CHM 696-11: Week 8

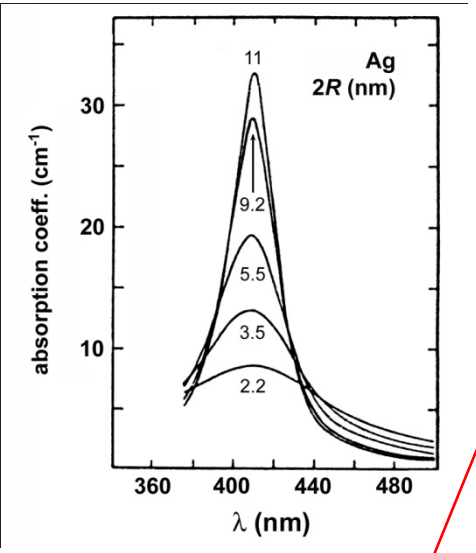
Instructor: Alexander Wei

Optical Properties of Metal Nanoparticles and Nanoparticle Assemblies

Review:

Wei, Q.; Wei, A. In *Supramolecular Chemistry of Organic–Inorganic Hybrid Materials* (Chapter 10), Mañez, R. M.; Rurack, K., Eds.; Wiley and Sons: New York, 2010; pp. 319-349

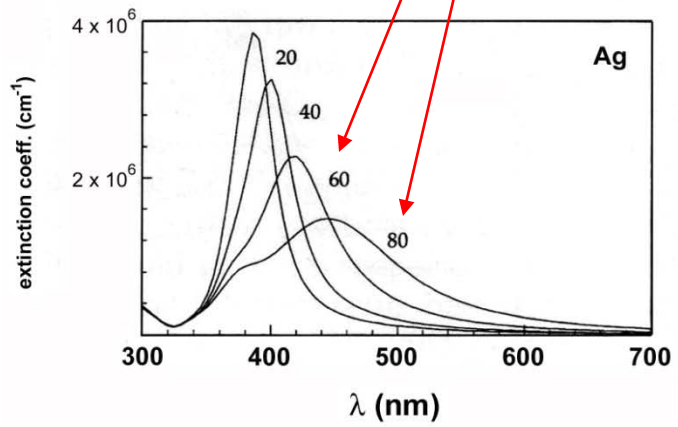
Size effects on localized SPRs

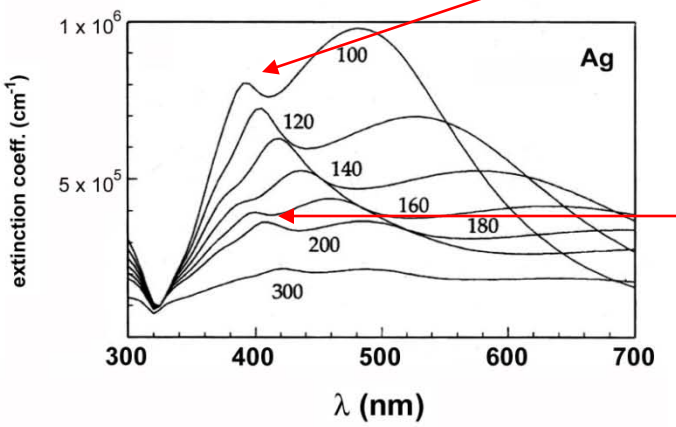


Surface scattering of oscillating electrons: plasmon lineshape (Γ) broadens with 1/R

Phase retardation: redshift and broadening of λ_{SP} for particles greater than L_E, the electron mean free path (40-50 nm)

Higher-order plasmon resonances: increase in probability with larger particle size (also a function of L_E)





Dipolar mode

Quadrupolar mode

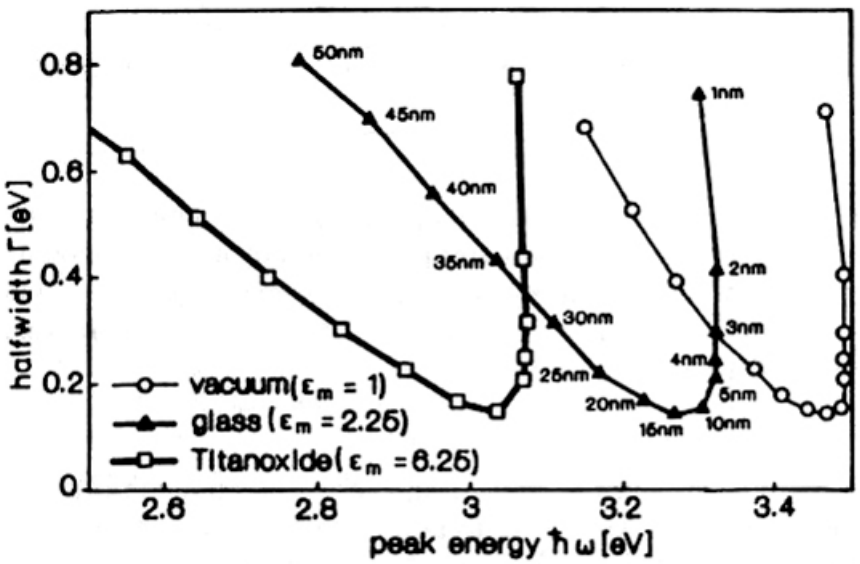
Octupolar mode

Calculated plasmon response from spherical Ag nanoparticles in H_2O:
Yguerabide, *Anal. Biochem*. **1998**, *262*, 137.

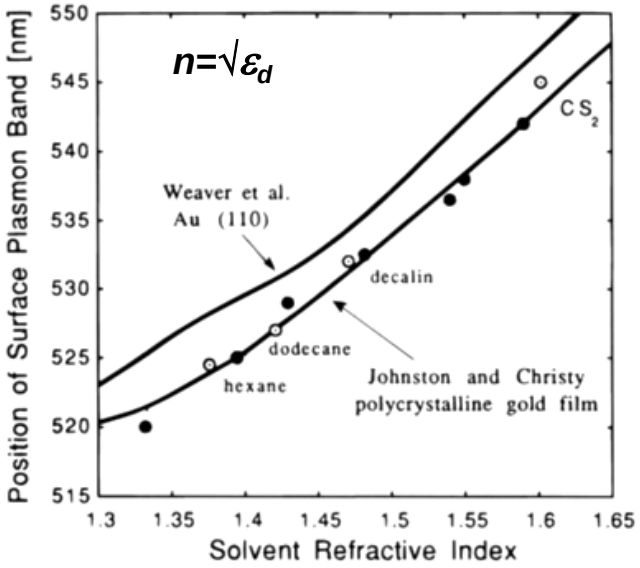
Dielectric effects: influence on LSPR wavelength

LSPRs and FWHM linewidths of Ag nanoparticles in different environments (calculated)

Kriebig and Vollmer,
*Optical Properties of Metal Clusters, c.*1995.



413 nm 387 nm 364 nm



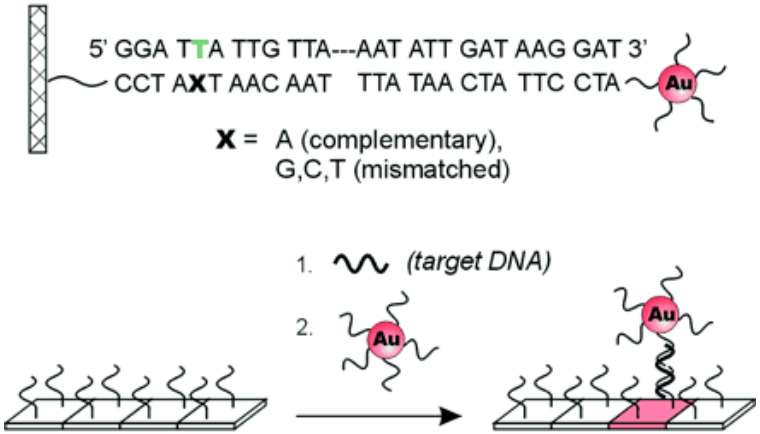
Solvatochromatism in polymer-stabilized 16-nm Au nanoparticles

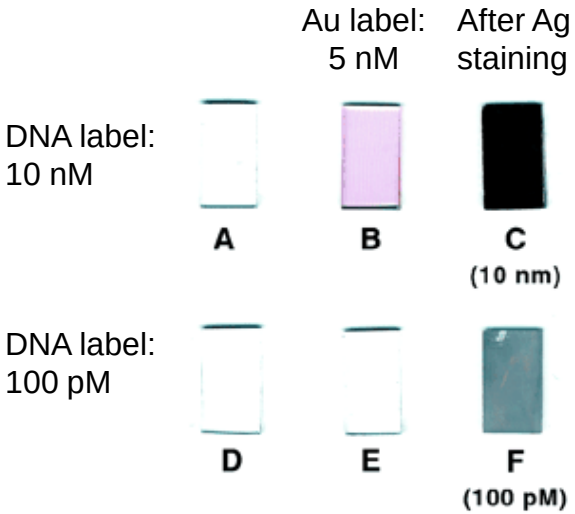
Underwood and Mulvaney,
Langmuir **1994**, *10,* 3427.

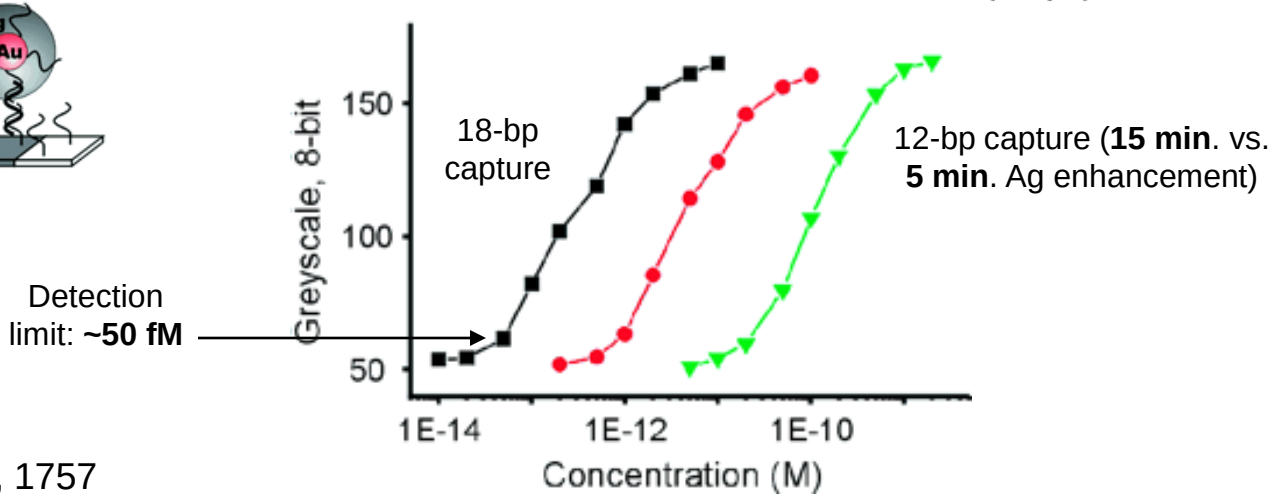
Metal nanoparticles as optical labels

A. Size-dependent optical extinction

Ag-enhanced detection of Au nanoparticle (NP) label:







Taton et al, *Science* **2000**, *289*, 1757

Metal nanoparticles as optical labels

B. Resonant light scattering

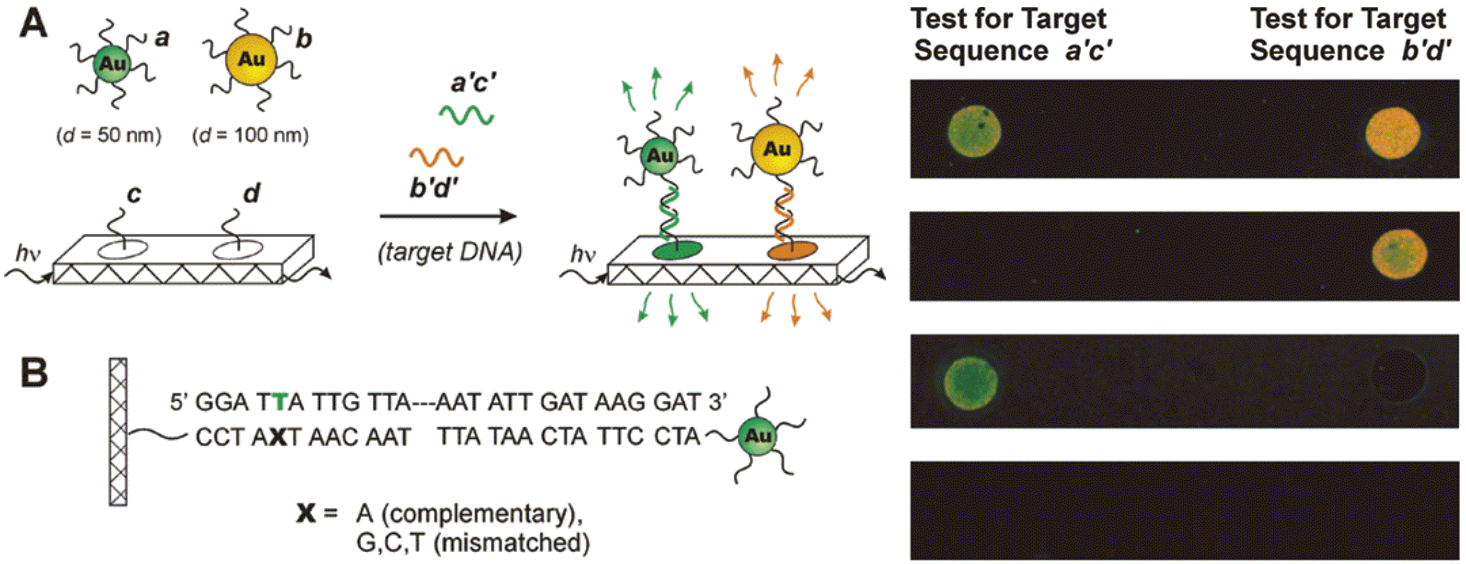
Size-dependent color response (Au NPs):

<50 nm: λ_{LSPR}= 520-530 nm (green)

80 nm: λ_{LSPR}= 560-570 nm (yellow)

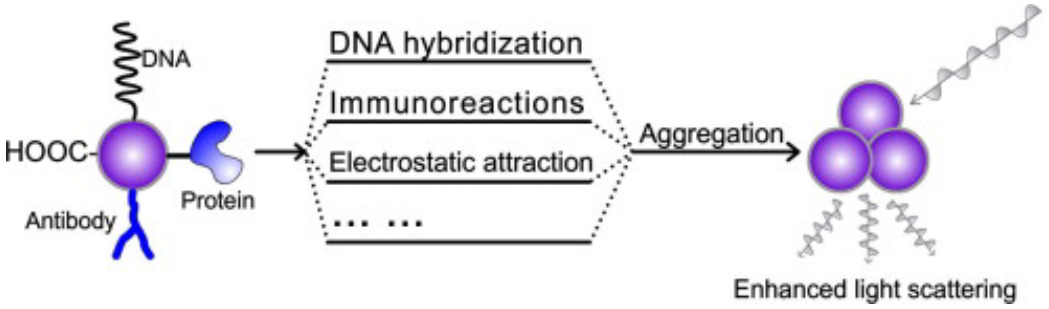
100+ nm: λ_{LSPR}= 580+ nm (orange)

Detection of DNA hybridization by darkfield (scattering) microscopy:



Taton, Lu, and Mirkin, *J. Am. Chem. Soc.* **2001**, *123*, 5164.

Aggregation-induced amplification of light scattering

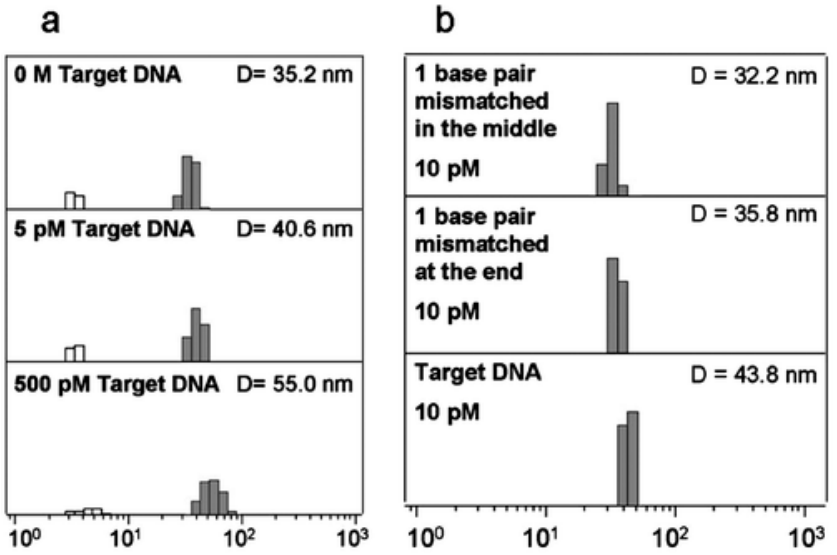


Ling et al, *Trends Anal. Chem.* **2009**, *28*, 447.

DNA-induced aggregation of 30-nm Au NPs monitored by dynamic light scattering (DLS)

low picomolar (pM) resolution;
sensitive to base-pair mismatches

Dai et al, *J. Am. Chem. Soc.* **2008**, *130*, 8138.

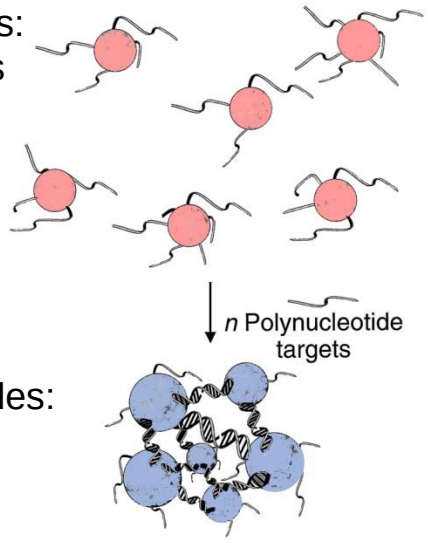


Metal nanoparticles as optical labels

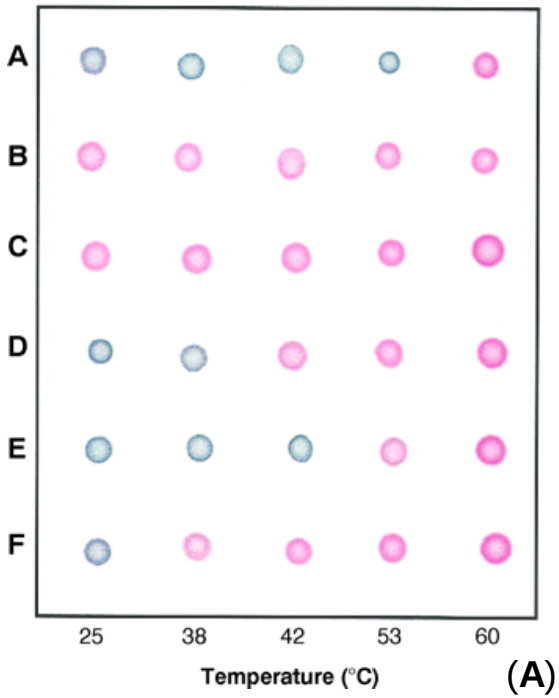
C. Aggregation-induced shifts in plasmon resonance (colorimetric assay)

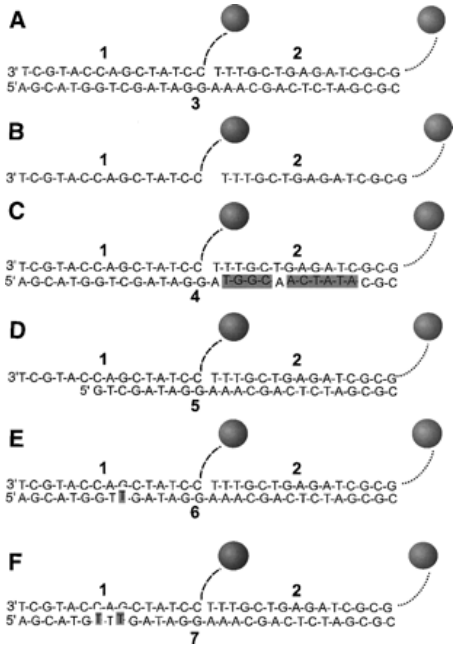
Ex. 1. DNA-induced aggregation of Au nanoparticles

Individual particles:
uncoupled LSPRs



aggregated particles:
collective SPR





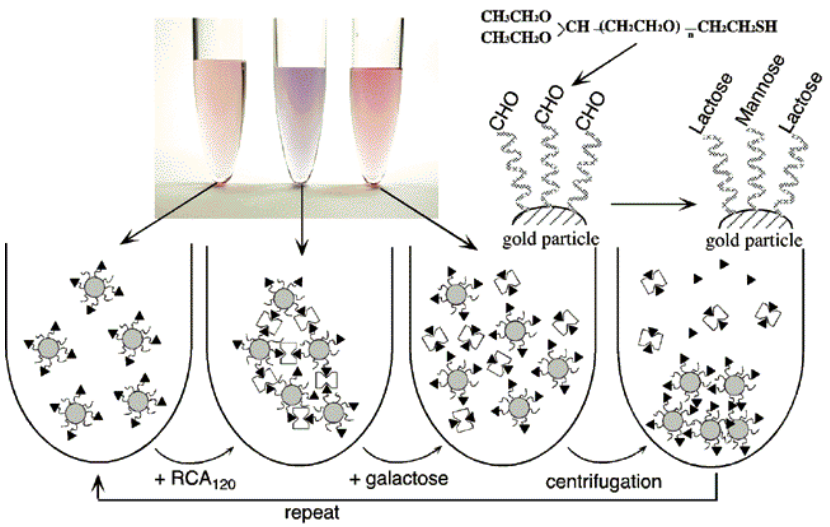
(**A**) complementary target
(**B**) no target
(**C**) complementary to one probe
(**D**) a 6-bp deletion
(**E**) a 1-bp mismatch
(**F**) a 2-bp mismatch

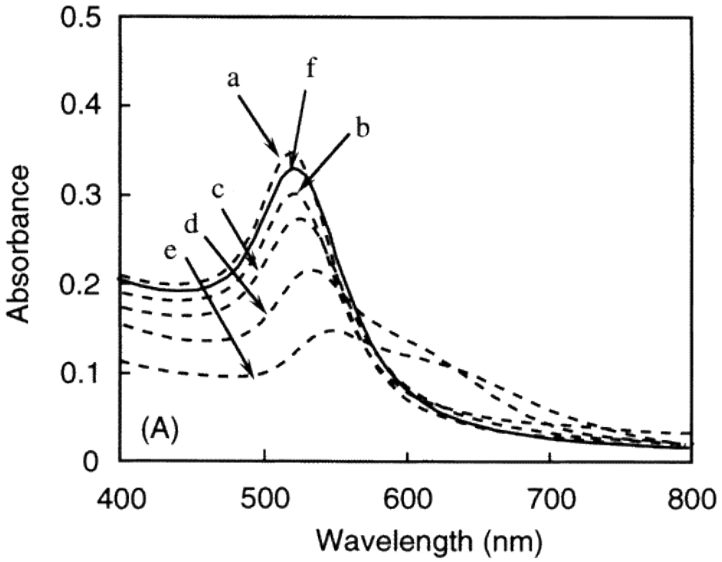
Variations in “melting” (dissociation) temperatures, T_m, as a function of base pairing:

Elghanian et al,
Science **1997**, *277*, 1078

Aggregation-induced shifts in plasmon resonance (cont'd)

Ex. 2: Lectin-induced aggregation of 9-nm Au NPs, with thiolated lactose (glyco-NPs)





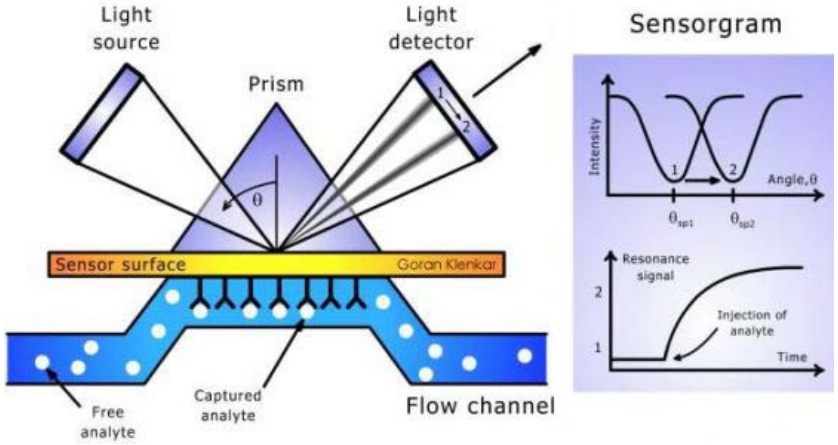
Otsuka, Akiyama, Nagasaki, and Kataoka, *J. Am. Chem. Soc.* **2001**, *123*, 8226.

After lectin addition (μg/mL): (a) 0; (b) 5; (c) 10; (d) 20; (e) 50. (solid line) redispersed NPs, after adding excess galactose.

For other examples of Au nanoparticles in colorimetric assays, see: *Inorganic Nanoprobes for Biological Sensing and Imaging*, Eds. H. Mattoussi, J. Cheon, Artech House:New York, 2009; Chapter 8 (Rotello and coworkers)

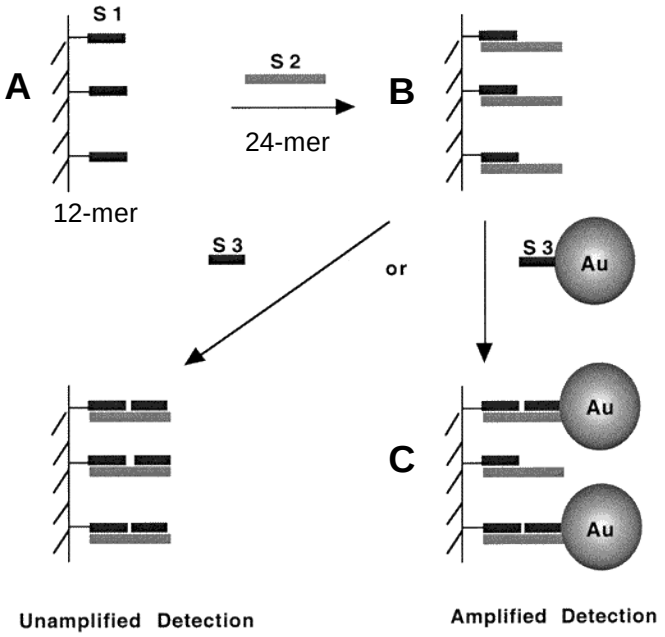
Metal nanoparticles as bio/chemical sensors

Adsorption-induced shifts in surface plasmon resonance (SPR)



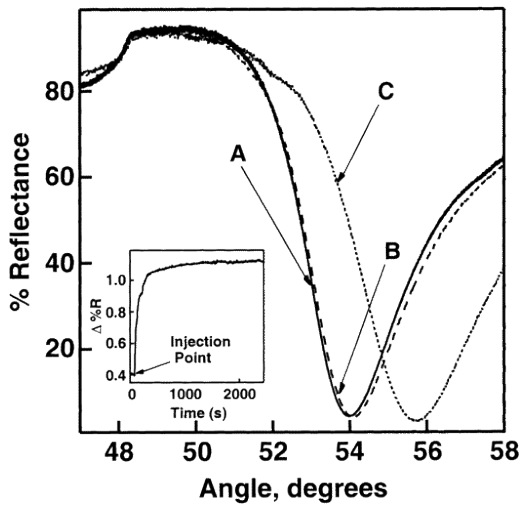
Surface adsorption changes the local refractive index of thin (50-nm) Au film, causes shift in "critical angle" for SPR absorption

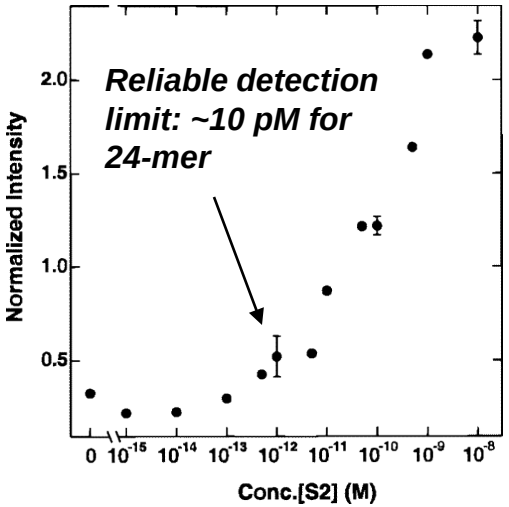
Works best for detecting biomolecular adsorption (e.g., proteins); small-molecule detection is harder



Nanoparticle-enhanced SPR detection of DNA oligonucleotides:

He et al, *J. Am. Chem. Soc.* **2000**, *122*, 9071

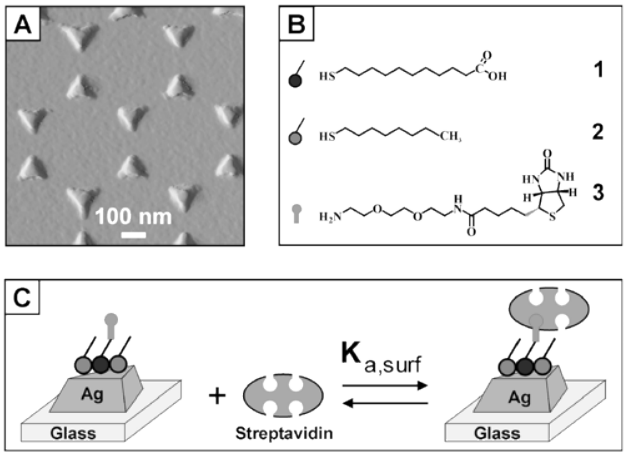


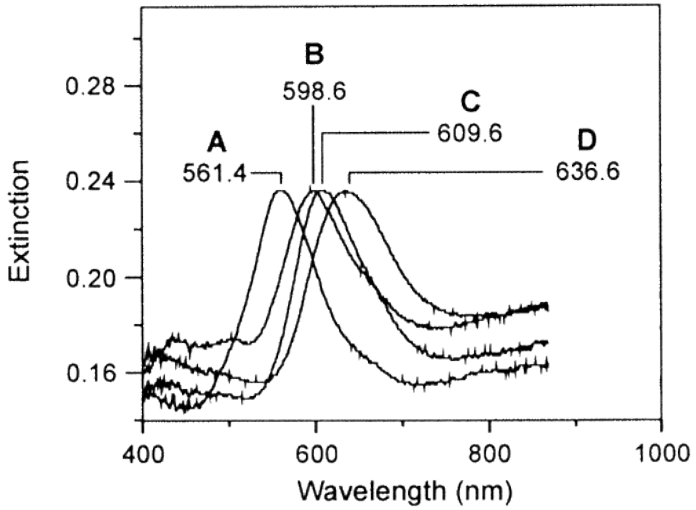


Anisotropic metal NPs as bio/chemical sensors

Adsorbate-induced shifts in LSPR: greater sensitivity

Localized SPR from Ag nanoprisms (*t* = 50 nm): Haes and van Duyne, *J. Am. Chem. Soc.* **2002**, *124*, 10596



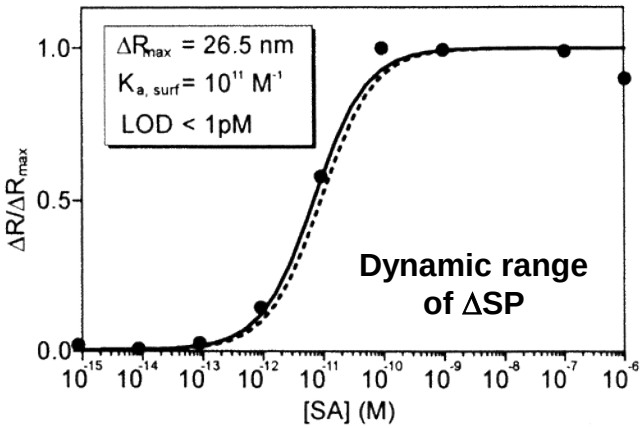


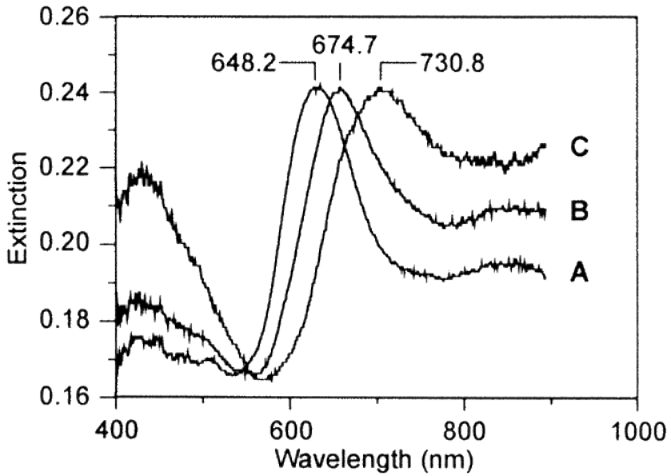
(A) Bare Ag nanoprisms

(B) Nanoprisms after modification with 1 mM 1:3 11-MUA/1-OT

(C) Nanoprisms after modification with 1 mM biotin

(D) Nanoprisms after exposure to 100 nM SA ($\Delta\lambda$ = 27 nm)





(A) Biotinylated nanoprisms

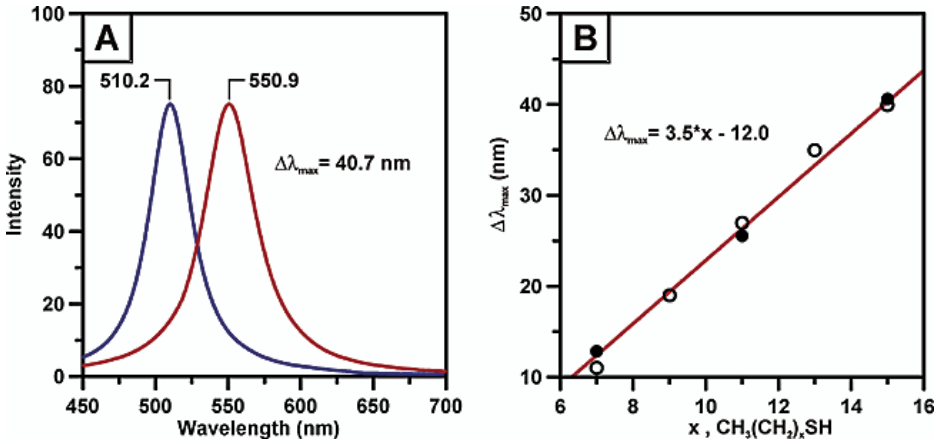
(B) Exposure to 100 nM SA ($\Delta\lambda$ = 27 nm)

(C) **Amplification of SA response using biotinylated Au colloids ($\Delta\lambda$ = 56 nm)**

Anisotropic metal NPs as bio/chemical sensors

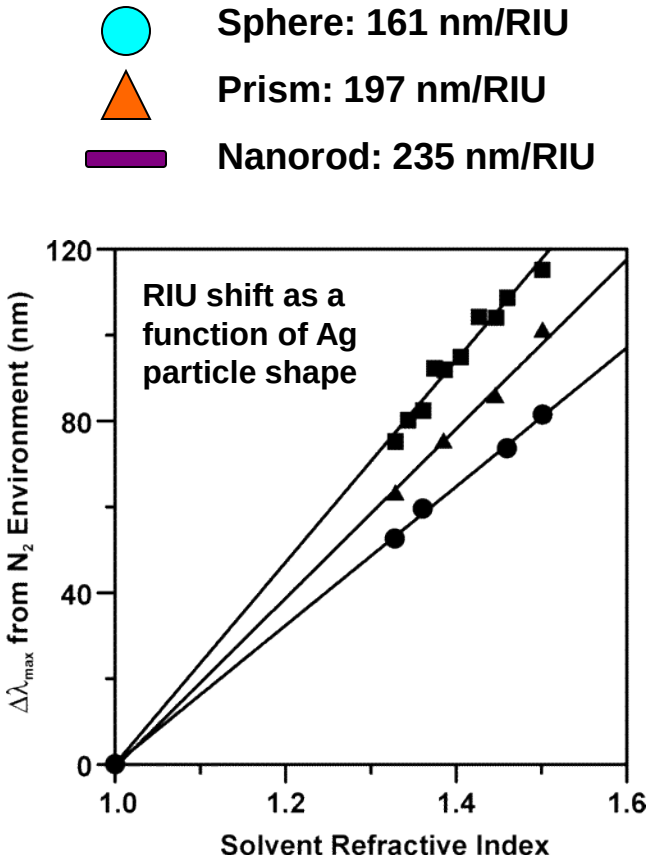
Changes in surface dielectric = LSPR shift

Single-nanoparticle SPR spectroscopy



(A) Ag NP before and after adsorption of C16-thiol.
(B) LSPR response vs. thiol chain length.

Anisotropic nanoparticles are more sensitive to local changes in surface dielectric; measured in refractive index units (RIU)

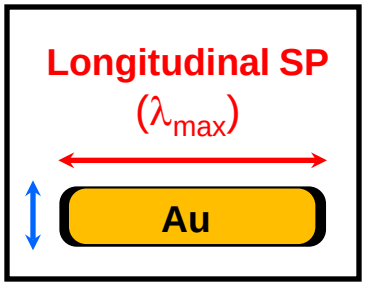


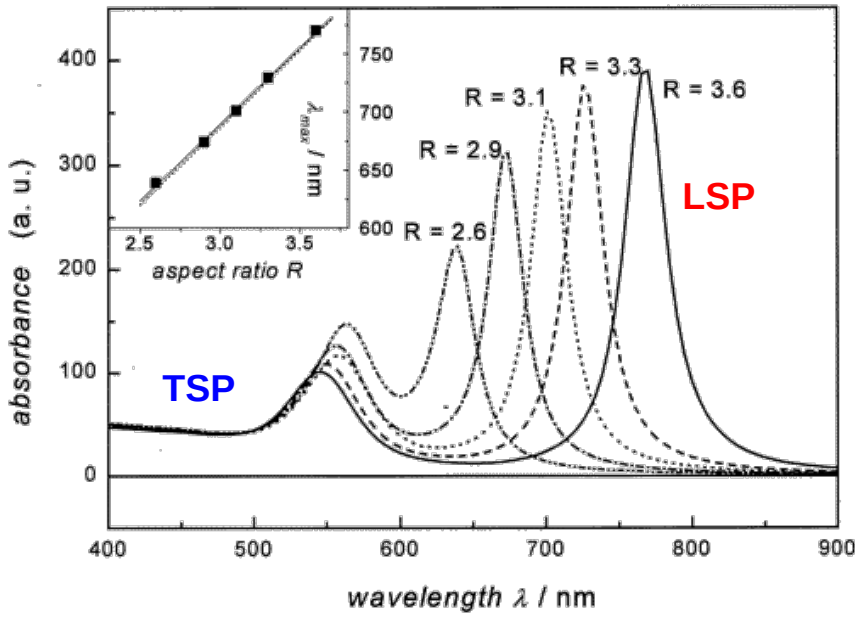
McFarland and van Duyne, *Nano Lett*. **2003**, *3*, 1057.

Anisotropic metal nanoparticles: Au nanorods

Au NRs: Tunable resonances in the NIR

Transverse SP

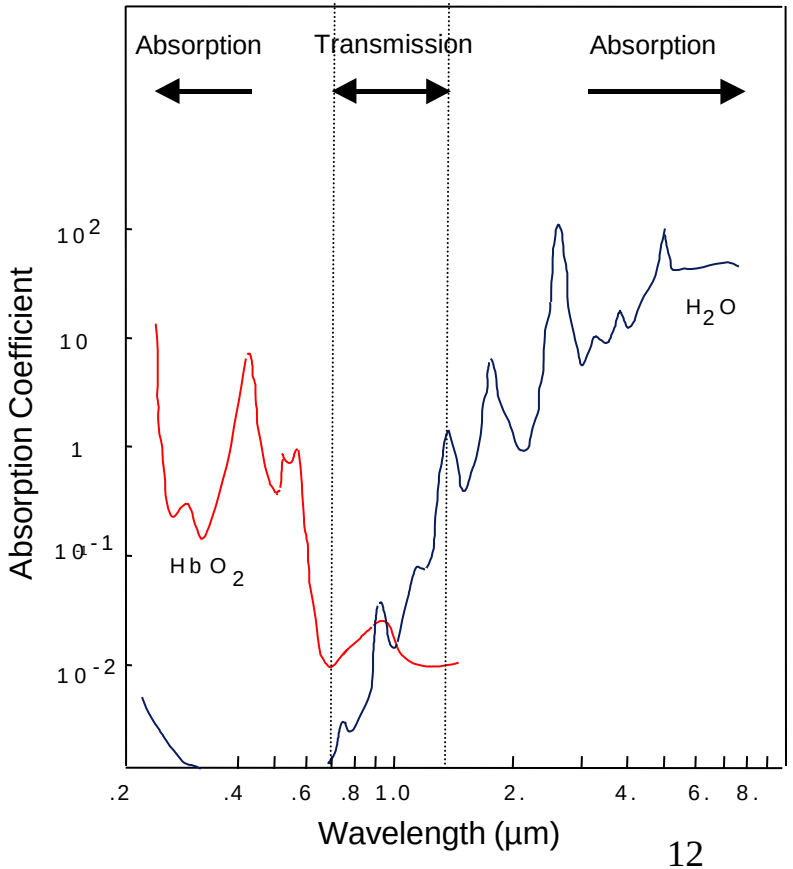




***SP modes as a function of aspect ratio*:**
Link and El-Sayed, *J. Phys. Chem. B* **1999**, *103*, 3073

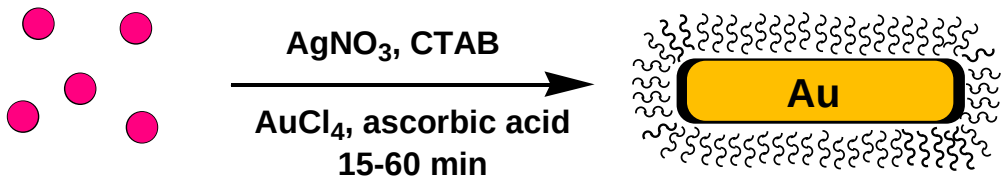
"Biological window" in tissue at NIR wavelengths:

Attenuation is minimized between 750 nm and 1.3 *μ*m



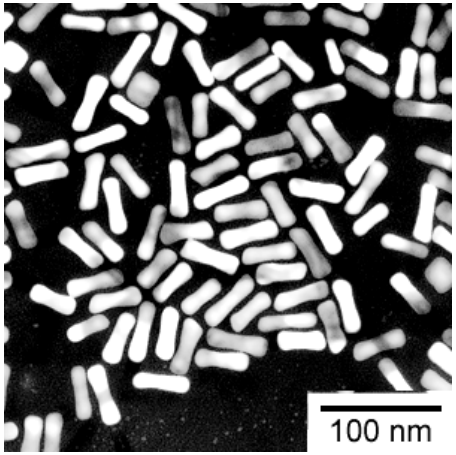
Synthesis of NIR-resonant Au nanorods

Seeded growth using micellar surfactants (CTAB):



3-nm Au particle seeds

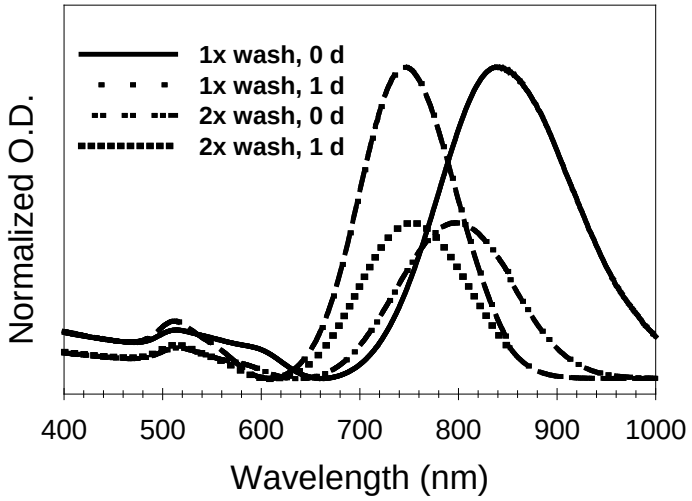
Sau and Murphy, *Langmuir* **2004**, *20*, 6414.
Zweifel and Wei, *Chem. Mater.* **2005**, *17*, 4256.

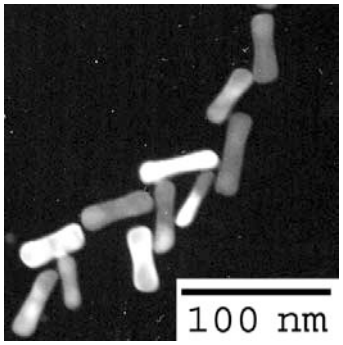


avg. width: 15-20 nm

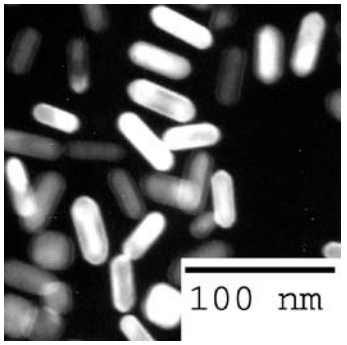
avg. length: 40-60 nm

Two-stage growth kinetics: effect on LPR wavelength





1st growth stage (fast): dumbbell-shaped NRs (stabilized after Na_2S)



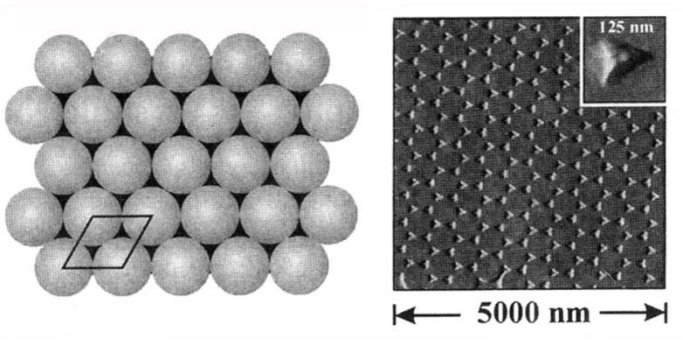
2nd growth stage (slow): Cylindrical NRs

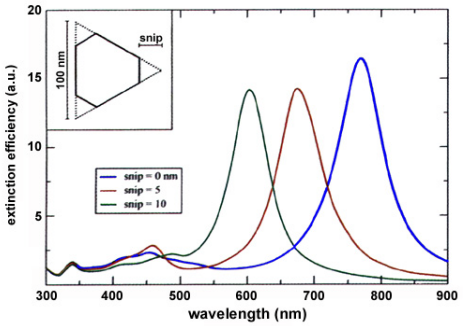
Other anisotropic Au nanoparticles

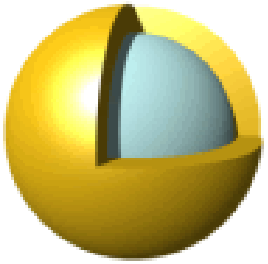
Nanoprisms (by nanosphere lithography)

Haynes and van Duyne, *J. Phys. Chem. B* **2001**, *105*, 5599.

Kelly et al, *J. Phys. Chem. B* **2003**, *107*, 668





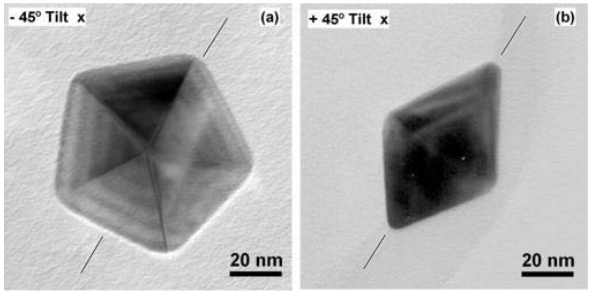


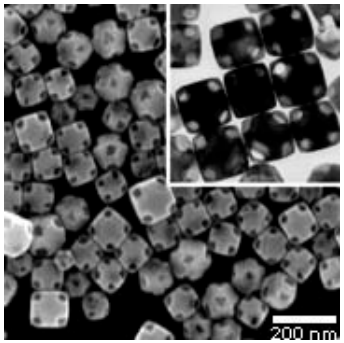
Nanoshells (SiO_2@Au)

Lal et al., *Acc. Chem. Res.* **2008**, *41*, 1842

Pentagonal bipyramids (decahedra)

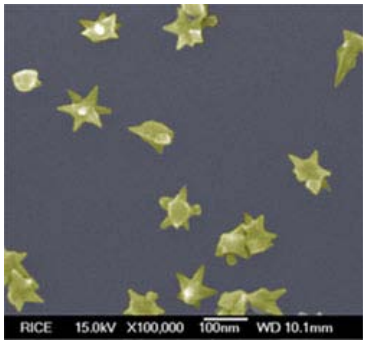
Sanchez-Igleisias et al, *Adv. Mater.* **2006**, *18*, 2529





Nanocages (growth on Ag nanocubes, with galvanic displacement)

Siekkinen et al, *J. Am. Chem. Soc.* **2006**, *128*, 14776

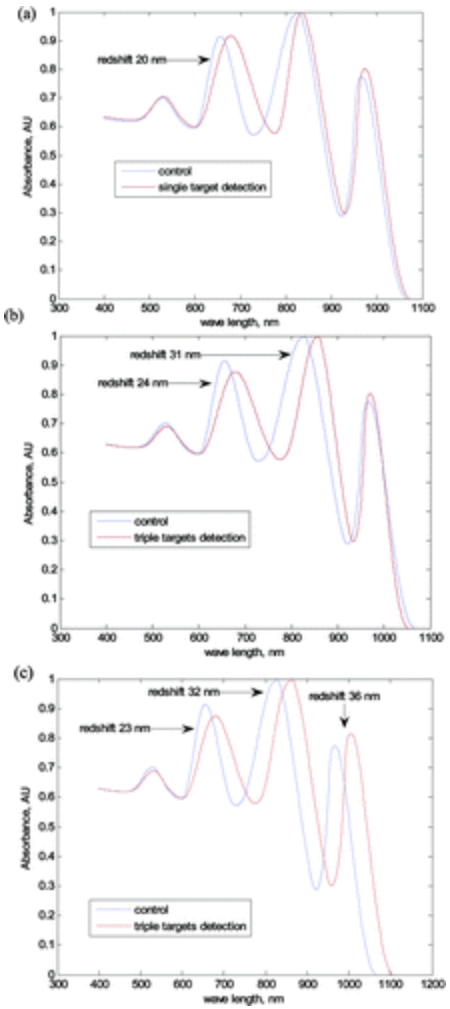


Nanostars (seeded growth from Au NPs)

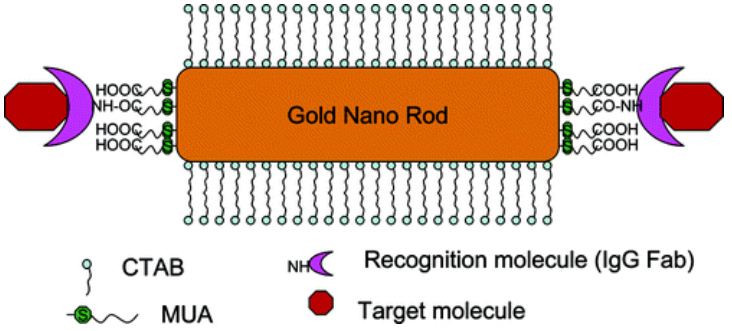
Nehl, Liao, and Hafner, *Nano Lett.* **2006**, *6*, 683

More examples of LSPR biosensing

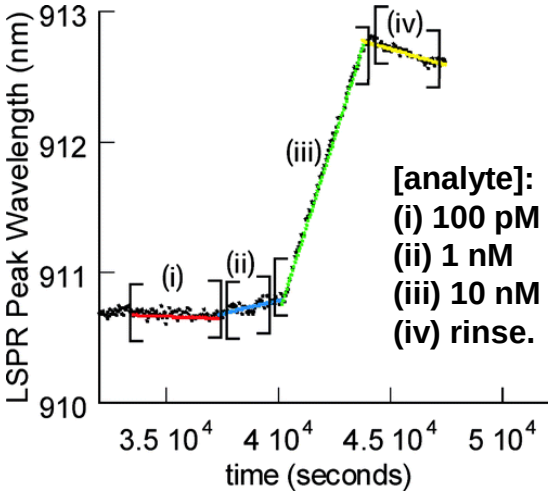
Antibody-labeled Au nanorods for multiplex biosensing

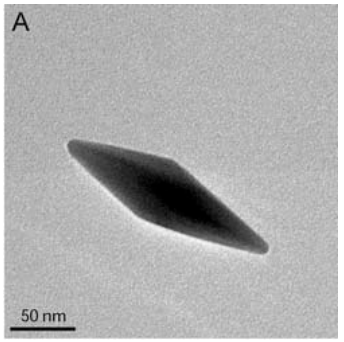


Yu and Irudayaraj, *Anal. Chem.* **2007**, *79*, 572



Real-time LSPR with antibody-labeled pentagonal bipyramids





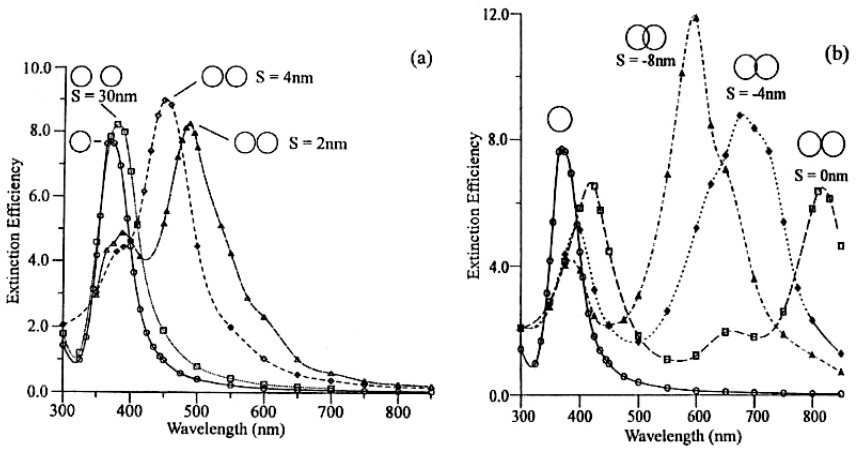
λ_{LSPR} = 750-900 nm

LSPR sensitivity: 280-380 nm/RIU

Lee, Mayer, Hafner, *Anal. Chem.* **2009**, *81*, 4450.

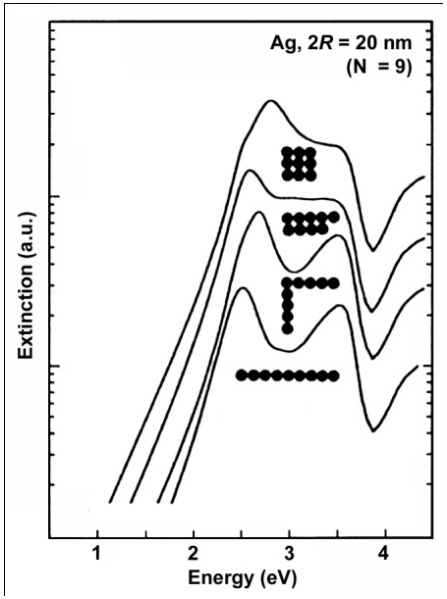
Collective optical properties of NP assemblies

Models of electromagnetic coupling between particles: large shift in collective SPR



Discrete dipole approximation (DDA) of 30-nm Ag particle dimer as a function of separation (S)

Jensen et al, *J. Cluster Sci.* **1999**, *10,* 295.



Simulation of (GMT) collective SPR of Ag NPs assembled into different geometries

Kriebig and Vollmer,
Optical Properties of Metal Clusters, 1995.

<u>Challenges in comparing experiment and theory</u>:

- calculations for particle sizes greater than 40 nm (quasistatic limit)
- Strong, highly nonlinear plasmon coupling between <u>closely</u> spaced particles (< 50% of diameter)
- Accounting for structural or surface charge defects ; establishing local dielectric constants (ε_d)