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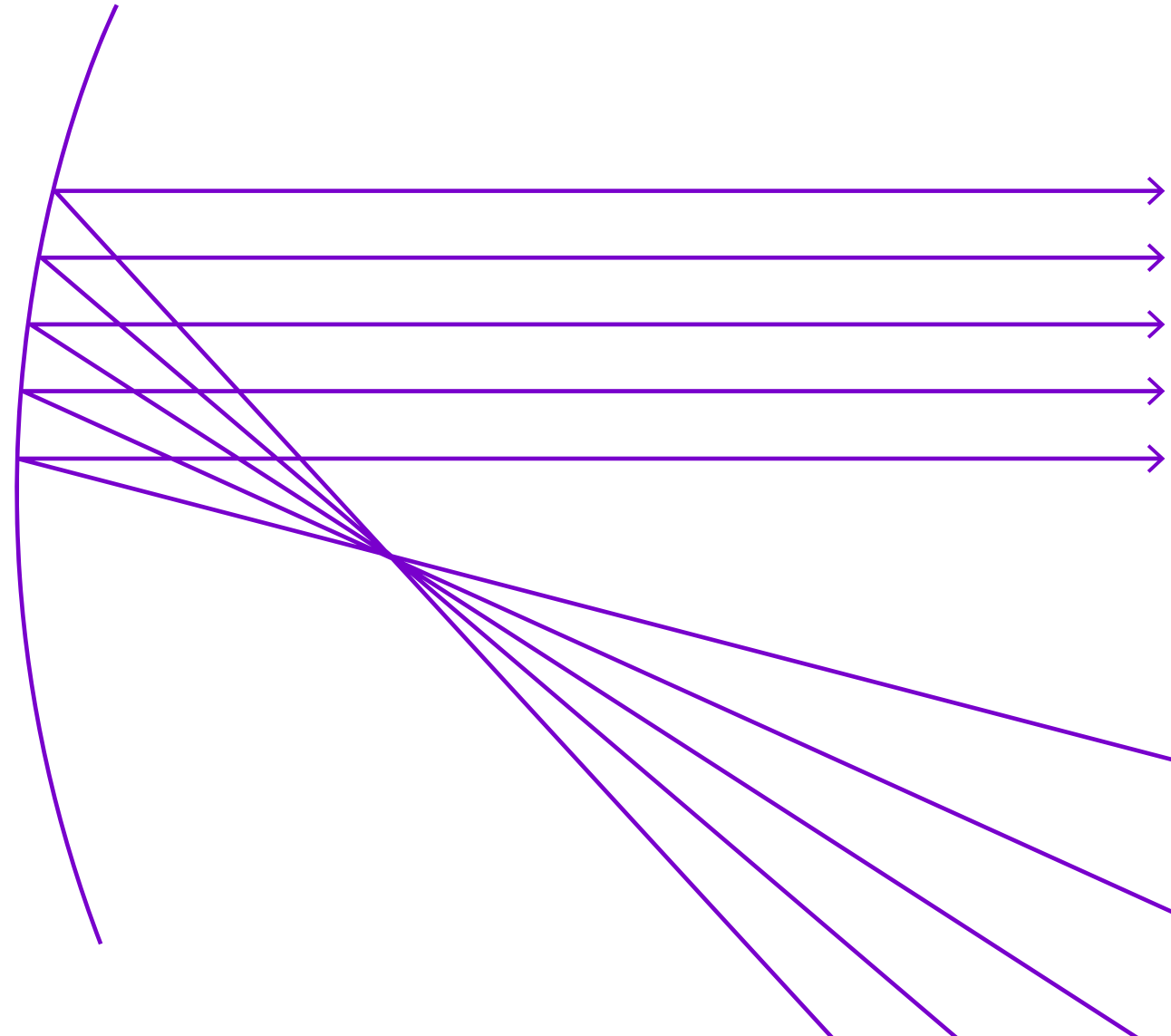
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Environmental Sensing Technical Group

Advanced Nanophotonic and Plasmonic Materials for Sensing Applications

Sreekanth Kandammathe Valiyaveedu, A*STAR

08 October 2021



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About the Environmental Sensing Technical Group

Our technical group focuses on tools and processing techniques to characterize the environment including DIAL and LIDAR, hyper-spectral monitoring, detection, processing and characterization, surveying applications, atmospheric propagation, pollution monitoring, and remote imaging.

Our mission is to connect the 1500+ members of our community through technical events, webinars, networking events, and social media.

Our past activities have included:

- Incubator Meeting on Agri-Photonics
- Webinar on Recent Advances in Quartz-Enhanced Photoacoustic Spectroscopy for Gas Sensing Applications
- Technical Group Poster Session at CLEO: 2018

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Connect with our Technical Group

Join our online community to stay up to date on our group's activities. You also can share your ideas for technical group events or let us know if you're interested in presenting your research.

Ways to connect with us:

- Our website at www.optica.org/ie
- On LinkedIn at www.linkedin.com/groups/12055528/
- Email us at TGactivities@optica.org

Today's Speaker



Sreekanth Kandammathe Valiyaveedu

*Institute of Materials Research and Engineering, A*STAR*

- Currently serving as a research scientist at the Institute of Materials Research and Engineering, A*STAR in Singapore
- Received his Ph.D. in photonics from Nanyang Technological University
- Served as a postdoctoral researcher at the Department of Physics, Case Western Reserve University and as a Senior Researcher at the Centre for Disruptive Photonic Technologies, Nanyang Technological University
- Editorial Board member for Scientific Reports and Chemosensors

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Advanced Nanophotonic and Plasmonic Materials for Sensing Applications

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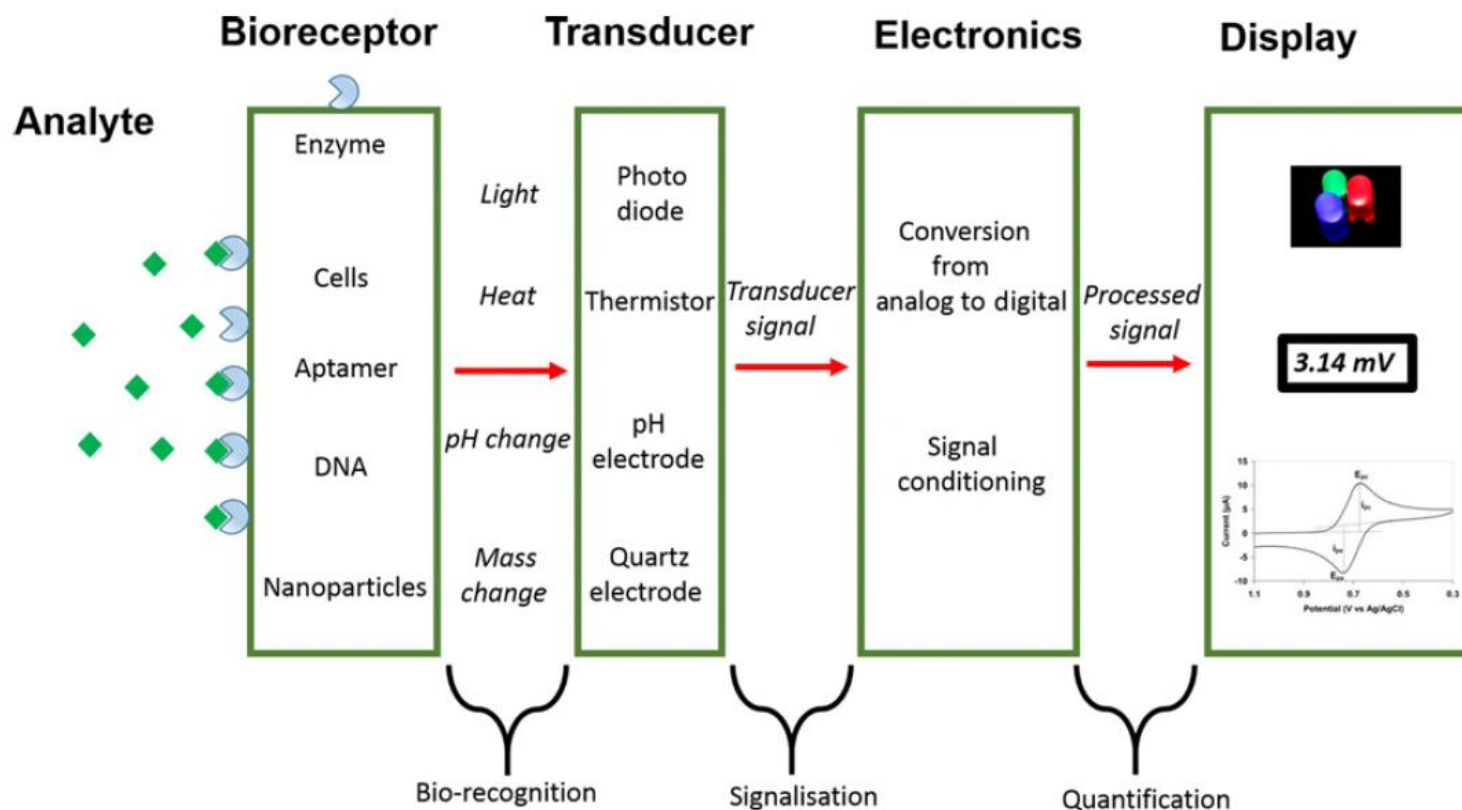
Outline

- Introduction
- Optical biosensors
- Conventional optical sensing methods
- Interrogation schemes
- Advanced materials and sensing methods
- Tunable sensing
- Intelligent sensing
- Summary and outlook

Introduction

Biosensor-is a device that measures biological and chemical reactions by generating signals proportional to the concentration of an analyte in the reaction

Components of a Biosensor



Introduction

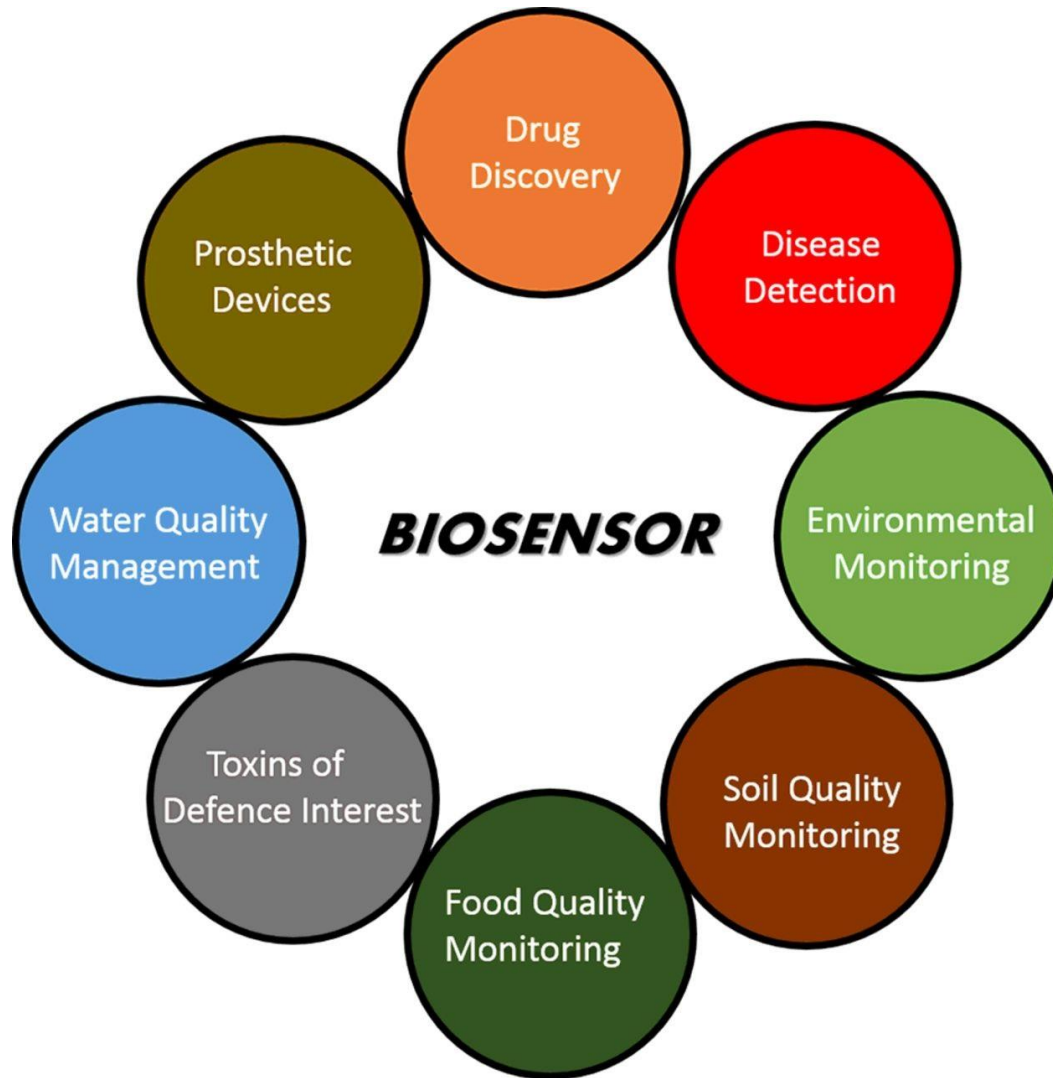
Basic Characteristics of a Biosensor

- Selectivity
- Reproducibility
- Stability
- Sensitivity
- Linearity

Types of Biosensors

- Electrochemical biosensors
- Thermometric (Calorimetric) biosensors
- Piezo-electric (Acoustic) biosensors
- Optical biosensors

Applications of biosensors



Optical Biosensors

An optical biosensor is a compact analytical device containing a biorecognition sensing element integrated with an optical transducer system

Optical principles for the transduction

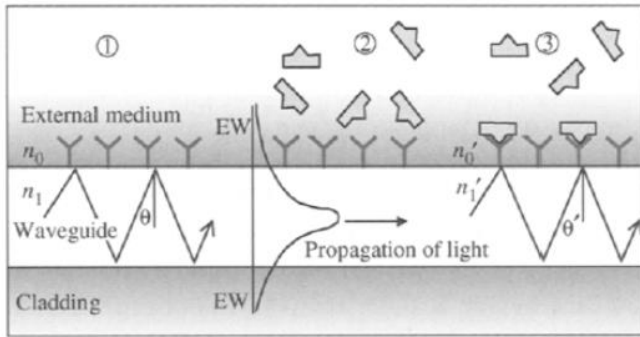
- Intensity, wavelength, phase, angle
- Fluorescence
- Refractive index

Advantages of Biosensors

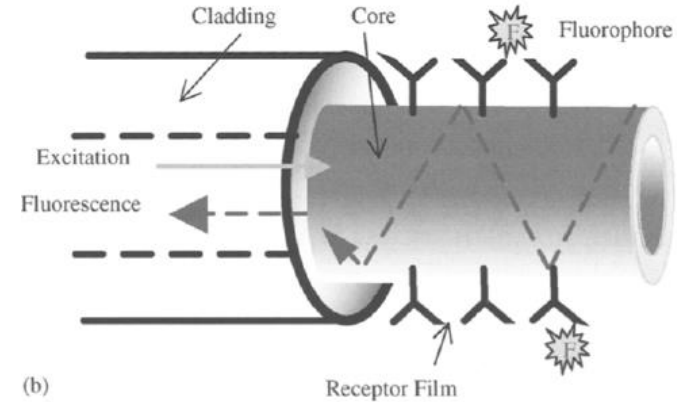
- Sensitive, fast and robust
- Suitable for miniaturization
- Can readily be multiplexed
- Free path or remote interrogation without the need for wire connections
- Label-free detection capabilities

Conventional optical sensing methods

Planar waveguide



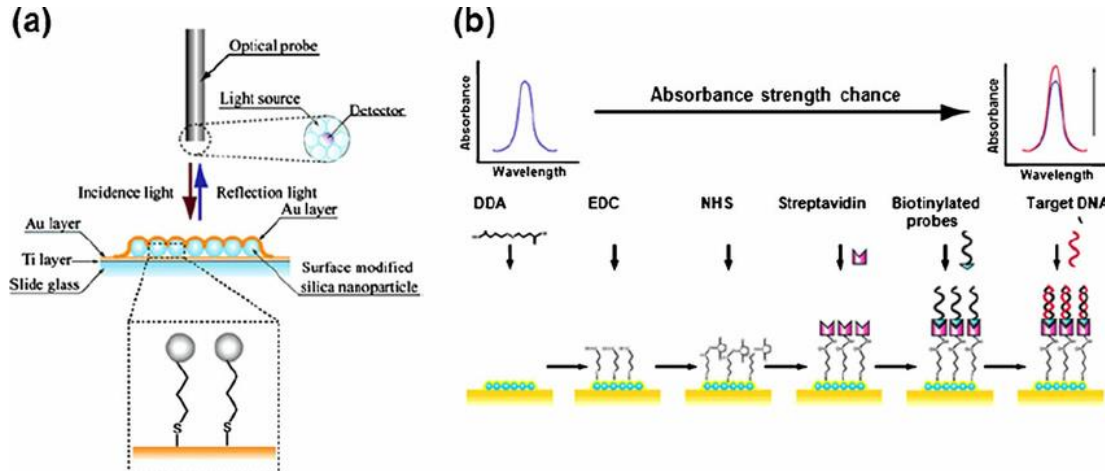
Label-free EW Intrinsic biosensors



EW fluorescence biosensors

Absorbance

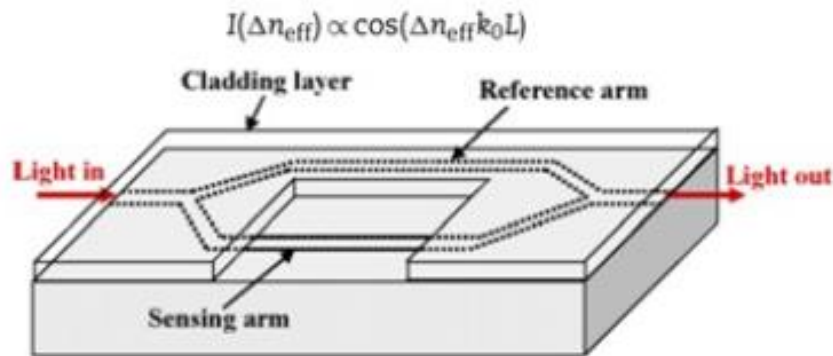
Based on the change of the imaginary part of the refractive index



Optical Biosensors, Elsevier, 83(2008)

Conventional optical sensing methods

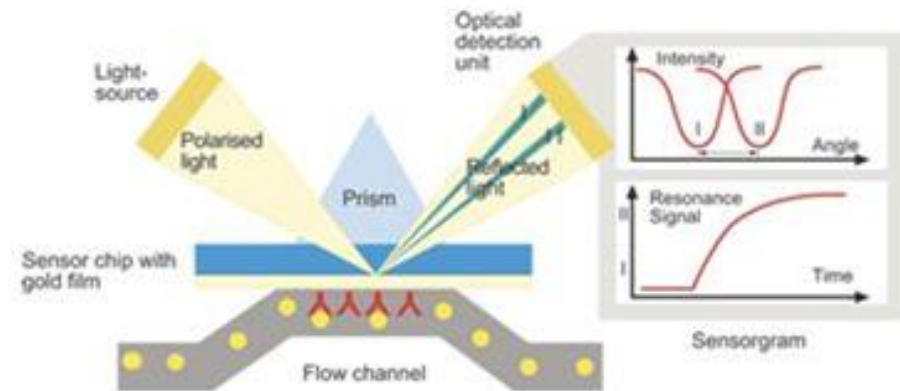
Optical interferometer



Mach-Zehnder interferometer

A change in the refractive index at the surface of the sensor arm results in an optical phase change on the sensing arm.

Surface plasmon resonance



SPR-based biosensors can be able to detect the real-time binding of biomolecules with the help of bio-receptors functionalized on a thin metallic film or metal nanoparticle.

Limitations

Sensing principle	Limit of detection (pg/mm ²)
SPR	1–5
Waveguide-SPR	2
Resonant mirror	5
Grating coupler	1–10
Mach-Zehnder interferometer	0.1
Differential mode interferometer	1
Young interferometer	0.7
Reflectometric interference spectroscopy (RifS)	1–5

Detection of Analyte concentration of the order of fg/mm²

Small molecule detection (<500 Da) at lower concentrations: low polarizability

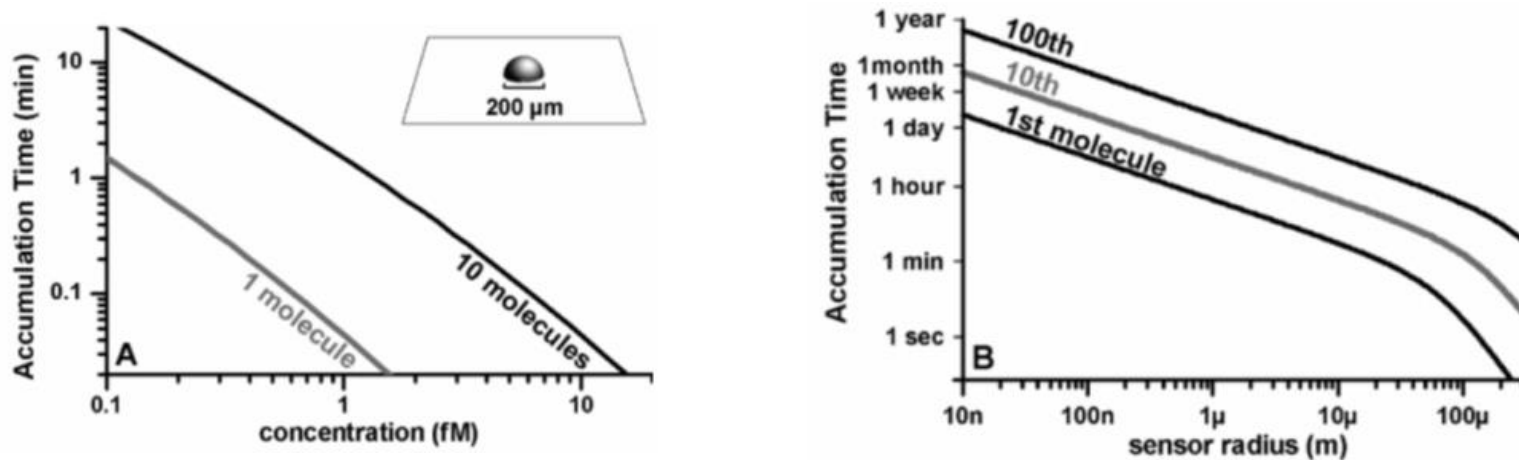
Point-Of-Care (POC) applications: cost-effective and scalable devices

Requirements for next generation biosensors

Sensitivity : Single or few small biomolecules detection (early-stage detection)

- The isolation and detection of circulating tumor cells and exosomes from bodily fluids- a real-time liquid biopsy
- Detection of airborne microorganisms (Corona virus, etc.)

Diffusion-limited transport : Nanobiosensors are statistically diffusion limited



Nano Lett. 5, 803 (2005)

Specificity : The ability of the receptors to bind parasitic molecules that cannot be easily distinguished from the targets

Interrogation schemes

The sensitivity of optical biosensors depends on the sensing interrogation scheme

➤ Spectral interrogation

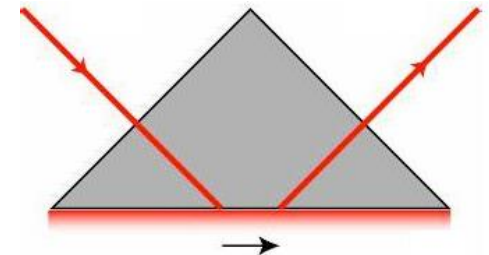
- By measuring the reflected, transmitted and absorbed (extinction) signal, which are spectral scan, angular scan, and intensity scan
- The resonance shift in the spectrum indicates the refractive index change caused by the capture of biomolecules at the sensor surface.
- The commercial SPR based optical biosensor works based on angular scan

➤ Phase sensitive detection

- The phase shifts in optical systems are more prominent than its amplitude counterpart
- This scheme can be integrated with imaging technology to realize high-throughput sensors

➤ Goos-Hänchen shift based detection

- The lateral beam displacement of the reflected light from the interface of two media when the angles of incidence are close to the critical angle

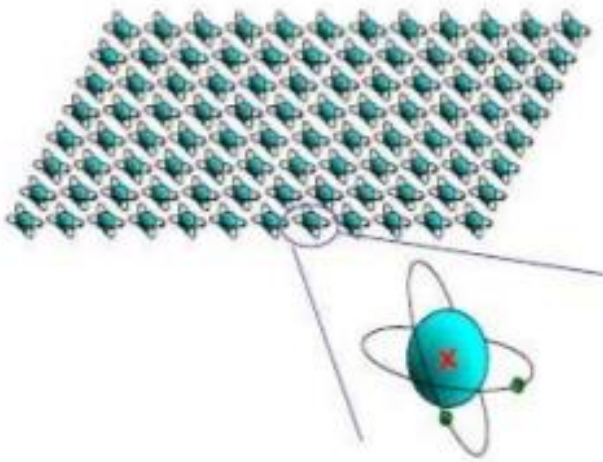


Advanced materials and sensing methods

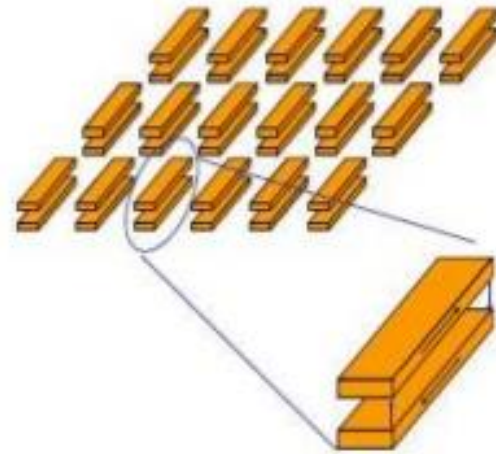
- Metamaterials and Metasurfaces
- Plasmonic nanoparticles
- Plasmonic nanoporous materials
- Nanophotonic cavities
- 2D materials integrated devices
- Quantum plasmonic sensing

Metamaterials and Metasurfaces

- A class of engineered materials with deep subwavelength building blocks that do not exist in nature and exhibit exotic and unusual electromagnetic properties that make them attractive for applications in bioengineering and biosensing
- They allow wavefront engineering, local phase and amplitude control of light along the surface
- Metals, semiconductors, dielectrics



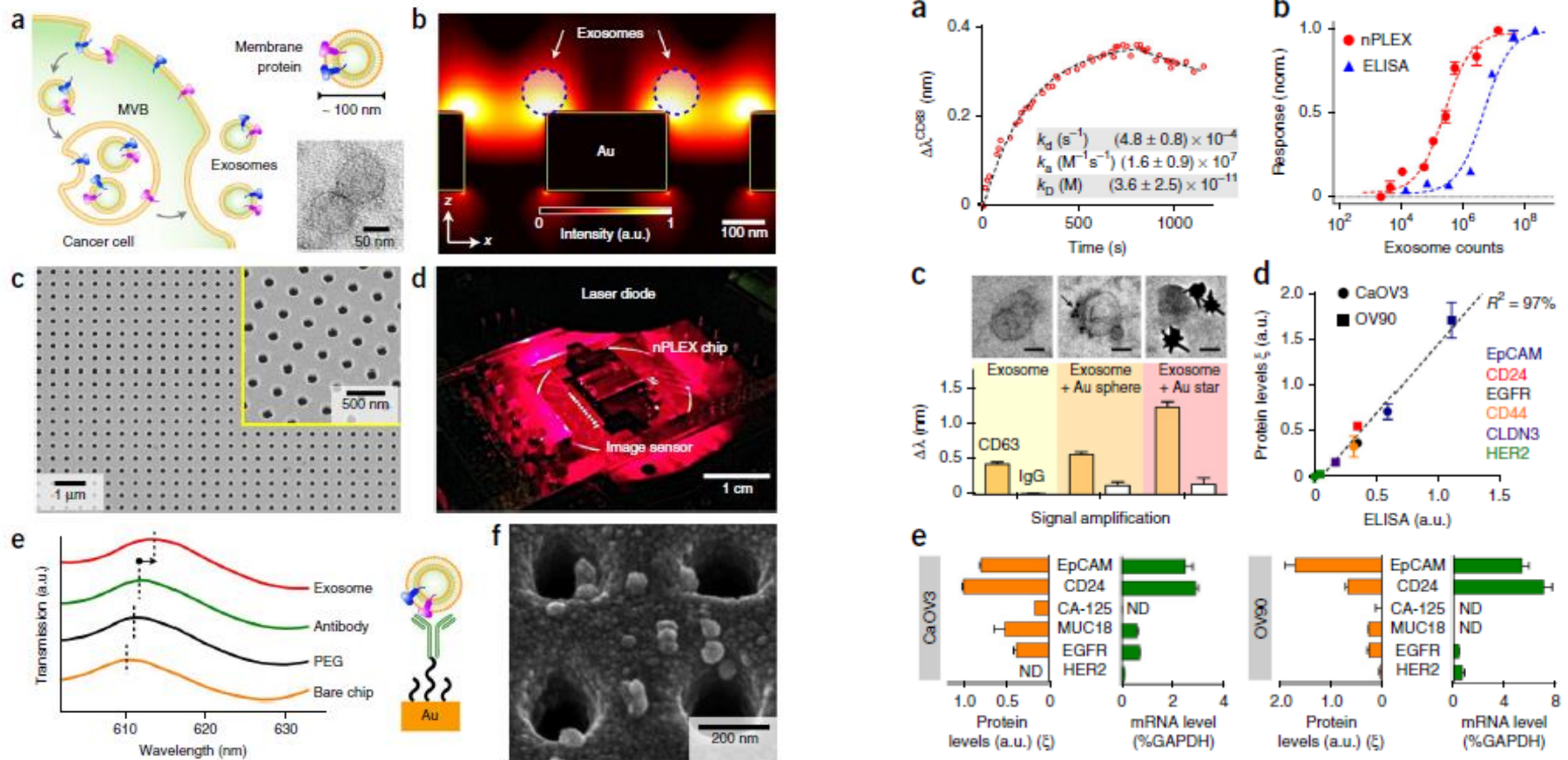
A natural material with its atoms



A metamaterial with artificially structured "atoms"

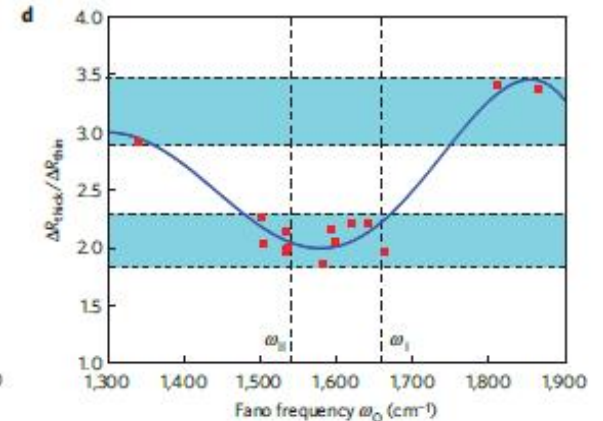
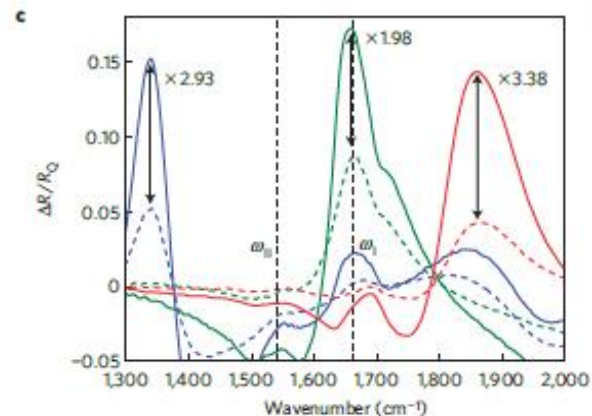
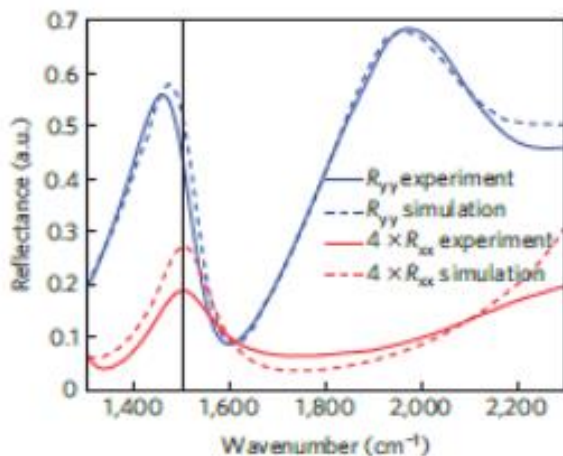
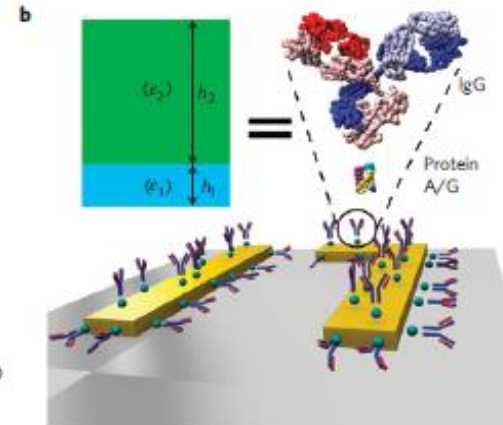
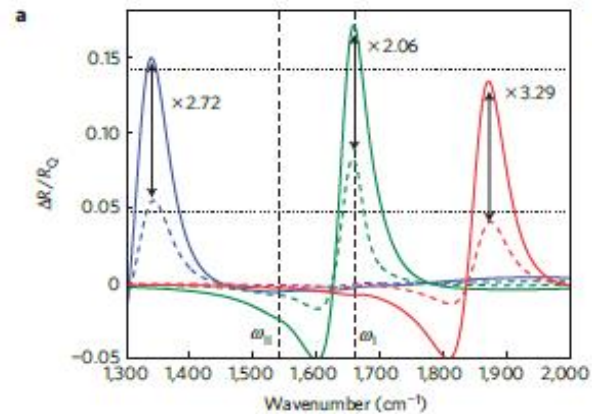
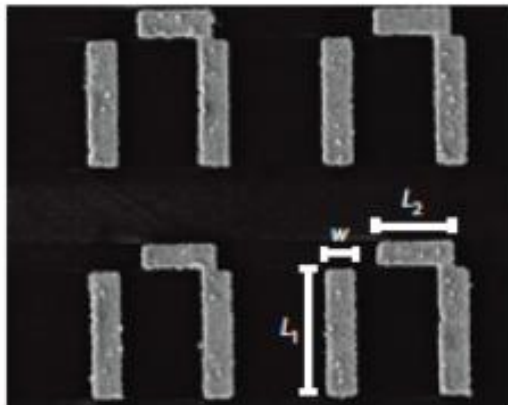
Metamaterial-based biosensors

- Plasmonic nanohole array metamaterials support enhanced light transmission at certain wavelengths due to surface plasmon excitation
- A very small volume of the biological sample can be characterized
- Detected low counts of exosomes:



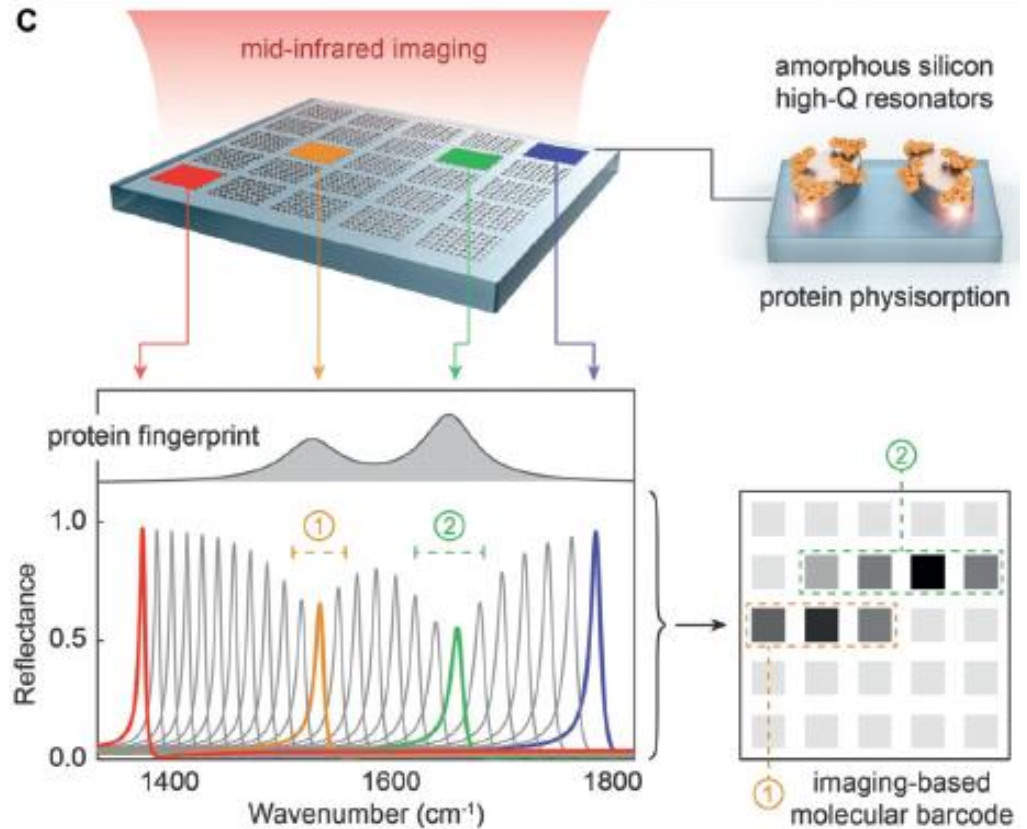
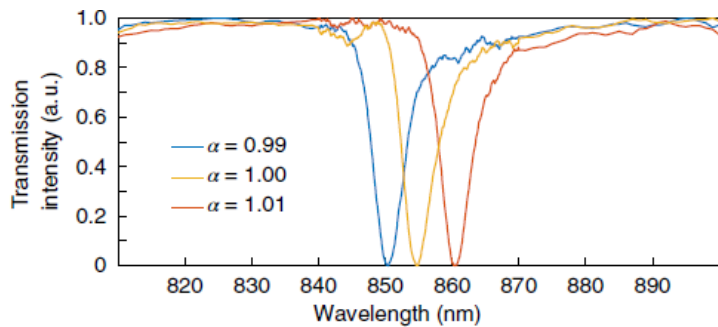
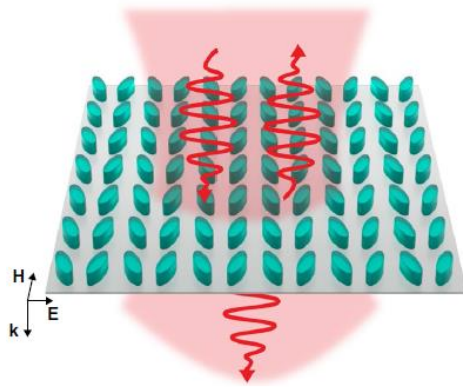
Metamaterial-based biosensors

- Fano-resonant asymmetric metamaterials show sharp plasmonic resonances in the infrared wavelengths
- To identify the molecular monolayers by detecting the vibrational modes of the target biomolecules



Bound states in the continuum

- All-dielectric asymmetric metasurfaces support quasi-BIC (high-Q mode)
- Extremely sharp resonances with strong light confinement

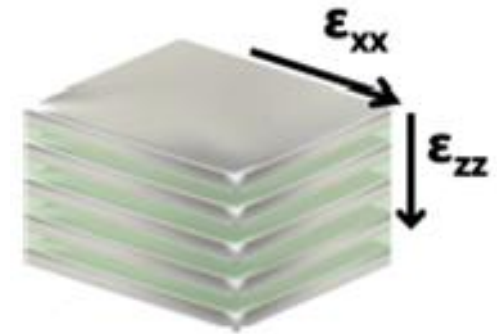


Hyperbolic Metamaterials

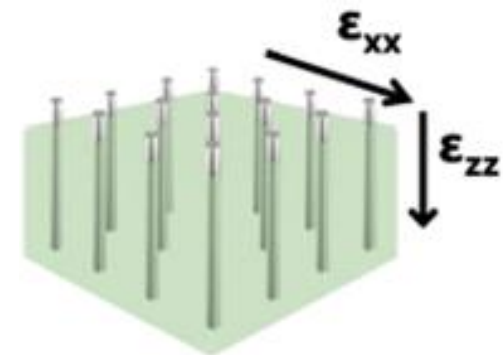
- HMMs are highly anisotropic optical materials whose permittivity tensors have diagonal components with simultaneously different signs
- HMM displays hyperbolic dispersion

UV	VISIBLE	Near-IR	Mid-IR and THz
Au, Al, Ag, PCMs	Au, Ag, PCMs, TiN	TiN, ZrN, AZO, GZO, ITO	InGaAs, AlInAs, SiC, Graphene, hBN, Topological insulators (Bi ₂ Te ₃ , Bi ₂ Se ₃), Superconductors (YBCO)
Plasmonic Materials		Alternate Plasmonic Materials	III-V Semiconductors Phonon Polaritonic Materials 2D Materials

Metal-dielectric multilayers

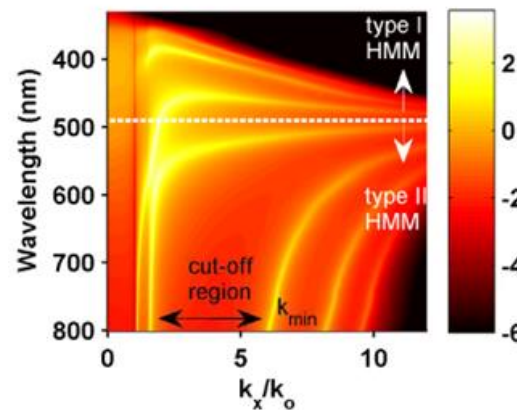
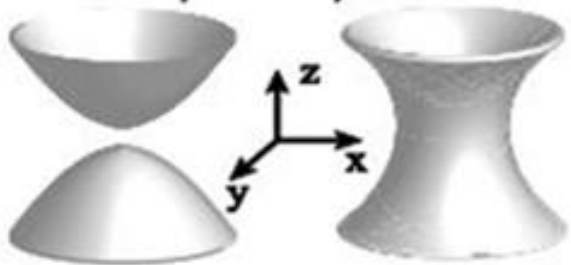


Metallic rods in dielectric host



3D HMM

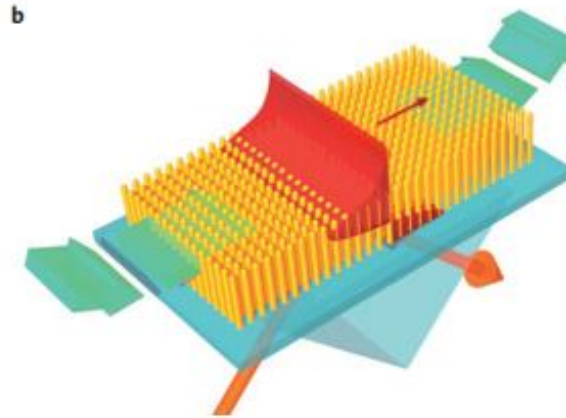
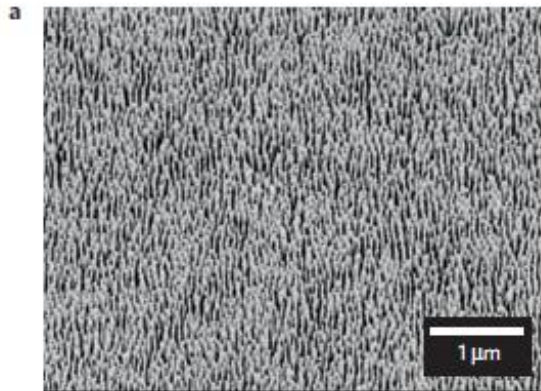
Isofrequency surface



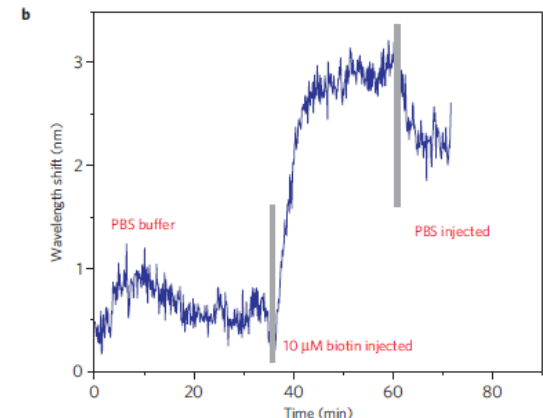
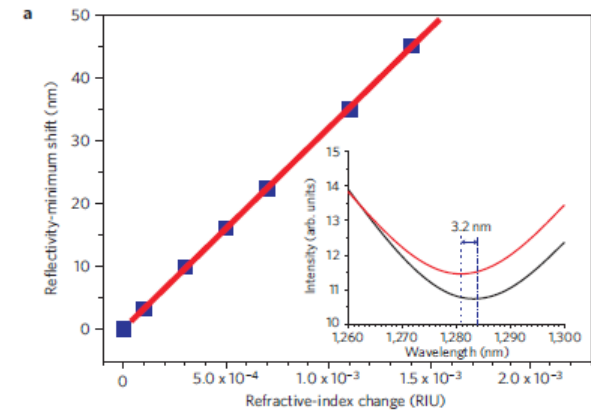
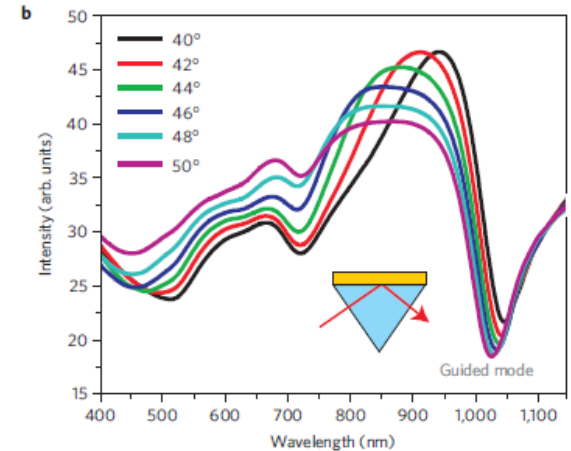
Biosensing with Type I HMM

- Bulk RI sensitivity= 30,000 nm/RIU
- FOM=330
- Streptavidin-biotin model
- Detected 10 μM biotin (MW=244Da)

$$FOM = \frac{\Delta\lambda}{\Delta n} \frac{1}{\Delta\phi}$$

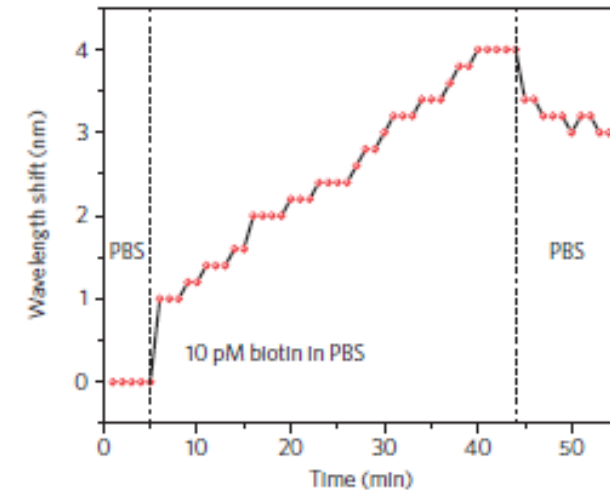
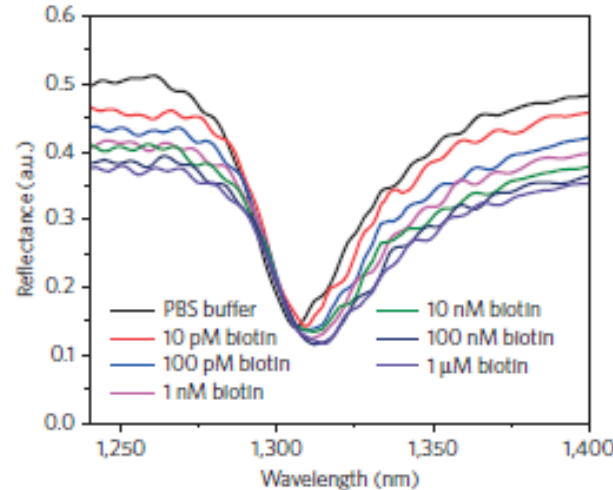
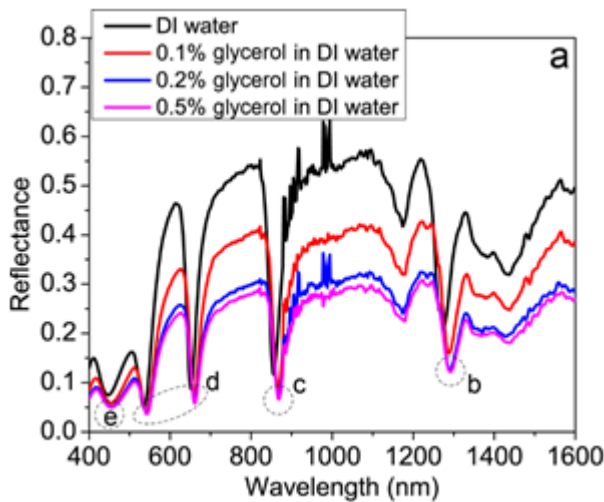
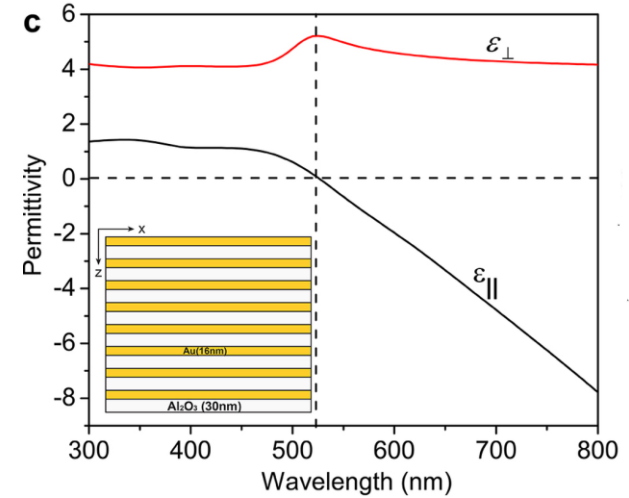
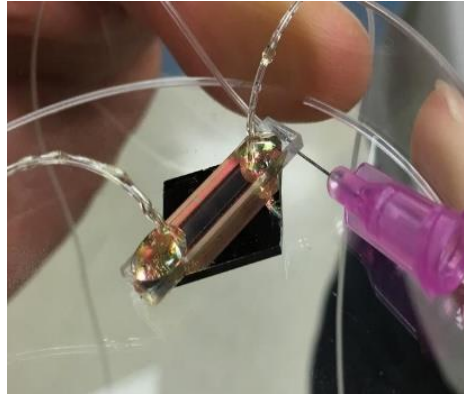
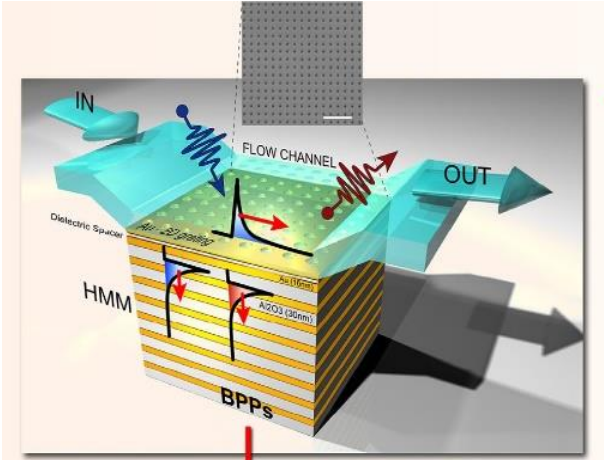


Nature Materials 8, 867 (2009)



Biosensing with Type II HMM

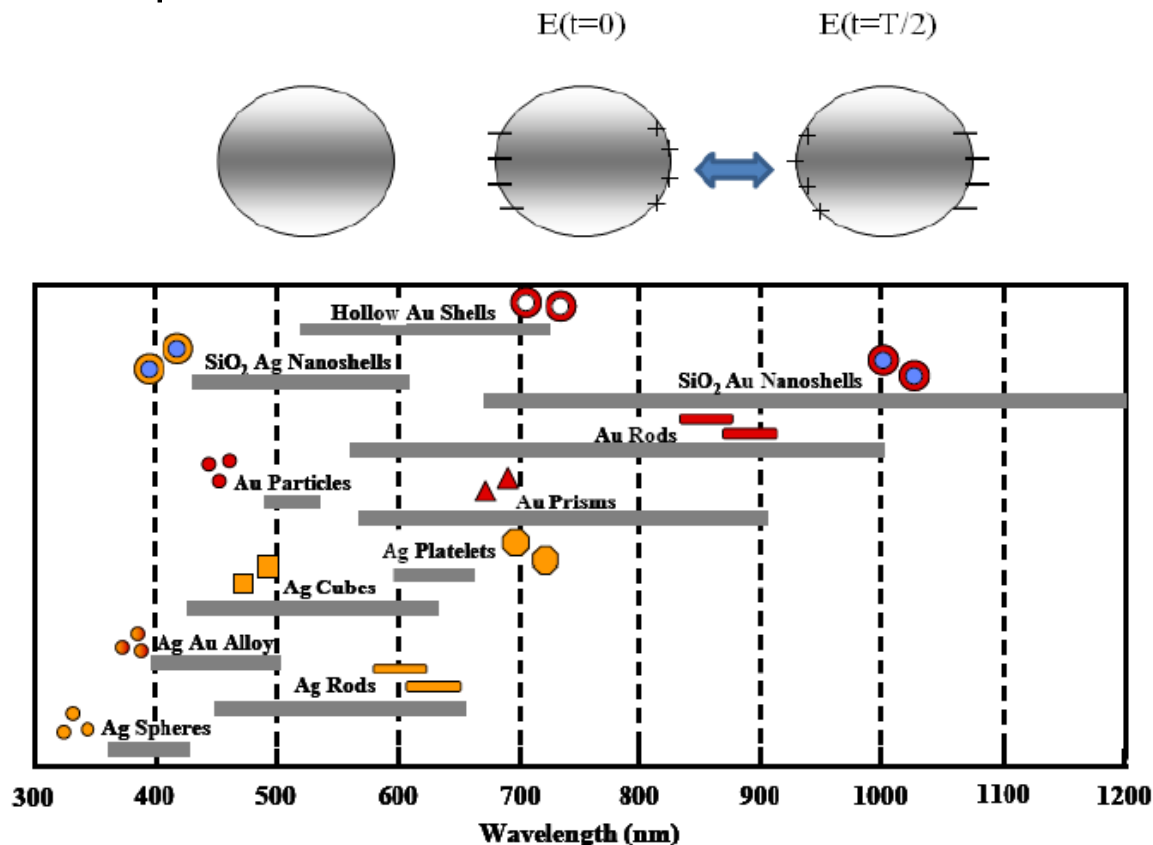
- Extreme sensitivity modes
- Maximum bulk RI sensitivity of **30,000 nm/RIU**
- Record FOM of **590**



Nature Materials 15, 621 (2016)

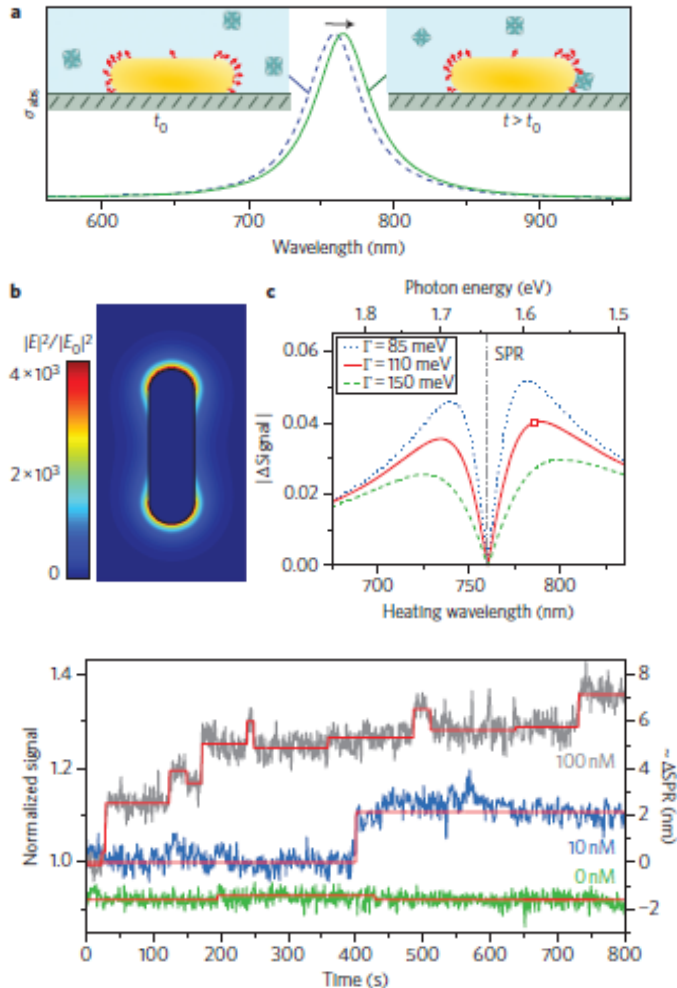
Plasmonic nanoparticles

- Plasmonic nanoparticles support localized surface plasmon (LSP) resonances, which are the localized electron oscillations on metal nanoparticles
- LSP sensors geometrically confine electromagnetic energy absorbed from large optical cross sections to significantly enhance local fields within 5–15 nm of the nanoparticle surface.

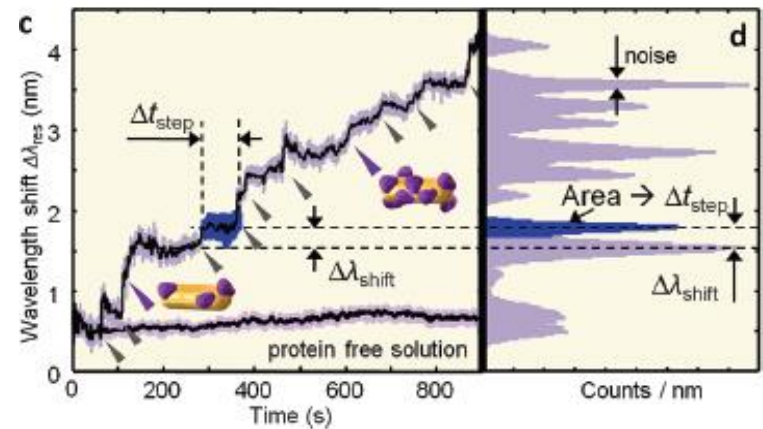
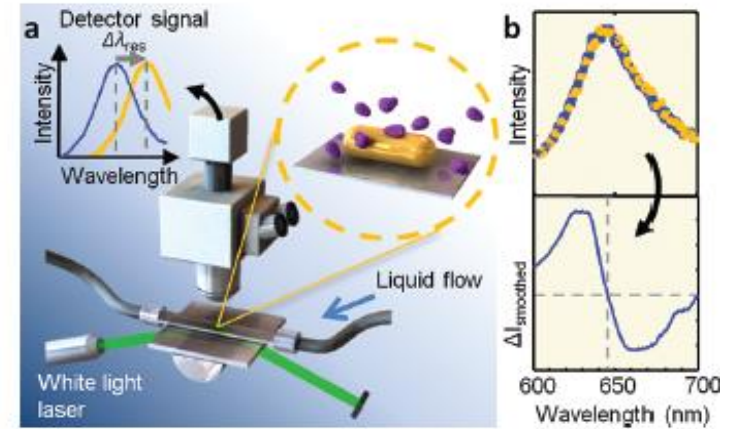


Plasmonic nanoparticle-based biosensors

- Single molecule binding events can be detected by measuring the photothermal signal from the plasmonic nanoparticle



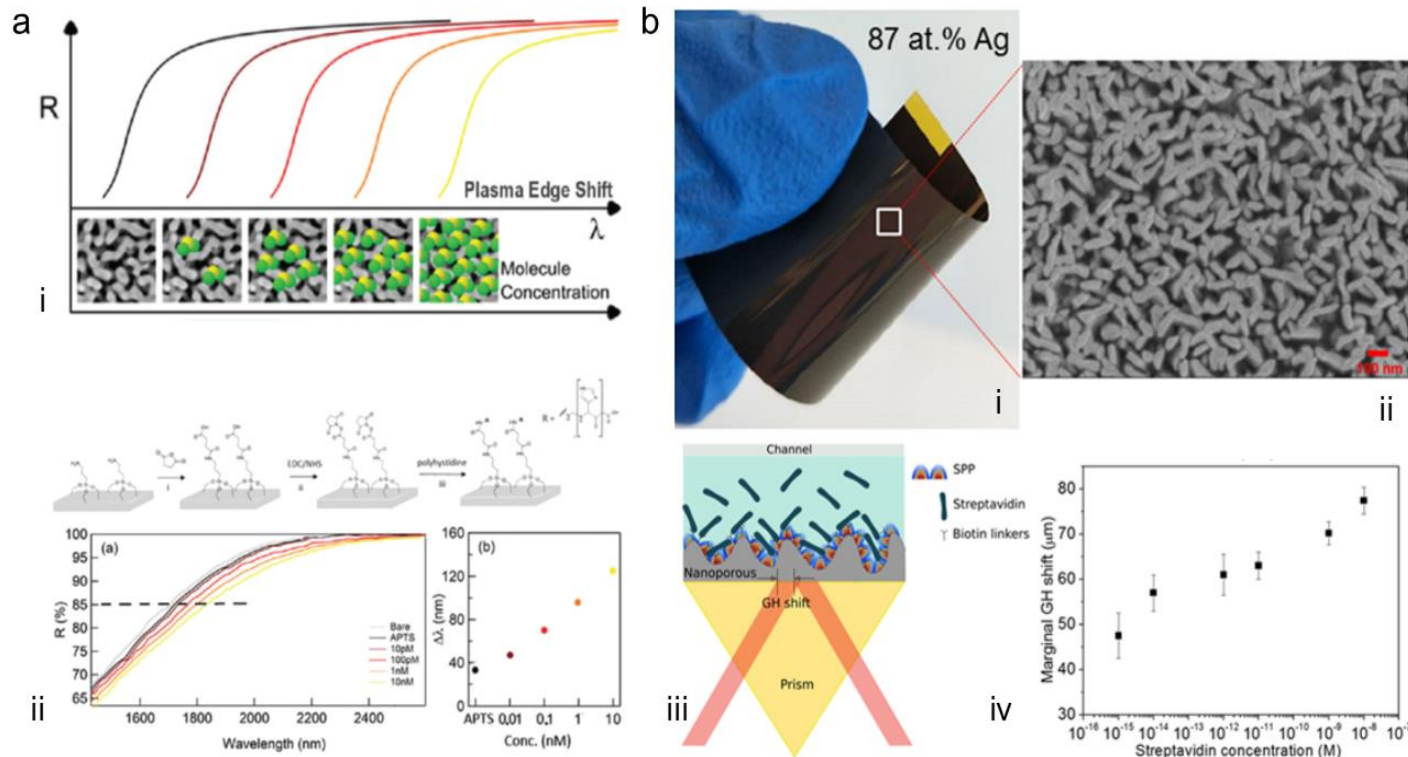
Nature Materials 7, 379 (2012)



Nano Lett. 12, 1092 (2012)

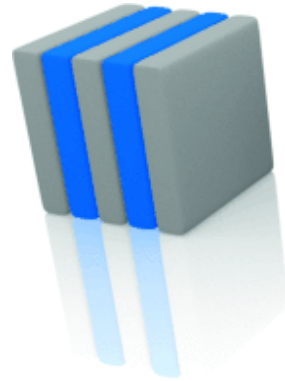
Plasmonic nanoporous-based biosensors

- Metallic-nanoporous materials show a plasmonic response
- High surface to volume ratio, which increases the number of biomolecules attached to the surface and increases the overlap between the local field and the biomolecules
- The fractal nature of the nanoporous geometry provides a high biomolecule diffusion rate and concomitantly lower sensing settling time

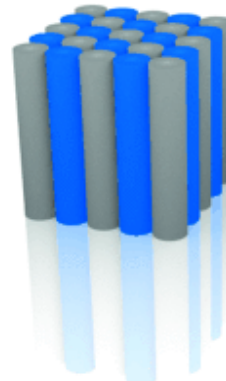


Nanophotonic cavities

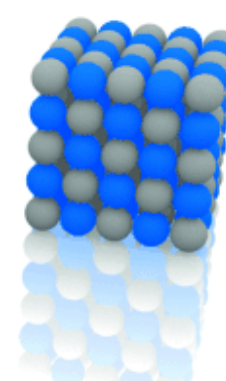
Photonic crystals



periodic in one dimension



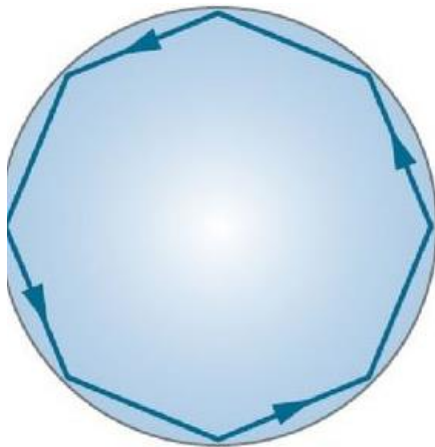
periodic in two dimensions



periodic in three dimensions

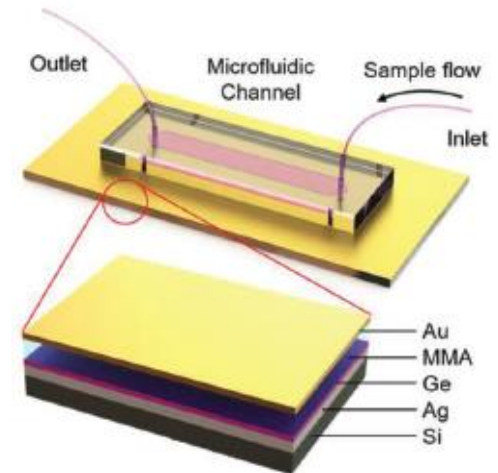
Angew. Chem. Int. Ed 53, 3318 (2014)

Microcavities



Adv. Opt. Photonics 7, 168 (2015)

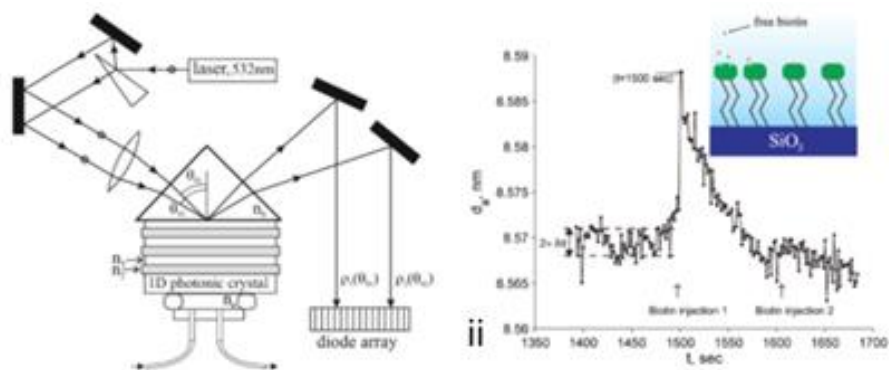
Fabry-Perot cavities



Adv. Opt. Mater. 1801313 (2019)

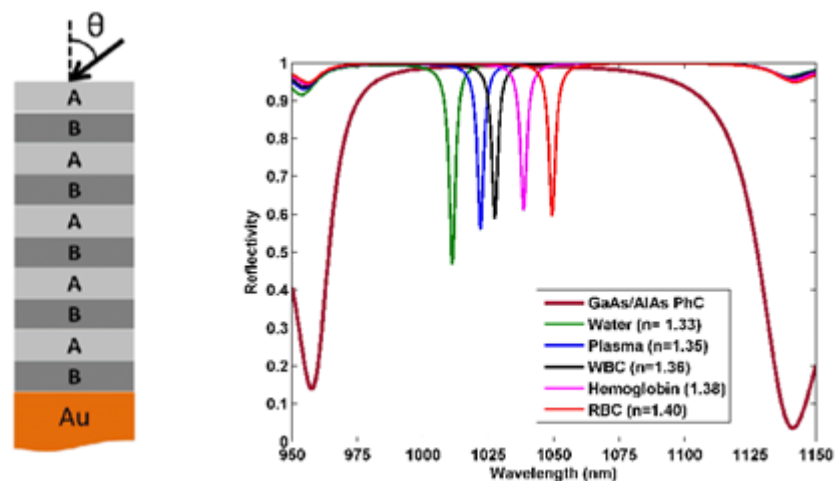
Photonic crystal-based biosensors

- By exciting the surface electromagnetic wave of the 1D PC
- Non-radiative electromagnetic modes that appear on the surface of semi-infinite 1D PC
- Single molecule level sensitivity is possible by combining 2D PC with plasmonic nanostructures



Anal. Chem. 79, 4729 (2007)

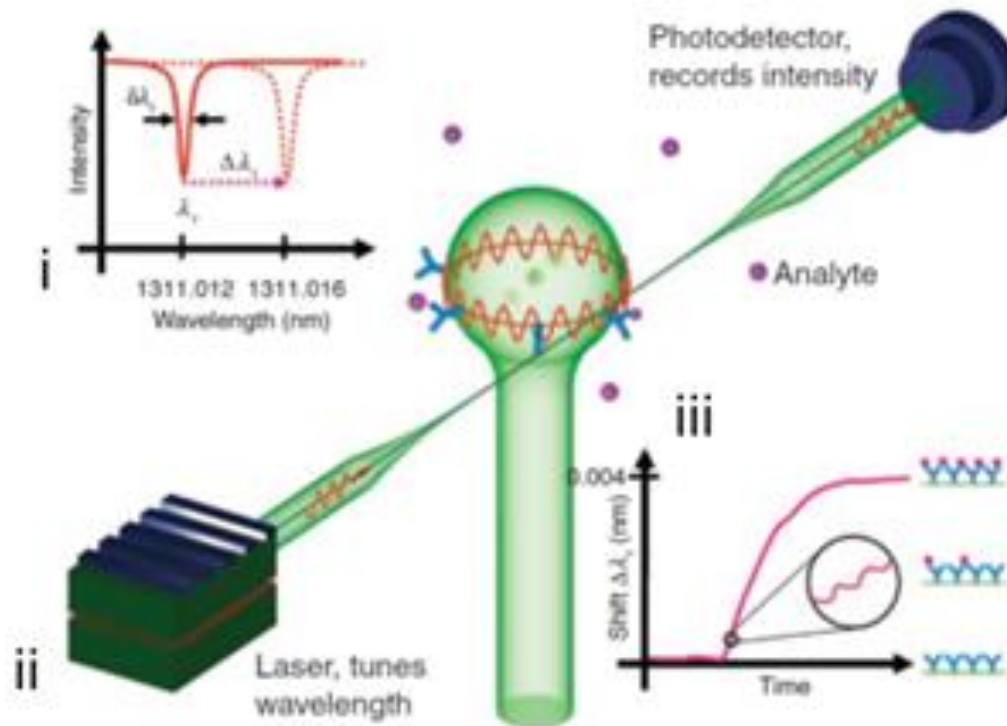
- By exciting Tamm plasmon polaritons (TPP)
- A TPP is an optical state that exists at the interface between a metallic layer and 1D PC
- Its dispersion lies within the light cone, thus it can be optically excited



J. Phys. Condensed Matter. 30 (2018)

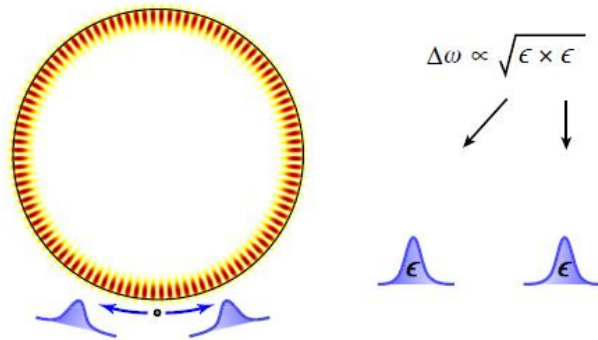
Whispering gallery mode-based biosensors

- Microcavities support whispering gallery mode (WGM) resonances
- Each photon guided by total internal reflection in a silica sphere with radius of $\sim 100 \mu\text{m}$ is recirculated many times
- WGM local field intensity can be further amplified by exciting the SPR in immobilized gold or silver nanoparticles

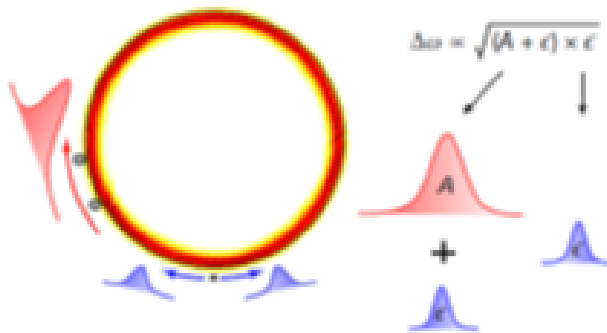


Exceptional point enhanced sensing

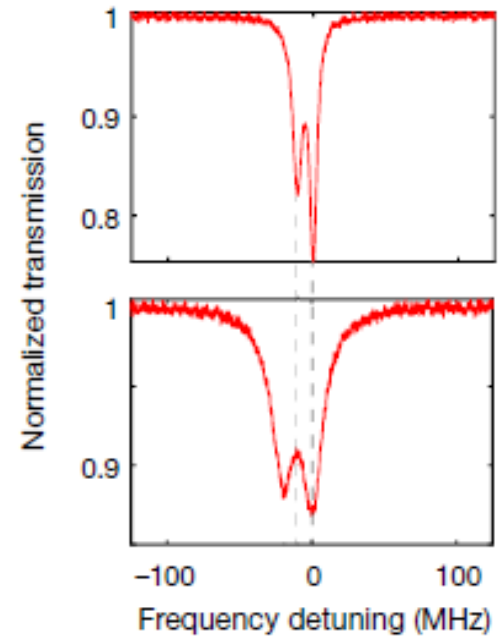
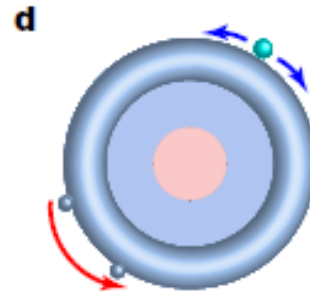
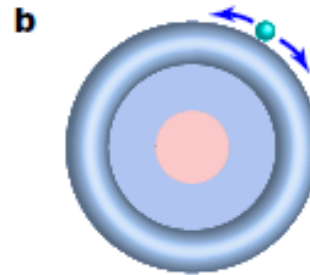
- Non- Hermitian singularities
- Eigenvalue splitting proportional to the square root of the perturbation strength



DP sensors



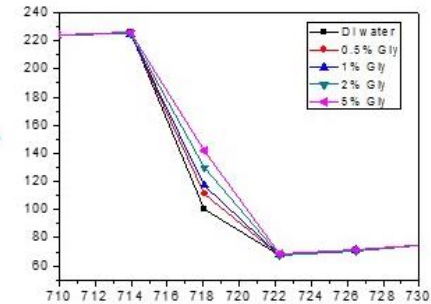
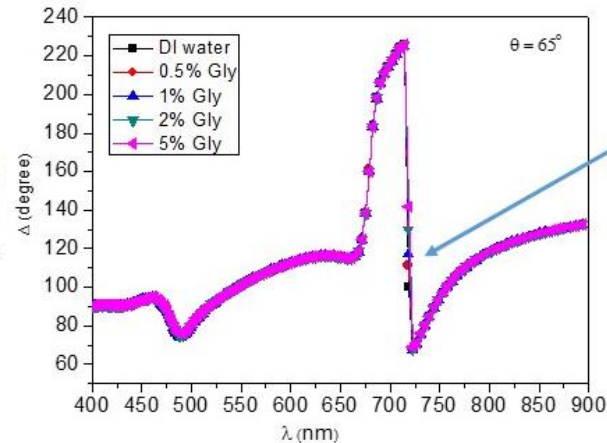
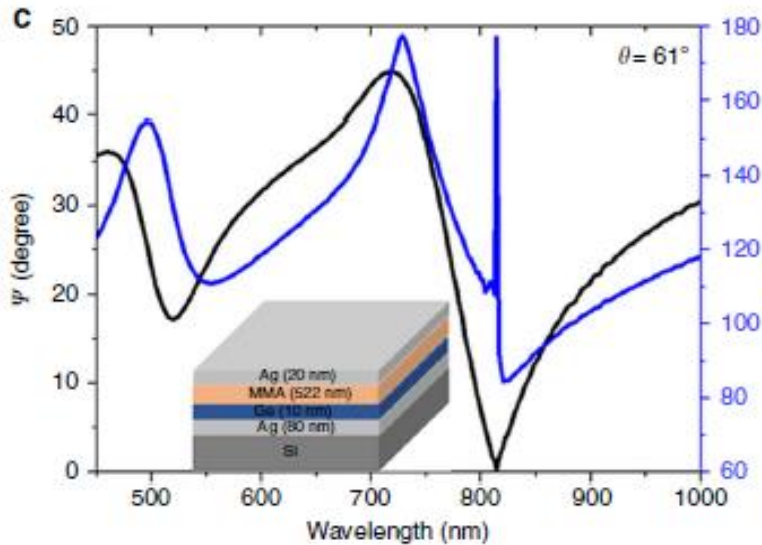
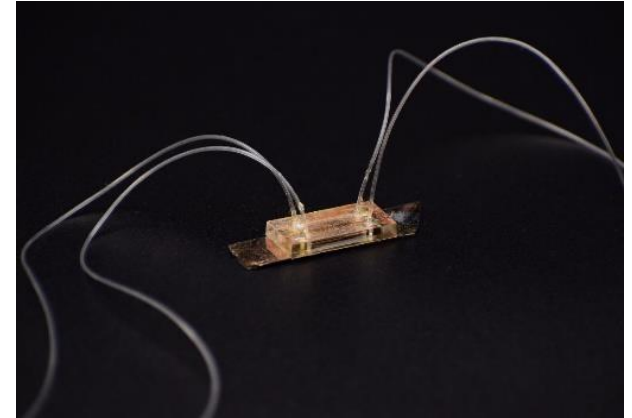
EP sensors



Nature 548, 192 (2017)

Singular phase thin film cavities for biosensing

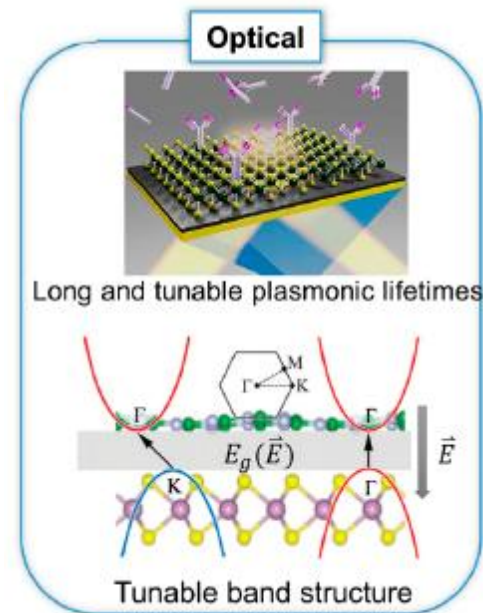
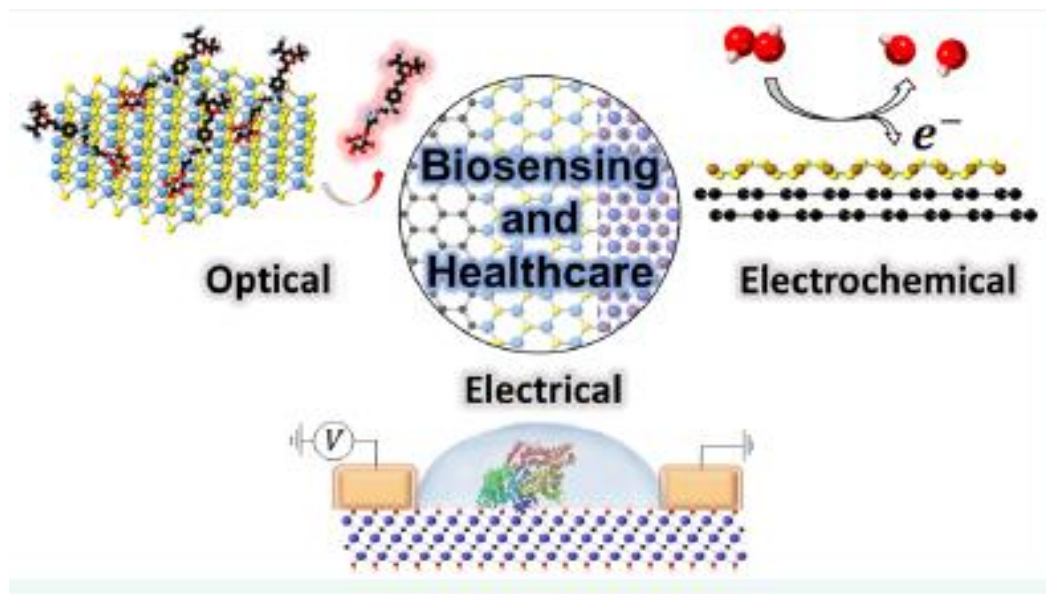
- Four-layered nanophotonic cavity
- Critical light coupling
- Singular phase at the point-of-darkness ($\psi \sim 0$)
- Phase sensitive detection
- Scalable sensor



Nature Communications 9, 369 (2018)

Adv. Opt. Mater. 7, 1801313 (2019)

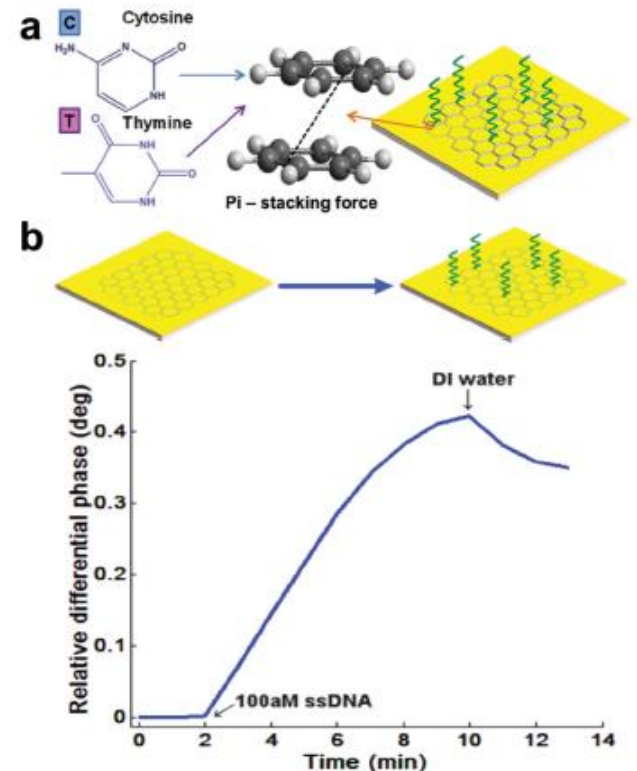
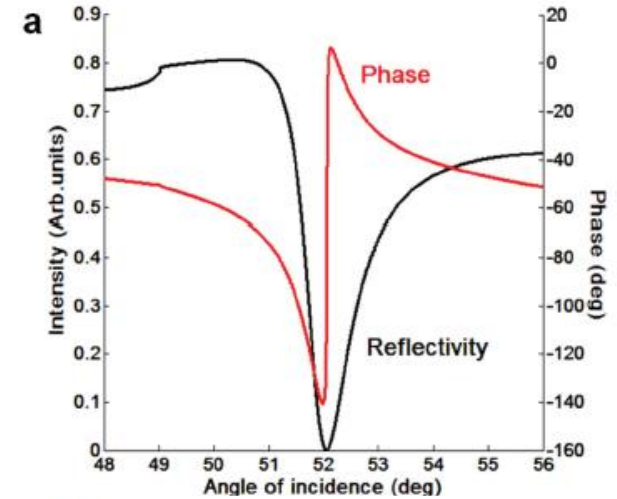
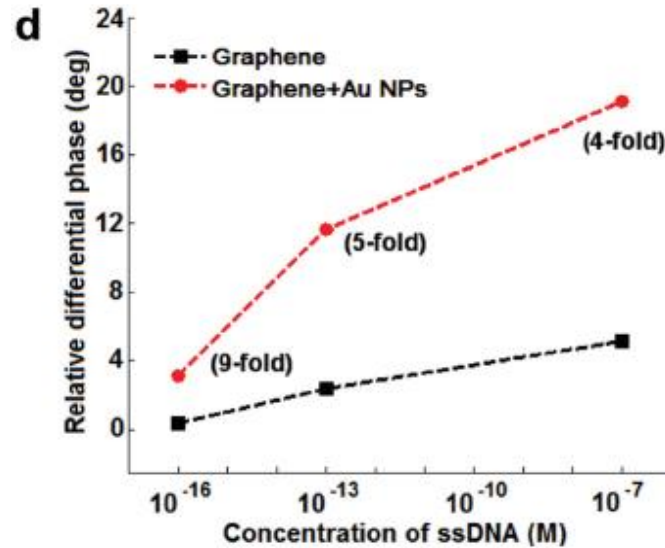
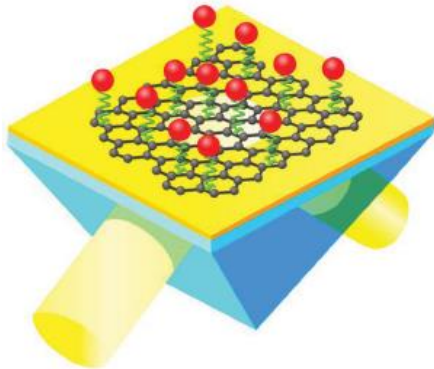
2D materials for biosensing



Nanomaterial	Bandgap	Bandgap Tunability	Carrier Mobility	Sensing Mechanism
Graphene	0 eV	+ 0.25 eV	$10^5 \text{ cm}^2/\text{Vs}$	O, E, Ec
Boron Nitride	5.9 eV	- 4 eV	N/A	O
Black Phosphorous	1.59 eV	0.10 eV	$10^3 \text{ cm}^2/\text{Vs}$	O, E
Transition Metal Dichalcogenides	0 - 3.4 eV	$\pm 1 \text{ eV}$	$1-10^2 \text{ cm}^2/\text{Vs}$	O, E, Ec

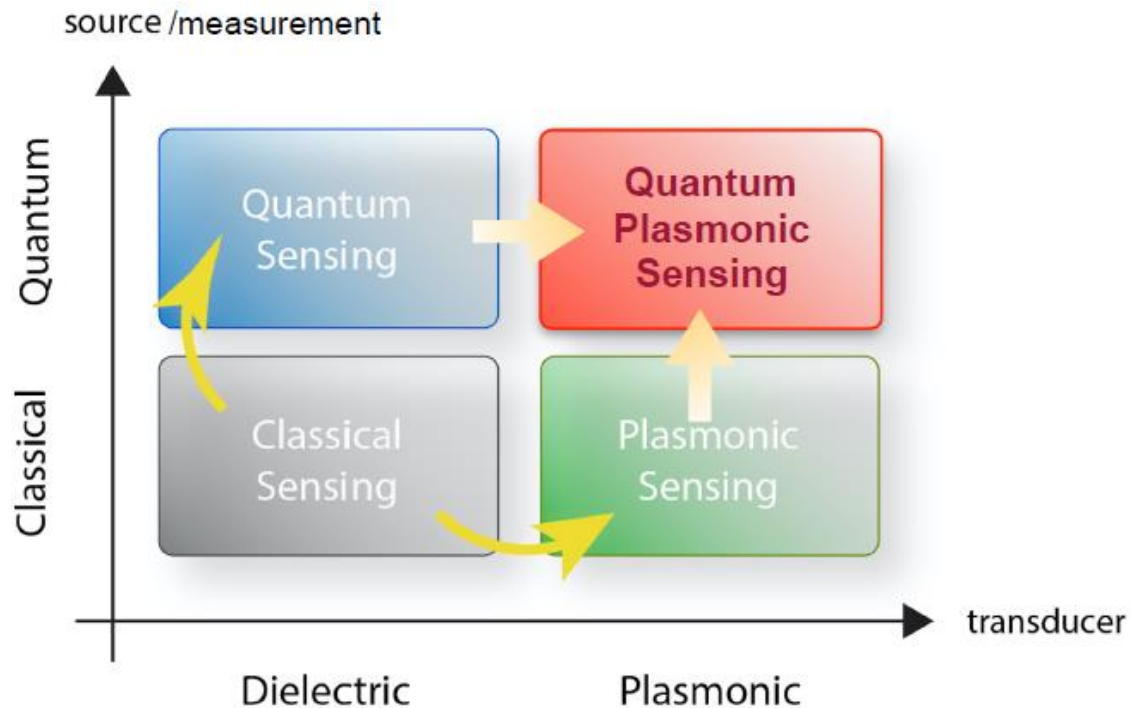
Graphene for optical biosensing

- Extreme singularities in phase of reflected light
- Signal enhancement using Au nanoparticle tags
- A unique platform to selectively detect aromatic ring structure biomolecules, which rely on pi-stacking forces



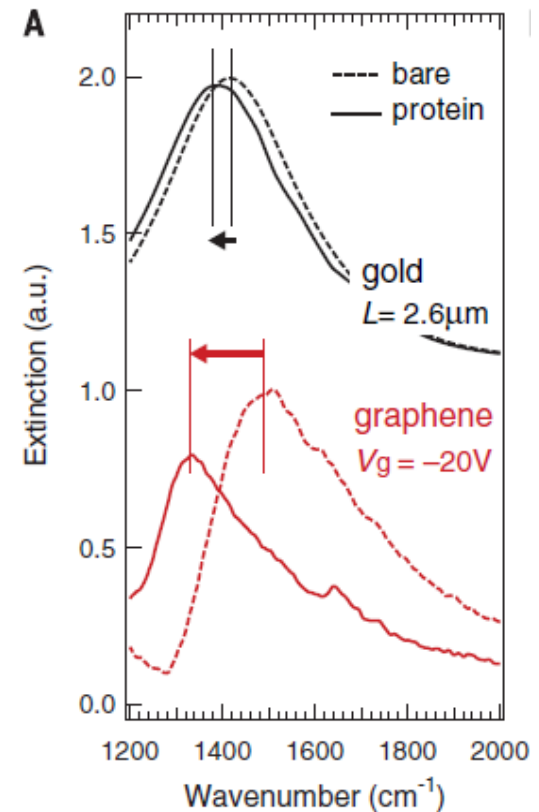
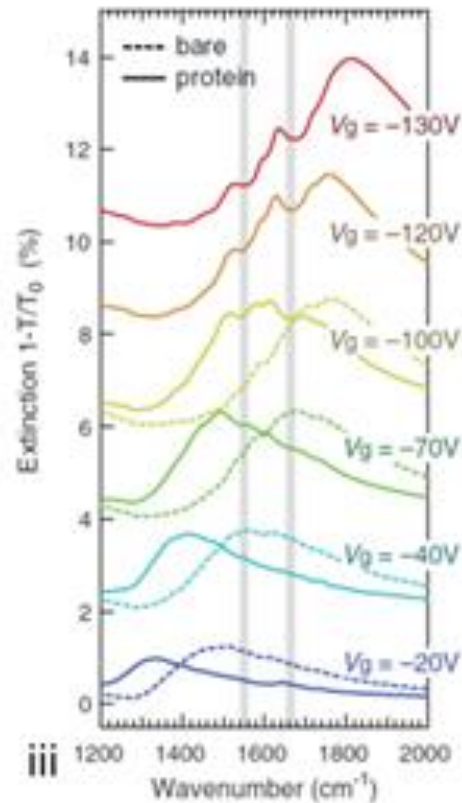
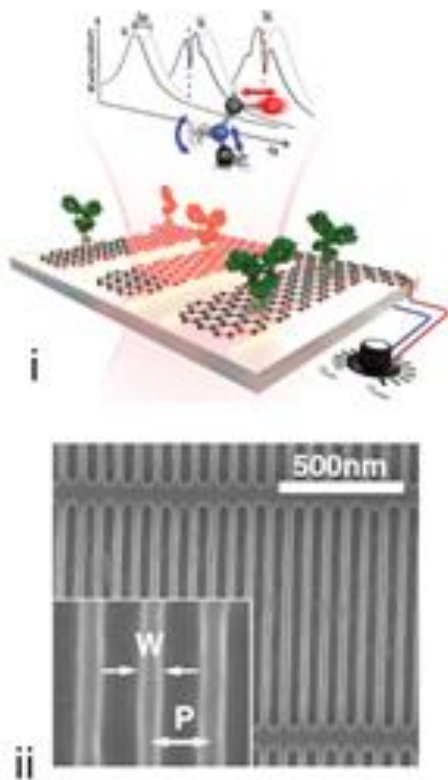
Quantum plasmonic sensors

- Beats short-noise limit
- Noise reduction by quantum sensing
- Enhanced sensitivity by plasmonic sensing



Tunable sensing

- A tunable sensor can be developed by incorporating functional materials in the optical system.
- It can differentiate between a multitude of fundamental biological building blocks including lipids, proteins, sugars, and nucleic acids



Chalcogenide phase change materials

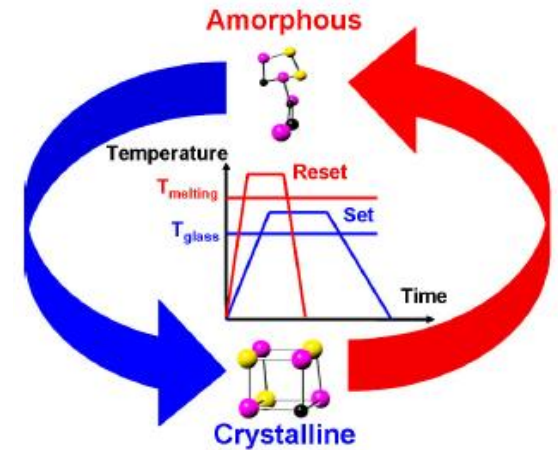
- Non-volatile switching
- A large optical contrast between two phases
- High speed and low power phase switching
- Reliable and repeatable switching over billions of switching cycles
- Long-term thermal stability of the amorphous phase

Forward switching: Amp to Cry

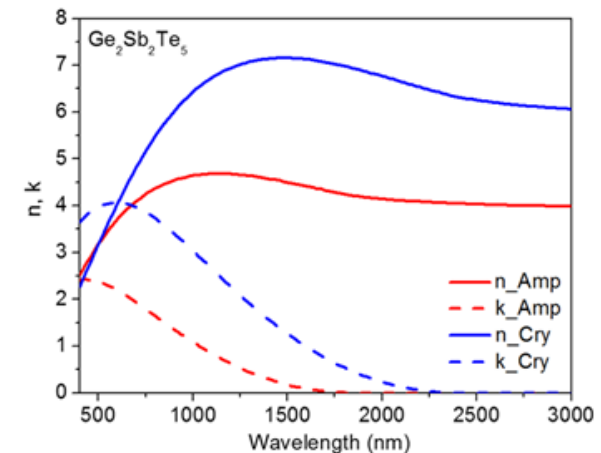
- It is an annealing process: heat the PCM above the glass-transition point (T_g), but below its melting point (T_m).
- Thermally, laser and electric current induced heating

Reverse switching : Cry to Amp

- The PCM should be heated at a temperature above T_m
- A melt-quenching process
- Only possible with a shorter, higher energy optical and electrical pulsed excitation

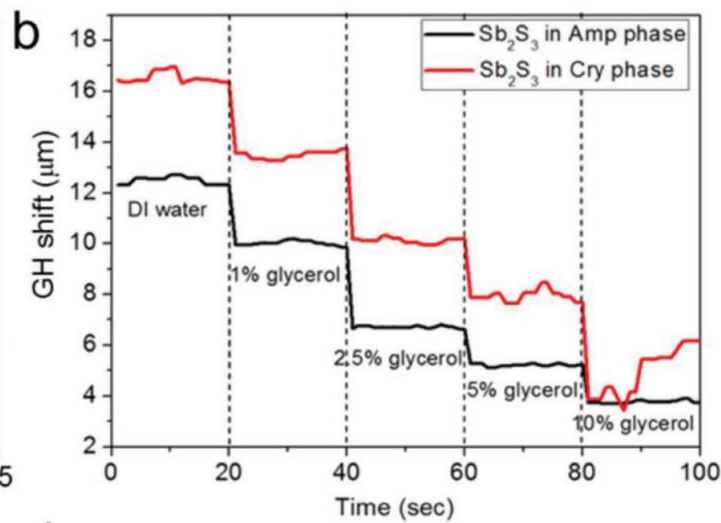
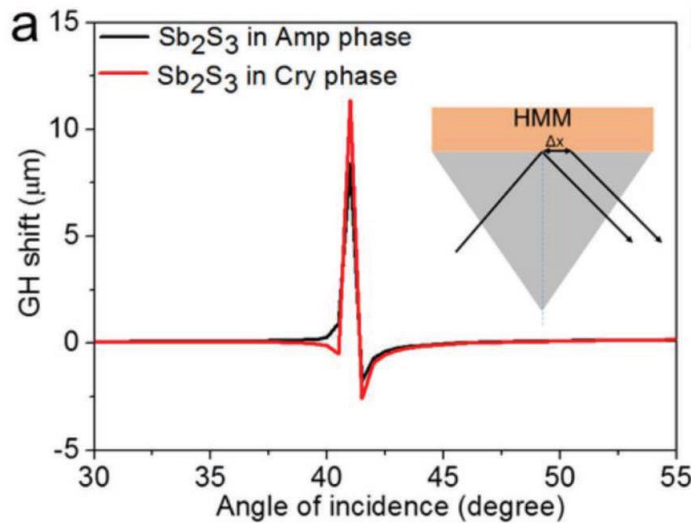
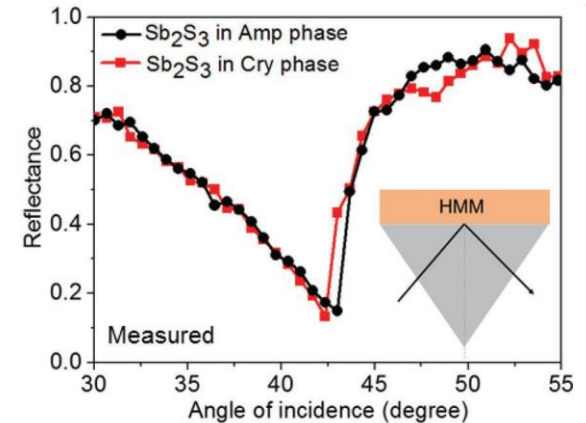
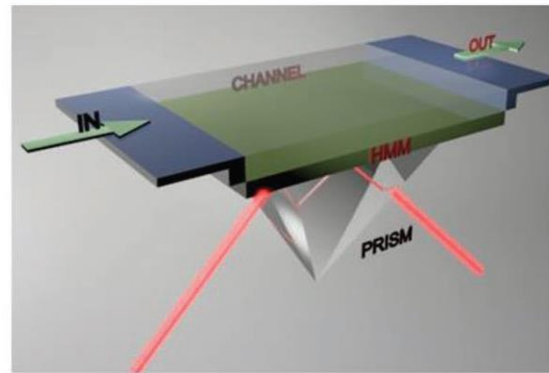
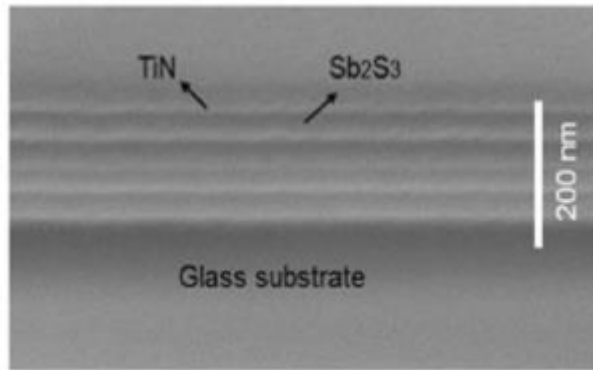


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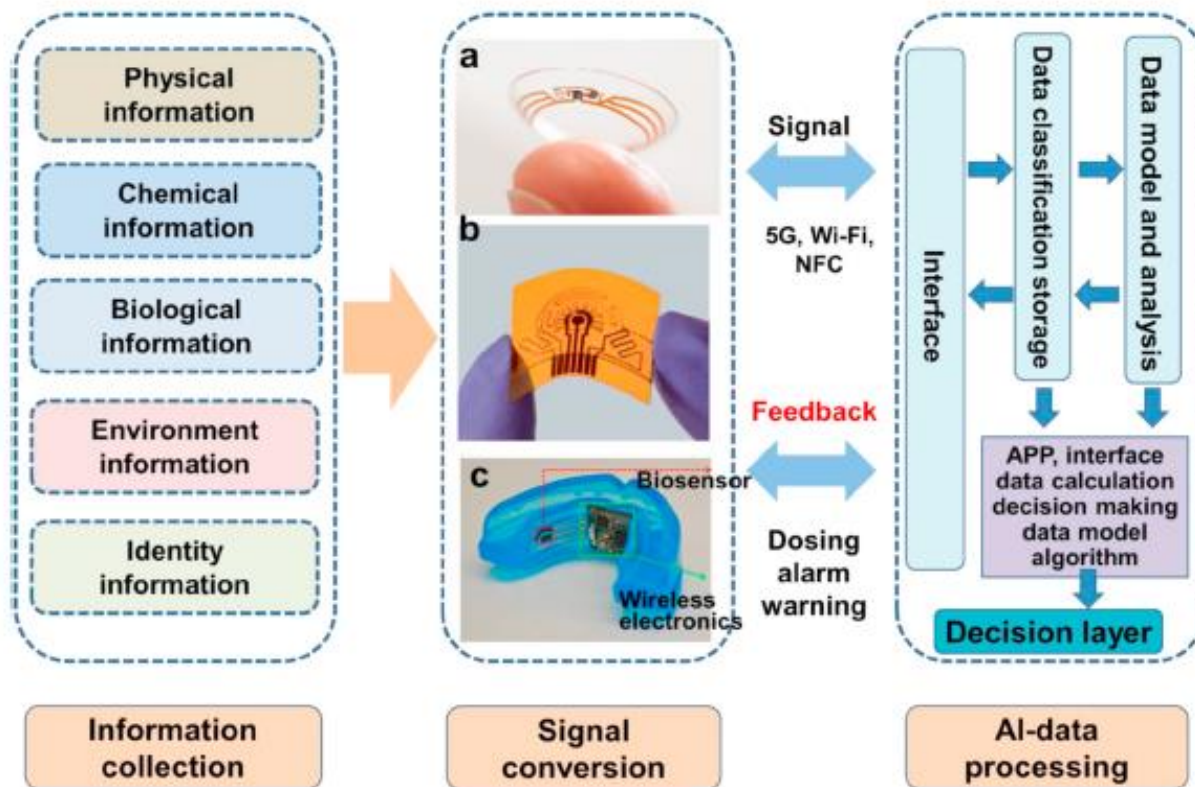
PCM-based tunable sensor

- Low-loss and tunable Sb₂S₃-TiN HMM
- Goos-Hänchen shift based interrogation scheme
- Realized tunable sensitivity by switching the phase of Sb₂S₃



Intelligent biosensing

- Artificial intelligence and deep learning
- Specificity of the detection can be improved
- Identification and kinetic characterization of complex biological entities
- Material innovation, biorecognition element, signal acquisition and transportation, data processing and intelligence decision system



Summary and outlook

- Advanced optical materials and new sensing methods improve the sensing performance of optical nanobiosensors
- The limit of detection of the order of fg/mm² can be achieved
- Miniaturized and scalable sensor devices can be developed
- The diffusion-limited transport issue of nanobiosensors could be solved by using super-hydrophobic grating and chiral grating coupled HMMs
- Interrogation scheme based on Imaging of phase and G-H shift can be used for high-throughput and high-efficiency sensing

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Thank You