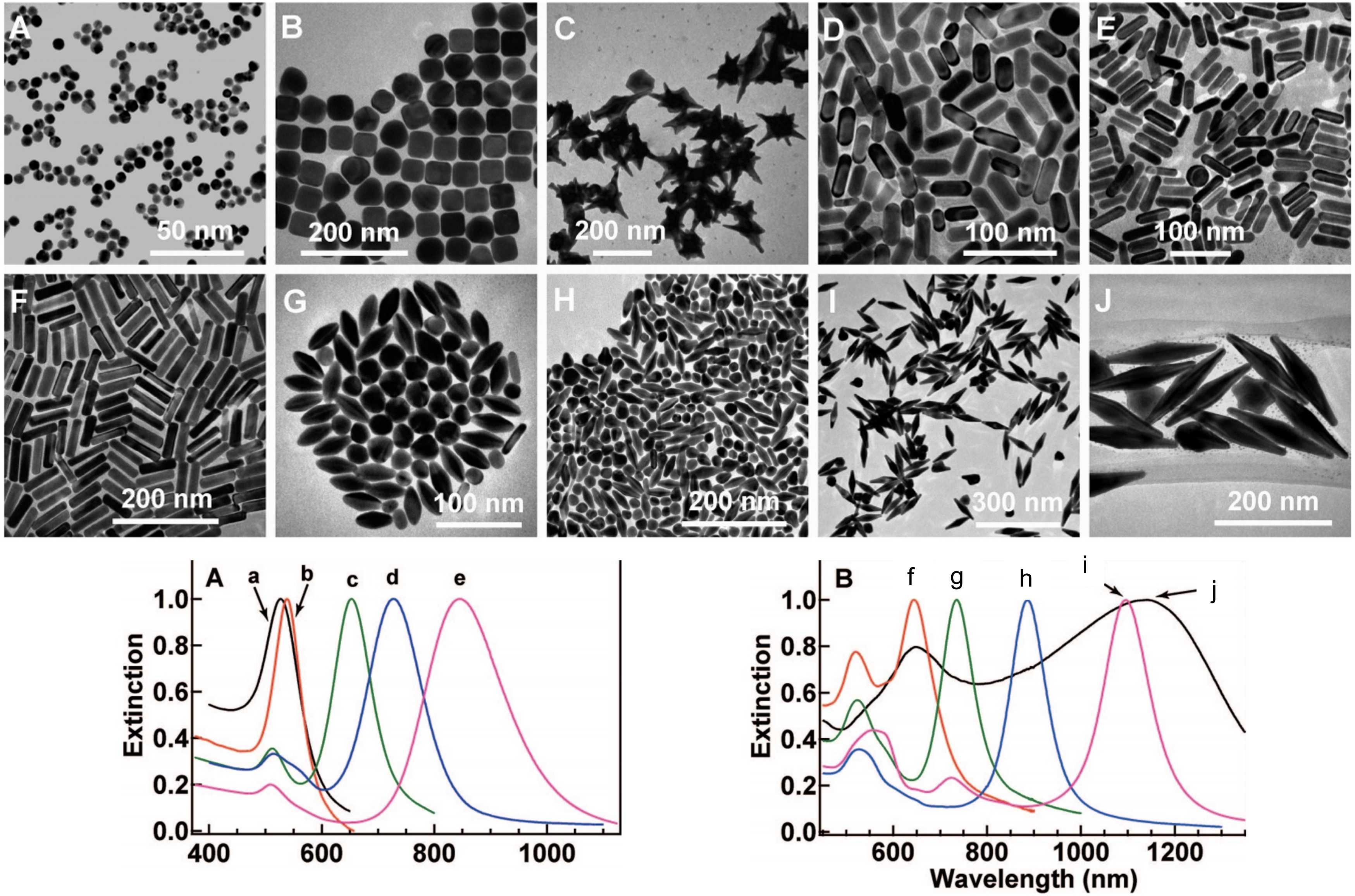
- *Spherical nanoparticle* resonance condition: $\epsilon'_r = -2\epsilon_{out}$
- For dielectrics typically used in biosensing (e.g. water), $\epsilon_{out} \sim 2.0$
- Therefore ϵ_r ~ -4 for resonance

X can range from 2-20 as aspect ratio increases

The dielectric function of gold supports resonance condition in optical frequencies



Effects of Nanoparticle Shape on Plasmonic Resonance



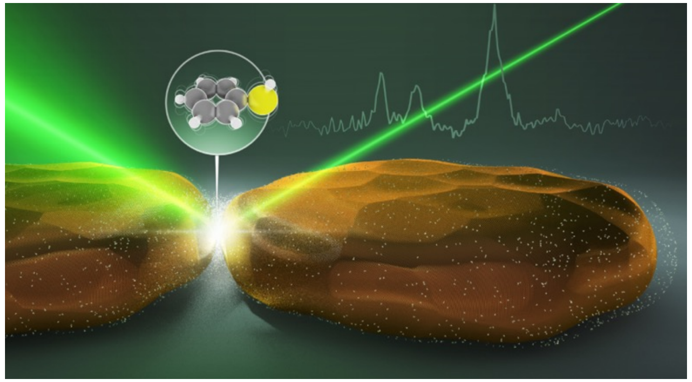
Chen, Langmuir, 2008

Case Study 1:
Nanoplasmonic Sensing at NASA

Work completed primarily by Timothy J. Palinski.
NASA prior role, current role: Honeywell International, Inc. Broomfield, CO. USA.

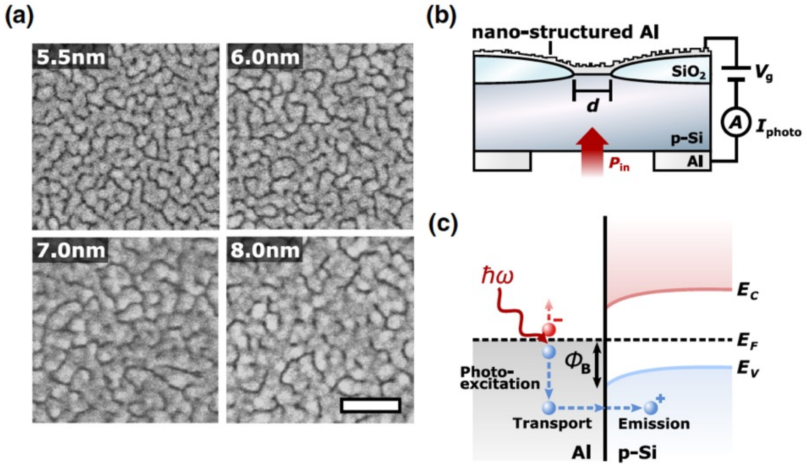
Applications of Plasmonic Fields

Biosensing



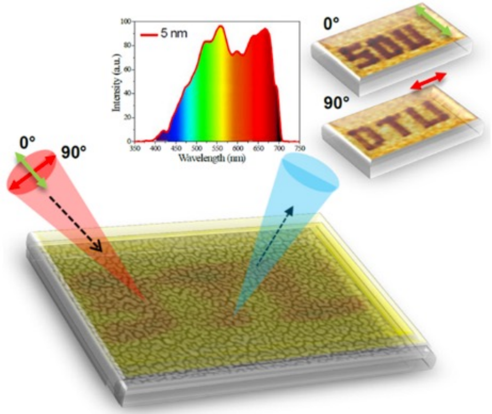
P. Roelli et al., *Nat. Nano.* 11, 164-169 (2016)

Enhanced photodetection



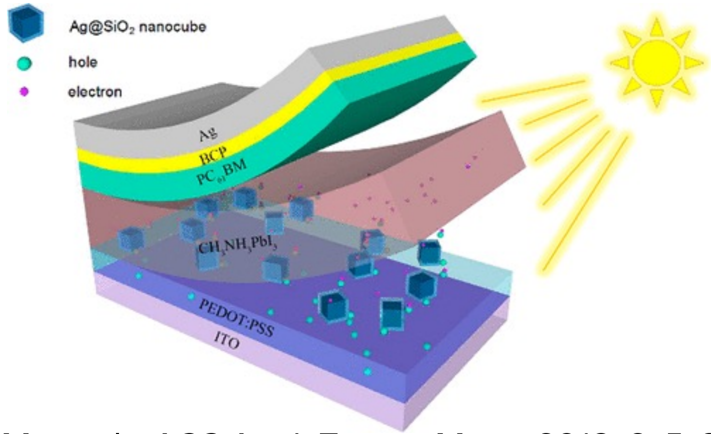
C. Frydendahl et al., *Optica*, vol. 7., no. 5, 2020

Light emission



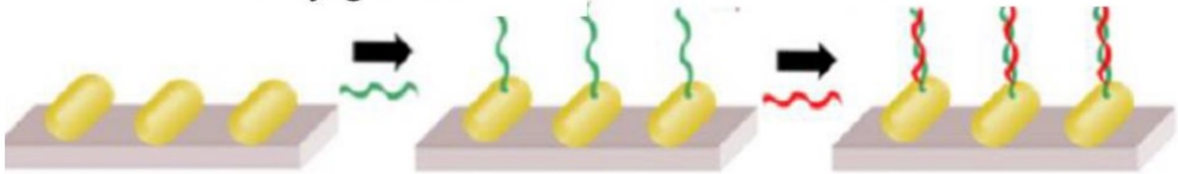
S. Novikov et al., *ACS Phot.* 2017, 4, 1207-1215

Energy harvesting



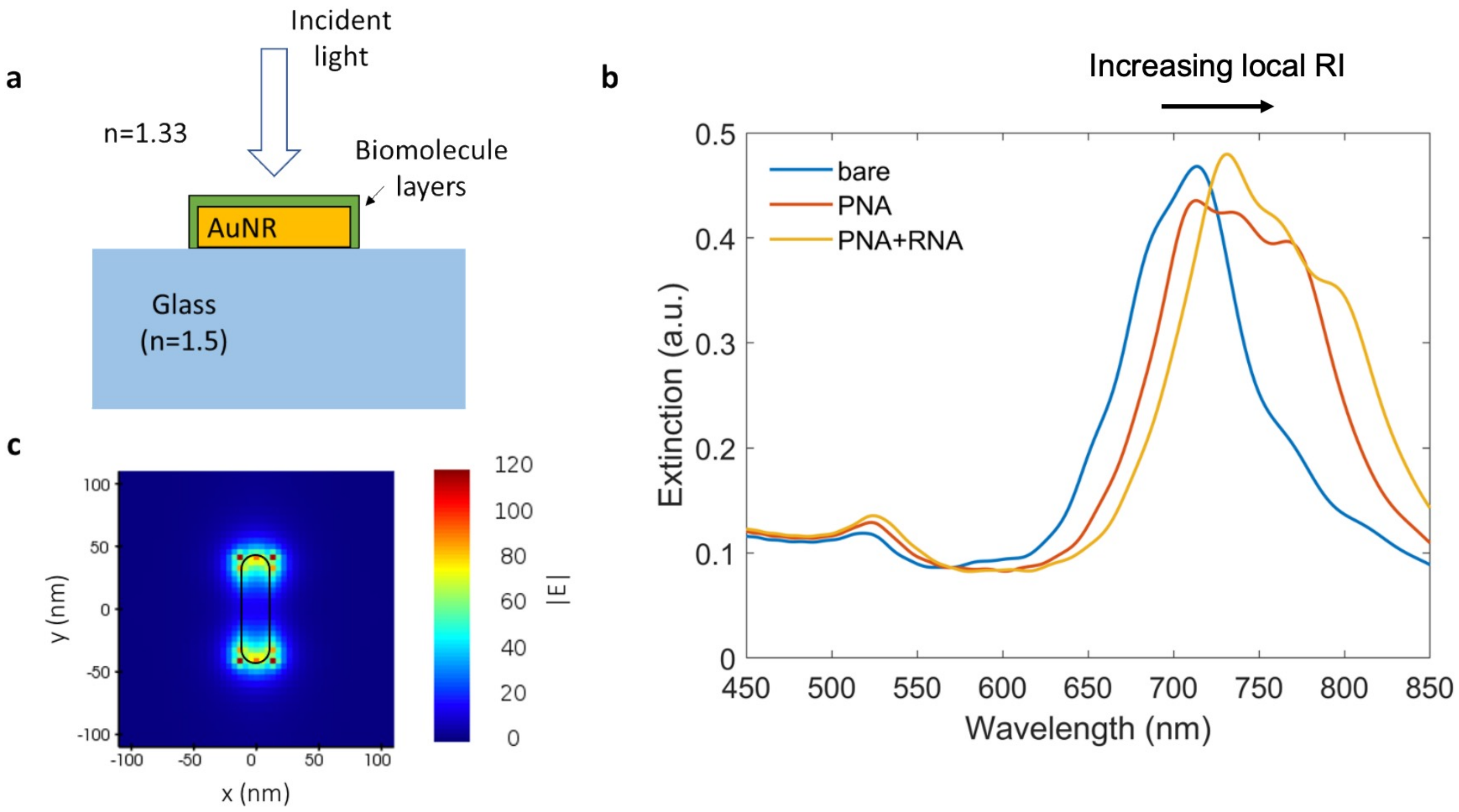
X. Ma et al., *ACS Appl. Energy Mater.* 2019, 2, 5, 3605-3613

Sequence-Specific Detection of SARS-CoV-2

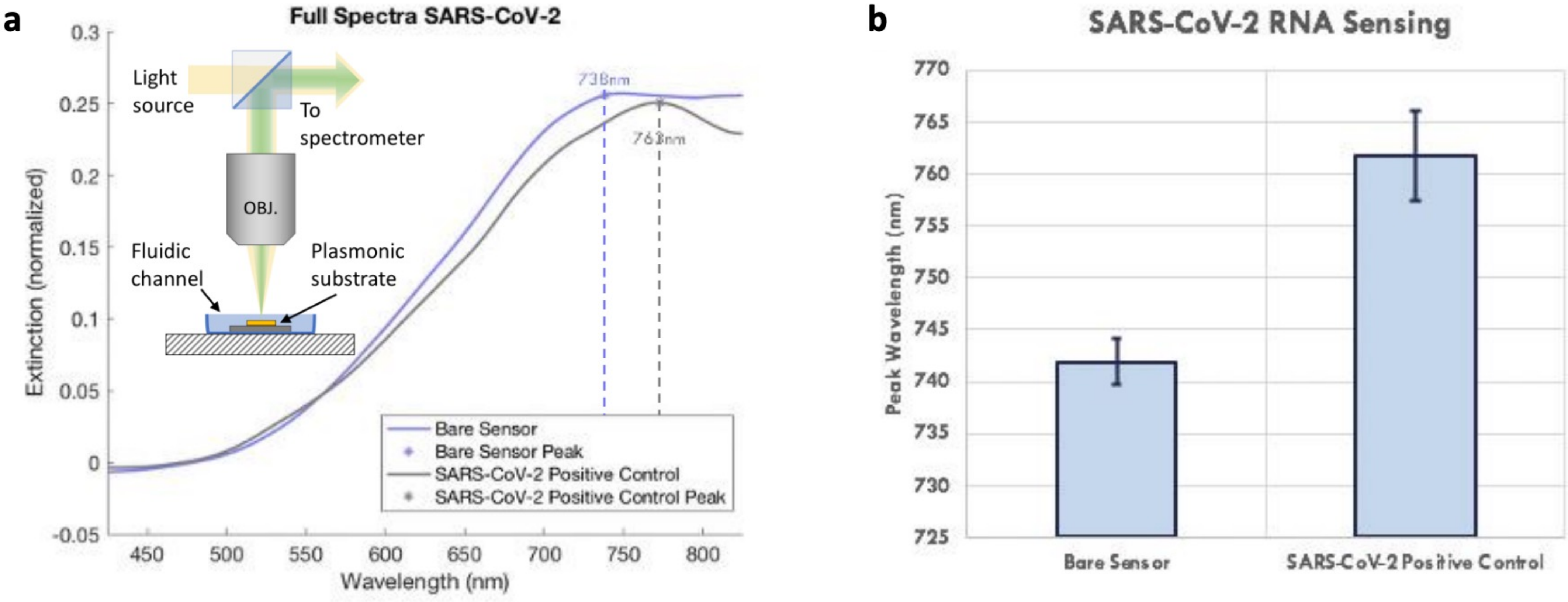


PNA Probe	Target Viral RNA Sequence
2019-nCoV_N1 Probe	**ACC CCG CAT TAC GTT TGG TGG ACC**
2019-nCoV_N2 Probe	ACA ATT TGC CCC CAG CGC TTC AG
B.1.1.7 SARS-CoV-2	ACC TCA AGG TAT TGG GAA CCT
B.1.351 SARS-CoV-2	CTG TTT TTC ATA GCG CTT CCA

Simulated Sensor Response

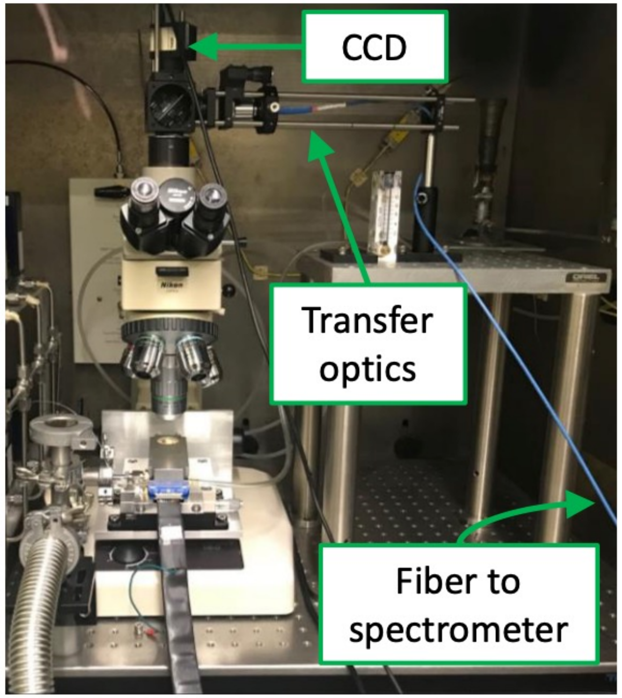


Experimental Sensor Response

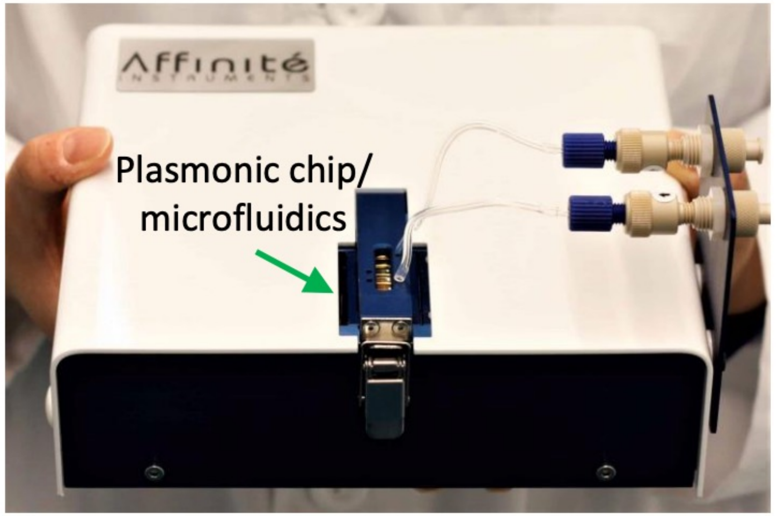


Towards a Portable Plasmonic Reader

Typical Lab-Based Setup



Portable Plasmonic Reader

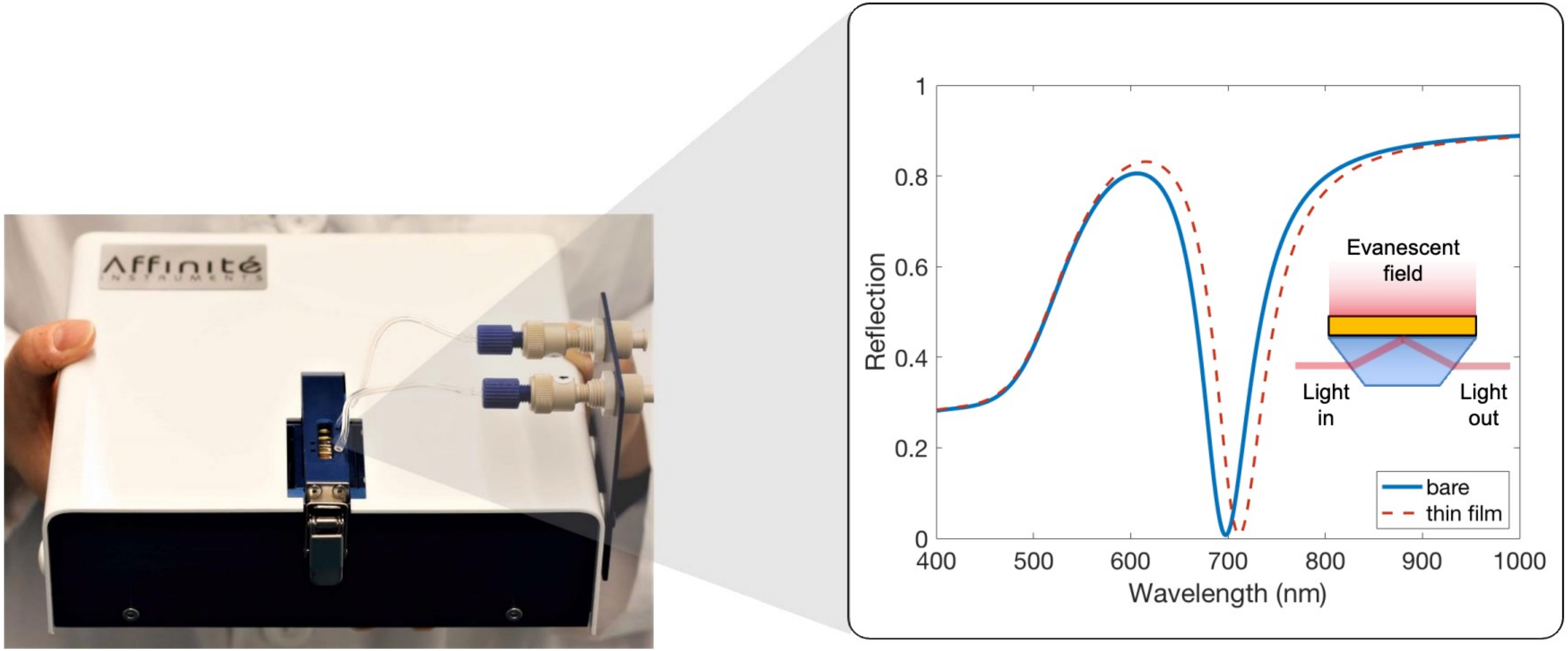


Self-contained light source/spectrometer

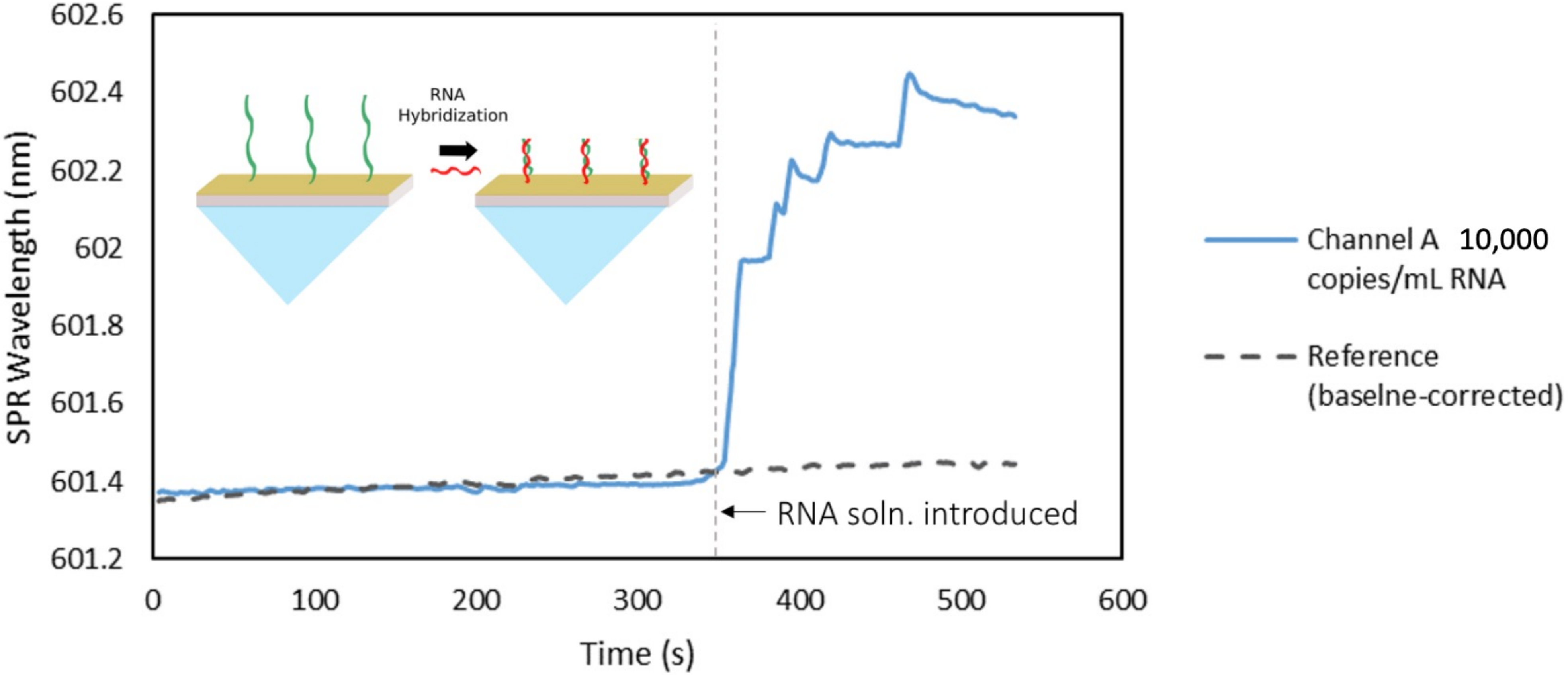
Affinité Instruments, P4SPR
https://www.affiniteinstruments.com

T. Brulé, J.F. Masson et al., *Analyst*, 2017, 142, 2161-2168

Towards a Portable Plasmonic Reader



RNA Detection Using a Portable System



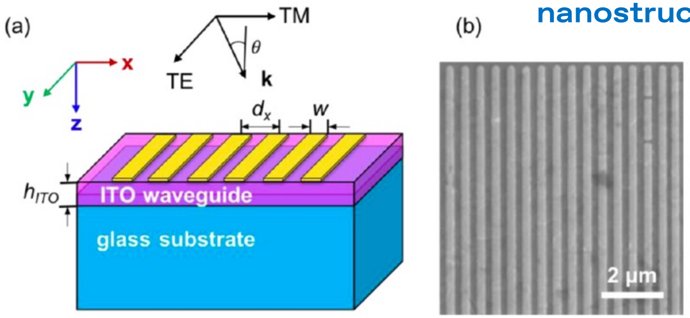
Summary

Our recent results

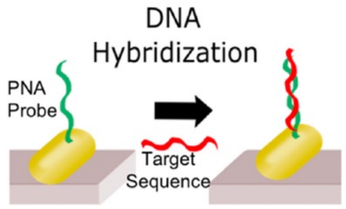
We have designed, fabricated, and tested plasmonic structures for sensitive, on-chip detection of target biomarkers. These structures consist of plasmonic gold nanoantennas coupled to a photonic waveguide. We demonstrate selective detection of target RNA sequences which is manifested as a well-defined shift in the resonance feature. Integration of plasmonic/photonic structures with photodetectors for on-chip field deployment is viable.

Device design

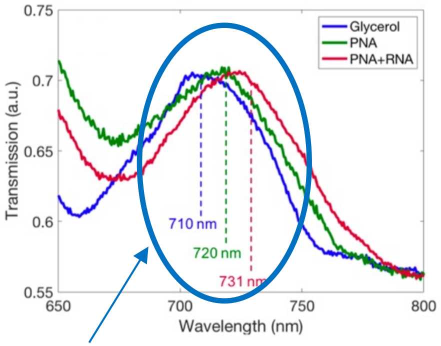
Plasmonic nanostructures



DNA/RNA detection

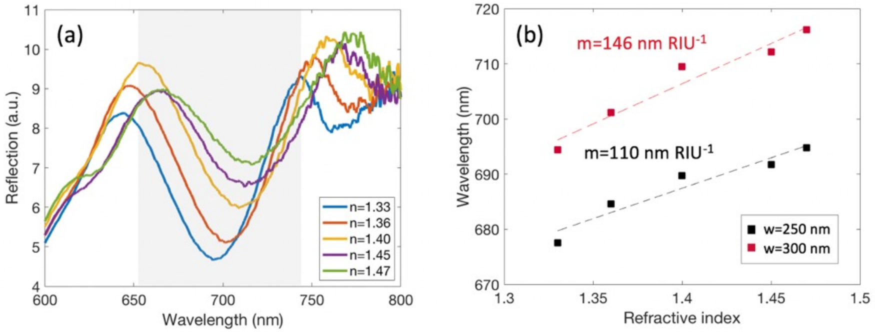


Tadimety *et al.*, Biosens. Bioelectron. **130,** 236-244, 2019



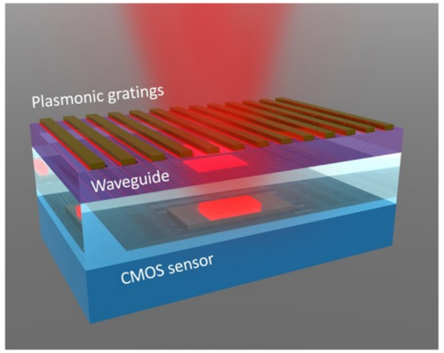
Resonance shift in response to selective RNA binding (green → red)

Refractive index sensitivity



Palinski *et al.*, Opt. Express. **27,** 11, 2019

On-chip integration



Plasmonic sensors typically rely on bulky lab equipment for signal excitation and readout (e.g., microscope, spectrometer, etc.)

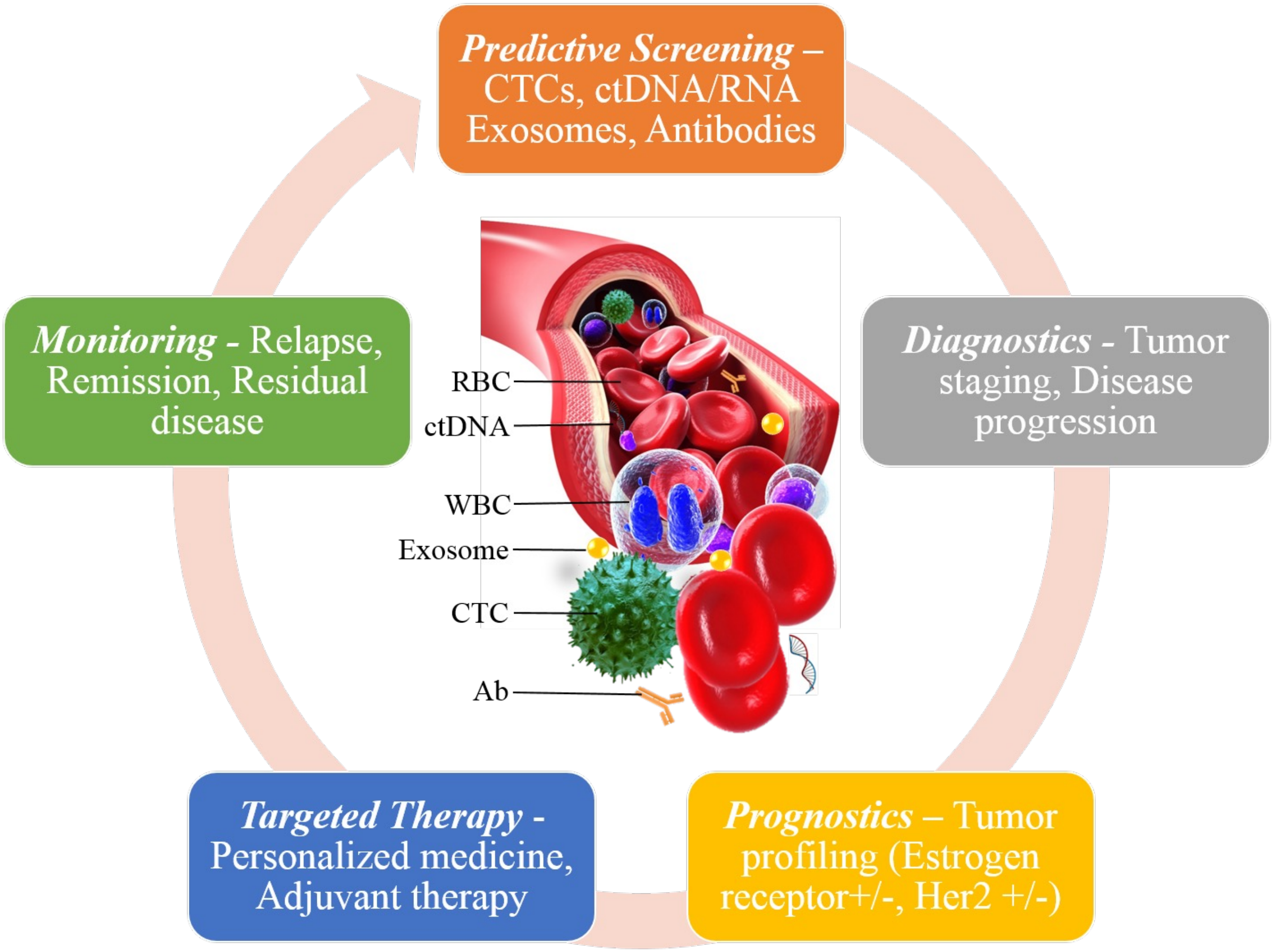
Integration into portable hardware achieved

COVID-19 detection demonstrated

Case Study 2:
Design and Testing of Nanoparticle Geometries for Liquid Biopsy

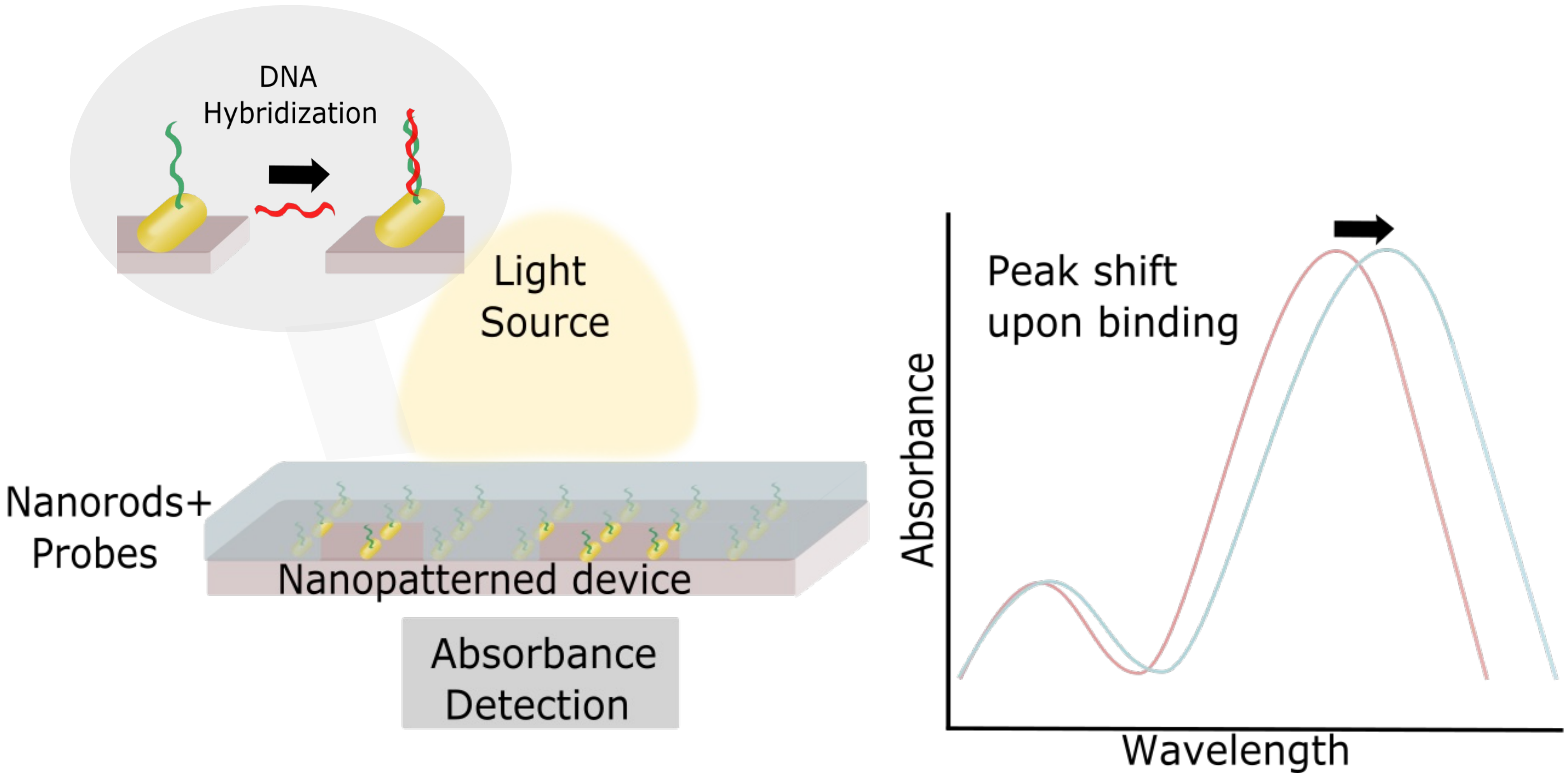
Work done under supervision of Dr. John X.J. Zhang & Dr. Gregory Tsongalis at Dartmouth College, funded by SONY Corporation

Liquid Biopsies for Screening, Diagnosis, and Monitoring



Tadimety, Syed, et al. *Integ. Biol.* 2017

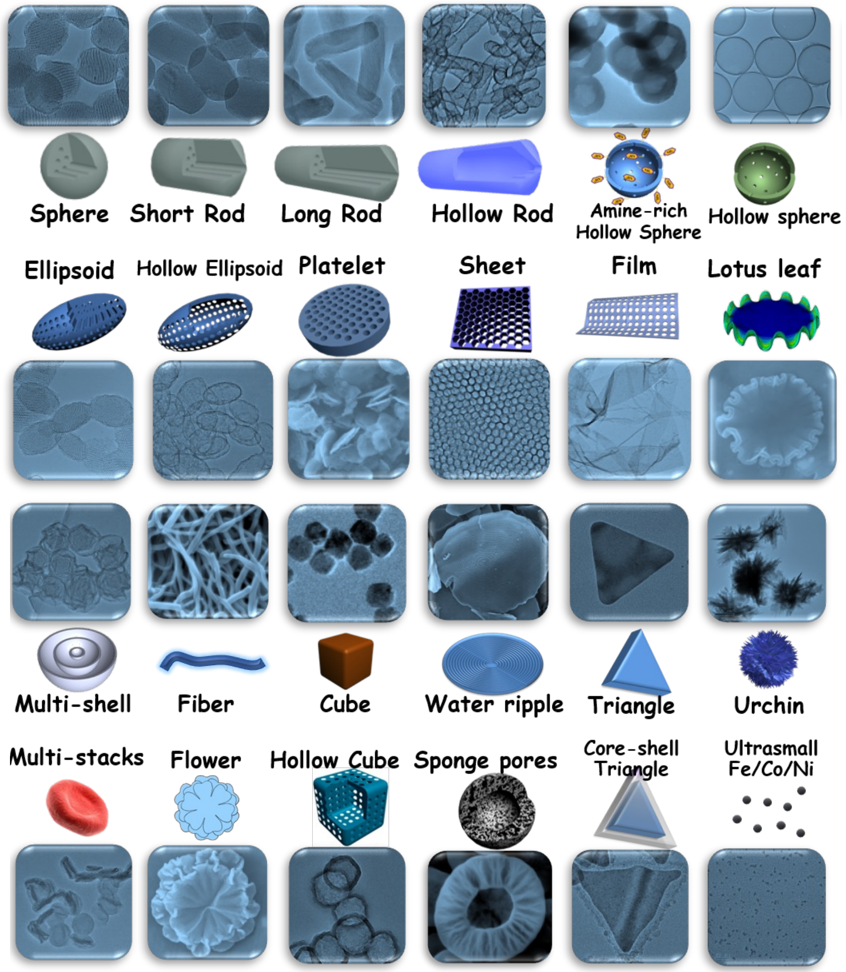
Liquid Biopsy Nanosensor: Principle of Operation



Tadimety et al. *Biosensors and Bioelectronics* 2019

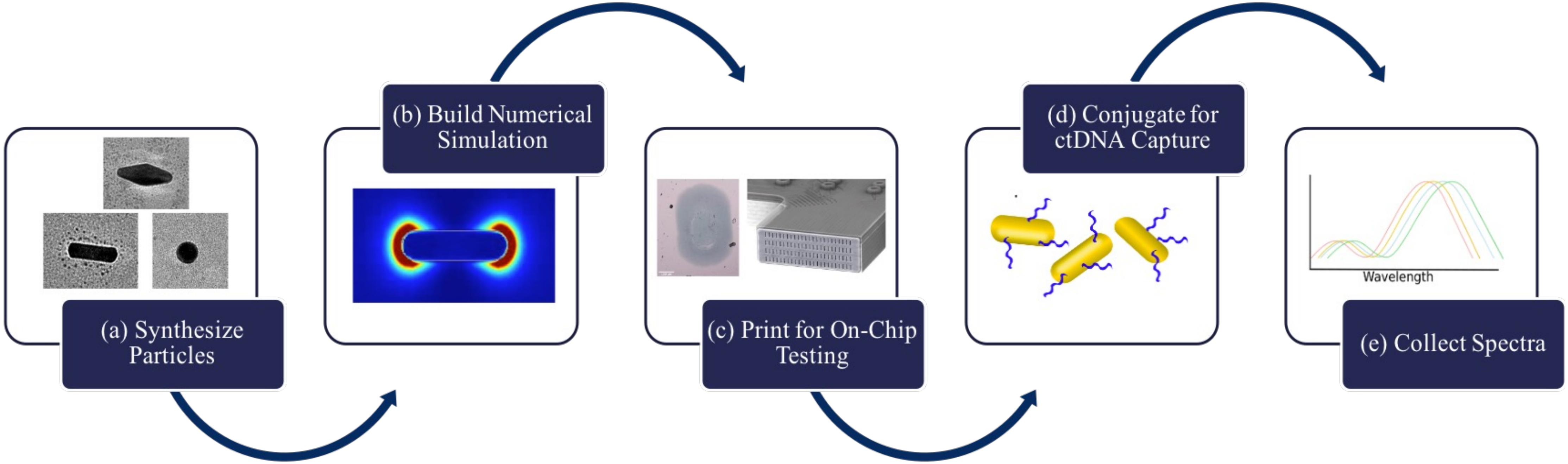
Study Overview

- Different nanoparticle shapes have different resonance features (plasmonic spectra)
- They also have different sensitivities
- Can we rationally design a particle better than a nanorod to improve limit of detection?
- How can we build simulations to inform our design?



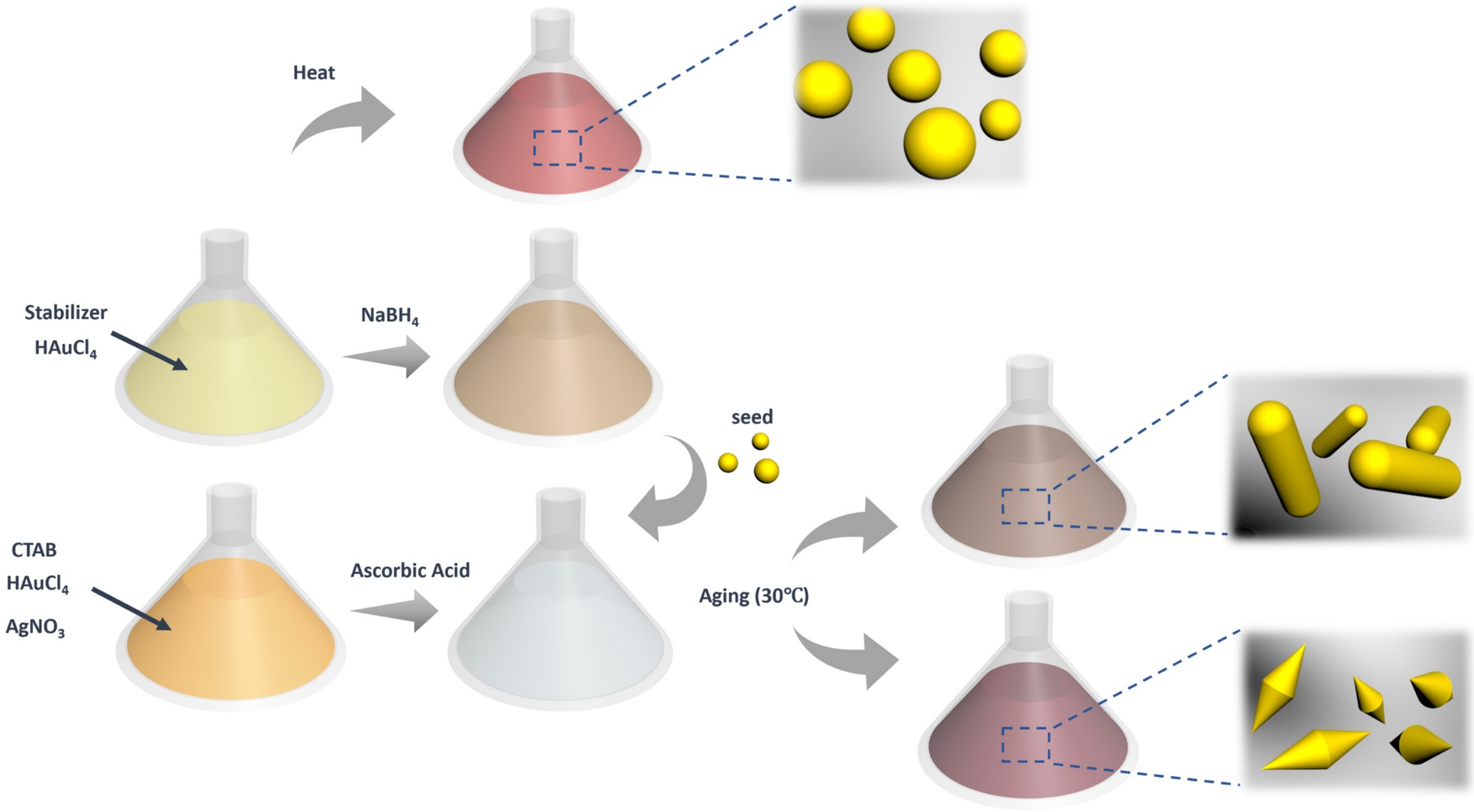
Tadimety*, Wu* et al. *Sci. Rep.* 2021, Nanoparticle Image Courtesy of Dr. Nanjing Hao

Study Workflow: Simulation, Experiment, and Testing



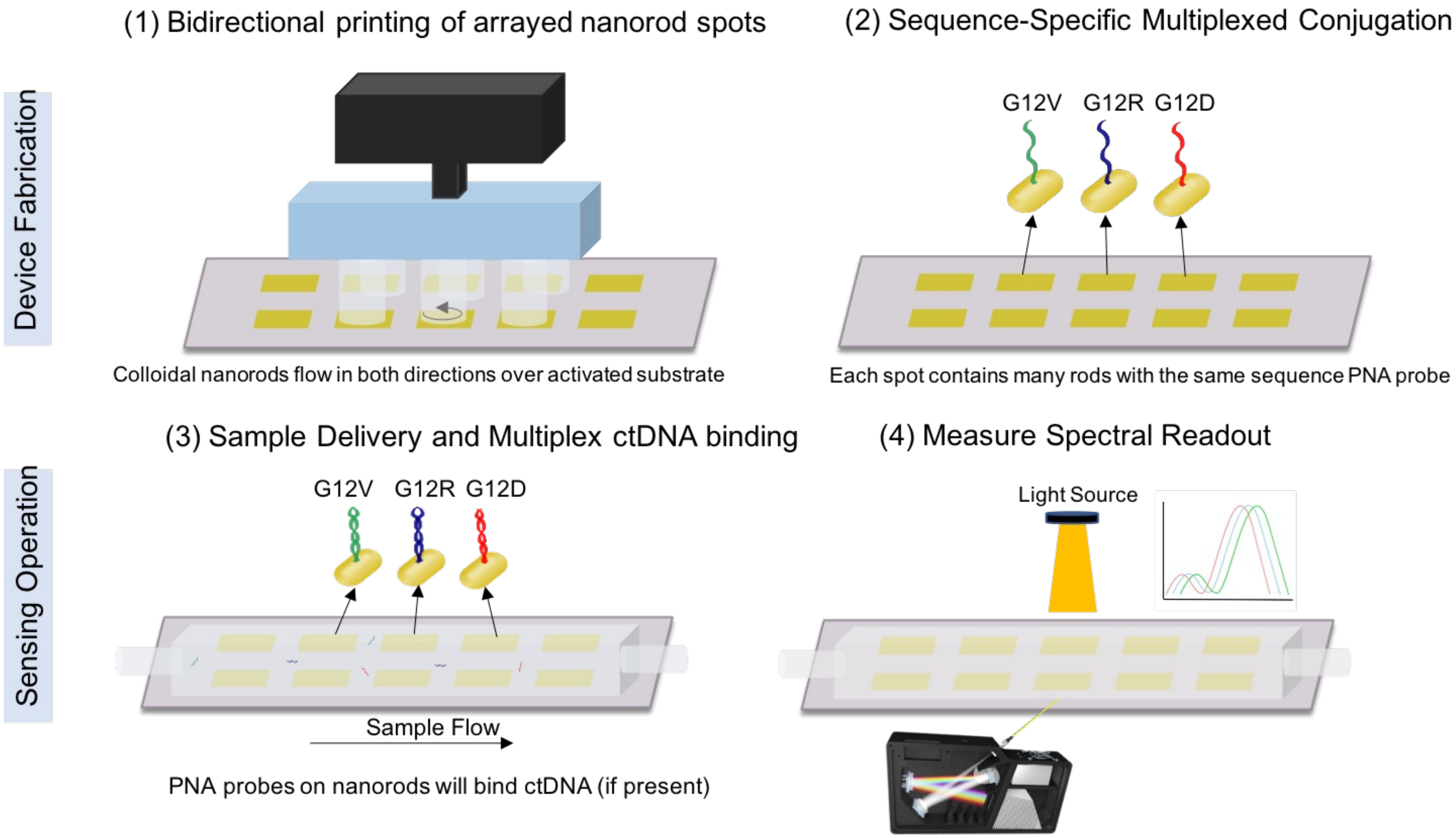
Tadimety*, Wu* et al. *Sci. Rep.* 2021.

Colloidal Nanoparticle Synthesis Workflow



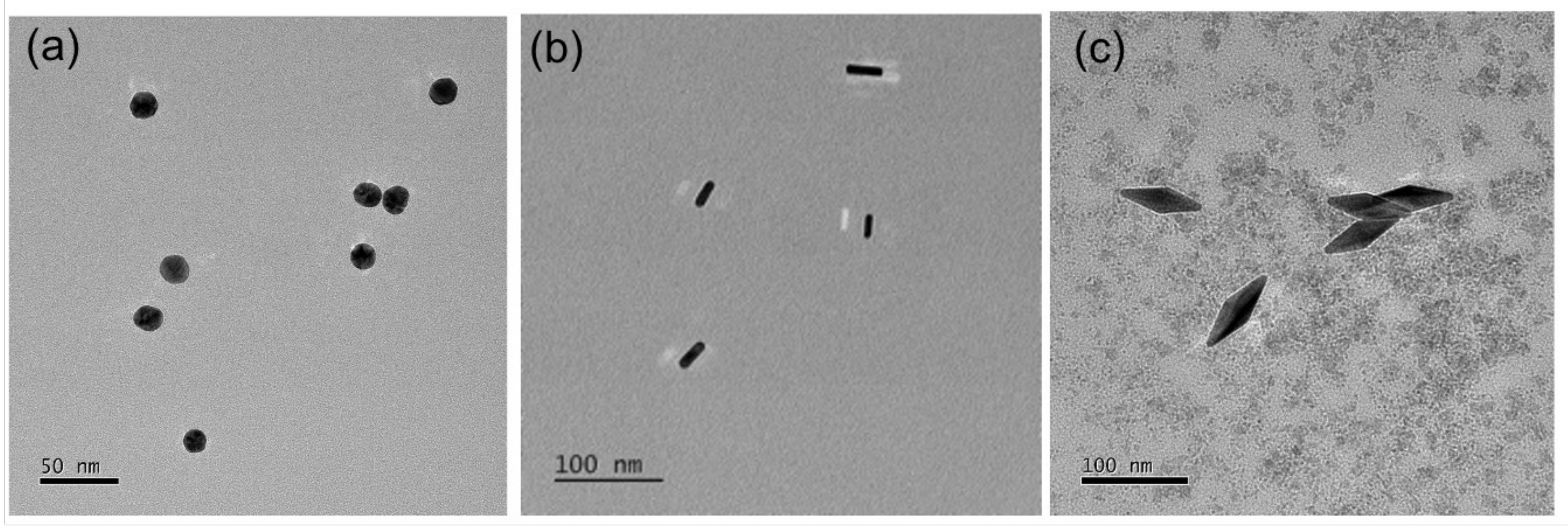
Tadimety*, Wu* et al. *Sci. Rep.* 2021.

Sensor Fabrication: Deposition of Colloidal Nanoparticles



Tadimety A. Ph.D. Thesis, Dartmouth College, 2020.

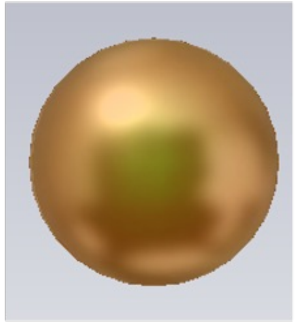
Colloidal Nanoparticle Characterization

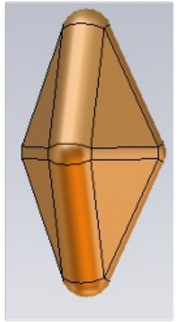


Nanospheres
(20nm)

Nanorods
(13nm x 45nm)

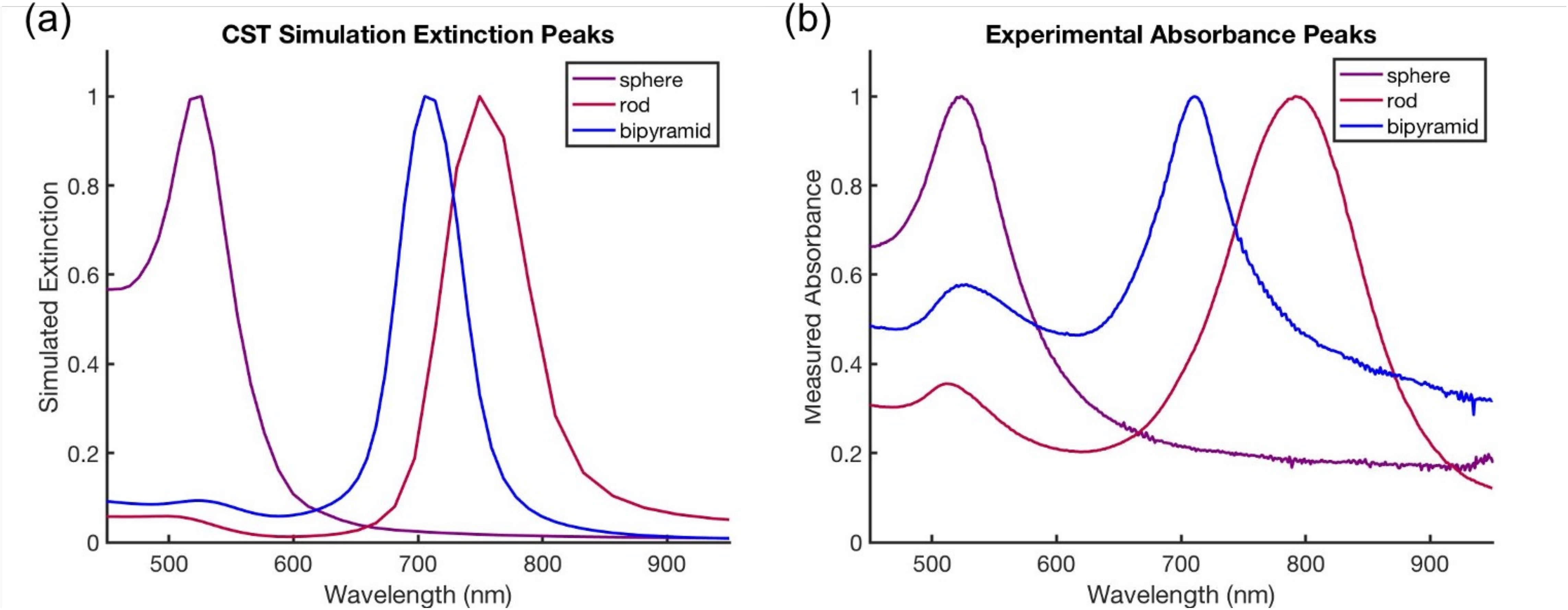
Nanobipyramids
(25nm x 70nm)





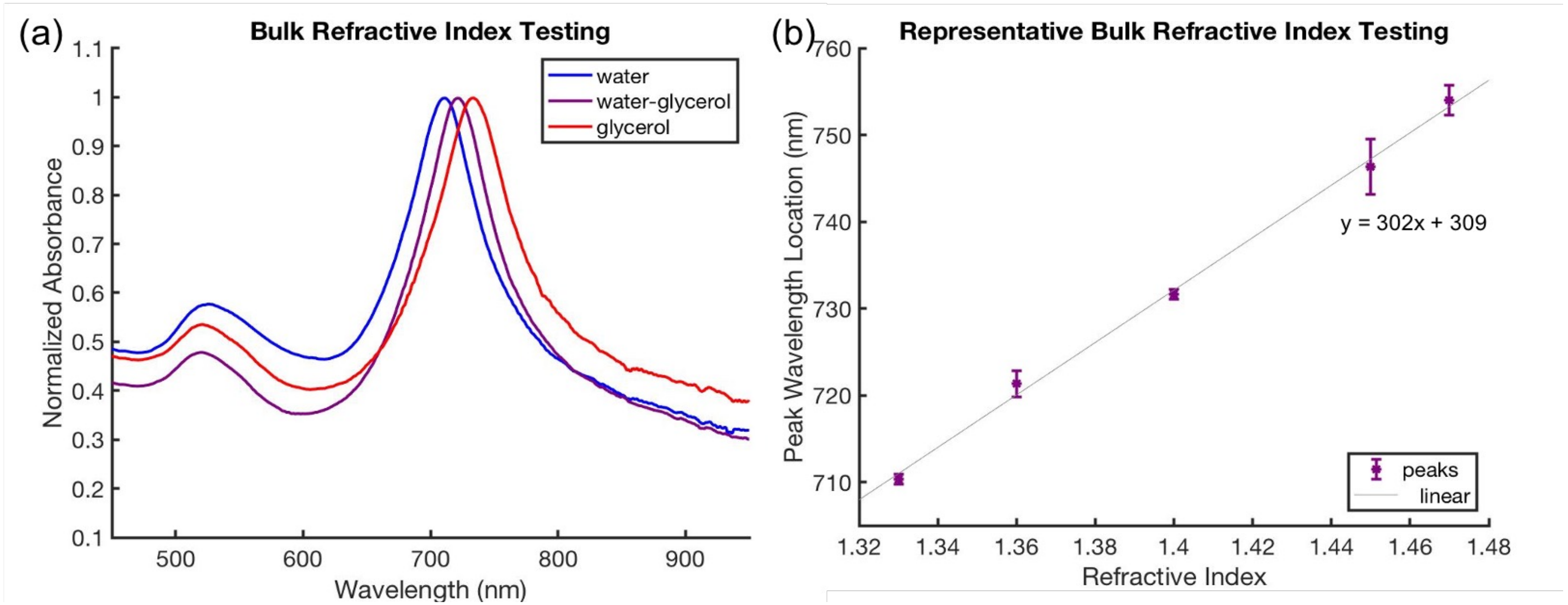
Tadimety*, Wu* et al. *Sci. Rep.* 2021.

Comparison of Simulation & Experiment: Resonance Spectra



Tadimety*, Wu* et al. *Sci. Rep.* 2021.

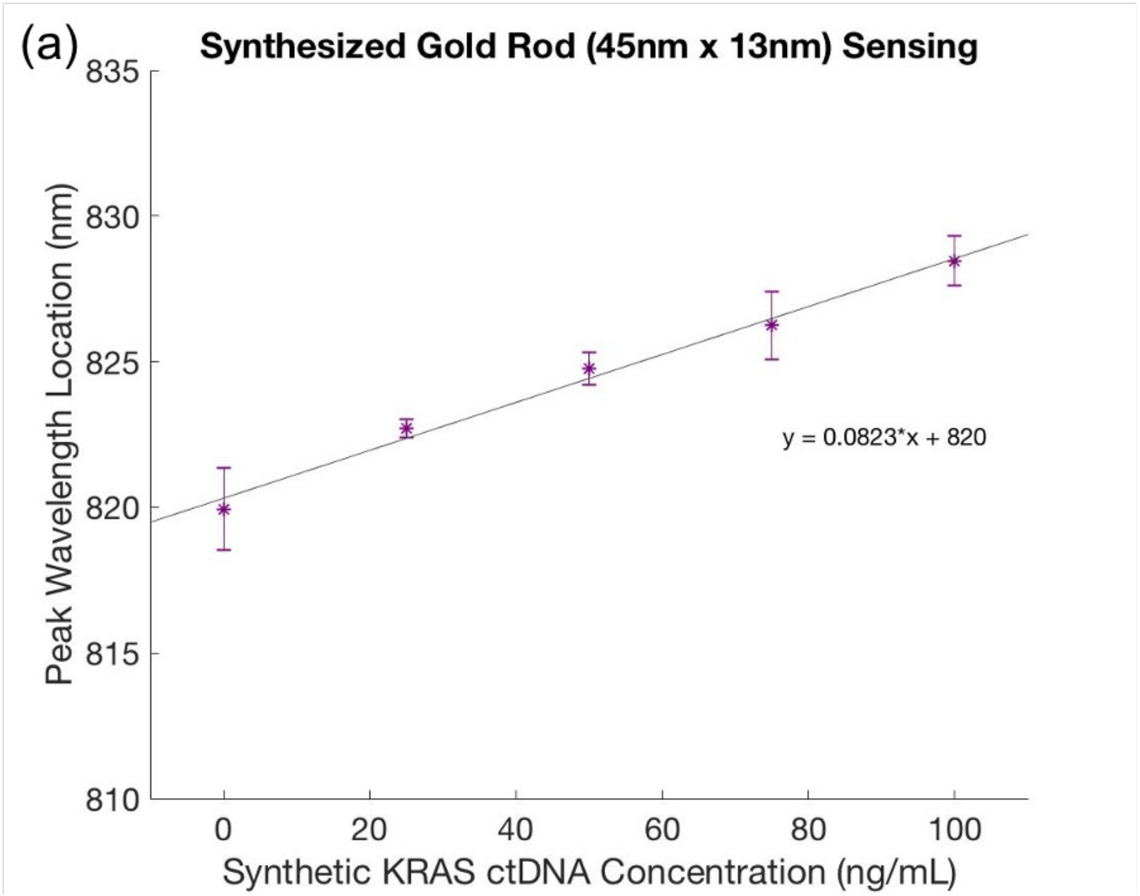
Comparison of Simulation & Experiment: Sensitivities

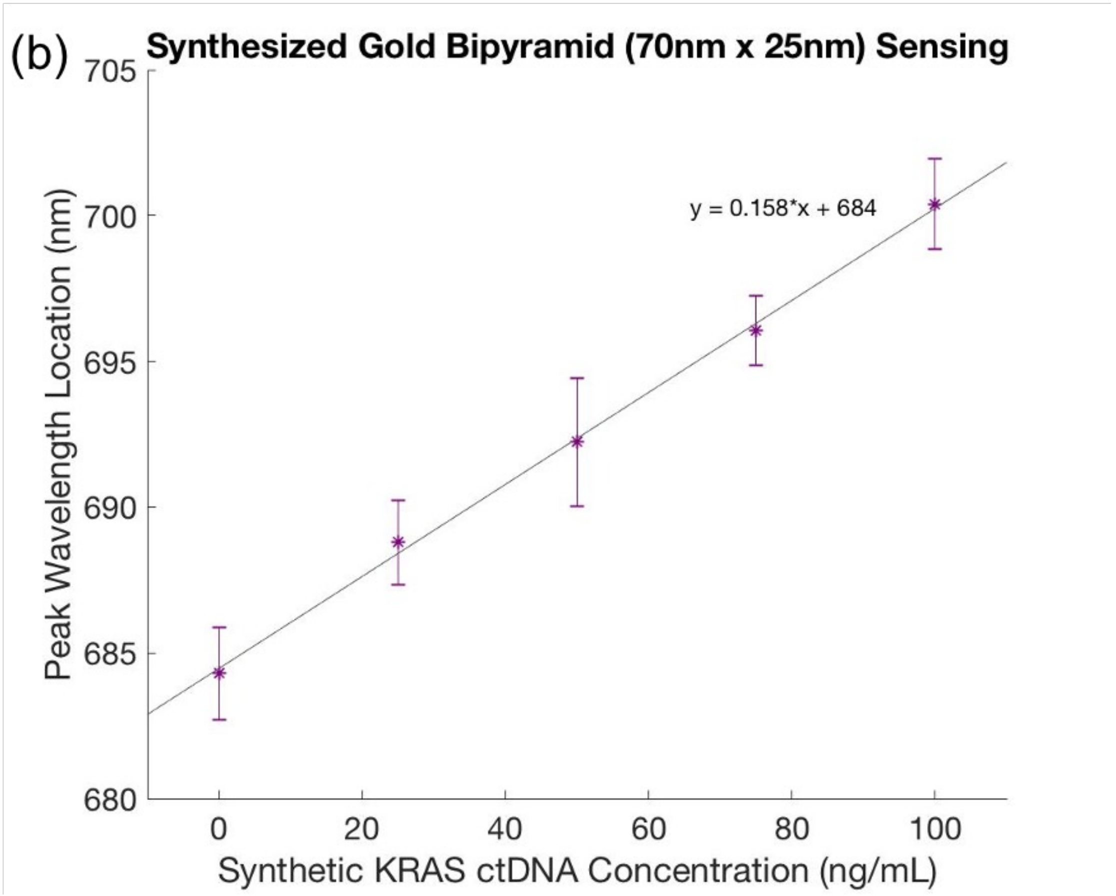


	Simulated RI Sensitivity (nm/RIU)	Experimental RI Sensitivity (nm/RIU)
Gold Rod (45nm x 13nm)	**212**	**228**
Gold Bipyramid (70nm x 25nm)	**367**	**302**
Gold Sphere (20nm radius)	**73**	**122**

Tadimety*, Wu* et al. *Sci. Rep.* 2021.

Comparison of Simulation & Experiment: ctDNA Sensing

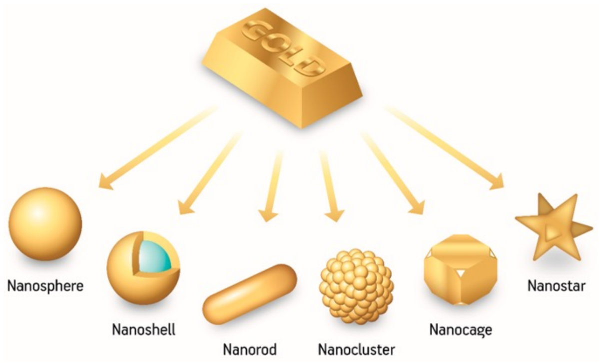


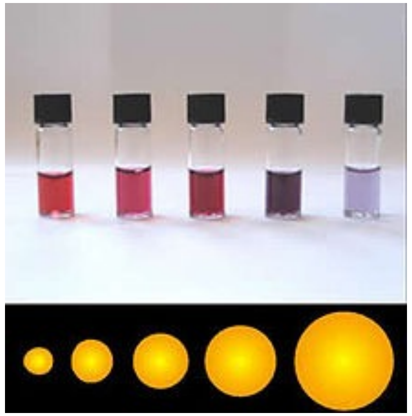


Tadimety*, Wu* et al. *Sci. Rep.* 2021.

Case Study 1: Conclusions and Continued Work

- We have built single particle simulations that align well with plasmonic particle behavior
- As hypothesized, nanobipyramids, with sharp edges, performed twice as well as nanorods
- This type of analysis can lower limit of detection and increase analytical sensitivity
- Continuing the work through pilot patient sample testing in collaboration with Dartmouth-Hitchcock Medical Center



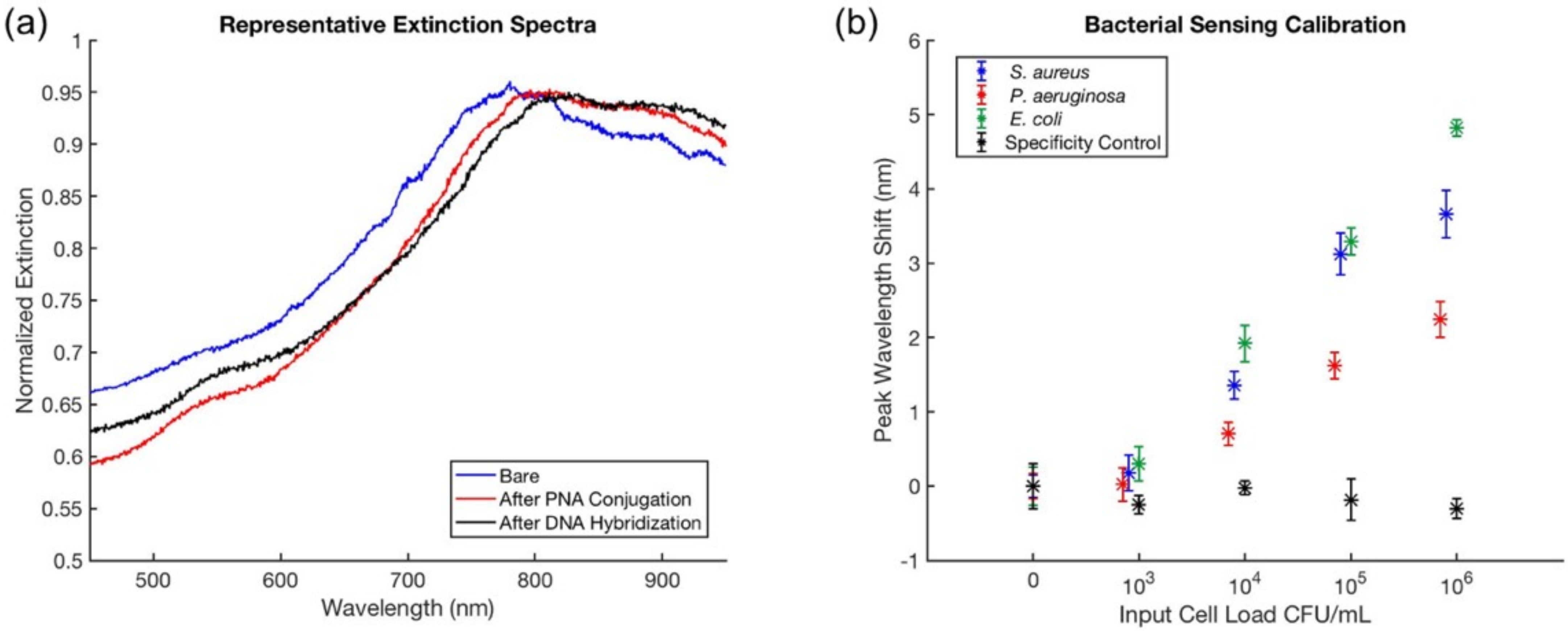


Tadimety*, Wu* et al. *Sci. Rep.* 2021.

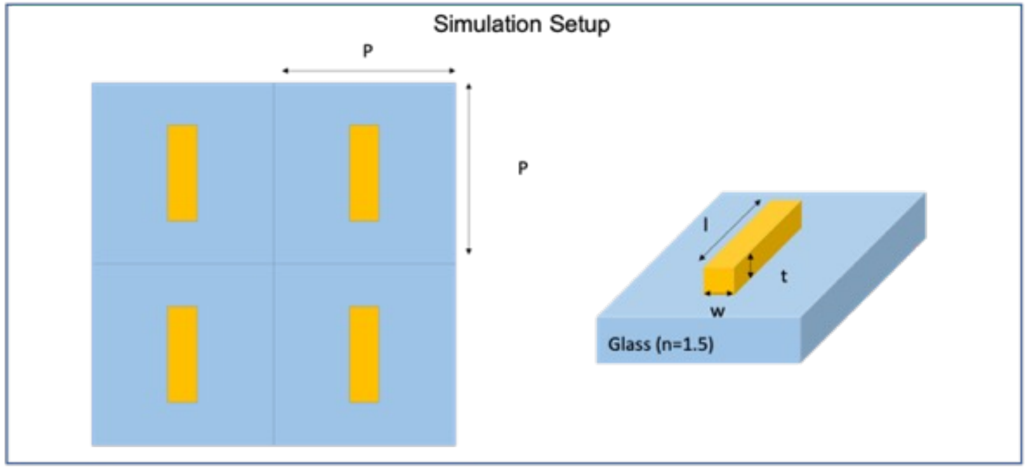
Case Study 3:
Rational Design of Nanoarray Geometries for Biosensing

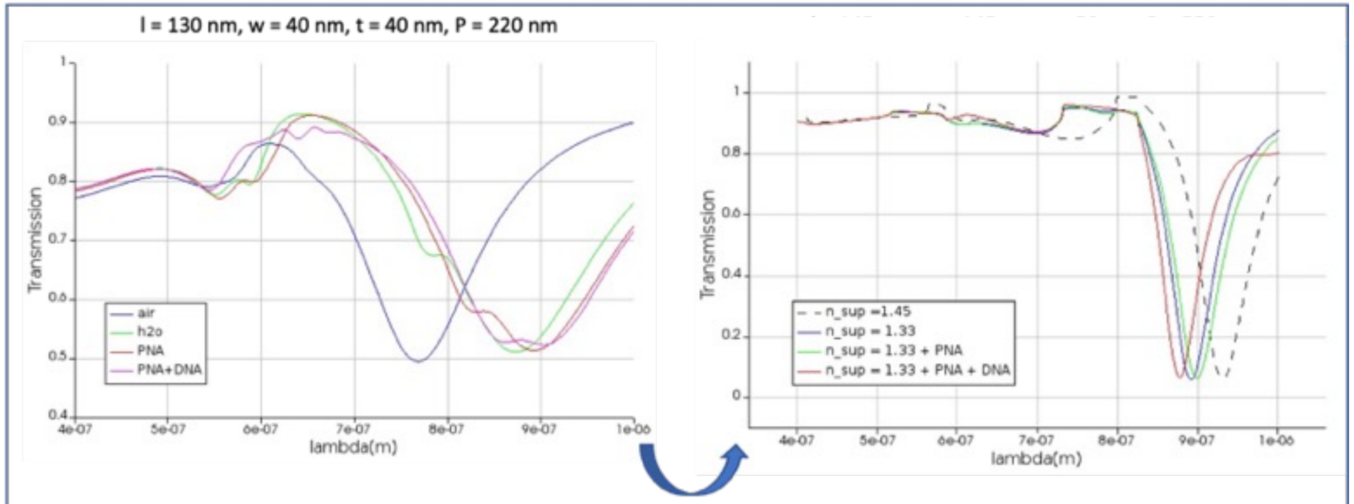
Work done in collaboration with NASA under funding from National Science Foundation

Plasmonic Nanosensing for Bacterial Detection



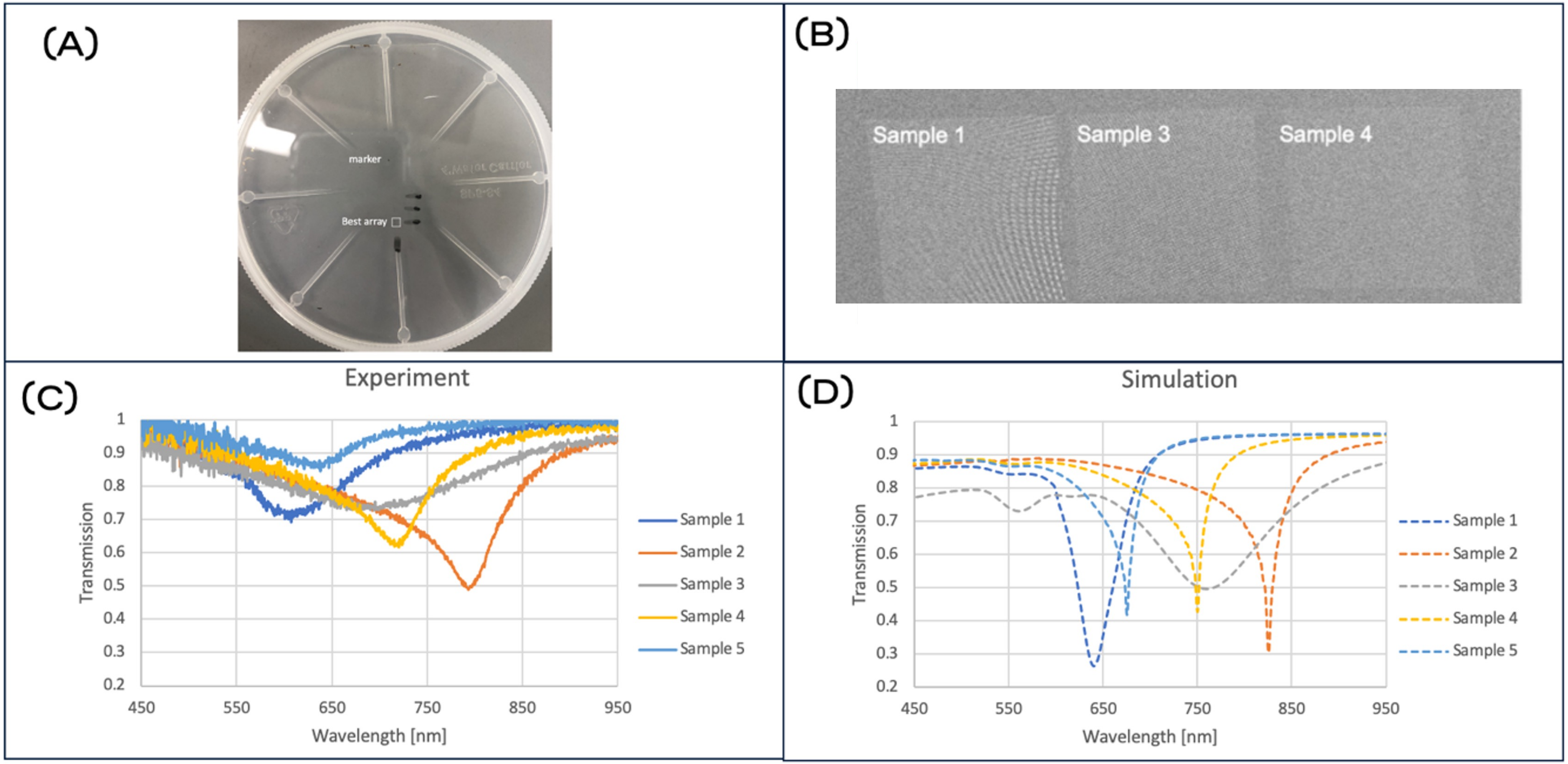
Project Overview: Introduction to Diffractive Coupling



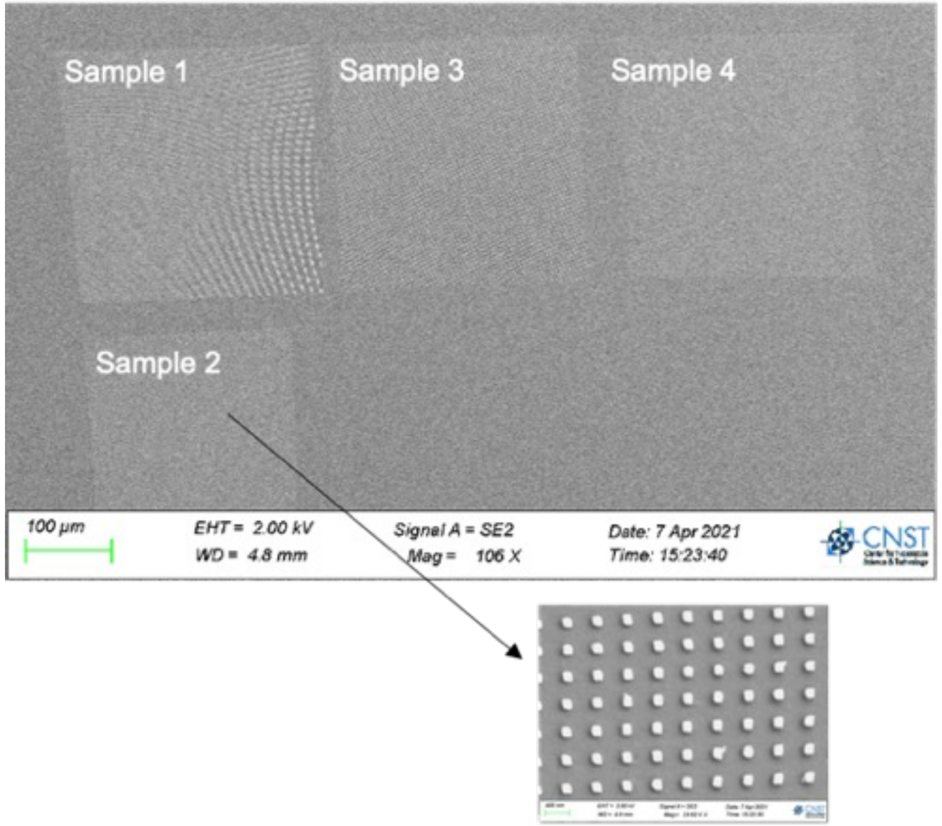


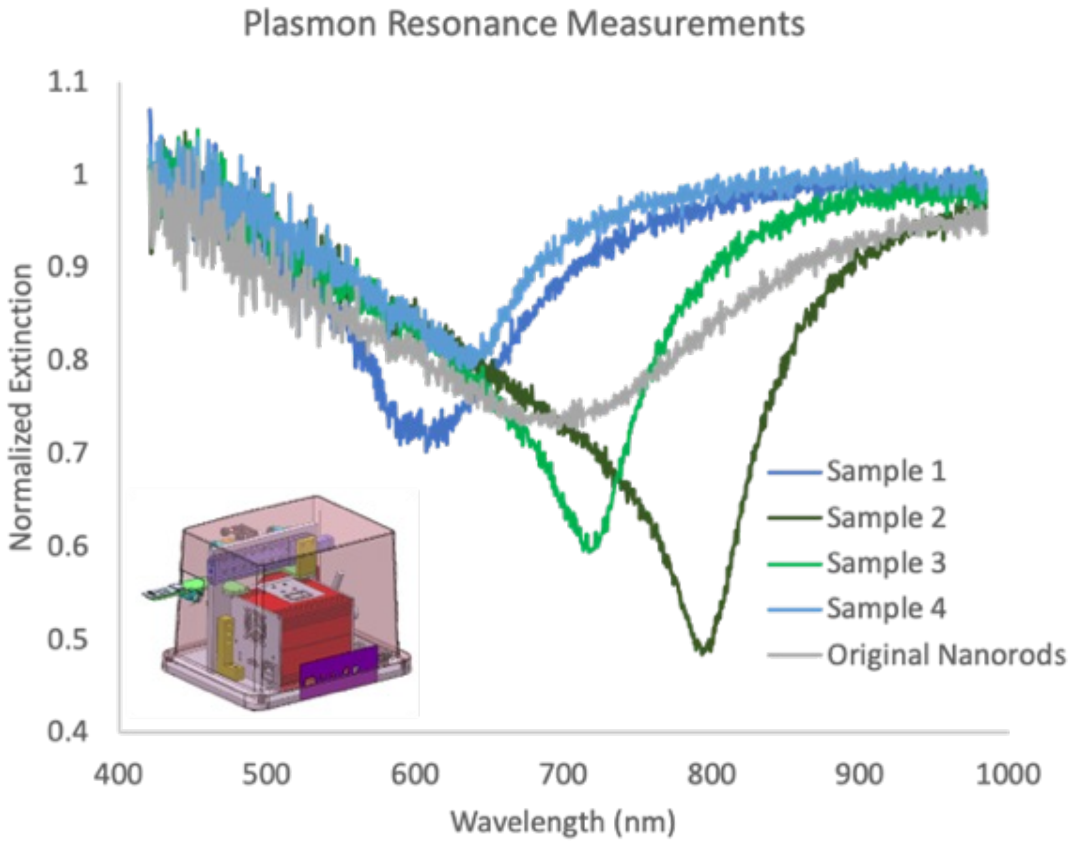
Rather than random (sparse) nanorod behavior, resonances can be narrowed and amplified through diffractive coupling

Design Workflow: Fabrication and Testing

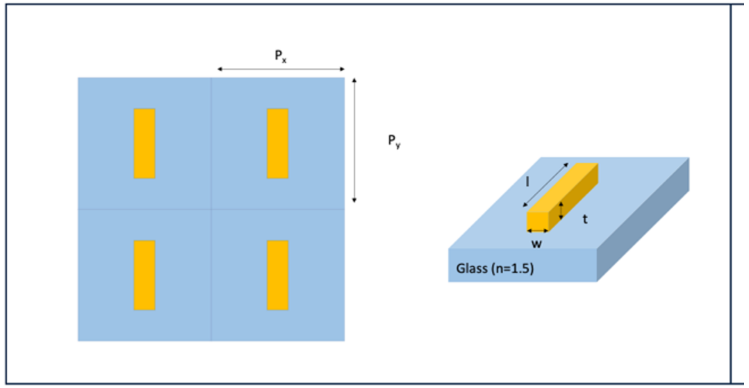


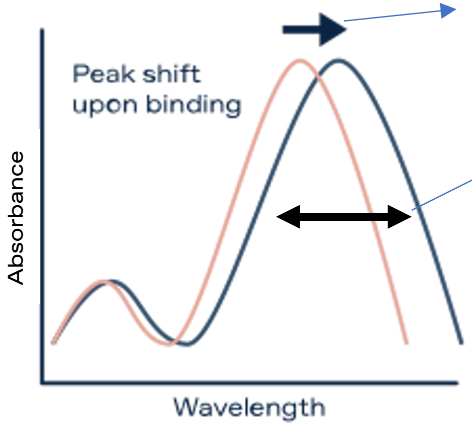
Experimental Testing of NIST Calibration Sample





Ongoing Projects: Improving Sensor Figure-of-Merit





Delta RI

FWHM

FOM = deltaRI / FWHM

Case Study 2: Ongoing Work

Figure of Merit Calculations from NASA Simulation

Width (nm)	Spacing (nm)	Thin	Medium	Thick
L	L	6.06	-	1.78
	M	-	1.87	-
	H	5.56	-	1.69
M	L	-	1.65	-
	M	7.20	7.99	10.56
	H	-	4.60	-
H	L	1.52	-	0.87
	M	-	3.85	-
	H	9.19	-	4.76

Purple is current sensor, green are only simulations that were better.
Takeaway – slight design tweaks may substantially improve sensor performance

References

Brolo, *Nature Photonics,* 2012

Brule T, Masson JF et. al., *Analyst,* 2017, 142, 2161-2168

Chen et al. , *Langmuir*, 2008

Mayer, *Chem. Rev,* 2011

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THANK YOU.

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