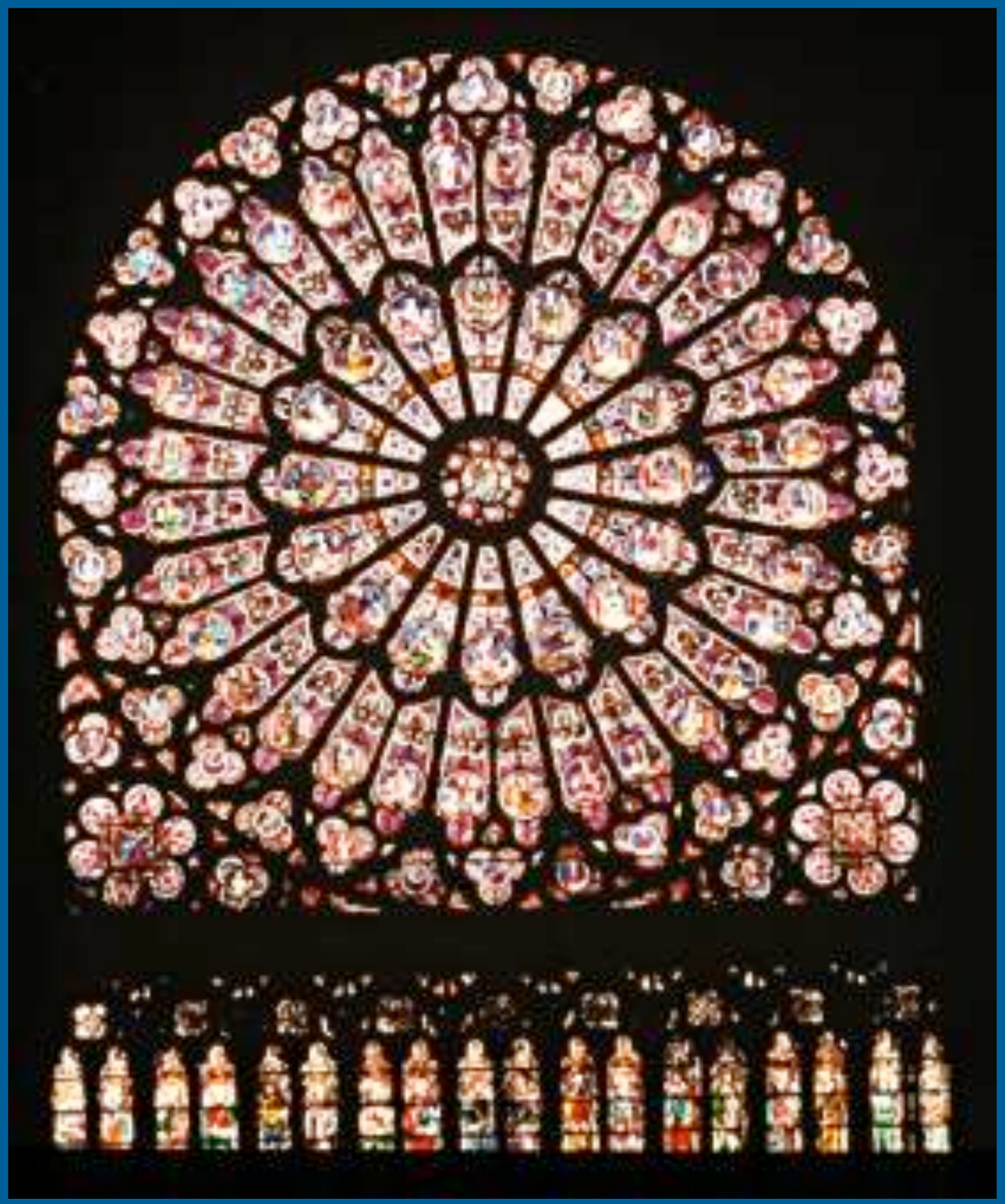
Surface Plasmon Resonance of Metallic Nanoparticles

Synthesis, Application, Characterization

James M. LeBeau

Examples from History

Notre Dame Cathedral: Rose Window



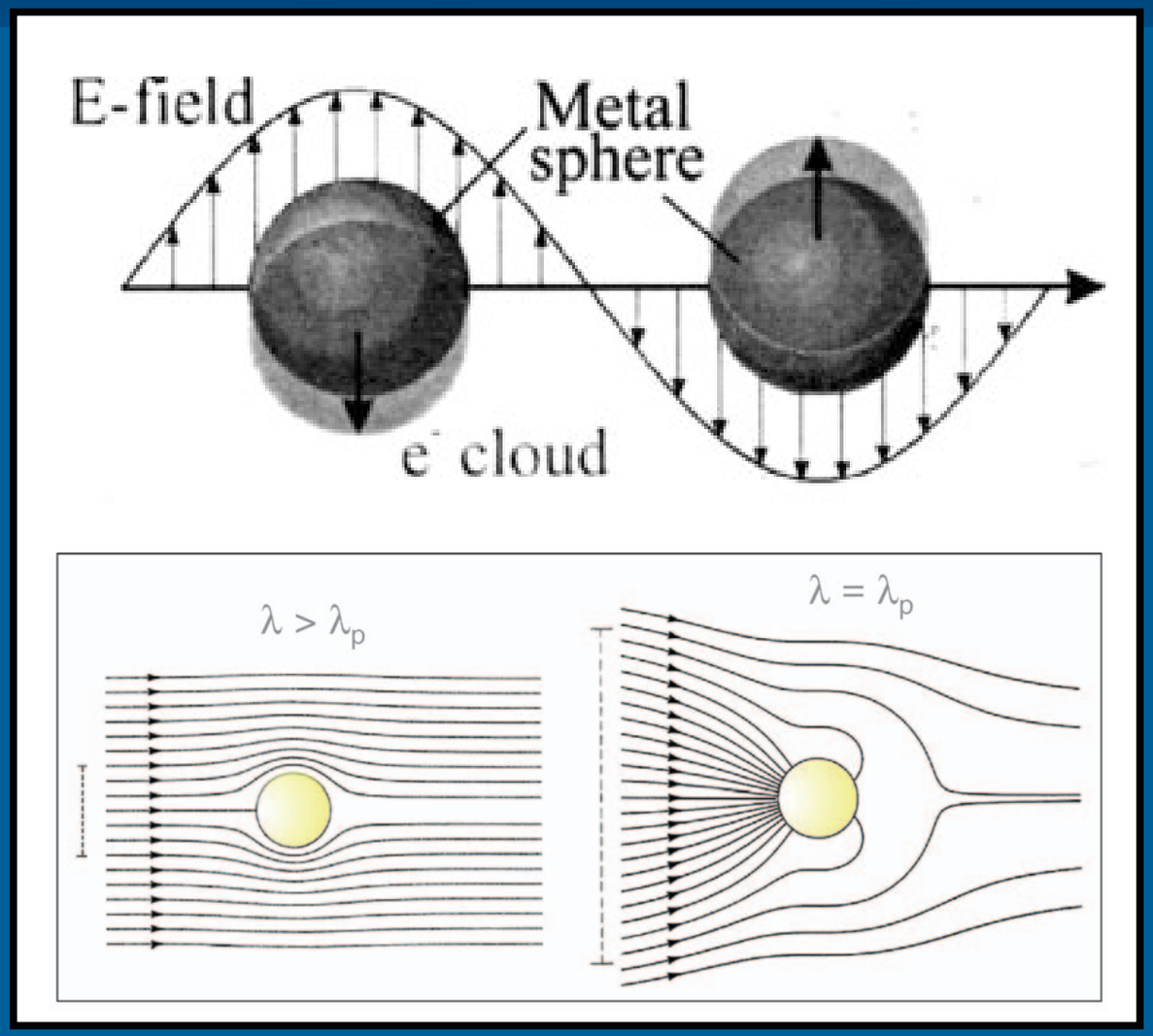
http://encarta.msn.com/media_461555912_761562615_-1_1/rose_window_notre_dame.html

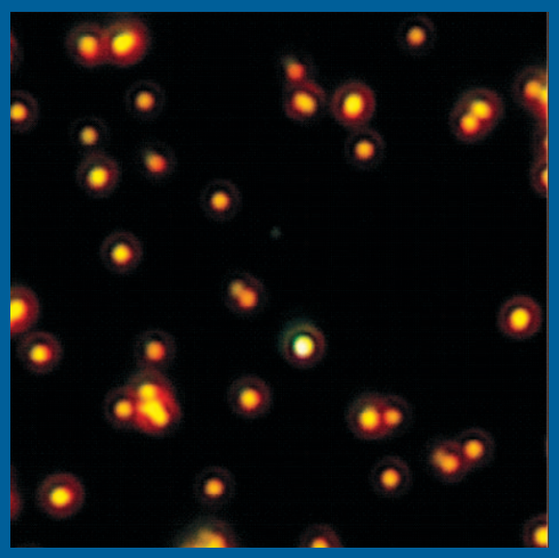
Lycurgus cup

www.ist-mona.org/ news/20070731.asp

Theory of Plasmon Resonance

- Collective oscillation of conduction electrons
- Resonance leads to absorption
- Absorption properties depend heavily:
  - Size
  - Size distribution
  - Shape
  - Local environment >> sensing





$$E(\lambda) = \frac{24\pi N_A a^3 \varepsilon_m^{3/2}}{\lambda \ln(10)} \left[\frac{\varepsilon_i}{(\varepsilon_r + 2\varepsilon_m)^2 + \varepsilon_i^2} \right]$$

[1] E. Hutter and J. H. Fendler. Advanced Materials, 16:1685, 2004.
[2] D. A. Stuart, et al. IEE Proceedings – Nanobiotechnology, 152(1):13–32, 2005.

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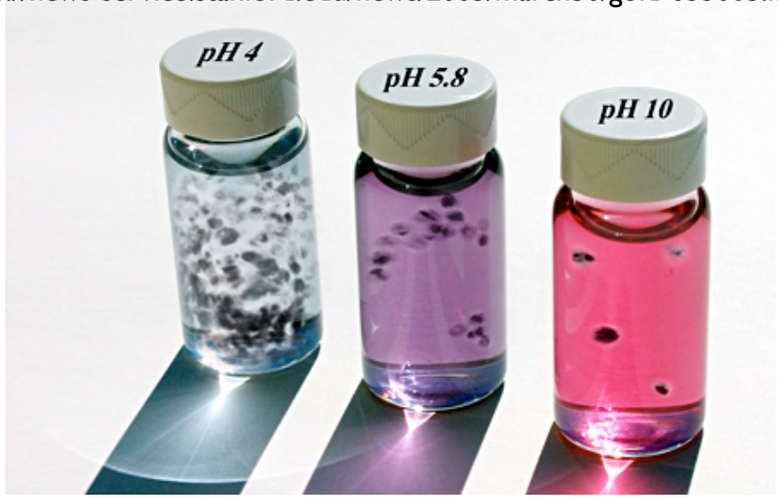
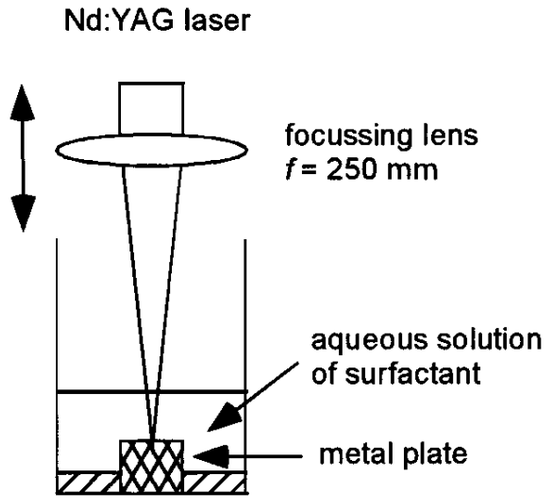
Synthesis Techniques

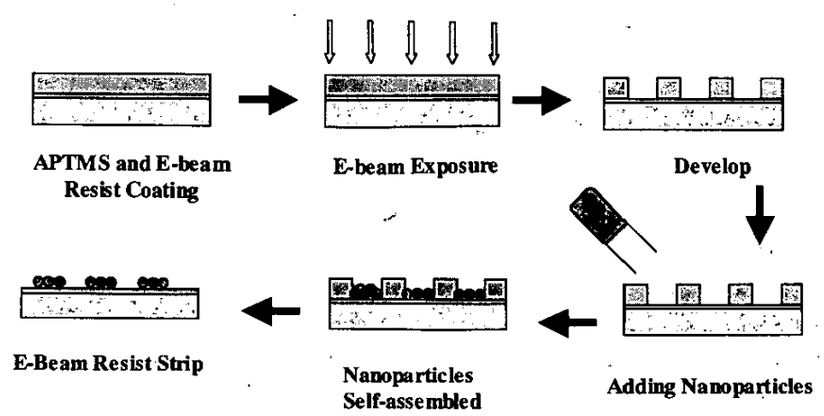
Solution Based

http://news-service.stanford.edu/news/2005/march30/gold-033005.html

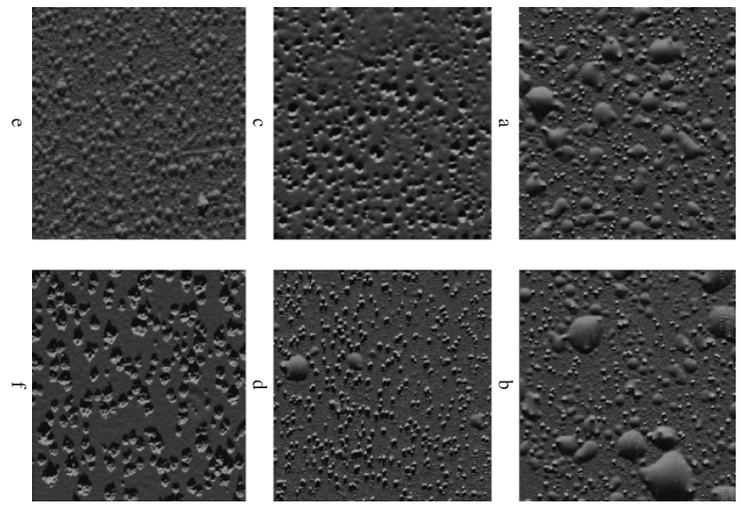




E-beam lithography



Laser Ablation



Electrodeposition

[1] X. DAI and R. G. COMPTON. Analytical Sciences, 22(4):567–570, 2006.

[2] C. I. Kuo, et al. Microprocesses and Nanotechnology Conference, 2003. Digest of Papers. 2003 International, pages 224–225, 2003.

[3] F. Mafune, et al. Journal of Physical Chemistry B, 105(22):5114–5120, 2001.

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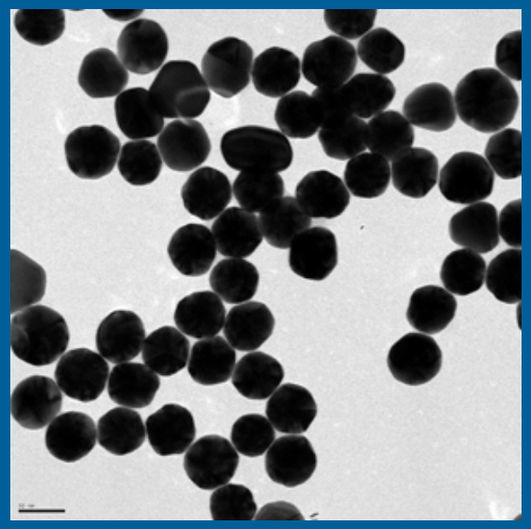
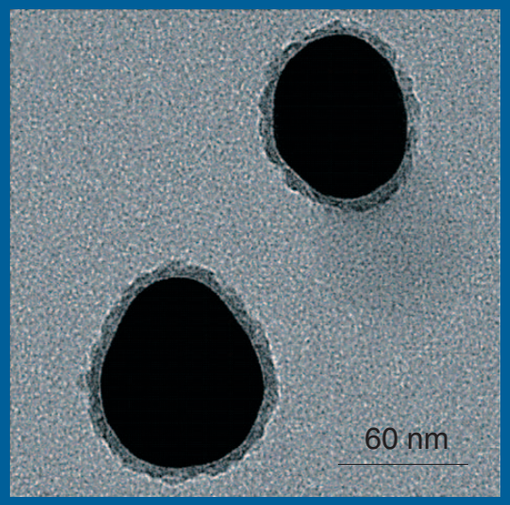
A Spectrum of Shapes and Sizes

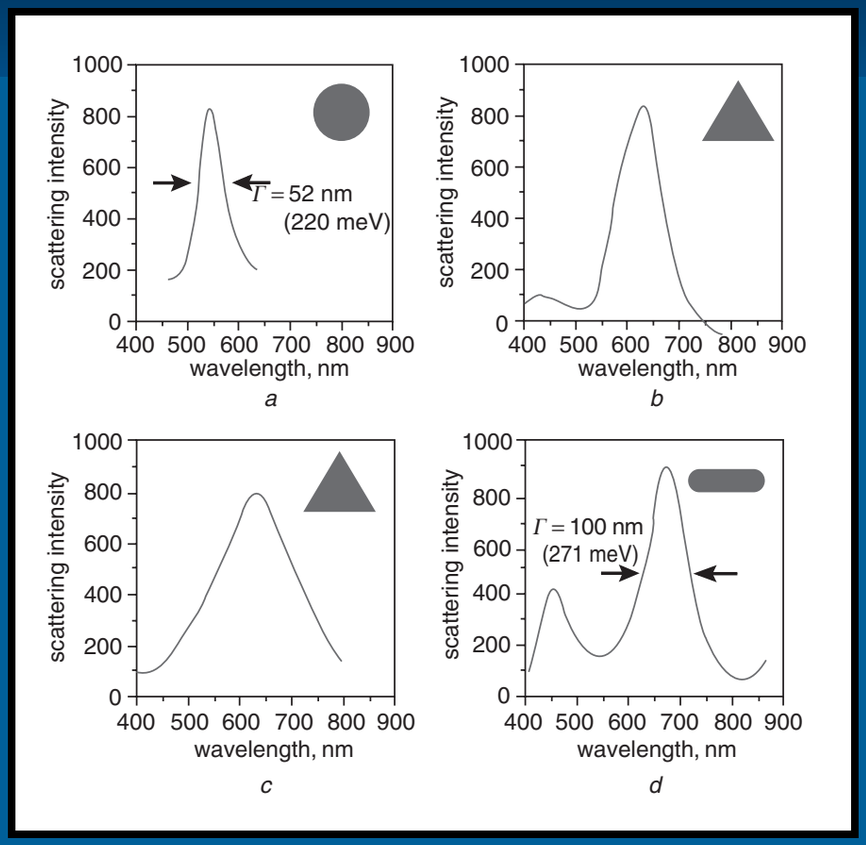
Spheres



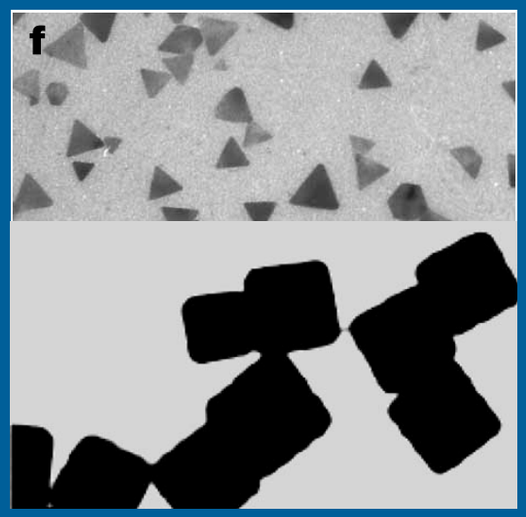
http://www.polysciences.com/Catalog/Department/Product/98/categoryId__412/productId__2695/

Core-shell

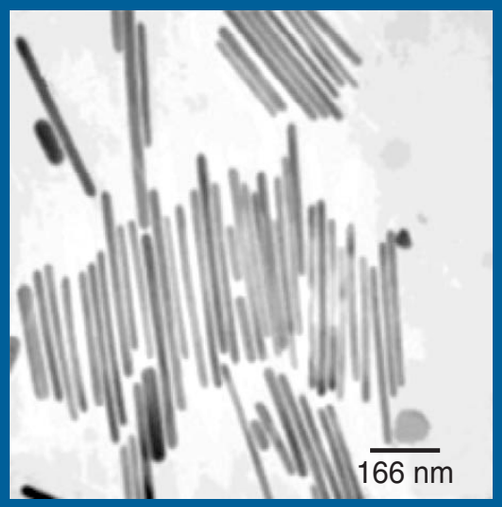




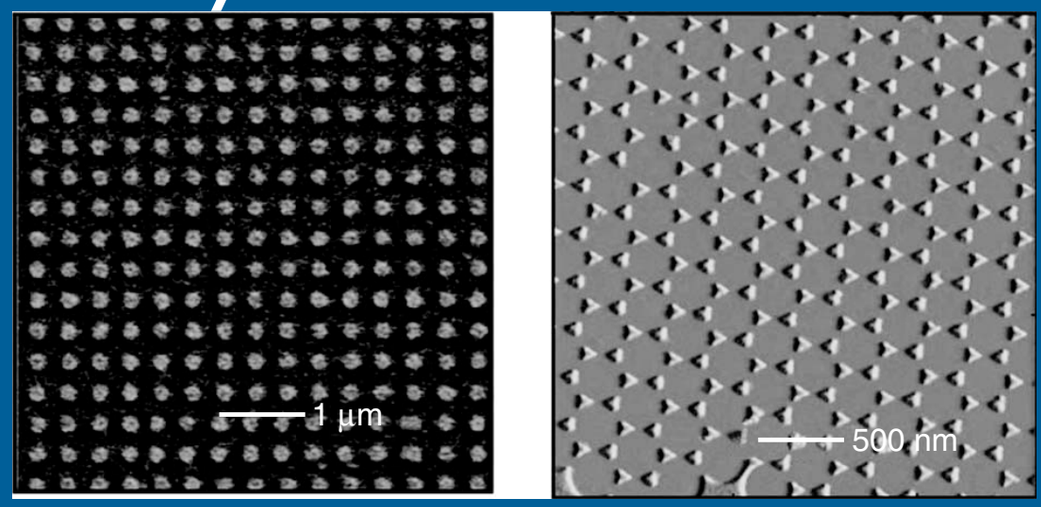
Prisms



Rods



Arrays



[1] R. Jin, et al. Nature, 425(6957):487–490, 2003.
[2] D. A. Stuart, et al., IEE Proceedings – Nanobiotechnology, 152(1):13–32, 2005.
[3] D. A. Stuart, et al. IEE Proceedings – Nanobiotechnology, 152(1):13–32, 2005.

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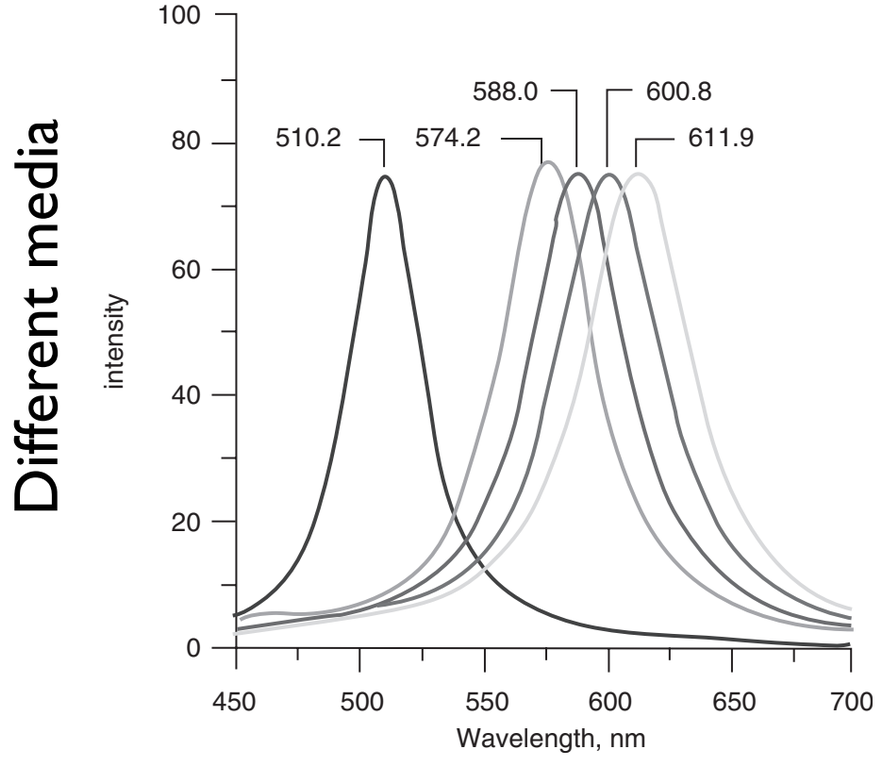
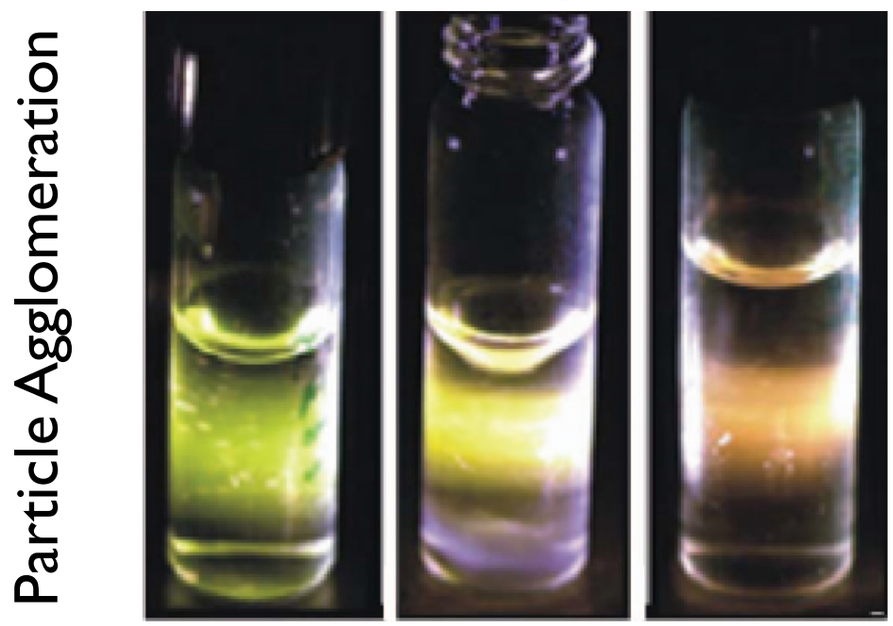
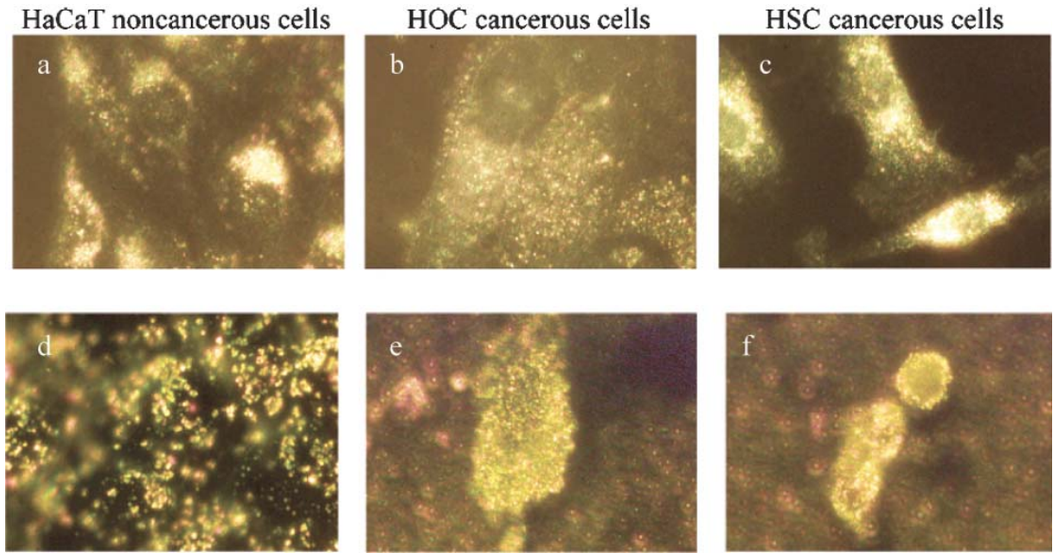
Colorimetric Detection

- Absorption spectra depends local environment and particle spacing
- Particles can be functionalized
  - Non-bleaching unlike fluorescence-based assays
    - 100 fold increase in sensitivity
- Color change based on presence of certain proteins
  - agglomeration
  - Antigen detection (pg/mL)
- Optical detection of cancer cells
  - Similar to QD's

[1] S. Eustis and M. A. El-Sayed. Chemical Society Reviews, 35(3):209–217, 2006.
[2] D. A. Stuart, et al. IEE Proceedings – Nanobiotechnology, 152(1):13–32, 2005.







Agglomeration: NaCl

http://www.mrsec.wisc.edu/Edetc/nanolab/gold/index.html

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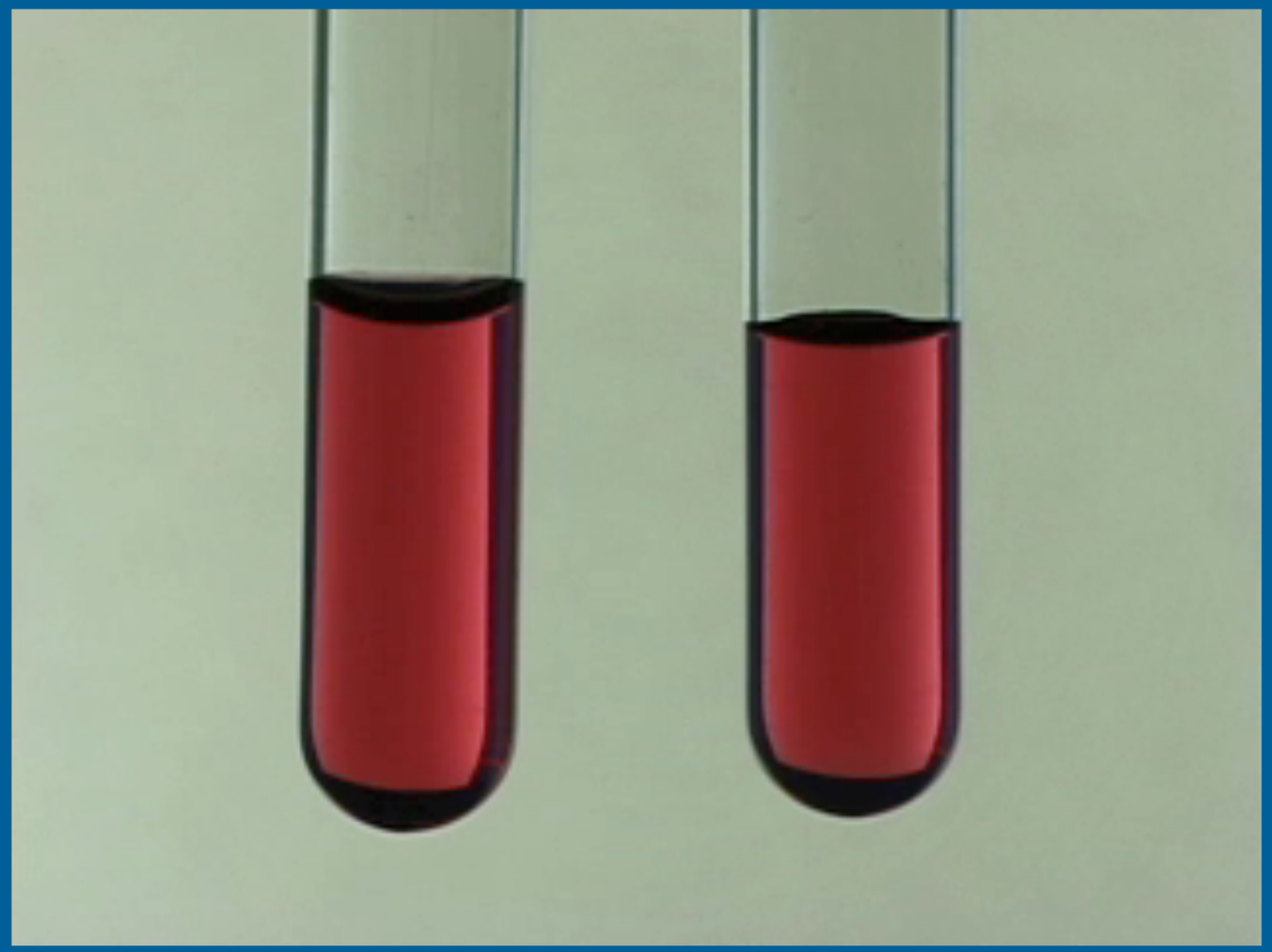

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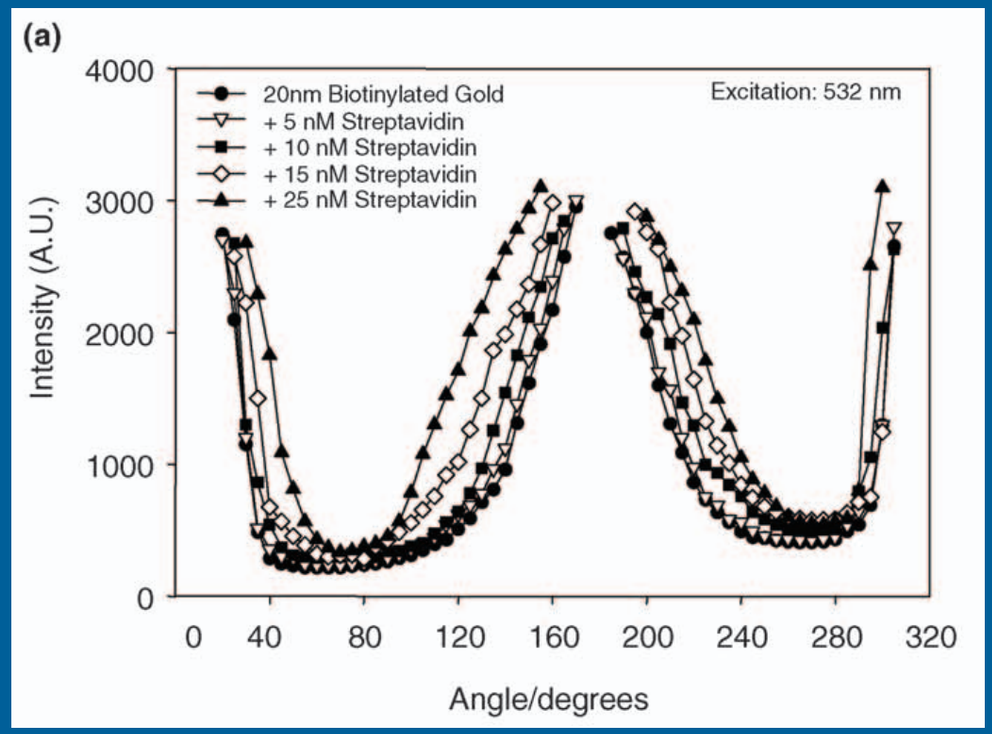
Scattering Dependence Detection

- Linearly polarized light has an angular dependence of scattering
- Agglomeration of particles changes the angular dependence
  - Rayleigh limit
  - Mie limit
- Ratio of scattering at two wavelengths
  - Independent of gold particle concentration
- Less studied than colorimetric detection

$$I \propto \frac{\cos^2 \theta}{\lambda^4}$$



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[1] K. Aslan, J. R. Lakowicz, and C. D. Geddes. Plasmon light scattering in biology and medicine: new sensing approaches, visions and perspectives. Current Opinion in Chemical Biology, 9(5):538–544, 2005.

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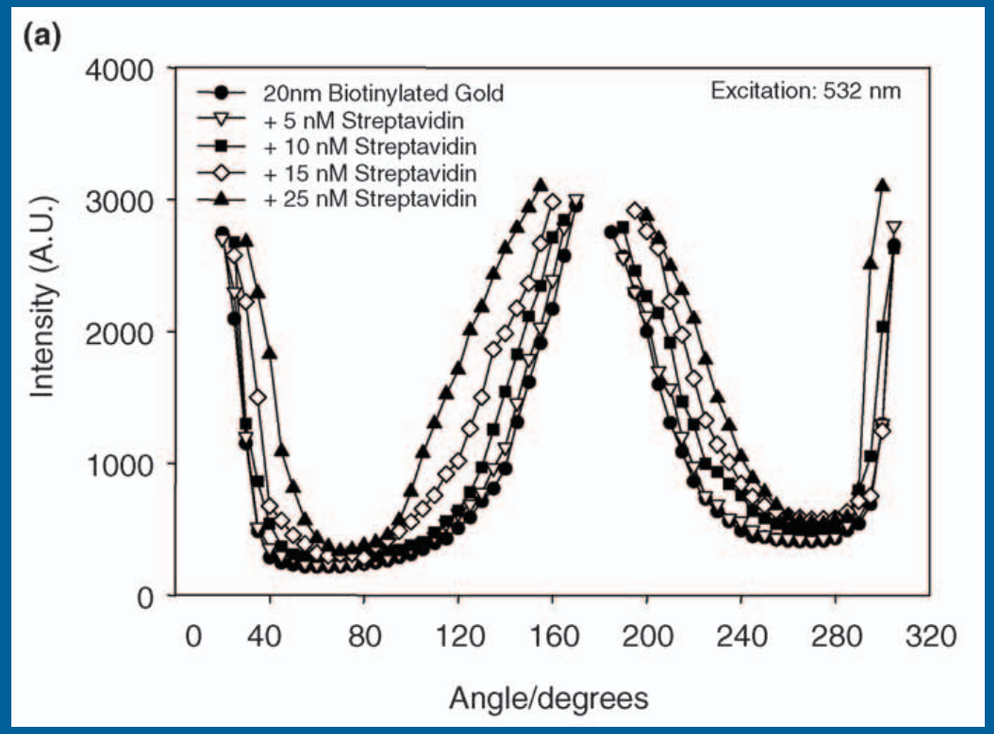

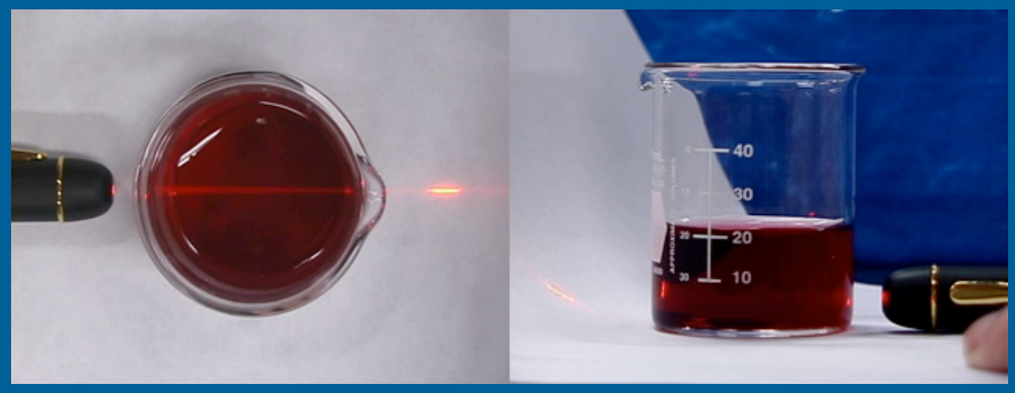

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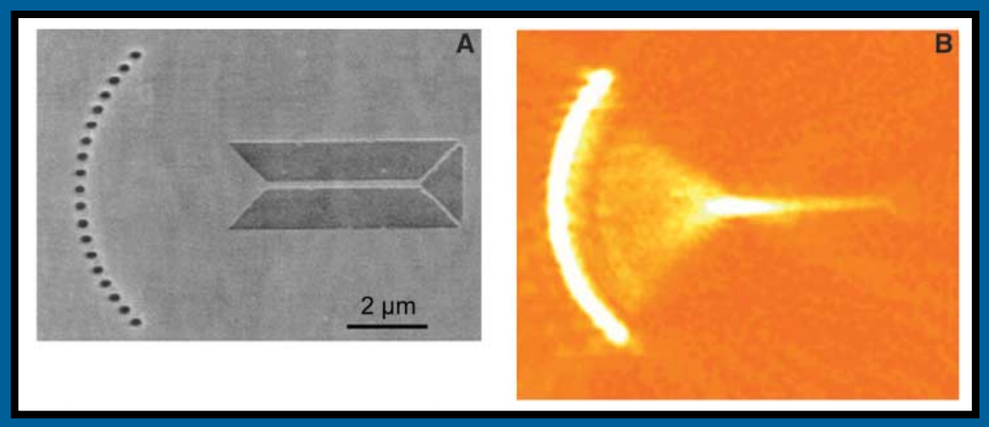
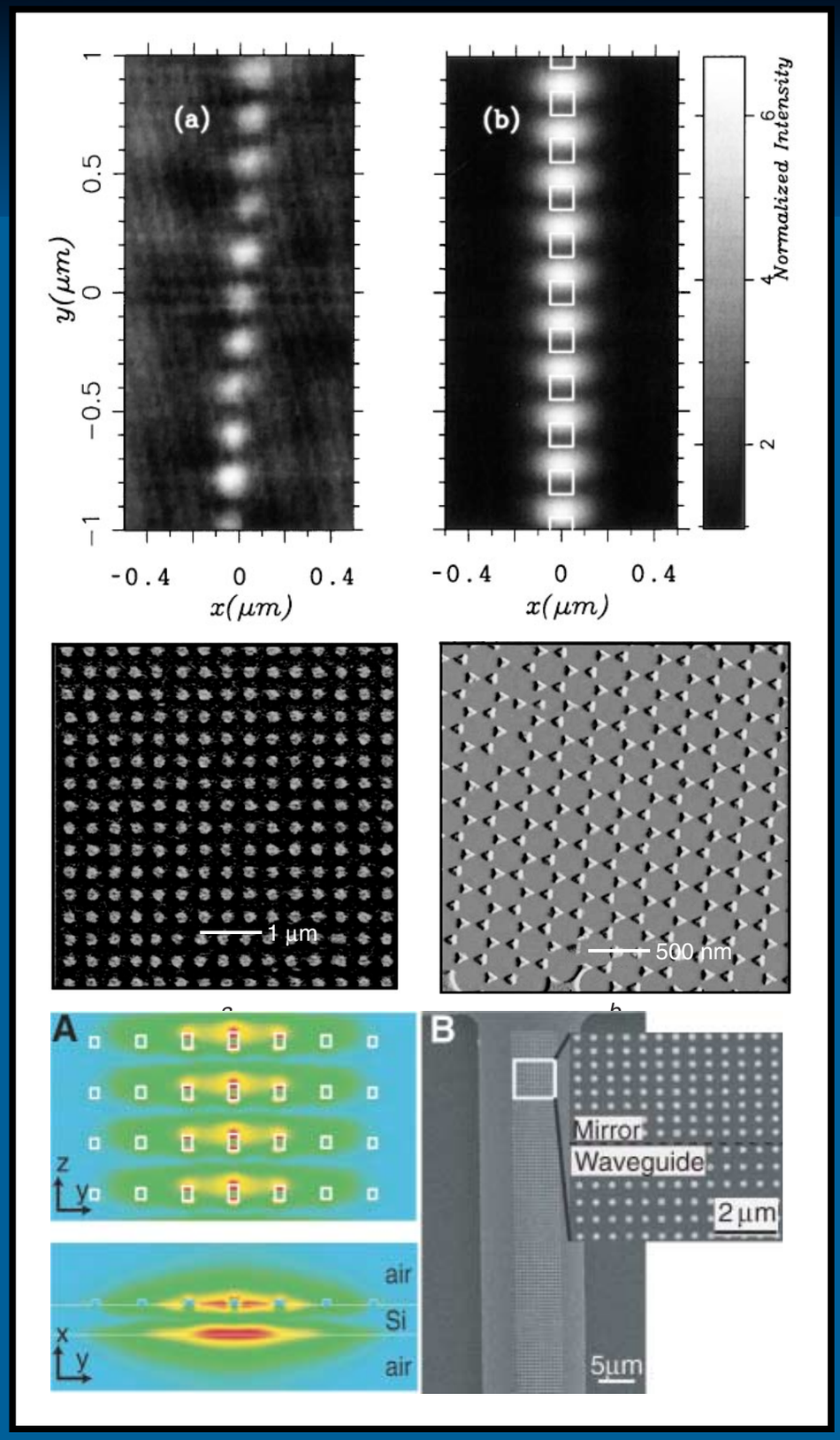
Plasmonic Waveguides

- Current photonic devices are μm scale, electronic devices are nm scale
- "Squeeze" light into plasmonic waveguide
  - Particles closely spaced will dipole-couple >> transmit information
    - Can also be done with nano metal wires
  - Propagation of light at sub-wavelength scale needed for optical-electronic integration
  - μm's of travel observed





[1] J. R. Krenn, et al. Squeezing the optical near-field zone by plasmon coupling of metallic nanoparticles. Phys. Rev. Lett., 82(12): 2590–2593, Mar 1999.
[2] E. Ozbay. Plasmonics: Merging Photonics and Electronics at Nanoscale Dimensions. Science, 311(5758):189–193, 2006.

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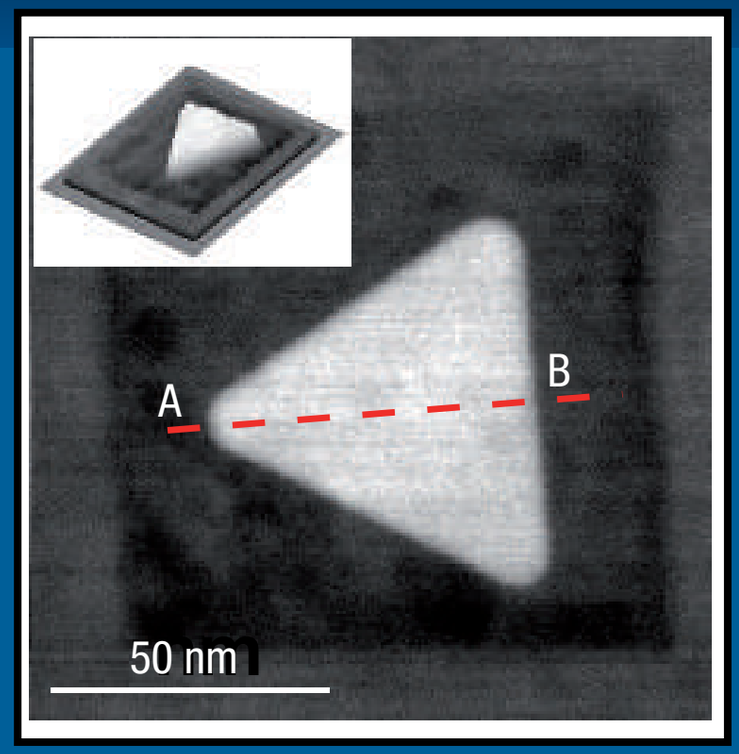
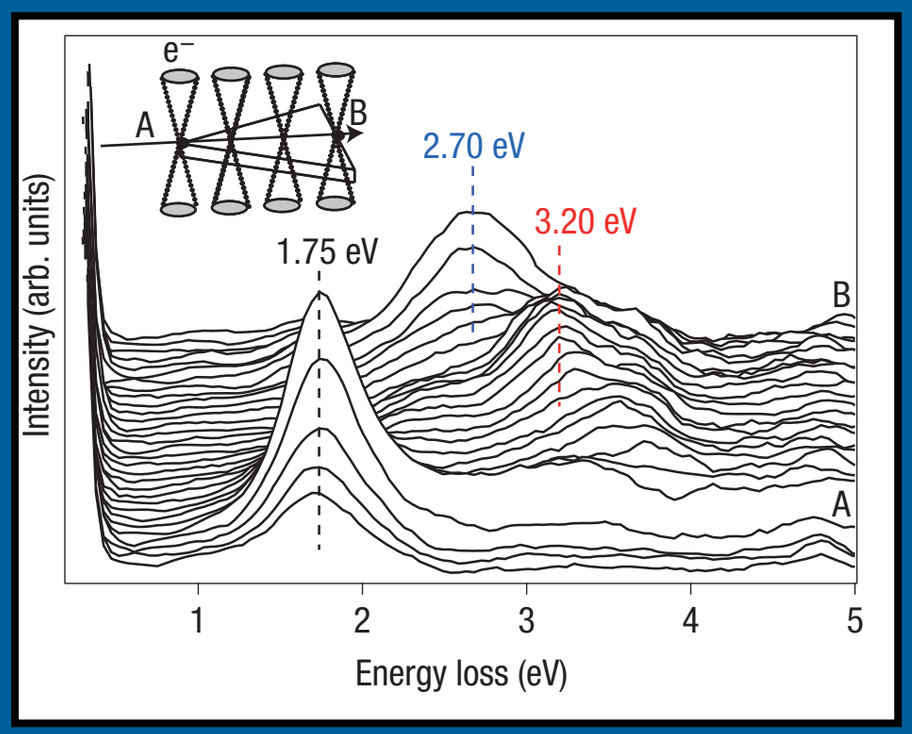
Localized Characterization

- Light spectroscopy techniques tell us about absorption energies
  - Non-local information!
- Can we characterize the particle plasmon excitations at the nanoscale?
- Electron energy loss spectroscopy with STEM
  - Fast electrons electrons passing through a material lose energy
    - Plasmon excitations
  - Localized information to roughly a nanometer





J. Nelayah, et al, Mapping surface plasmons on a single metallic nanoparticle. Nat Phys, 3(5):348–353, 2007.

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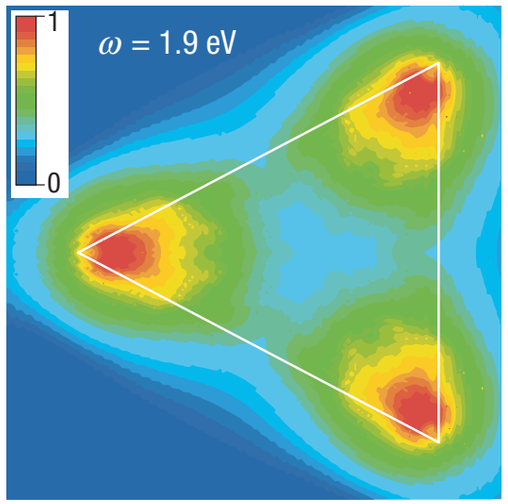
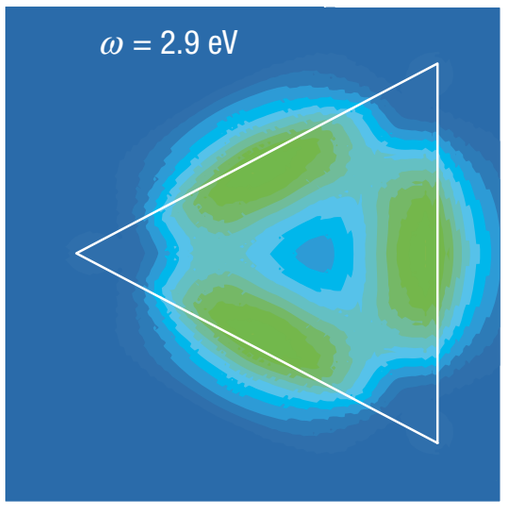
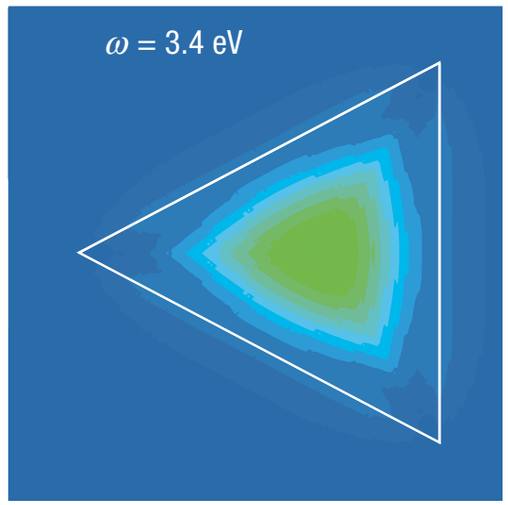
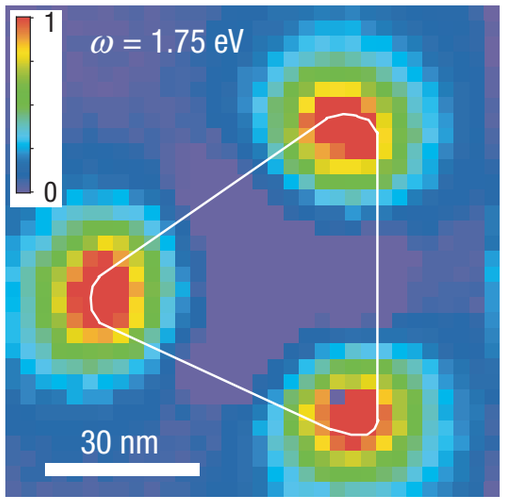
Spectrum Imaging

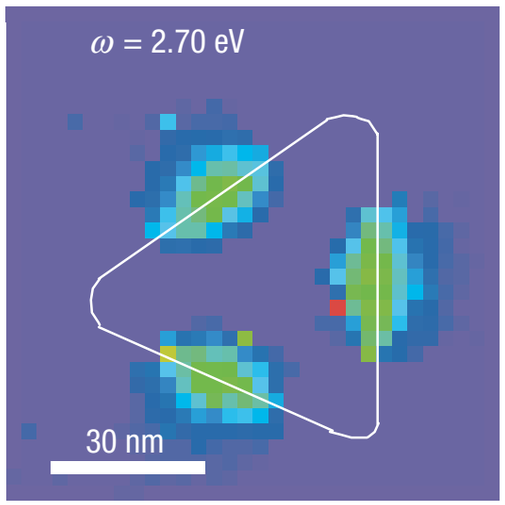
Silver nanoprisms

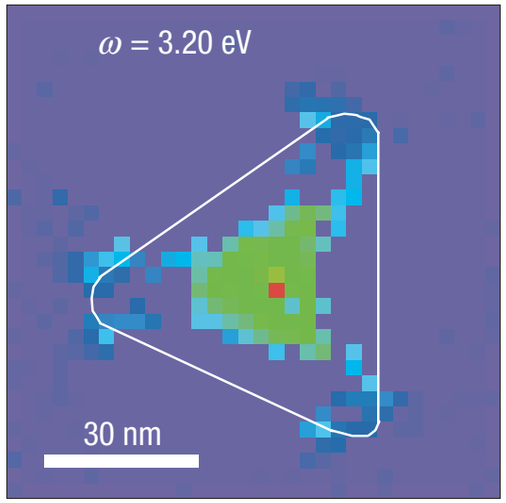




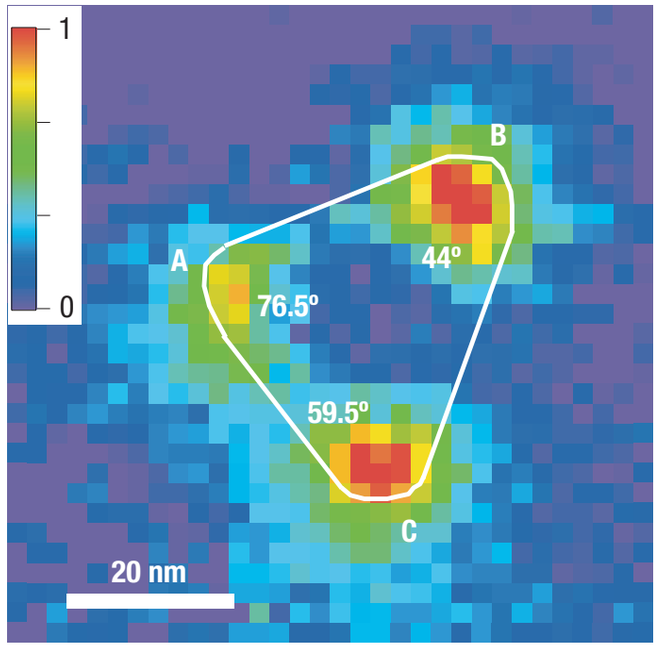








Asymmetric



- Localized information about energy eigenmodes of the particles, good match with theory
- Asymmetries alter the absorption properties, not observable with other techniques

J. Nelayah, et al, Mapping surface plasmons on a single metallic nanoparticle. Nat Phys, 3(5):348–353, 2007.

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Conclusions

- Localized surface plasmon resonance in nanoparticles provides novel plasmonic detection systems
- Far reaching applications with significant promise for future development
  - Two different routes: colorimetric and scattering dependence
    - Exceptionally tunable: size, shape, etc
  - Possibilities to integrate photonic devices with electronic devices
- New characterization techniques provide detailed information about plasmon excitations

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