Optics at the Nanoscale

Merging Nanoparticles with Light

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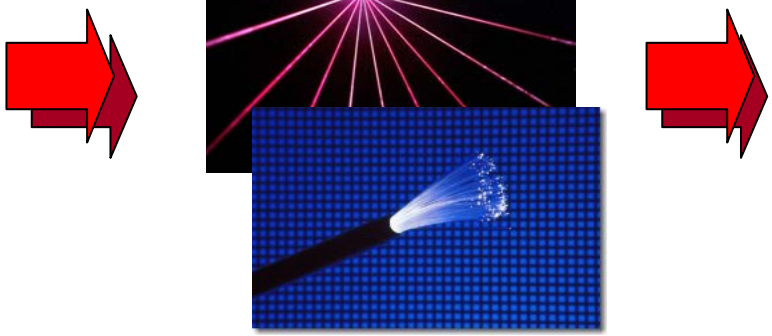
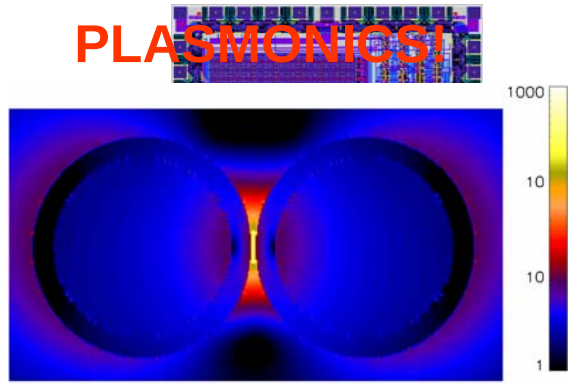
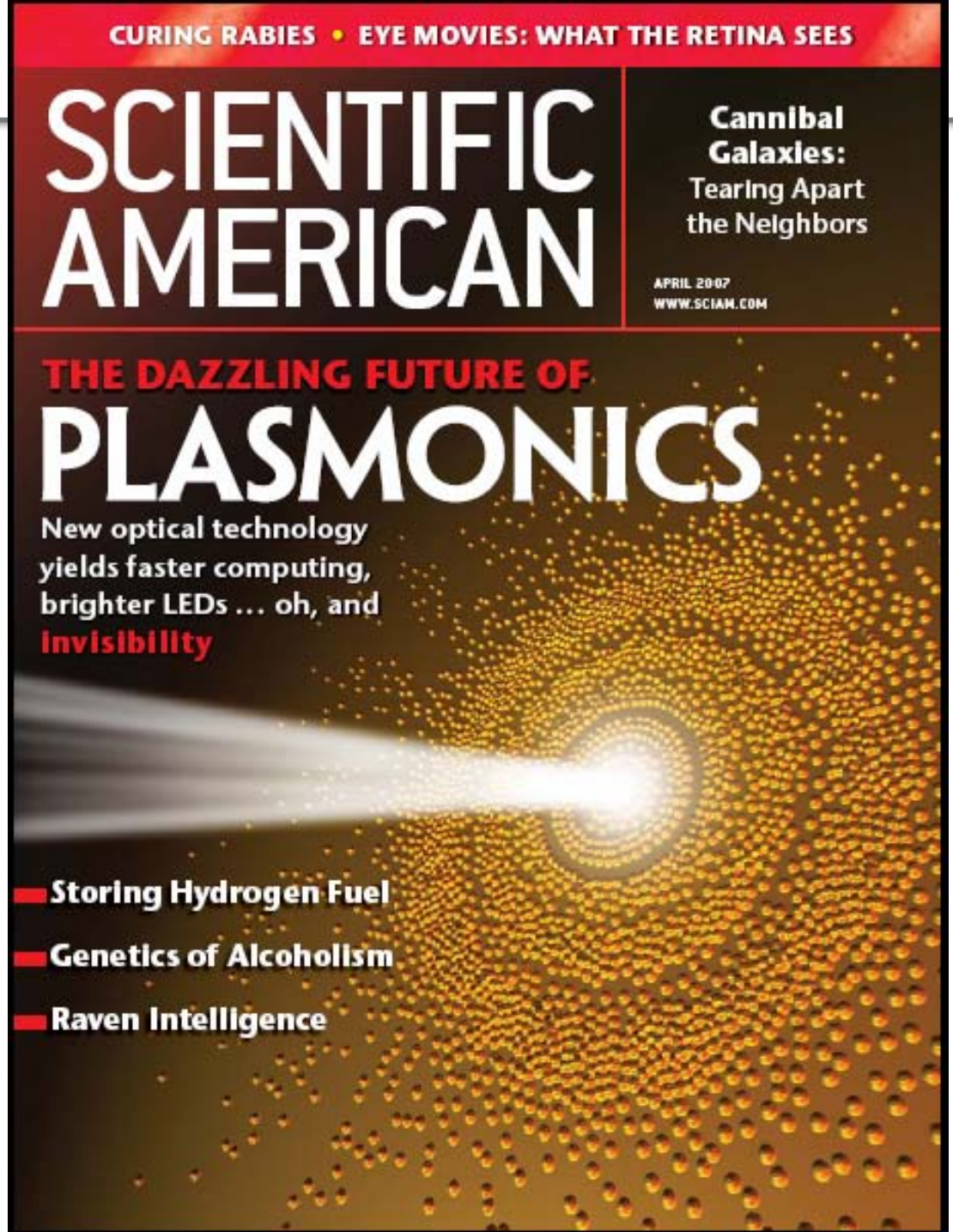
Nanophotonics: an emerging technology



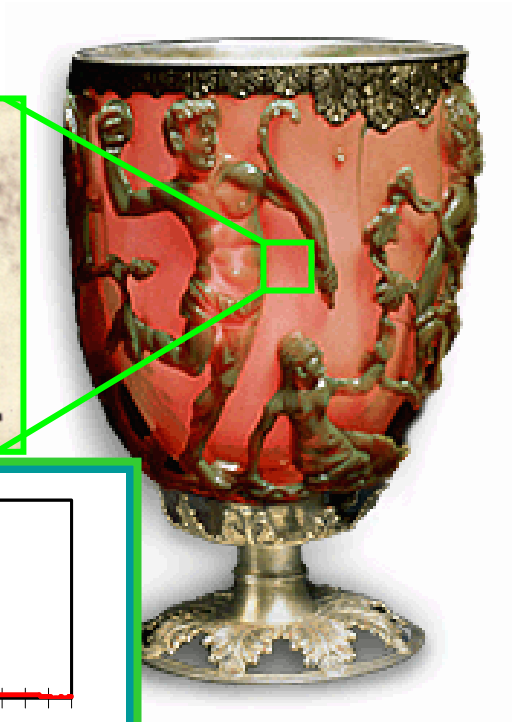


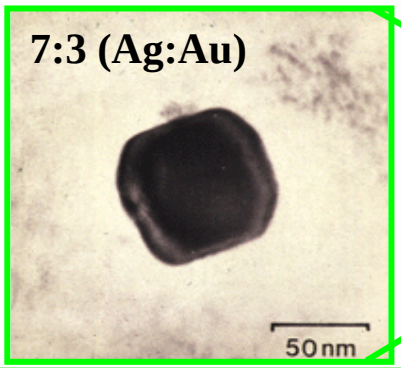
Optics at the nanoscale !

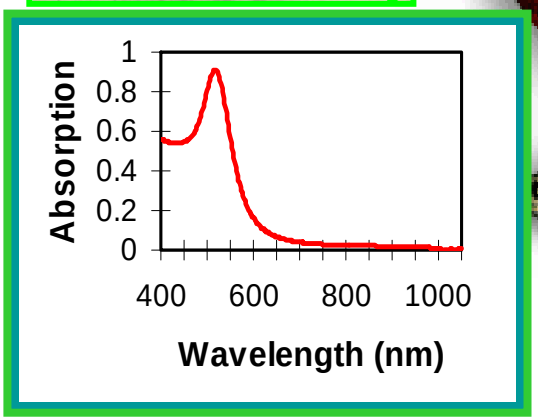

CURING RABIES • EYE MOVIES: WHAT THE RETINA SEES
SCIENTIFIC AMERICAN
Cannibal Galaxies: Tearing Apart the Neighbors
APRIL 2007
WWW.SCIAM.COM
THE DAZZLING FUTURE OF
PLASMONICS
New optical technology yields faster computing, brighter LEDs ... oh, and invisibility
Storing Hydrogen Fuel
Genetics of Alcoholism
Raven Intelligence

Plasmonic nanoparticles: shape matters!

Lycurgus Cup
4th Century A.D., Roman

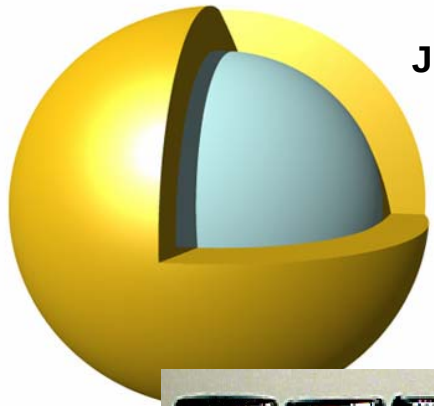






Gustav Mie, Ann. Physik 25, 377 (1908)

A.L. Aden and M. Kerker, J. Appl. Phys. 22, 1242 (1951)

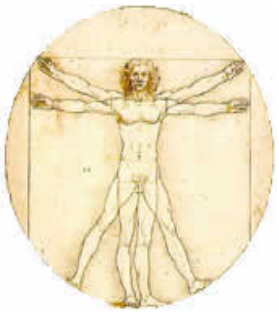


S. Oldenburg et al.,*CPL* **288**, (1998) 243-247.

E. Prodan et al., ***Science* 302** (2003) 419-21.

Getting a sense of the nanometer scale:

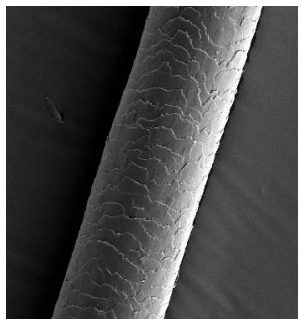
Person
1.7
meters



Pencil lead
2
millimeters

850 pencil leads per person

Human hair
70
micrometers

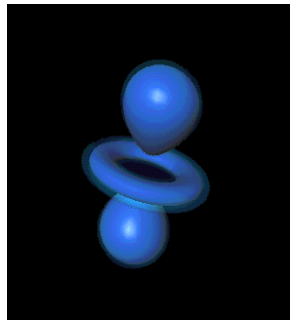


30 human hairs per pencil lead

Nanoshell
100
nanometers

700 nanoshells per human hair

Atom
0.15
nanometers



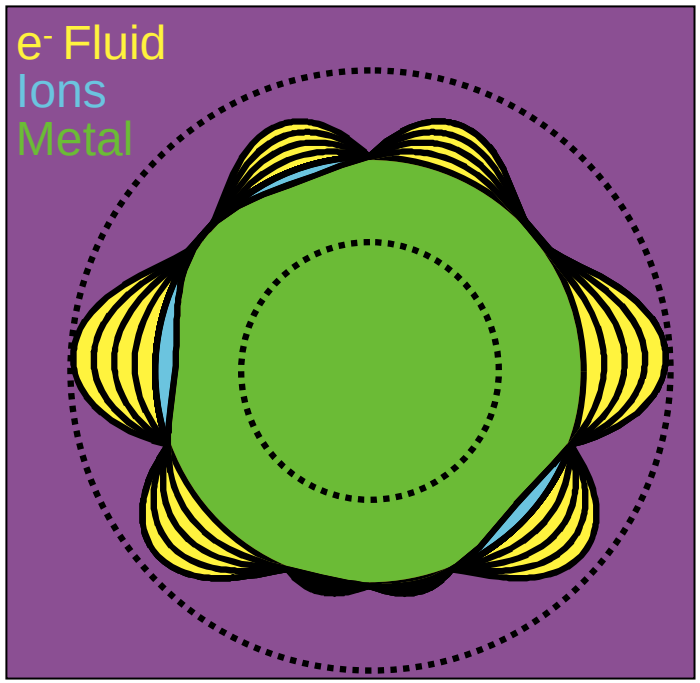
670 atoms per nanoshell diameter

Anything 1 billionth - 1 millionth of a meter in size:

- Molecules
- Viruses
- Transistors

Nanoparticle Plasmons

Metal = Fixed Ions + Incompressible Electron Fluid



Metal Sphere

↓

Excitation

=

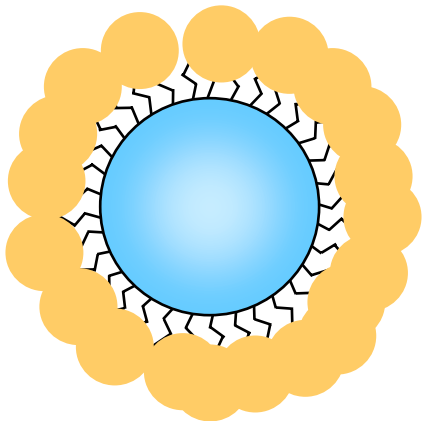
Incompressible Deformation

↓

Oscillates

Fabrication of Silica-Gold Nanoshells

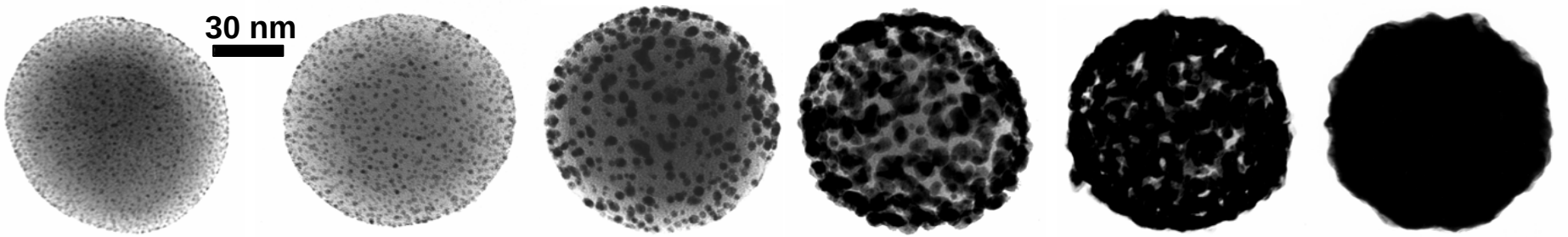
SiO_2 nanoparticle core (~100 nm)



surface terminated with amines

ultrasmall (1-2 nm) gold colloid attached

additional gold plated until gold shell is complete

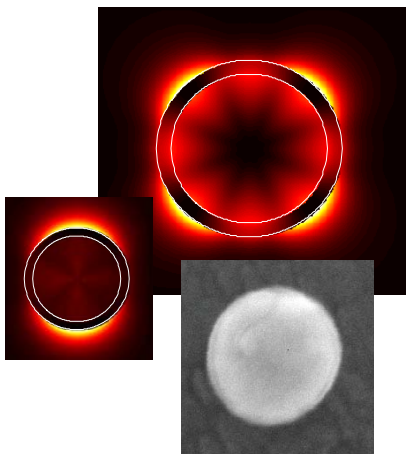


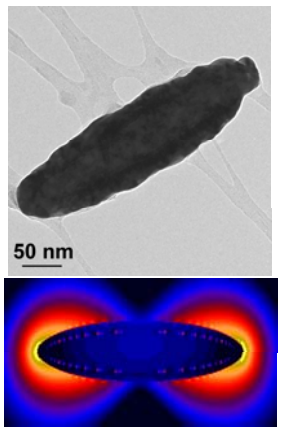
Plasmonics: manipulating light at the nanoscale

Plasmon: collective oscillation of all delocalized electrons in a metal

Properties: energies, near field spatial distributions, linewidths controlled by metal, shape and interactions

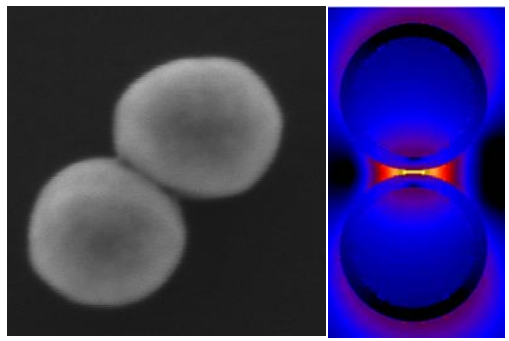
nanoshells

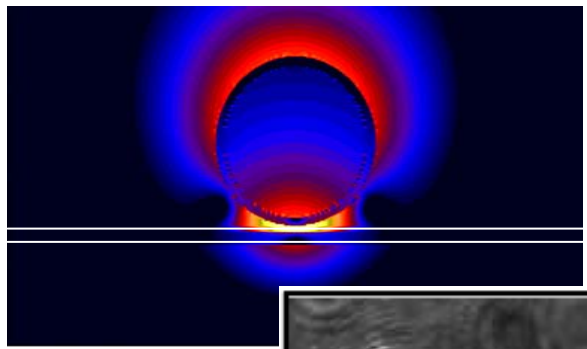




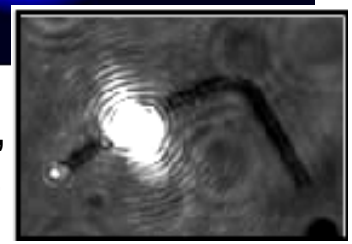
nanorice

“dimers”: nanocavities





Particle-film, particle-wire



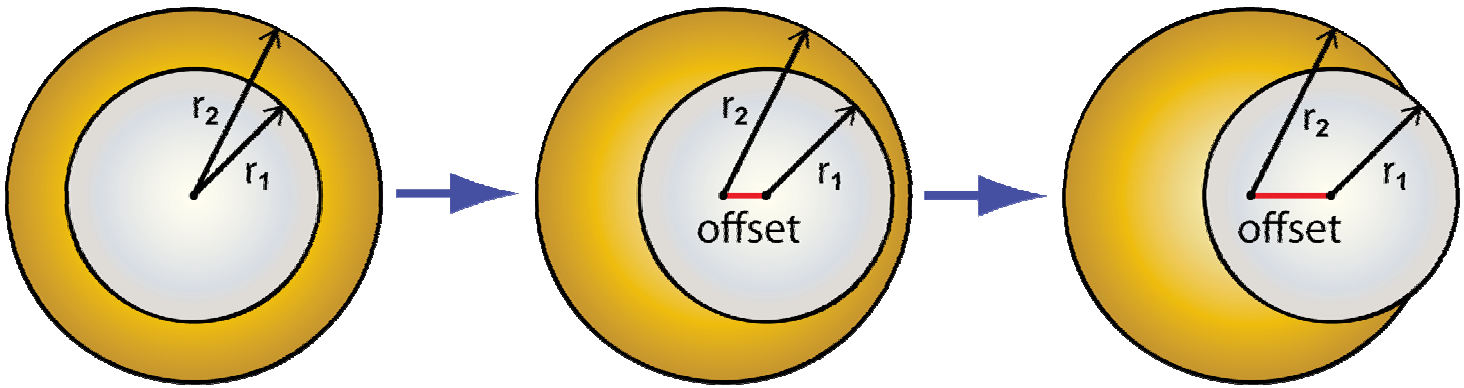
Symmetry breaking at the nanometer scale:

Nanoshells to Nanoeggs to Nanocups

Nanoshells, Nanoeggs, Nanocups

- Three related particle types, all based on core-shell geometry
  - Dielectric core: silica ($\varepsilon = 2.04$)
  - Metallic shell: J&C gold, linear interpolation

Johnson P and Christy R *Phys. Rev. B* **6** 4370–9 (1972)



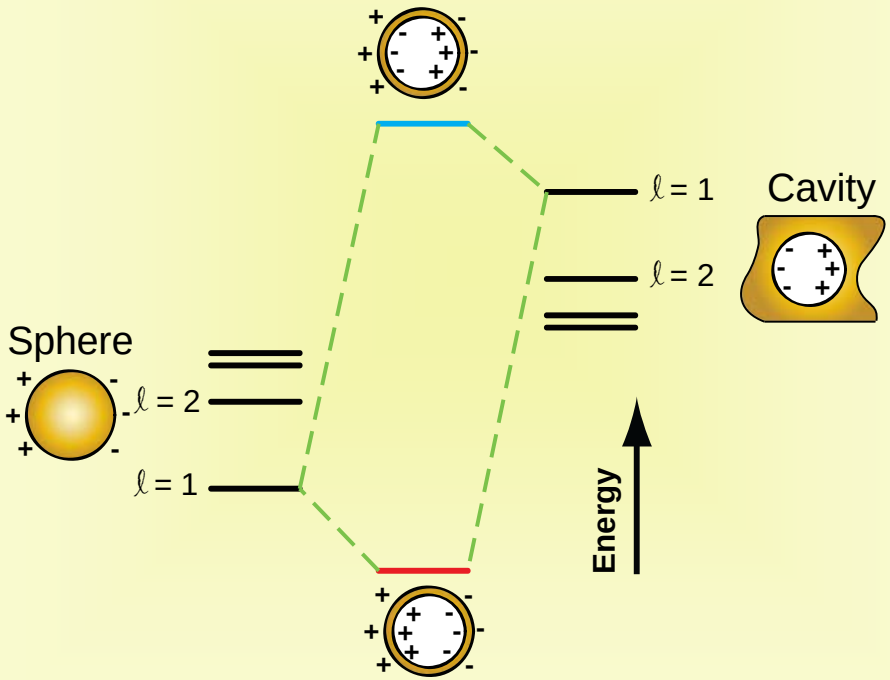
- Single symmetry parameter

$$D = offset/(r_2 - r_1)$$

- Parameters considered
  - Near-field enhancements
  - Far-field absorption, scattering spectra

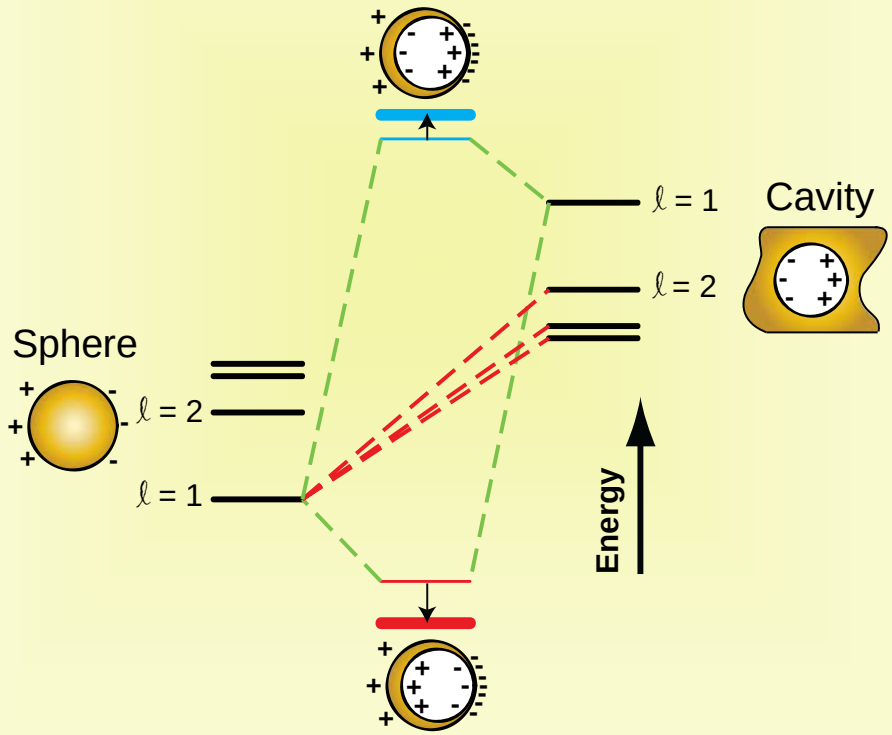
Plasmons interact just like electron wave functions

Nanoshells



- Only primitive modes with identical angular momentum indices hybridize

Nanoeggs, nanocups

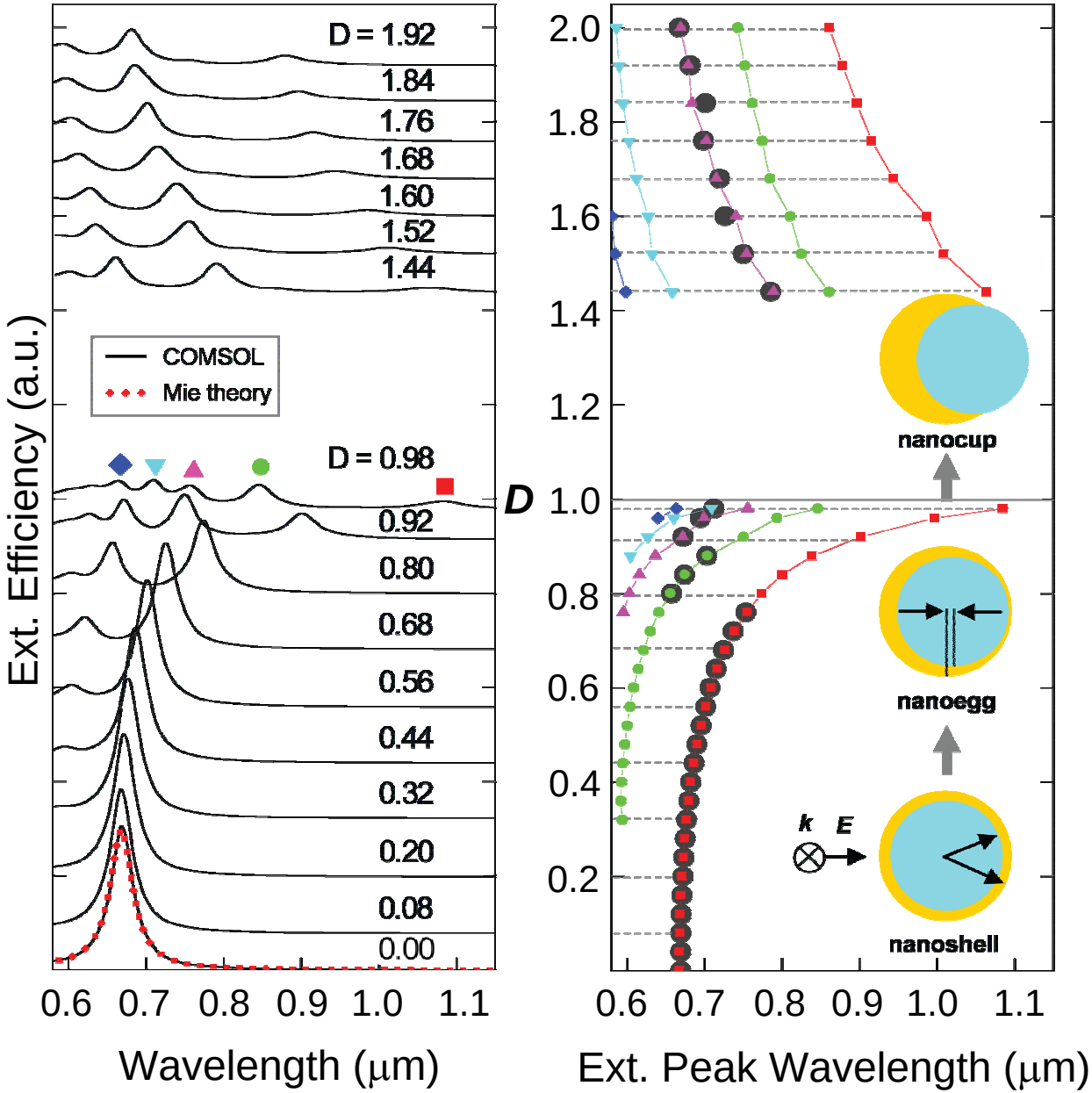


- All primitive modes can hybridize
- Core offsets approaching shell thickness cause stronger hybridization, larger energy level splitting

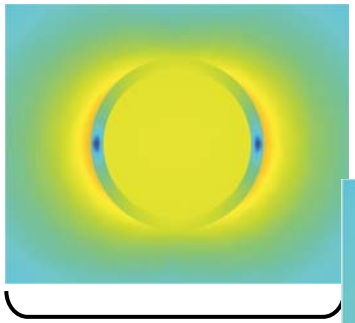
E. Prodan et al., ***Science 302*** *(2003) 419-21.*

Far-field Spectra of Nanoparticles

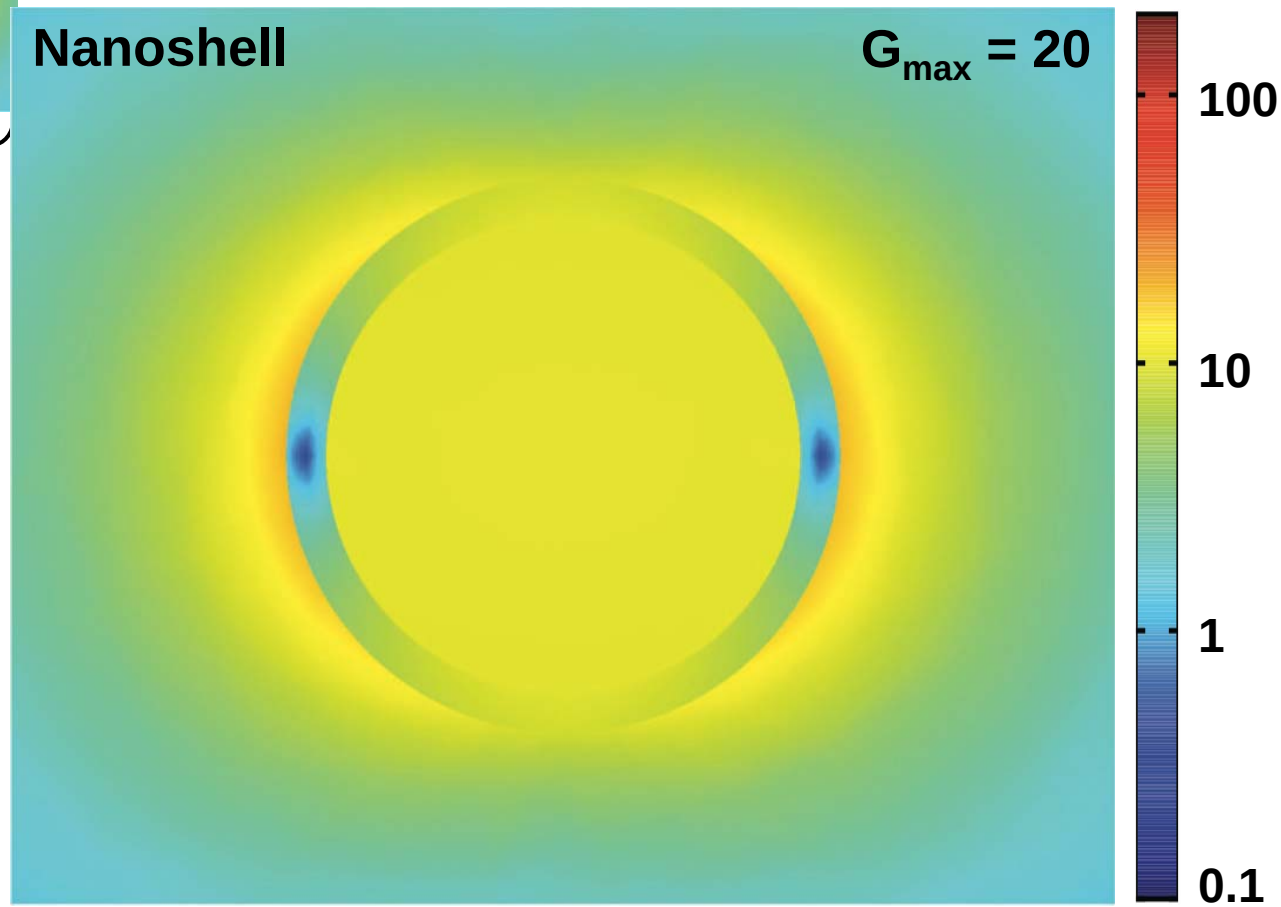
- Increased offsets cause:
  - Redshift hybridized peaks
  - Higher order peaks
- Hybridization view
  - Mixed higher-order primitive modes become dipole active with increased offsets
  - Hybridization strongest with thinnest shell



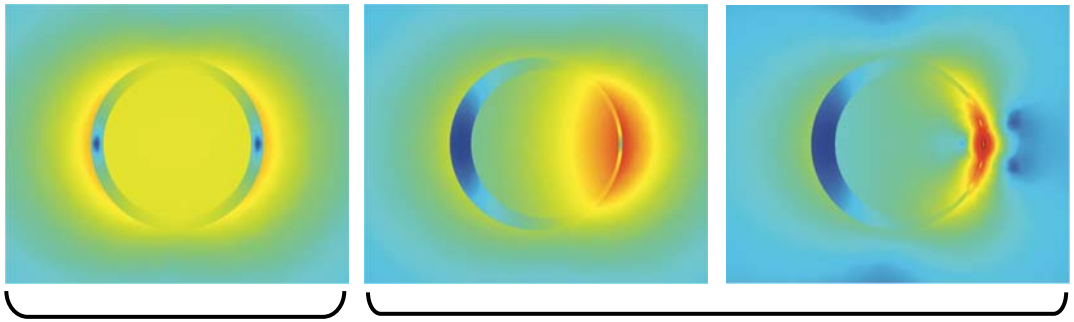
Near-field Enhancements – [30, 35] nm



Nanoshell

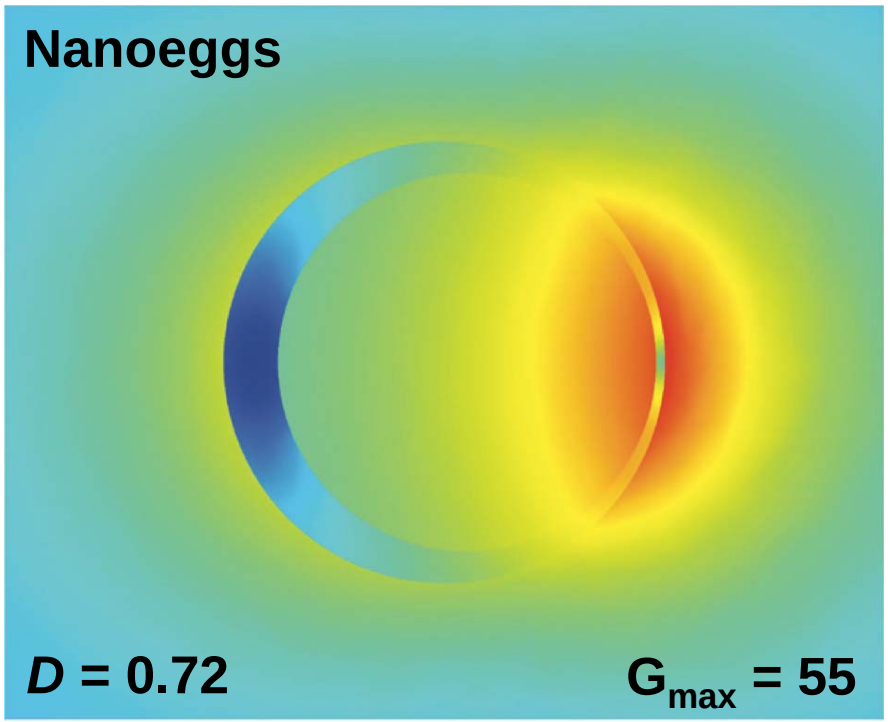


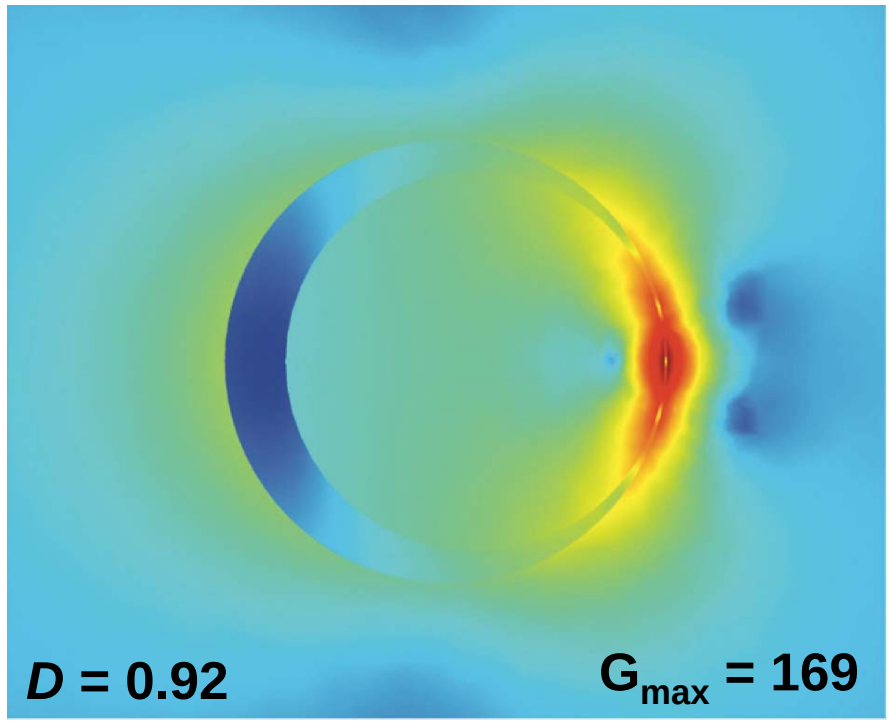
Near-field Enhancements – [30, 35] nm



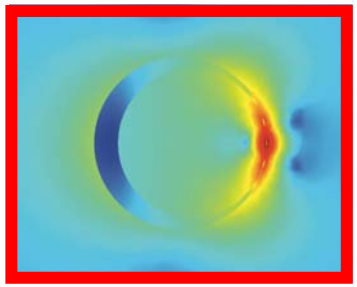
Nanoshell

Nanoeggs





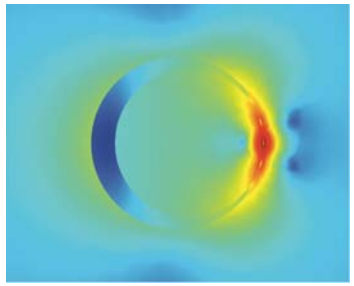
Near-field Enhancements – [30, 35] nm



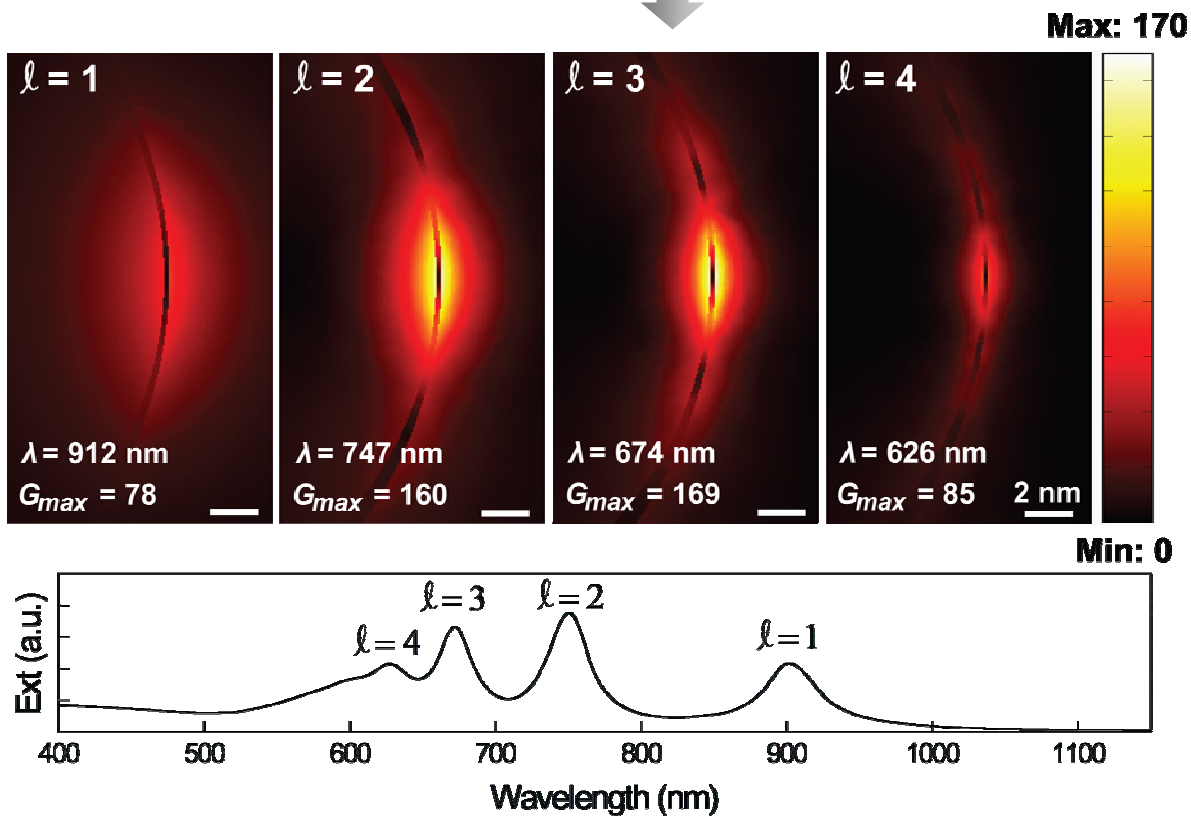
Nanoshell **Nanoeggs** **Nanocups**

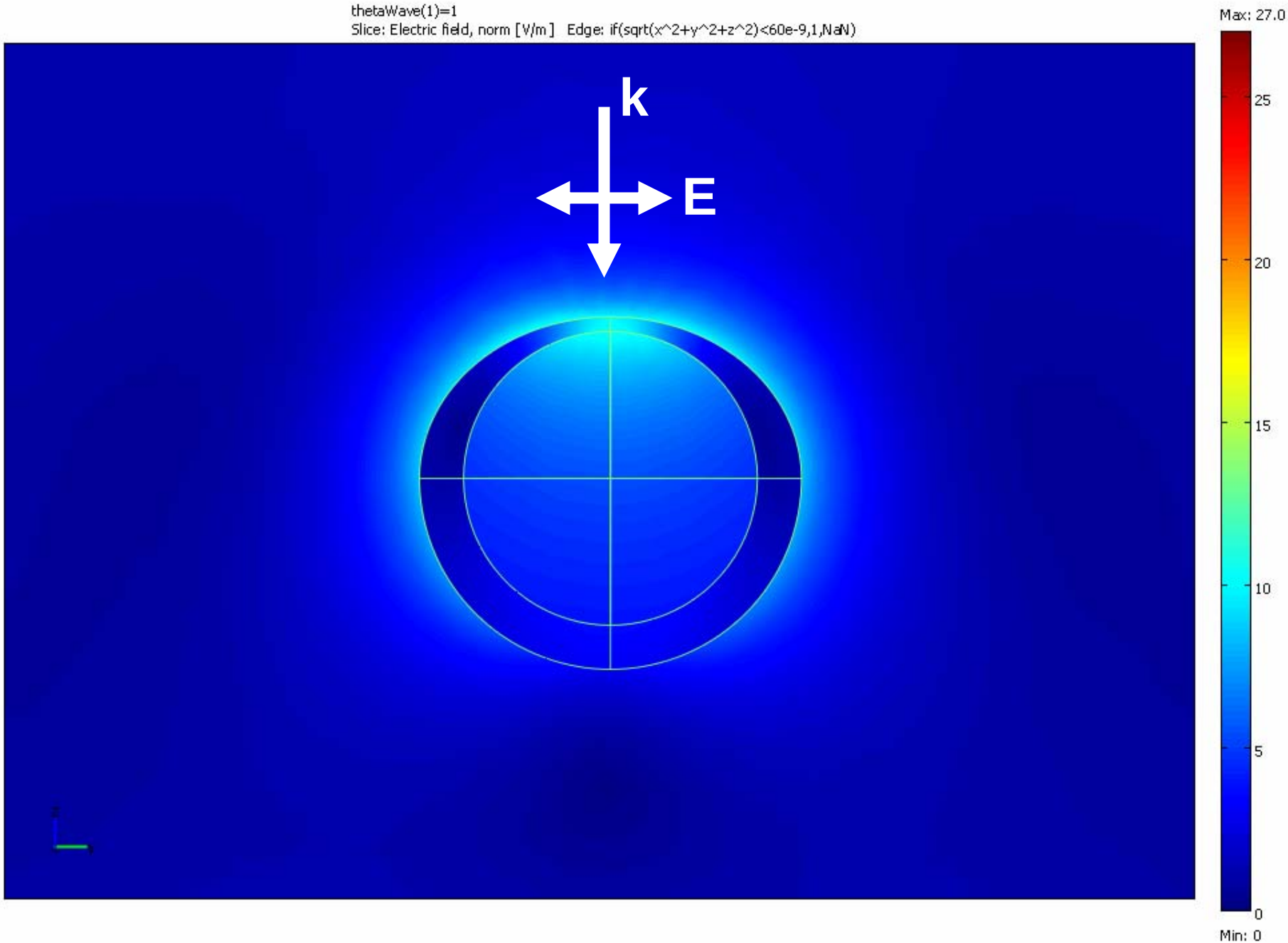
- Offsets near $D = 1$ give largest enhancements
- Field enhancements are on an open surface, not a gap
  - Potential for use as surface-enhanced spectroscopy substrate
- For each offset, other resonances also show significant enhancements

Near-field Enhancements – [30, 35] nm



- Near-field focusing depends on which resonance is excited
- Nanoeggs function as chromatic nanolenses
- Maximum enhancement does not correspond to largest extinction peak




thetaWave(1)=1
Slice: Electric field, norm [V/m] Edge: if(sqrt(x^2+y^2+z^2)<60e-9,1,NaN)
k
E
Max: 27.0
25
20
15
10
5
0
Min: 0

Coupling Light into a Nanowire

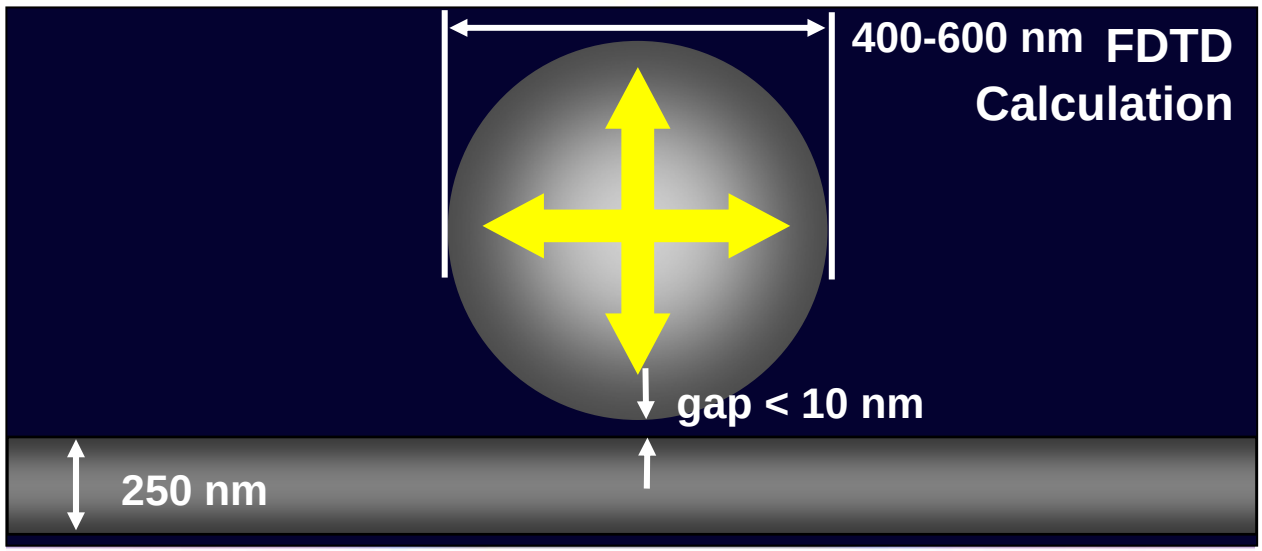
Connecting nanoscale optics to the macroscale

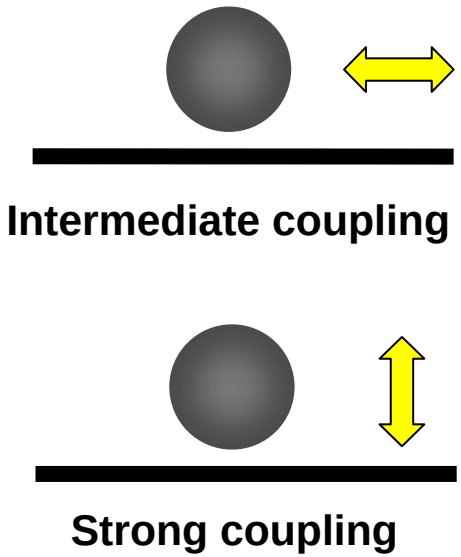
Desired: *Simple input/output port for nanowire waveguides*

Possible use: basic geometry scalable, possibly useful for planar on-chip interconnects

Experimental test of particle/wire plasmon hybridization

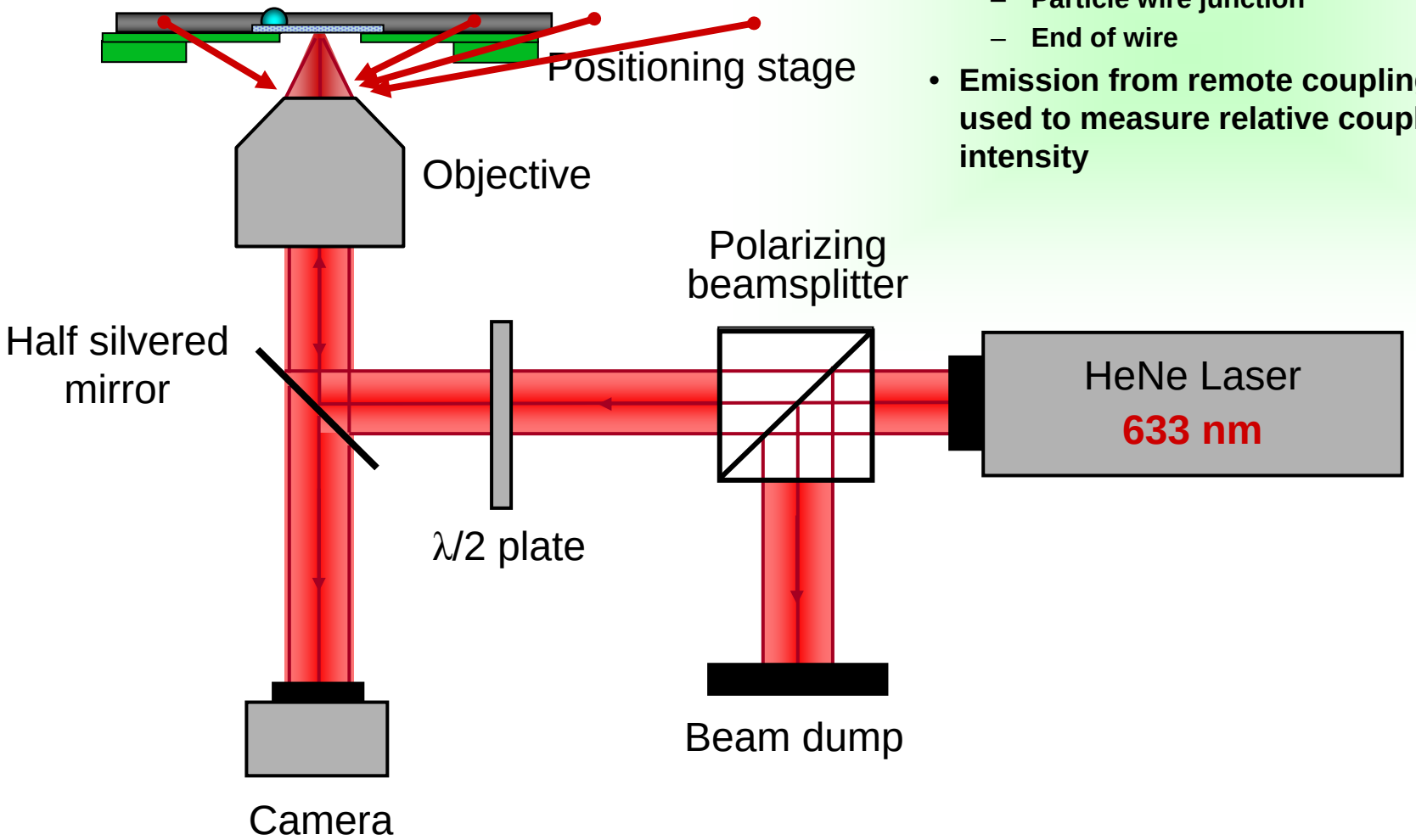
- **Theory**: F. Hao and P. Nordlander. *Appl. Phys. Lett.,* **89**, 103101 (2006)
- Increasing particle diameter relative to wire diameter redshifts resonance
- Decreasing gap relative to particle diameter increases coupling intensity





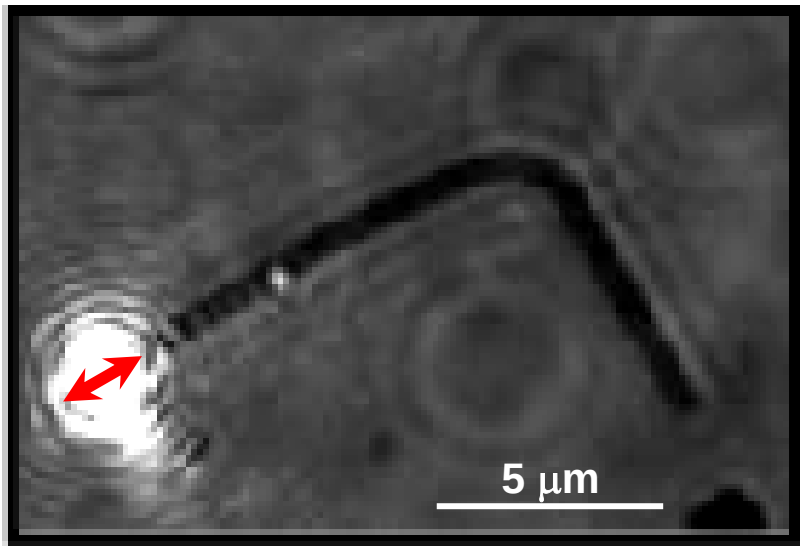
Experiment:

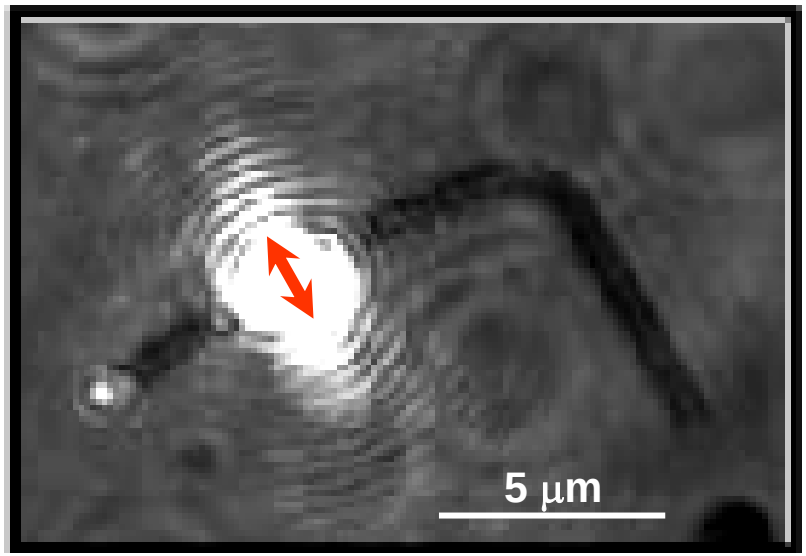
Nanowires on glass coverslip
Nanowire sample



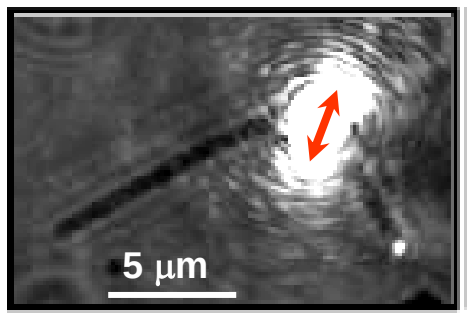
- **Wires, particles deposited via drop casting**
- **Laser used to excite plasmons at:**
  - **Particle wire junction**
  - **End of wire**
- **Emission from remote coupling sites used to measure relative coupling intensity**

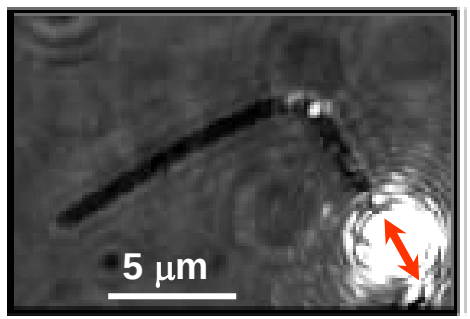
Images of Coupling into a Nanowire



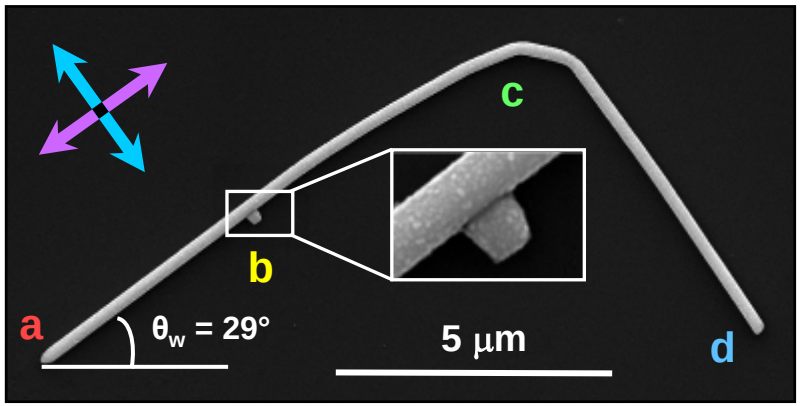


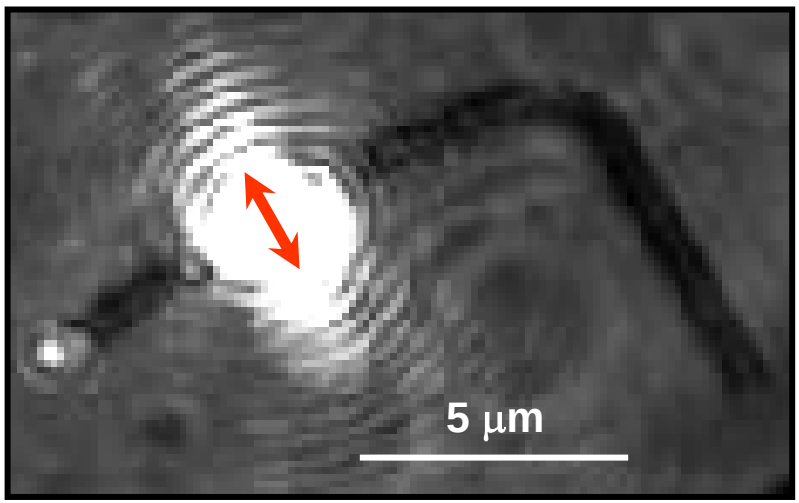
- All sites of broken symmetry can be used to couple light into the nanowire:
  - Ends
  - Kink
  - Particle
- Red arrows indicate excitation laser polarization

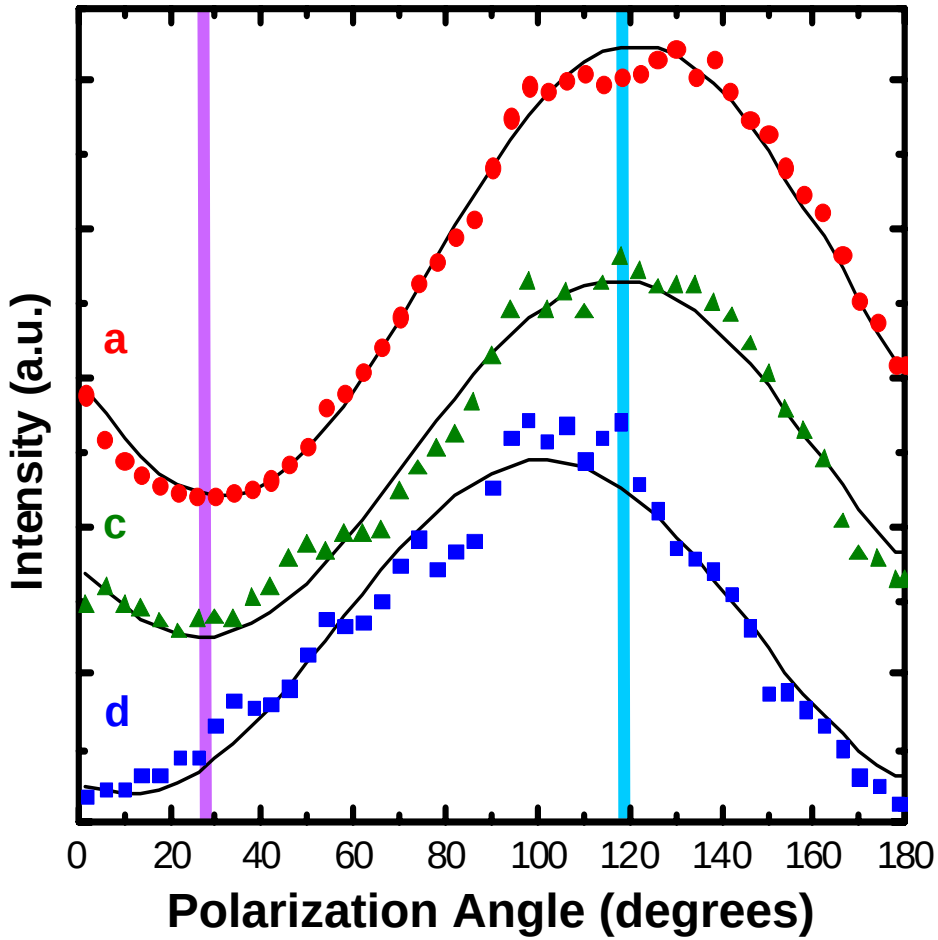




Polarization Dependence of Long Wire Coupling

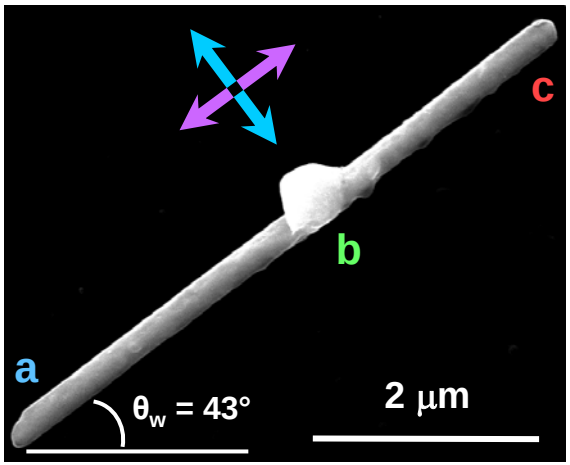


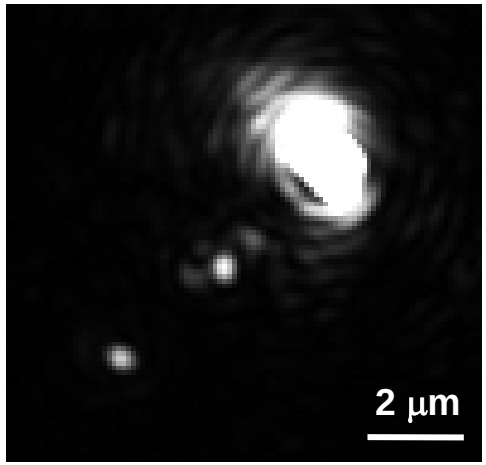


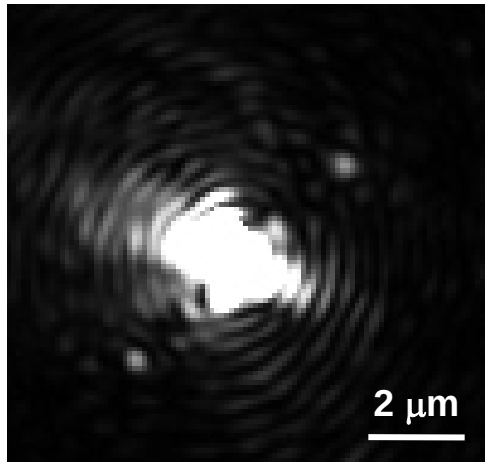


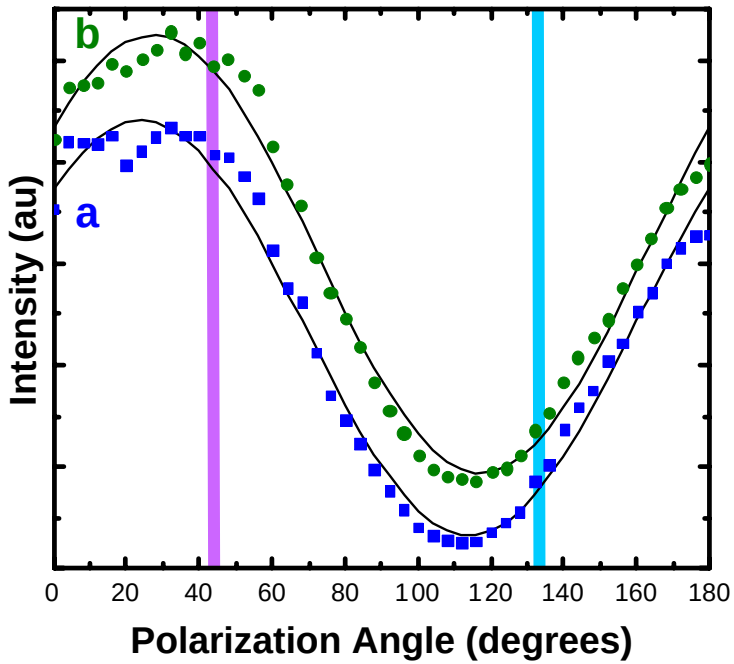
In agreement with theory, long wires show aligned emission peaks

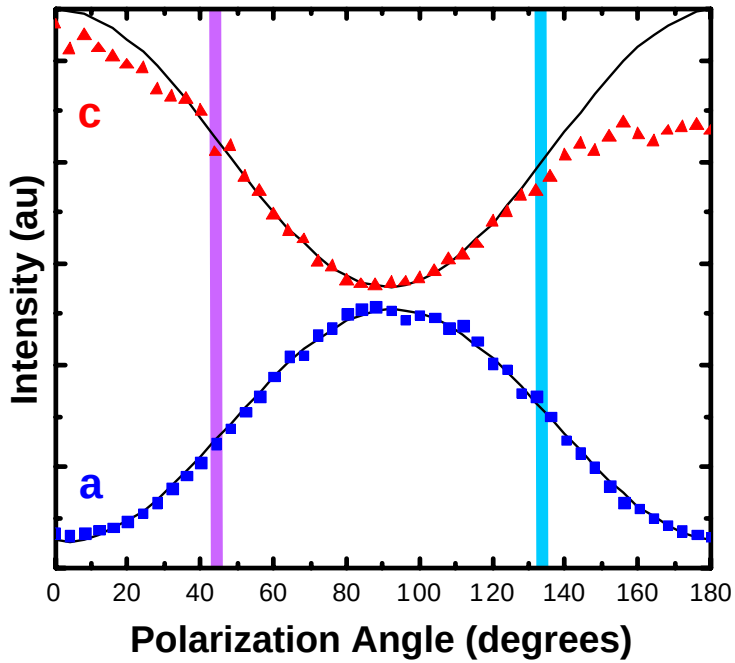
Short Wires behave differently!







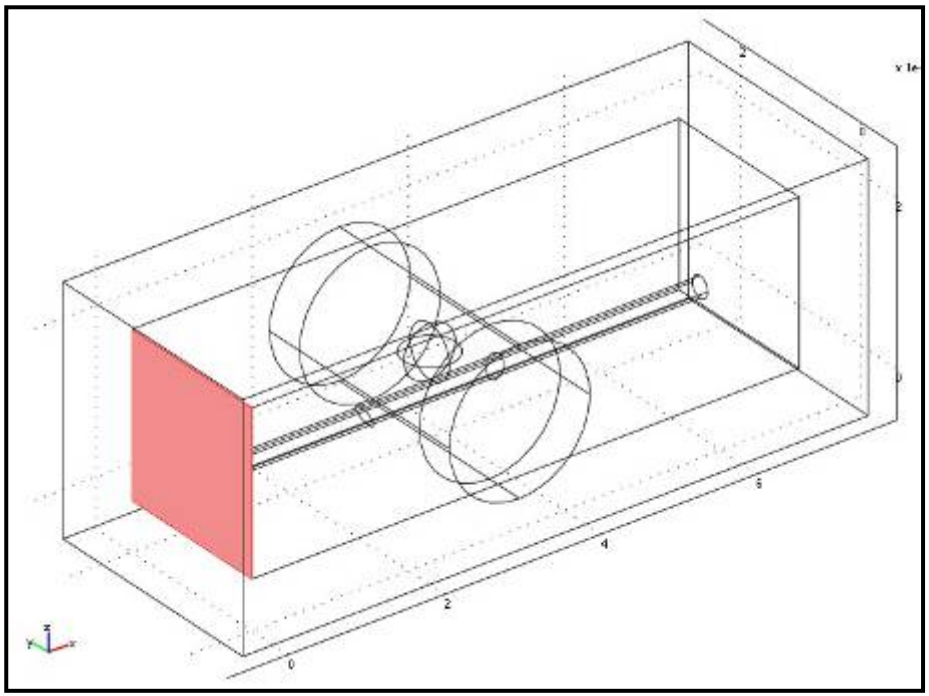


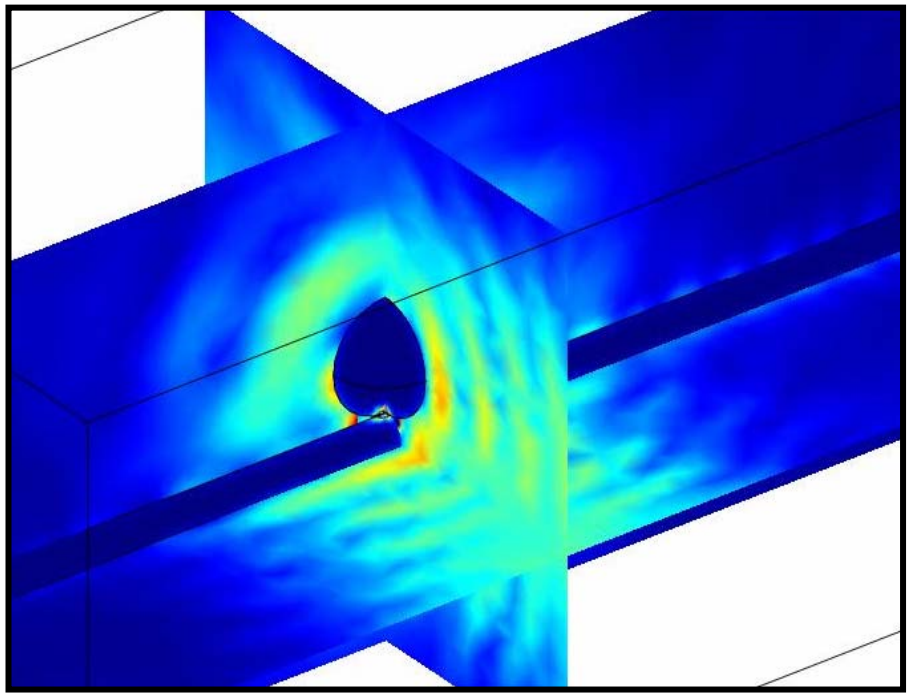


Localized Plasmons + Extended Structure = Multiscale

- FDTD, FEM both useful for isolated nanoparticles
- For multiscale problems, the fixed Cartesian grid size used in FDTD makes determining a solution computationally difficult
- Adaptive meshing in COMSOL allows treatment of extended, multiscale structures
  - Particle & wire problem

COMSOL Simulations of Short Wire

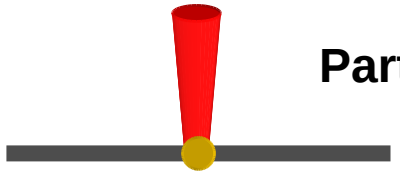




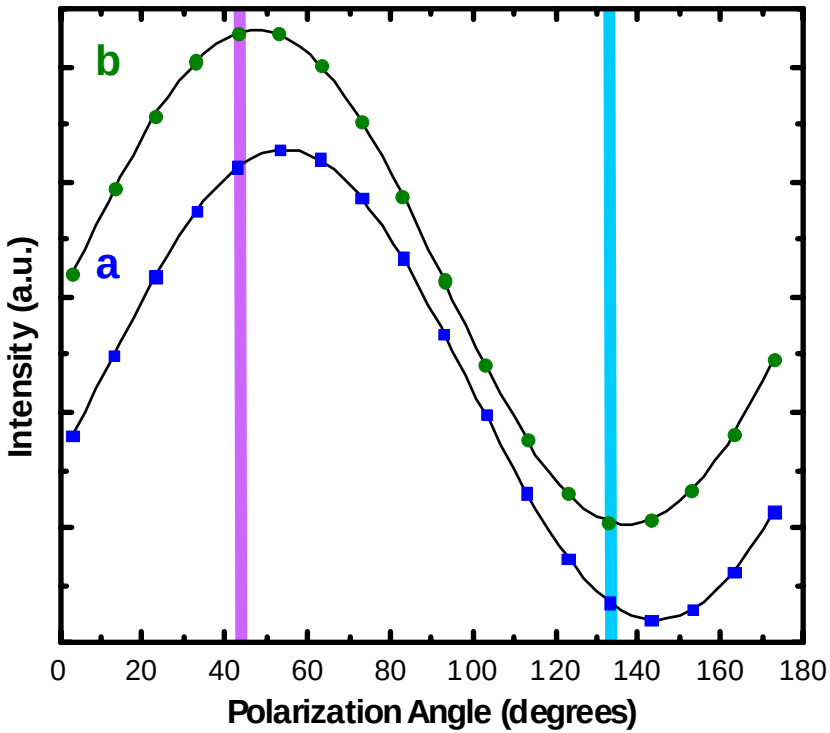
- Model dimensions identical to measured dimensions of nanowire/particle pair
- Scattering boundaries on outer surface
- Polarized, Gaussian beam used for excitation
- Far-field transforms applied near each point of broken symmetry to calculated far-field emissions

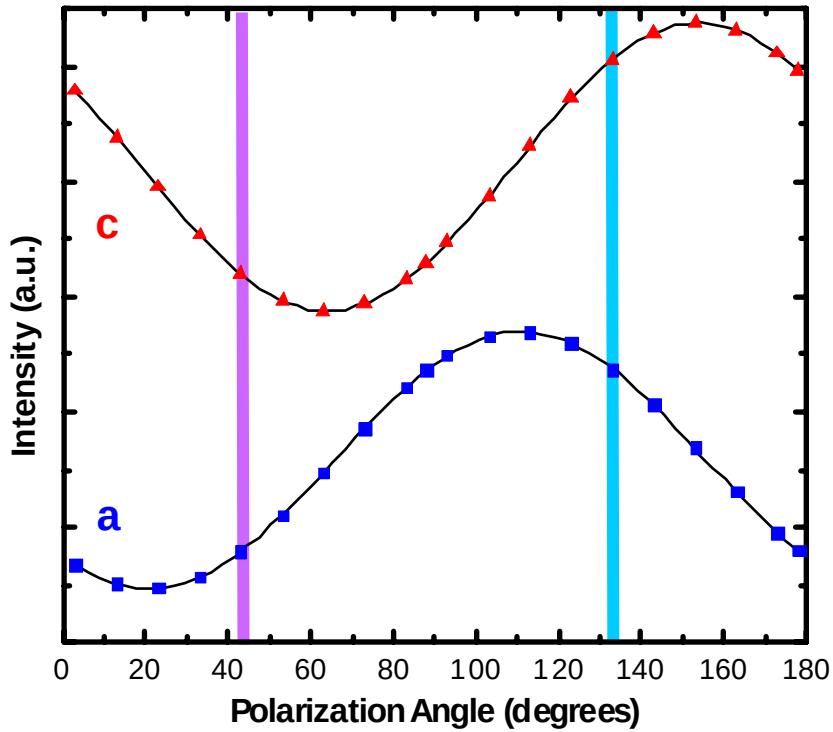
Calculated Polarization Dependence

End excitation



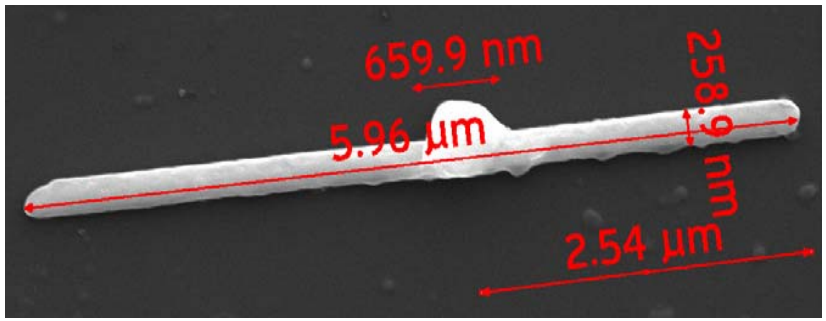
Particle excitation

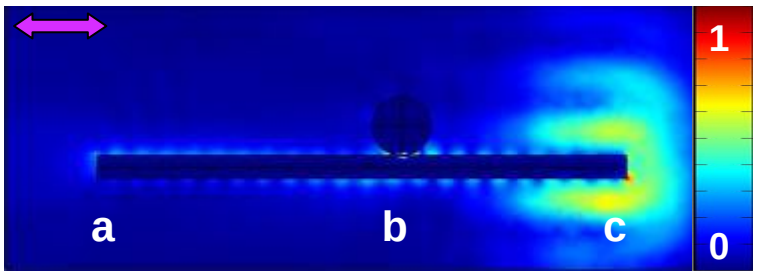


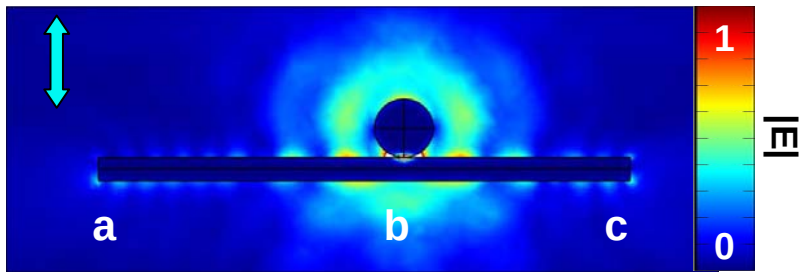


- Normalized far-field intensities show the same trend observed experimentally
- Sensitive dependence on wire length corresponds to Fabry-Perot response of plasmonic cavity

Standing-wave response of wire







- Near-field response of nanowire shows standing waves

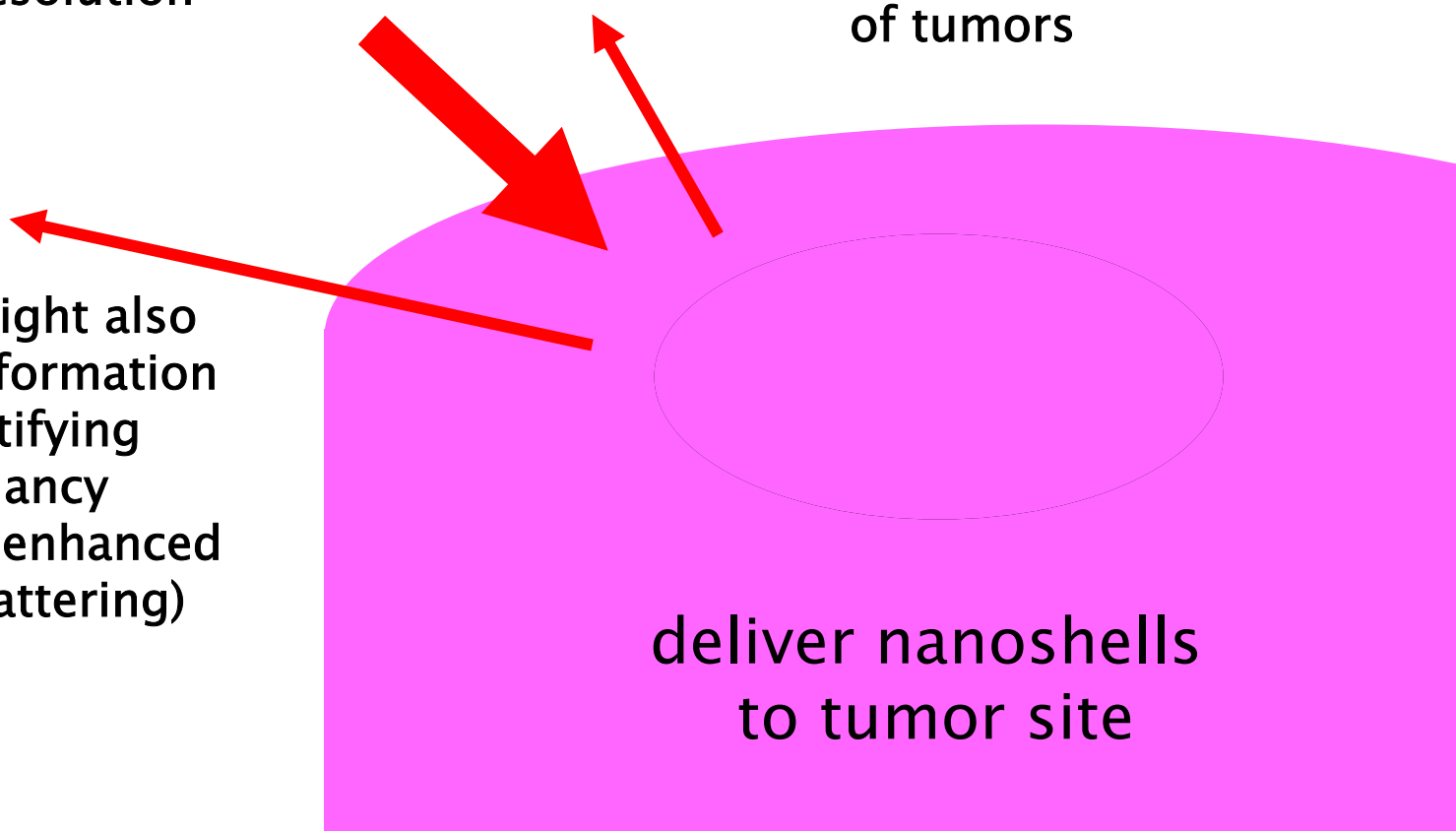
Plasmonic Nanocups

Effects of Geometry and Dielectric Resonance

Nanoshell-assisted Seamless Integration of Screening and Therapy: “See and Treat”

nanoshells provide vivid contrast enhancement, increase image resolution

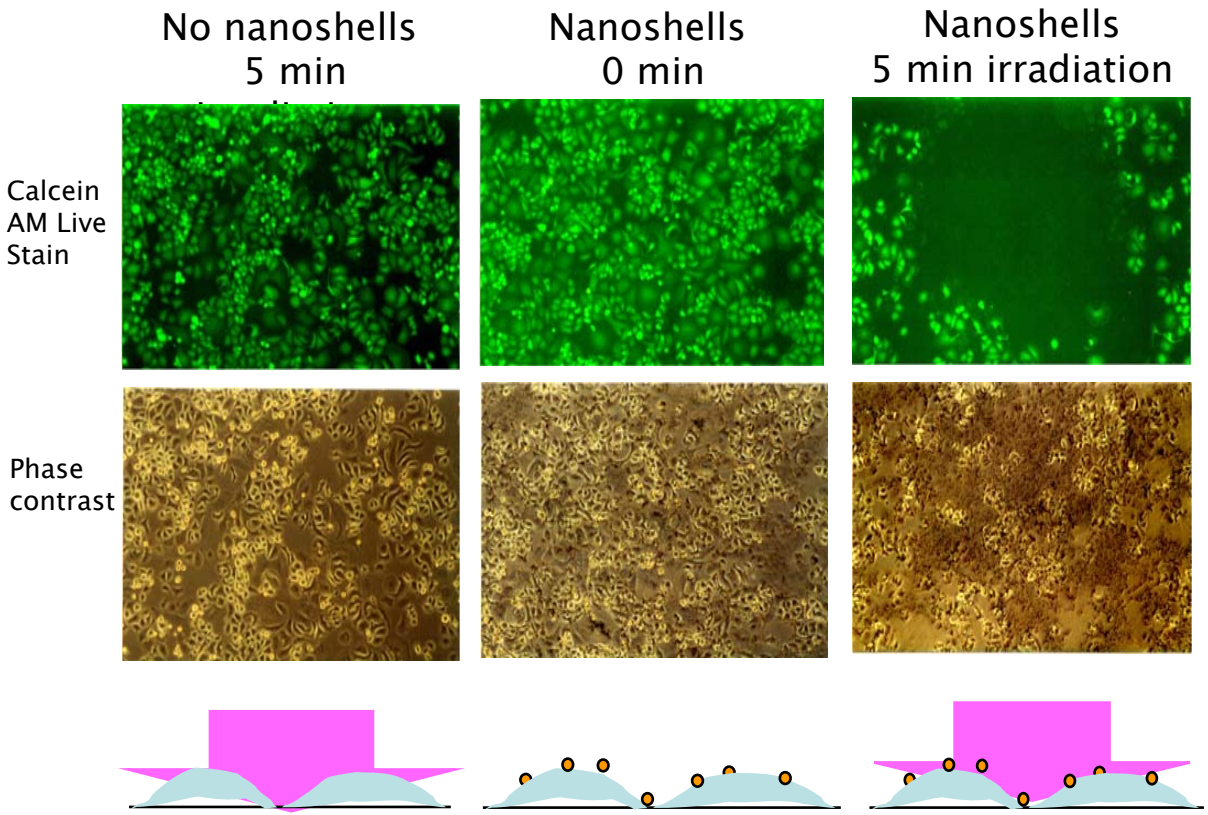
nanoshells are a photothermal heat source for remote destruction of tumors



scattered light also provides information for identifying malignancy (Nanoshell-enhanced Raman Scattering)

deliver nanoshells to tumor site

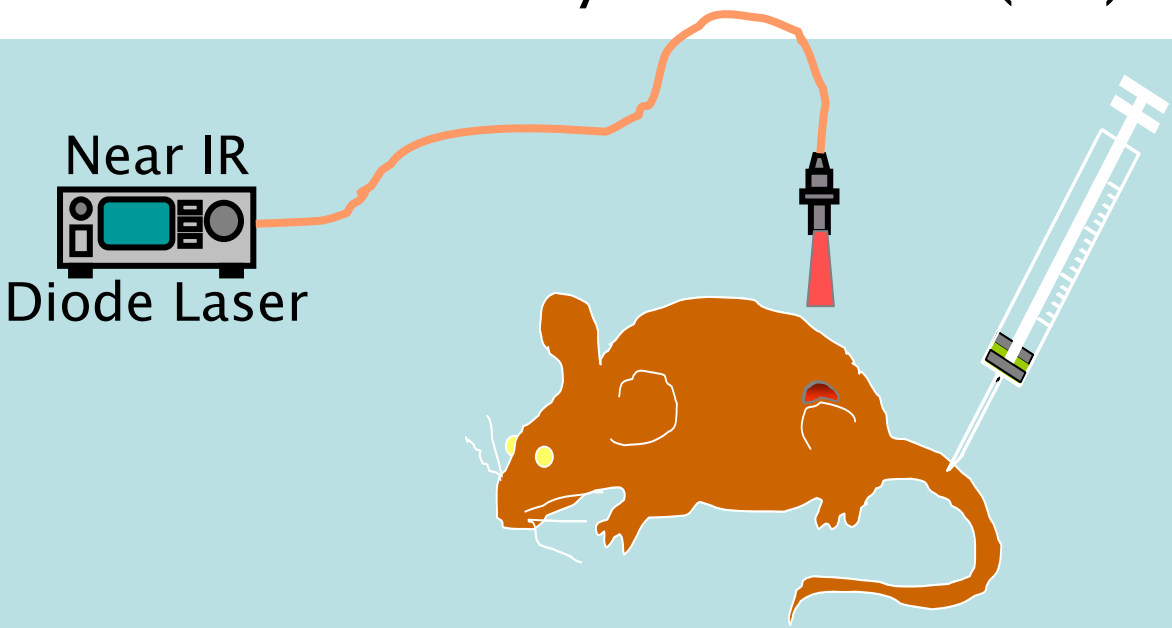
Nanoshell-assisted Cancer Therapy



L. R. Hirsch, R. J. Stafford, J. A. Bankson, S. R. Sershen, R. E. Price, J. D. Hazle, N. J. Halas, and J. L. West, "Nanoshell-Mediated Near Infrared Thermal Therapy of Tumors Under MR Guidance" , PNAS 100, 13549-13554 (2003).

Systemically delivered nanoshell therapy

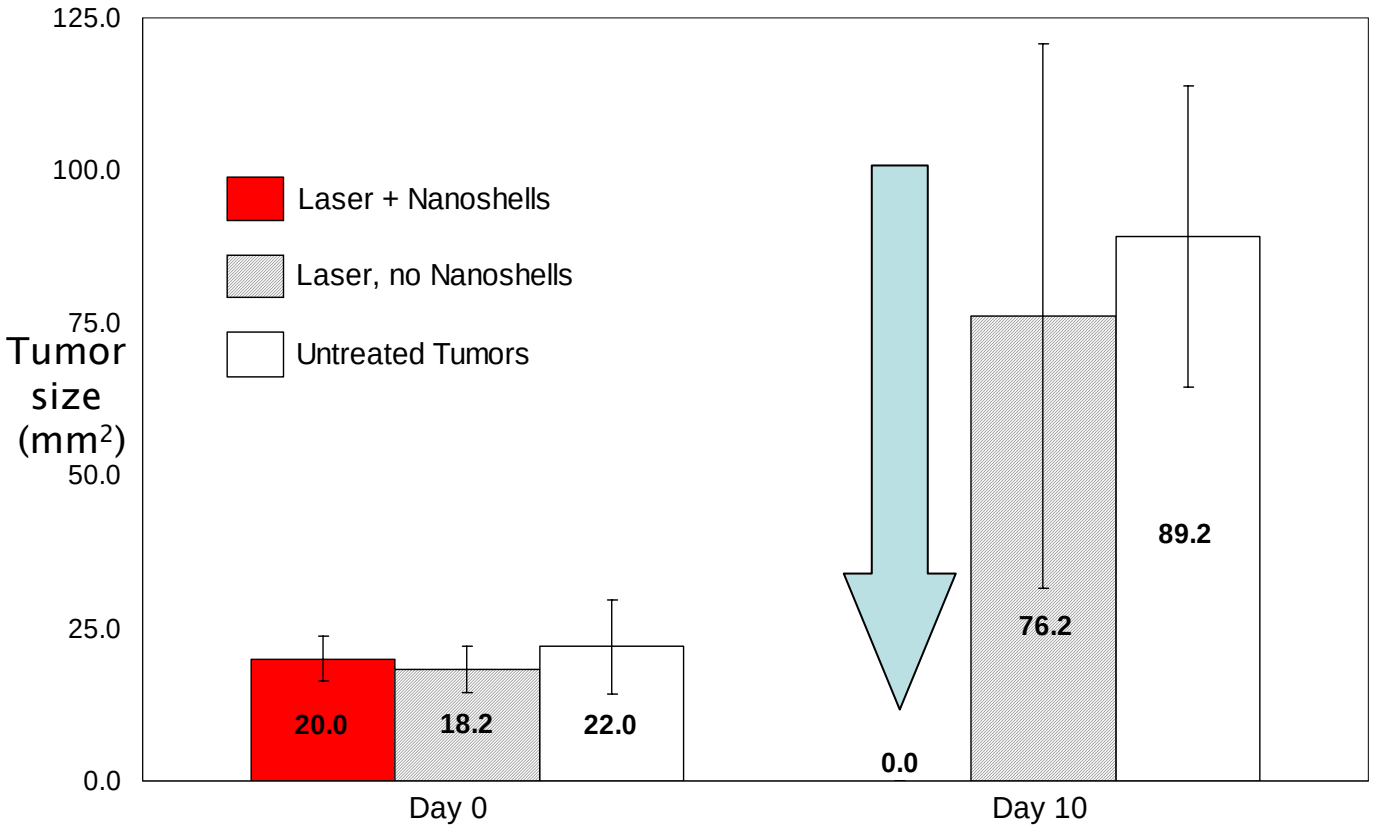
Nanoshell uptake entirely due to Enhanced Permeability and Retention (EPR) Effect



- BALB/c mice innoculated with CT26.wt mouse colon carcinoma cell line
- Systemically delivered pegylated nanoshells via tail vein injection
- 6 hrs post injection, tumors irradiated with 4 W/cm^2 810 nm diode laser source for 3 min
- Tumor surface temp. monitored using infrared thermometer.
- Resultant tumor size monitored for up to 2 months

P. O'Neal, L. R. Hirsch, J. D. Payne, N. J. Halas, and J. L. West, Cancer Letters 209 (2004) 171-176.

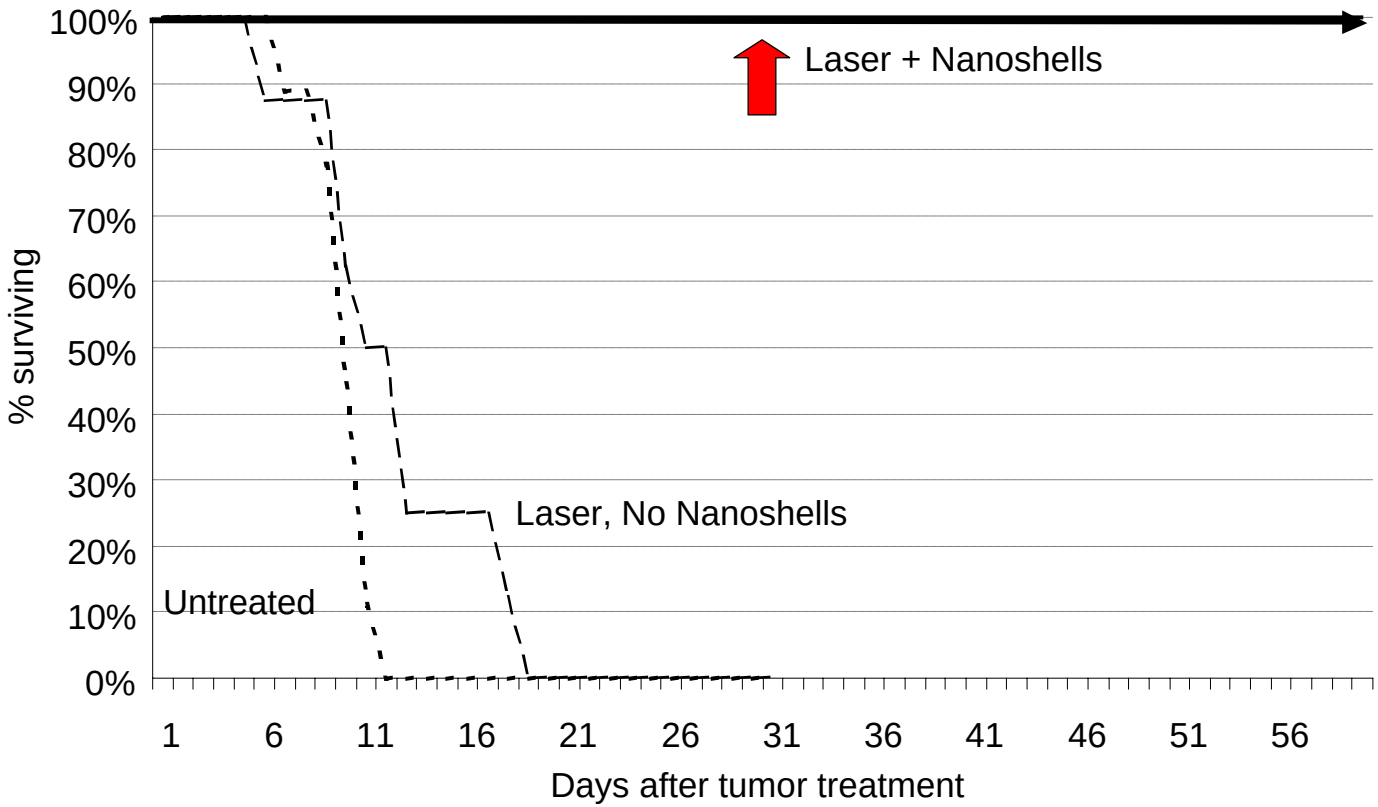
Tumor size before and after therapy



No measurable tumor mass was found in any nanoshell/laser treatments after 10 days

Complete regression of all tumors receiving nanoshell/laser treatments

Mouse Survival after Therapy



Untreated tumors:

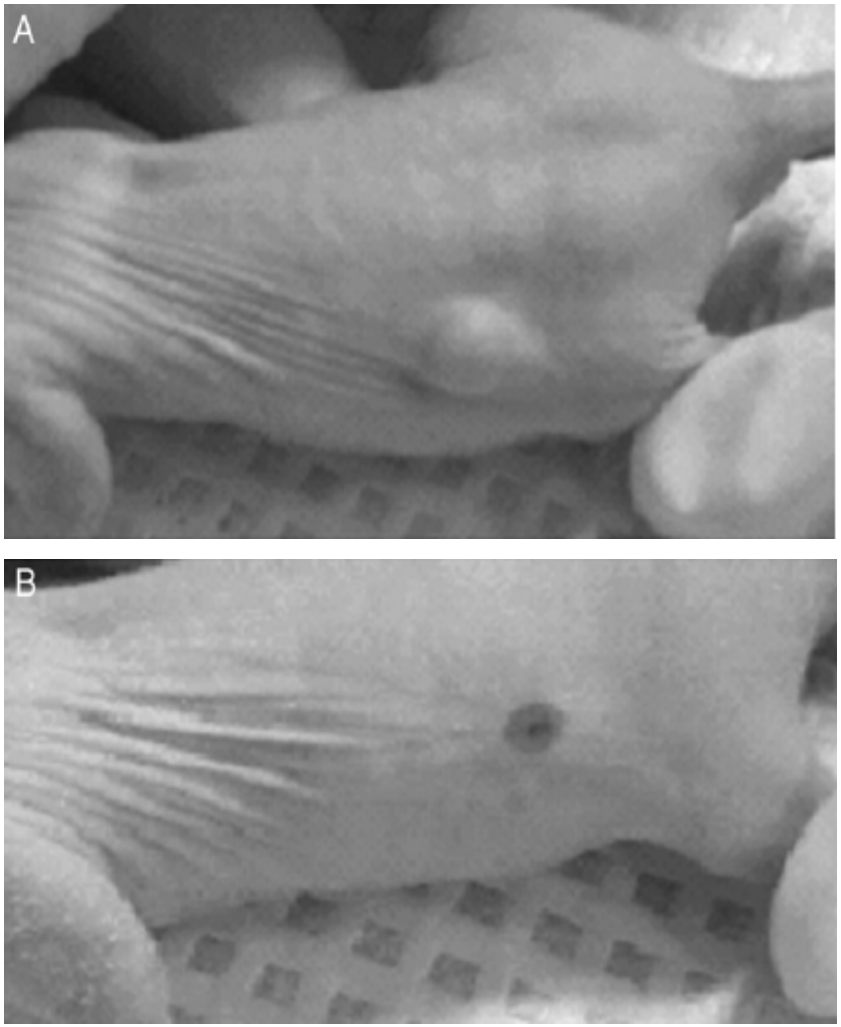
- Mean survival of 10 days

Laser controls:

- Mean survival of 12.5 days

100% of all mice receiving nanoshell/laser therapy survived to end of study (60 days)

Nanoshell-based photothermal cancer therapy



J. Cadeddu et al., J. Urology 179, 748-753 (2008)

Pilot-phase clinical trials of AuroLase™ therapy FDA-approved and ongoing 2008: untargeted head and neck cancer
UT San Antonio, UTSW Dallas, BCM (Houston), Tulane (NO)

Conclusions

Plasmonics: an emerging science and technology

Simulations help both theorists and experimentalists!

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NASA NSF AIR FORCE OFFICE OF SCIENTIFIC RESEARCH UNITED STATES AIR FORCE SCIENCE TO SHAPE THE FUTURE OF THE ARMY ARMY RESEARCH LAB 1951 THE Welch FOUNDATION Advancing Chemistry. Improving Life.

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