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Support:

Nanoplasmonics:
Optical Properties of Plasmonic Nanosystems

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Lecture 2:

Nanoplasmonics of Nanosystems

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LECTURE 2

Nanoplasmonics of Nanosystems

1. Introduction; Local fields of a sphere and lifetimes
2. Localized SP resonances (SPs or LSPRs): Quasistatic eigenmodes
3. Nanoshells, their eigenmodes and absorption cross section
4. SERS
5. Applications to nanoscopy
6. Aggregates of nanospheres; nanolenses
7. Extreme nanoplasmonics (optional)

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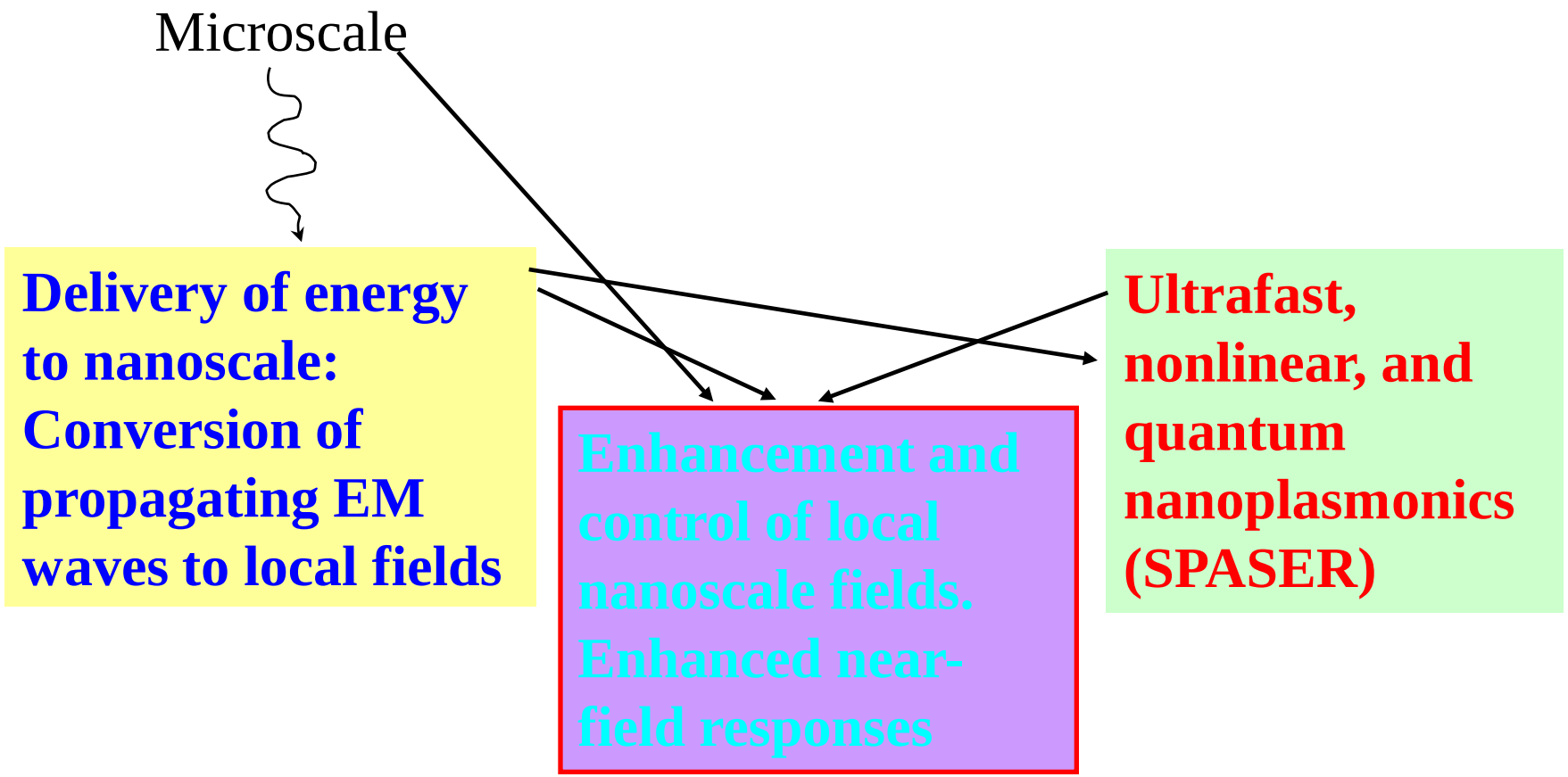
PROBLEMS IN NANOOPTICS



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Plasmonic Hot Spots

19th Anniversary

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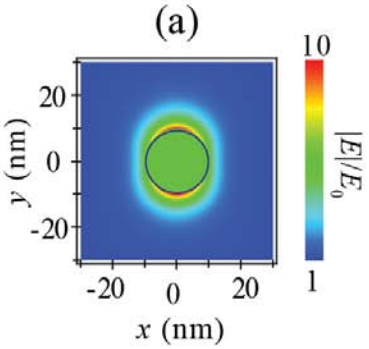
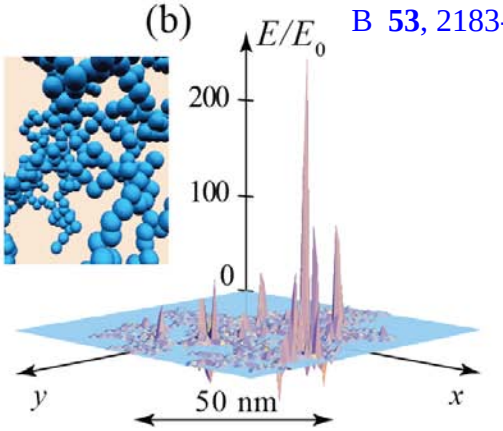
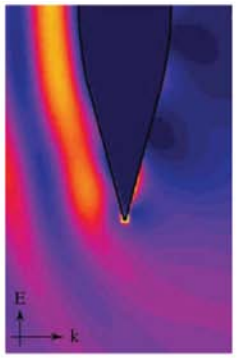
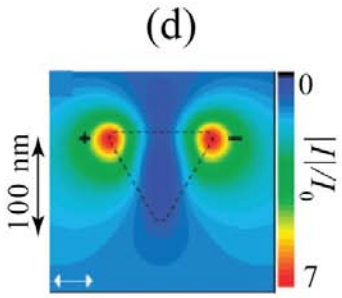
- M. I. Stockman, L. N. Pandey, and T. F. George, Phys. Rev. B **53**, 2183-2186 (1996)







L. Novotny and S. J. Stranick, Annual Rev. Phys. Chem. **57**, 303-331 (2006)



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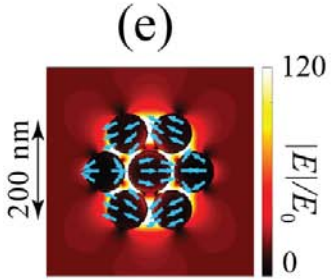
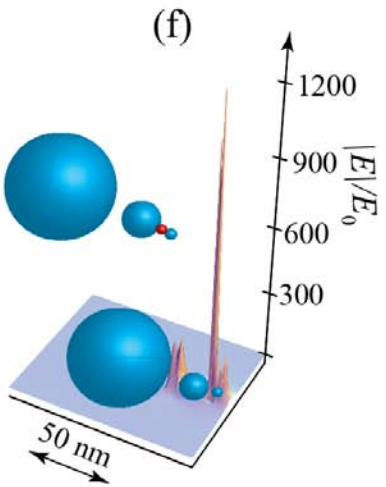
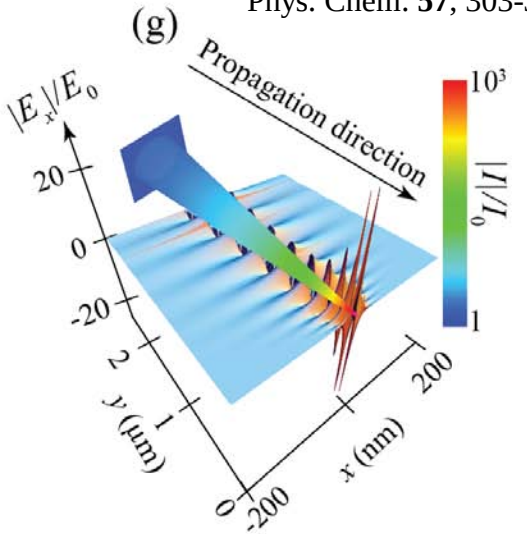


- J. A. Fan et al., Science **328**, 1135 (2010)
- M. Hentschel et al., Nano Lett. **10**, 2721 (2010)



K. Li, M. I. Stockman, and D. J. Bergman, Phys. Rev. Lett. **91**, 227402 (2003)



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Quasistatic Approximation and Eigenmodes

For a nanosystem, size is much less than the radiation wavelength and skin depth. In this case, one can neglect retardation, and describe the system by quasistatic equations for electrostatic potential.

Quasistatic approximation does not imply that the excitation processes are slow. Just to the opposite, the neglectable retardation allows one to use and study ultrafast processes in nanostructures.

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Quasistatic Field Equations and Boundary Conditions

$$\frac{\partial}{\partial \mathbf{r}}\varepsilon(\mathbf{r},\omega)\frac{\partial}{\partial \mathbf{r}}\varphi(\mathbf{r})=0\,,\ \varphi(x,y,0)=0\,,\ \varphi(x,y,L_z)=1\,,$$

$$\left.\frac{\partial}{\partial x}\varphi(x,y,z)\right|_{x=0,L_x}=\left.\frac{\partial}{\partial y}\varphi(x,y,z)\right|_{y=0,L_y}=0\,.$$

Quasistatic Fields as Expansion over Eigenmodes for Spherical Particles

$$\varphi_2(l,m,r,\theta,\varphi)=\left[a_2(l,m)\frac{1}{r^{l+1}}+b_2(l,m)r^l\right]Y_{lm}(\theta,\varphi),$$

$$\varphi_1(l,m,r,\theta,\varphi)=\left[a_1(l,m)\frac{1}{r^{l+1}}+b_1(l,m)r^l\right]Y_{lm}(\theta,\varphi).$$

Consider 1 as internal region and 2 as external.

Unity field at the infinity is given by a choice $b_2(l,m)=-1$;

Regularity in the center requires $a_1(l,m)=0$.

Maxwell boundary conditions at the surface of the sphere:

$$\varphi_1(l,m,R,\theta,\phi)=\varphi_2(l,m,R,\theta,\phi);$$

$$\varepsilon_1\frac{\partial}{\partial R}\varphi_1(l,m,R,\theta,\phi)=\varepsilon_2\frac{\partial}{\partial R}\varphi_2(l,m,R,\theta,\phi).$$

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Coefficients of eigenmodes expansion for L-multipole mode:

$$a_2(l,m)=\frac{R^{2l+1}l(\varepsilon_1-\varepsilon_2)}{\varepsilon_2+l(\varepsilon_1+\varepsilon_2)};\quad b_1(l,m)=\frac{(1+2l)\varepsilon_2}{\varepsilon_2+l(\varepsilon_1+\varepsilon_2)};\ .$$

$l-$multipolar polarizability: $\alpha_l=R^{2l+1}\dfrac{l(\varepsilon_1-\varepsilon_2)}{\varepsilon_2+l(\varepsilon_1+\varepsilon_2)};$

Dipolar polarizability: $\alpha_1=a_2(1,m)=R^3\dfrac{\varepsilon_1-\varepsilon_2}{\varepsilon_1+2\varepsilon_2}$;

In usual notations ($1\rightarrow$ m, $2\rightarrow$ d): $\alpha=R^3\dfrac{\varepsilon_m-\varepsilon_d}{\varepsilon_m+2\varepsilon_d}.$

Surface plasmon resonance of a sphere: $\mathrm{Re}\,\varepsilon_m(\omega_{sp})=-2\varepsilon_d$.

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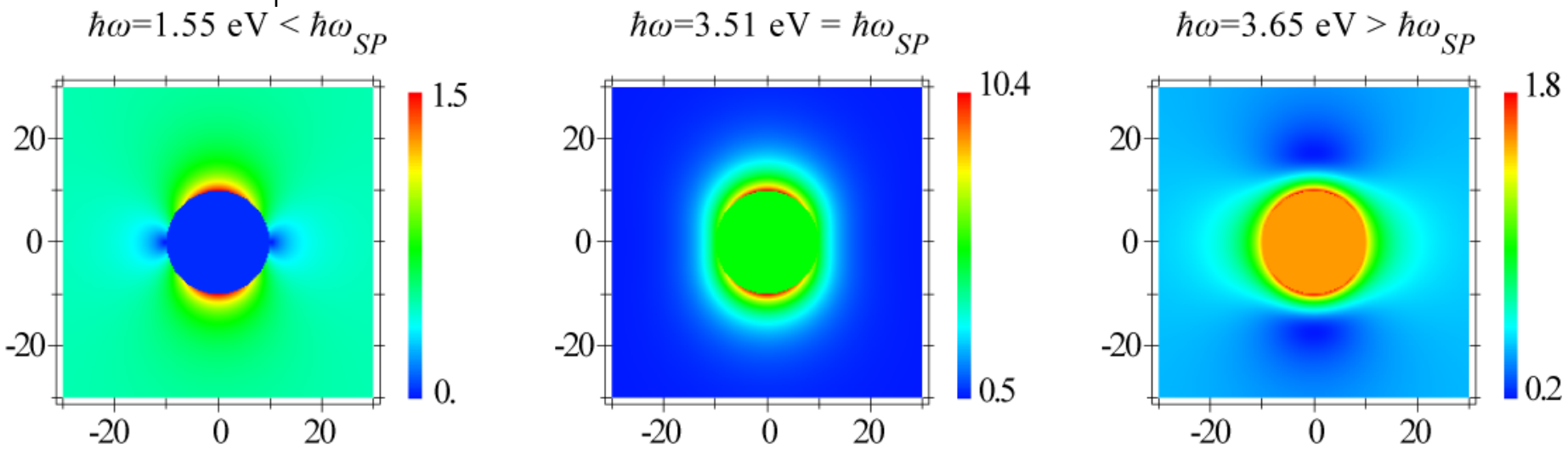
Quasistatic Local Field Magnitude for Silver Nanosphere in Vacuum

Excitation Polarization



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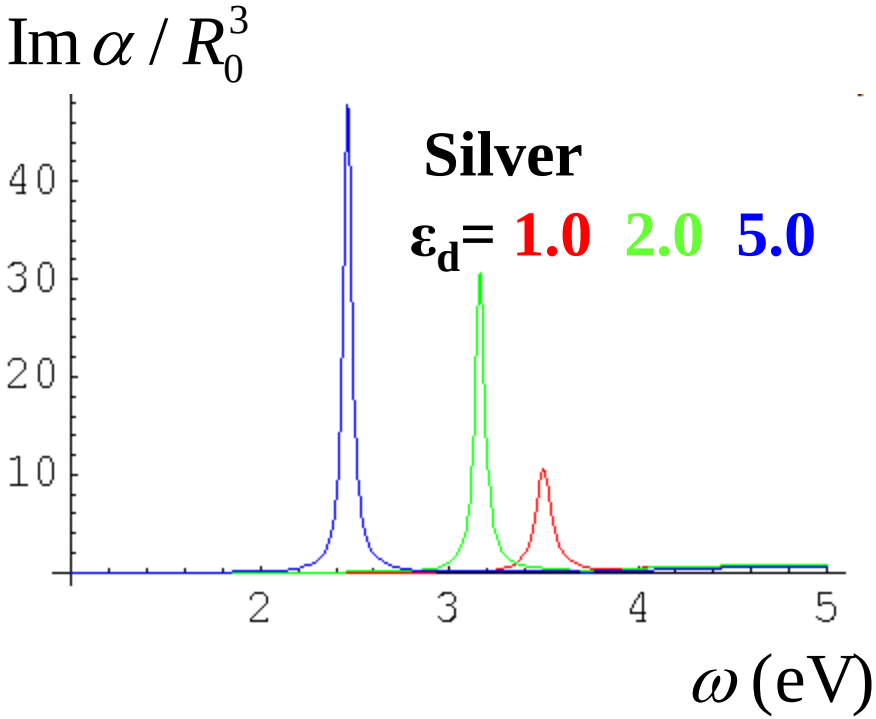
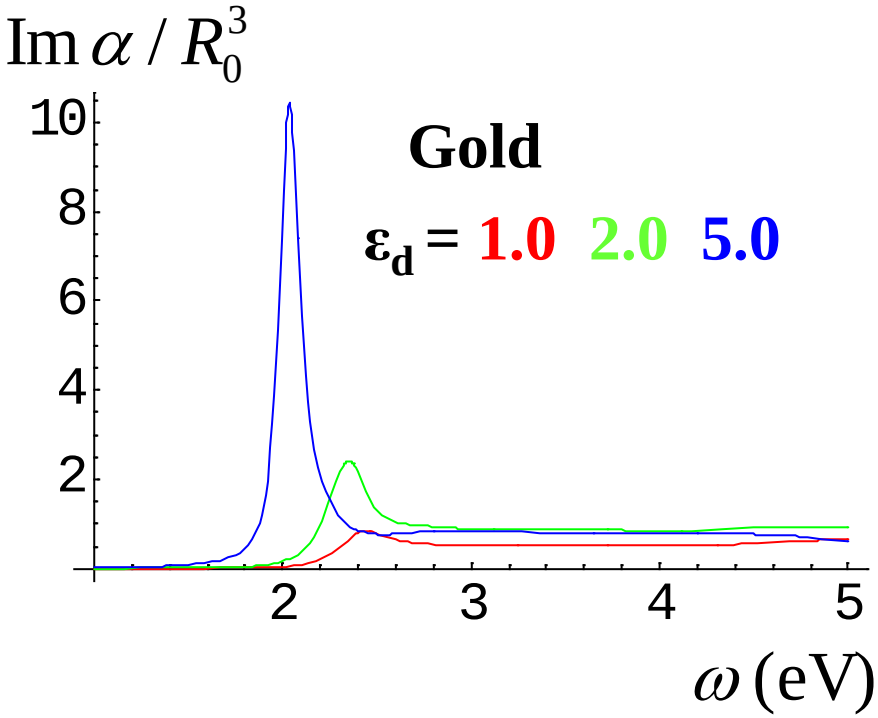
Total extinction (absorption + scattering) cross section

(Optical Theorem) $\sigma_{tot} = 2\pi \frac{\omega}{c} \mathrm{Im}\,\alpha,\ \alpha = R_0^3 \frac{\varepsilon_m - \varepsilon_d}{\varepsilon_m + 2\varepsilon_d}$



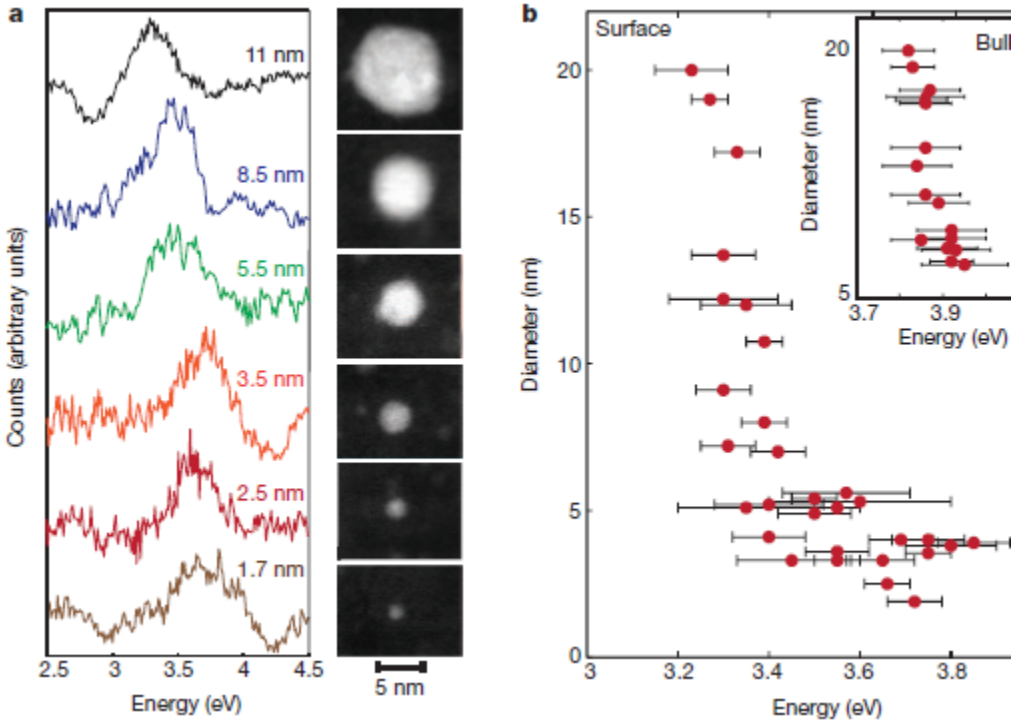


doi:10.1038/nature10904

Geo U

Quantum plasmon resonances of individual metallic nanoparticles

Jonathan A. Scholl[1], Ai Leen Koh[2] & Jennifer A. Dionne[1]



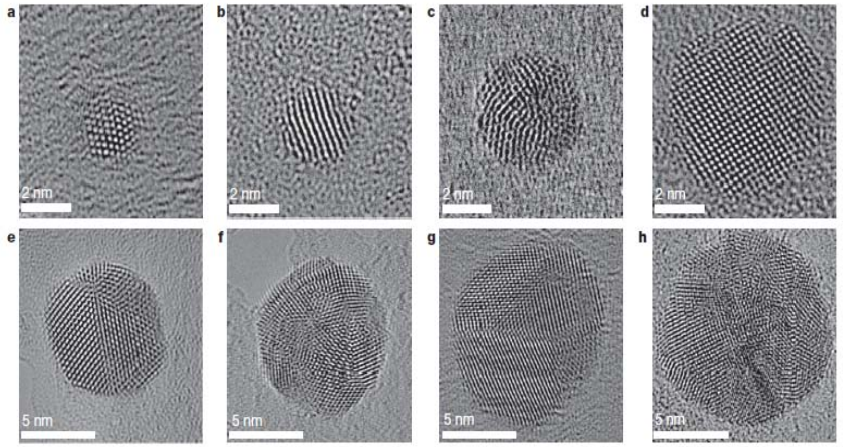


Figure 1 | Aberration-corrected TEM images of silver nanoparticles synthesized free of stabilizing ligands. Particles with diameters of 2 nm (a), 3 nm (b), 4.5 nm (c), 6 nm (d), 7.5 nm (e), 9 nm (f), 10.5 nm (g), and 12 nm (h) are shown. Scale bars: a–d, 2 nm; e–h, 5 nm.

Figure 3 | Correlating Ag nanoparticle geometry with plasmonic EELS data. **a**, Collection of normalized, deconvoluted EELS data from particles ranging from 11 nm to 1.7 nm in diameter and the corresponding STEM image of each specimen. The electron beam was directed onto the edge of the particles so that only the surface resonance is shown. **b**, Plot of the surface plasmon resonance energy versus particle diameter, with the inset depicting bulk resonance energies. Horizontal error bars indicating 95% confidence intervals were generated with a curve fitting and bootstrapping technique (see Methods). Vertical error bars are contained within the size of the data points.

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Plasmon Lifetimes

General behavior of polarizability close to a (plasmon) pole
[See: V. B. Berestetskii, E. M. Lifshits, and L. P. Pitaevskii, *Quantum Electrodynamics* (Pergamon Press, Oxford and New York, 1982)]:

$$\alpha = \frac{\left|\mathbf{d}_{0p}\right|^2}{\hbar\left(\omega - \omega_p\right)}$$

Compare this to the polarizability of a nanosphere:

$$\alpha = R^3 \frac{\varepsilon_m(\omega) - \varepsilon_d}{\varepsilon_m(\omega) + 2\varepsilon_d} \approx R^3 \frac{-3\varepsilon_d}{\left(\omega - \omega_p\right)\left.\frac{\partial\left(\mathrm{Re}\,\varepsilon_m(\omega)\right)}{\partial\omega}\right|_{\omega=\omega_p}},$$

where $\mathrm{Re}\,\varepsilon_m(\omega_p) = -2\varepsilon_d$

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From this, we find the transition dipole of a plasmon:

$$\left|\mathbf{d}_{0p}\right|^2 = \hbar R^3 \frac{3\varepsilon_d}{\left.\frac{\partial\left(\mathrm{Re}\,\varepsilon_m(\omega)\right)}{\partial\omega}\right|_{\omega=\omega_p}}$$

Substituting it into standard formula for radiative decay rate,

$$\gamma_n^{(r)} = \frac{4}{3}\frac{\omega_n^3\sqrt{\varepsilon_d}}{\hbar c^3}\left|(\mathbf{d})_{n0}\right|^2$$

, we obtain:

$$\boxed{\gamma_r = 4\left(\frac{\omega R}{c}\right)^3 \frac{\varepsilon_d}{\left.\frac{\partial\left(\mathrm{Re}\,\varepsilon_m(\omega)\right)}{\partial\omega}\right|_{\omega=\omega_p}}}$$

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Nonradiative decay rate can be found from the pole of the polarizability

$$\varepsilon_m(\omega_p - i\gamma_{nr}) + 2\varepsilon_d = 0$$

Expanding, we find the non-radiative rate

$$\gamma_{nr} = \frac{\mathrm{Im}\,\varepsilon_m(\omega_p)}{\left.\frac{\partial\left(\mathrm{Re}\,\varepsilon_m(\omega)\right)}{\partial\omega}\right|_{\omega=\omega_p}}$$

Comparing to the radiative rate:

$$\frac{\gamma_r}{\gamma_{nr}} = 4\left(\frac{R}{\lambda\!\!\!^{-}}\right)^3 \frac{1}{\mathrm{Im}\,\varepsilon_m(\omega_p)}$$

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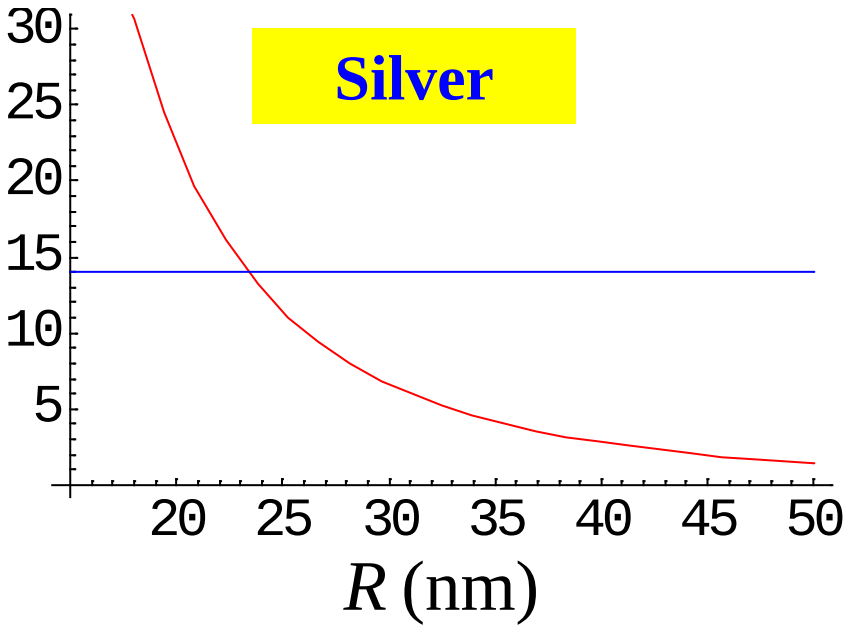
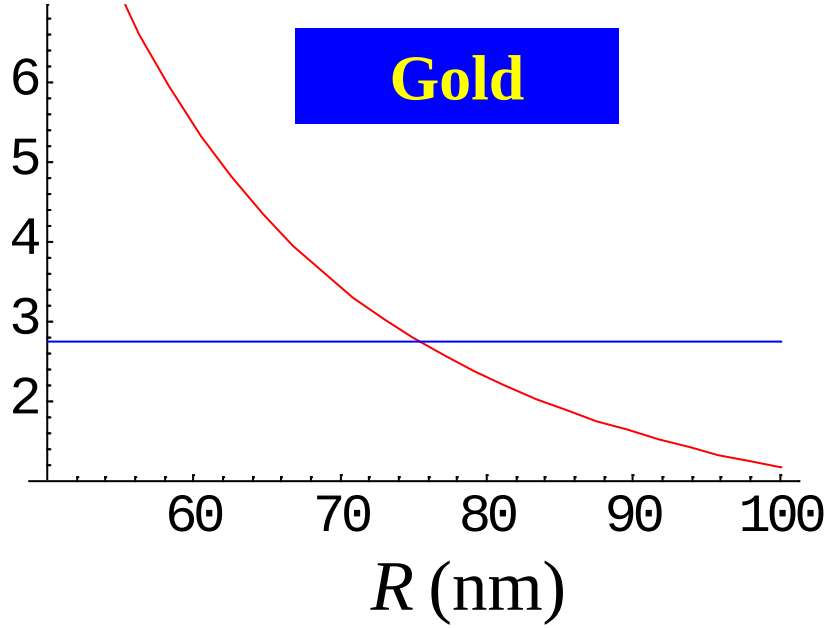
$$\text{Nonradiative lifetime (fs)}: \quad \tau_{nr} = \frac{1}{\gamma_{nr}}$$

$$\text{Radiative lifetime (fs)}: \quad \tau_{r} = \frac{1}{\gamma_{r}}$$





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We will follow the spectral theory that allows one to *separate the material and geometric properties of the system.*

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Quasistatic Field Equations and Boundary Conditions

$$\frac{\partial}{\partial \mathbf{r}}\varepsilon(\mathbf{r},\omega)\frac{\partial}{\partial \mathbf{r}}\varphi(\mathbf{r})=0\,,\ \varphi(x,y,0)=0\,,\ \varphi(x,y,L_z)=1\,,$$

$$\left.\frac{\partial}{\partial x}\varphi(x,y,z)\right|_{x=0,L_x}=\left.\frac{\partial}{\partial y}\varphi(x,y,z)\right|_{y=0,L_y}=0\,.$$

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Material properties of the system is convenient to express in terms of the spectral parameter

$$s(\omega) = \left(1 - \frac{\varepsilon_{\mathrm{m}}(\omega)}{\varepsilon_d(\omega)}\right)^{-1}$$

Field Equation

$$\left[\frac{\partial}{\partial \mathbf{r}}\theta(\mathbf{r})\frac{\partial}{\partial \mathbf{r}} - s(\omega)\frac{\partial^2}{\partial \mathbf{r}^2}\right]\varphi(\mathbf{r};\omega) = 0$$

$\theta(\mathbf{r}) = 1$ in metal, $\theta(\mathbf{r}) = 0$ in dielectric

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Physical surface plasmons are elementary excitation whose complex frequency can be found from an equation $s(\omega_n + i\gamma_n) = s_n$,

where the spectral parameter $s(\omega) = \left(1 - \frac{\varepsilon_{\text{metal}}(\omega)}{\varepsilon_{\text{host}}(\omega)}\right)^{-1}$

Retarded Green's function

$$\left[\frac{\partial}{\partial \mathbf{r}}\theta(\mathbf{r})\frac{\partial}{\partial \mathbf{r}} - s(\omega)\frac{\partial^2}{\partial \mathbf{r}^2}\right]G^r(\mathbf{r},\mathbf{r}';\omega) = \delta(\mathbf{r}-\mathbf{r}')$$

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Local fields on nanoscale for harmonic excitation with external field $\varphi_0(\mathbf{r},\omega)$ at frequency ω:

$$\varphi(\mathbf{r},\omega) = \varphi_0(\mathbf{r},\omega) - \int \varphi_0(\mathbf{r}',\omega)\nabla_{\mathbf{r}'}\theta(\mathbf{r}')\nabla_{\mathbf{r}'}G(\mathbf{r},\mathbf{r}';\omega)\, d^3r',$$

Local fields on nanoscale for short-pulse excitation with pulse field $\varphi_0(\mathbf{r},t)$

$$\varphi(\mathbf{r},t) = \varphi_0(\mathbf{r},t) - \int \varphi_0(\mathbf{r}',t')\nabla_{\mathbf{r}'}\theta(\mathbf{r}')\nabla_{\mathbf{r}'}G(\mathbf{r},\mathbf{r}';t-t')\, d^3r'\, dt',$$

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Eigenmode problem (homogeneous equations; dependent only on geometry, material independent!)

$$\frac{\partial}{\partial \mathbf{r}}\theta(\mathbf{r})\frac{\partial}{\partial \mathbf{r}}\varphi_n(\mathbf{r}) = s_n \frac{\partial^2}{\partial \mathbf{r}^2}\varphi_n(\mathbf{r}),$$

where $\theta(\mathbf{r} \in \text{metal}) = 1$ and $\theta(\mathbf{r} \in \text{dielectric}) = 0$;

$$\varphi_n(x, y, 0) = \varphi_n(x, y, L_z) = 0 ,$$

and

$$\left.\frac{\partial}{\partial x}\varphi_n(x, y, z)\right|_{x=0,L_x} = \left.\frac{\partial}{\partial y}\varphi_n(x, y, z)\right|_{y=0,L_y} = 0 .$$

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In terms of the eigenmodes, Green's function spectral expansion is very simple

$$G^r(\mathbf{r},\mathbf{r}';\omega)=\sum_n \frac{\varphi_n(\mathbf{r})\varphi_n^*(\mathbf{r}')}{s(\omega)-s_n}$$

Irrespectively of the precision with which the eigenfunctions and eigenvalues are found (as long as the eigenfunction are properly orthonormal and the eigenvalues satisfy the corresponding sum rule, this Green's function *exactly* satisfies the general requirements of the theory due to its correct analytical structure.

In particular, it has only simple poles in the lower half-plane of complex frequency. Thus it satisfies Kramers-Kronig causality relations.

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The poles of this Green's function describe SP plasmon modes. The resonant (singular) part of the Green's function is

$$G^r(\mathbf{r}',\mathbf{r};\omega) = \frac{1}{s'(\omega_n)}\sum_n \frac{\phi_n^*(\mathbf{r}')\phi_n(\mathbf{r})}{\omega-\omega_n+i\gamma_n}\;;\quad s(\omega_n)=s_n;\quad \gamma_n = \left.\frac{\operatorname{Im}\varepsilon_m}{\omega\dfrac{\partial \operatorname{Re}\varepsilon_m}{\partial\omega}}\right|_{\omega=\omega_n}$$

At a resonant pole, the Green's function and local fields are increased by the plasmonic quality factor,

$$Q = \frac{\omega}{2\gamma} = \frac{\omega\dfrac{\partial \operatorname{Re}\varepsilon_m}{\partial\omega}}{2\operatorname{Im}\varepsilon_m}$$

$$E_\alpha(\mathbf{r},\omega) = E_\alpha^{(0)}(\mathbf{r},\omega) + \int \frac{\partial^2 G^r(\mathbf{r},\mathbf{r}';\omega)}{\partial r_\alpha \partial r'_\beta} E_\beta^{(0)}(\mathbf{r}',\omega)d^3r'$$

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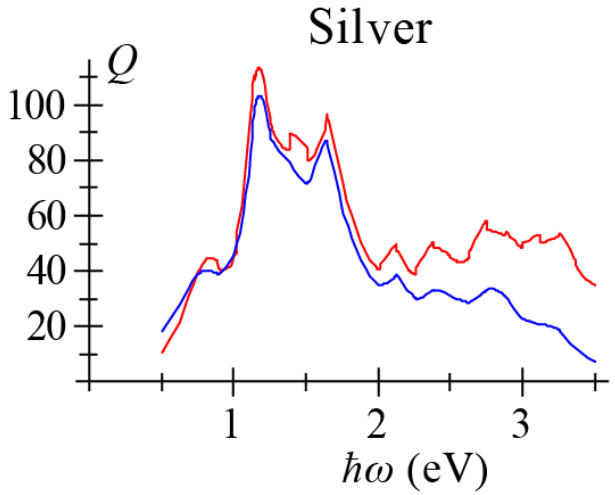
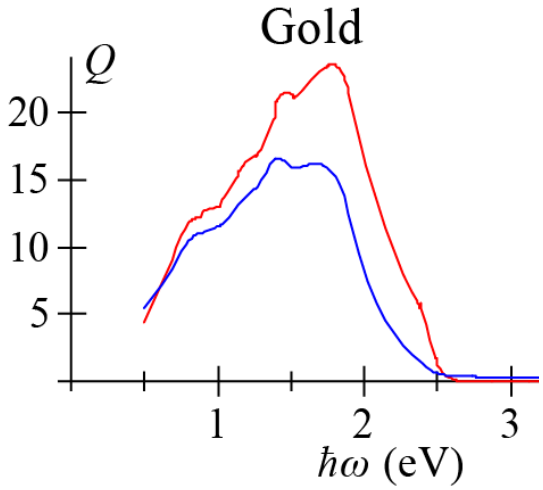
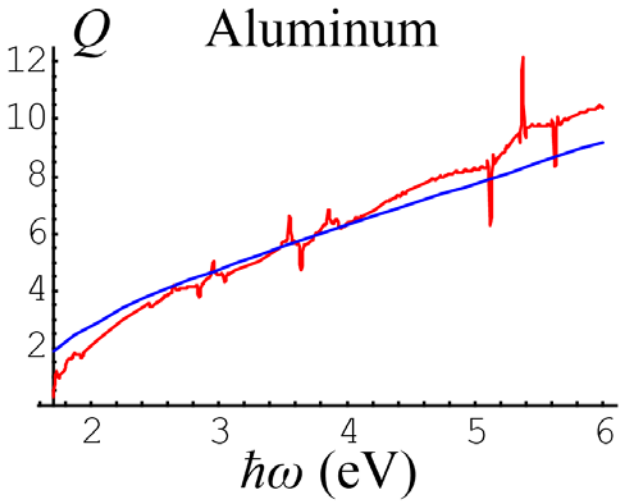
Quality Factor of SP Resonances







$$Q = \frac{\omega}{2\gamma} \approx \frac{\omega \frac{\partial \mathrm{Re}\varepsilon_m(\omega)}{\partial \omega}}{2\mathrm{Im}\,\varepsilon_m(\omega)}$$

$$Q = \frac{-\mathrm{Re}\,\varepsilon_m(\omega)}{\mathrm{Im}\,\varepsilon_m(\omega)}$$

Exact

Simplified

These two definitions coincide for the extreme Drude case: $\varepsilon_m = -\frac{\omega_p^2}{\omega^2}$

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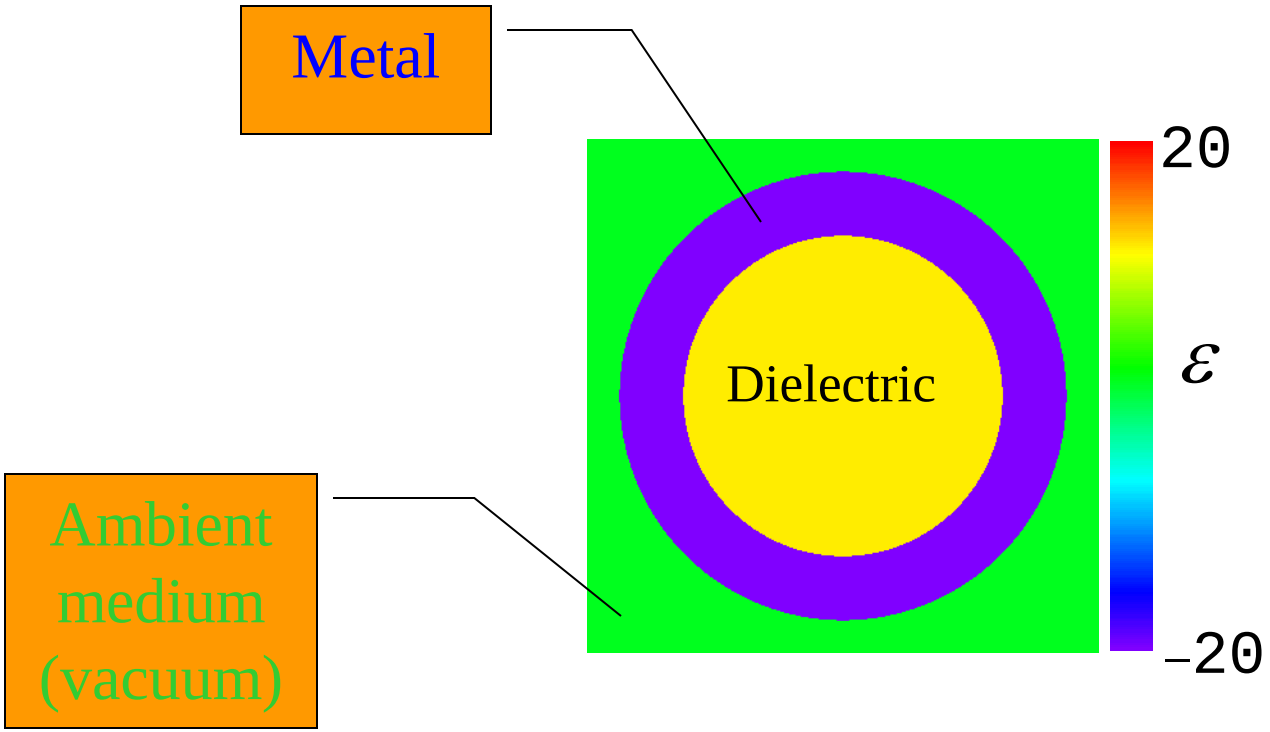
Nanoshells



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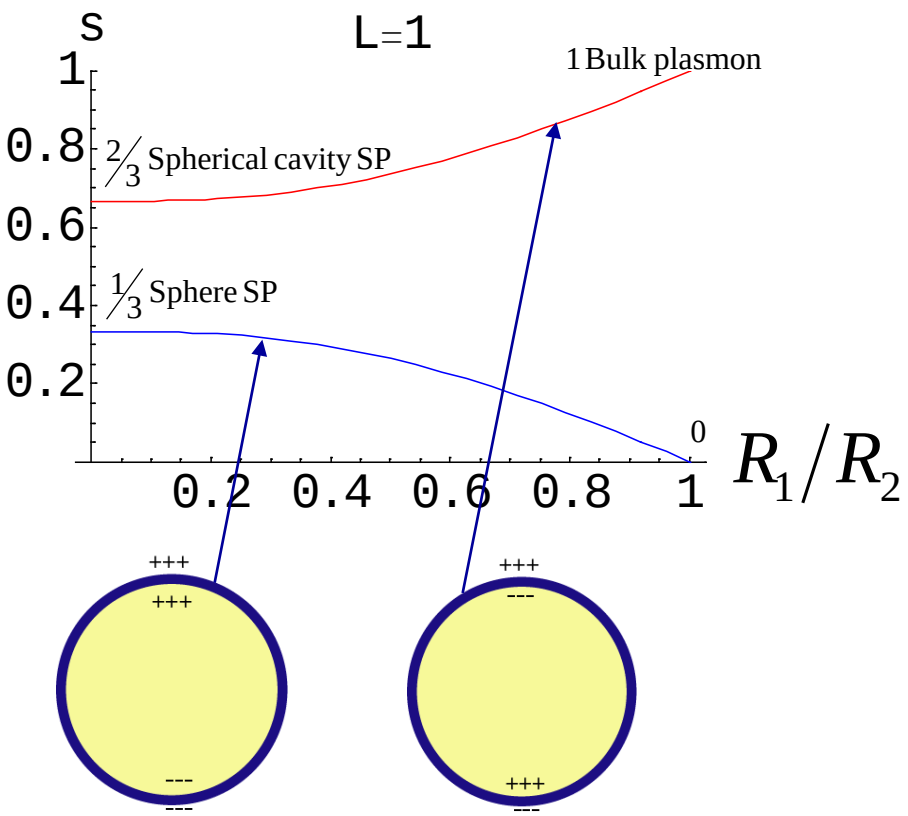
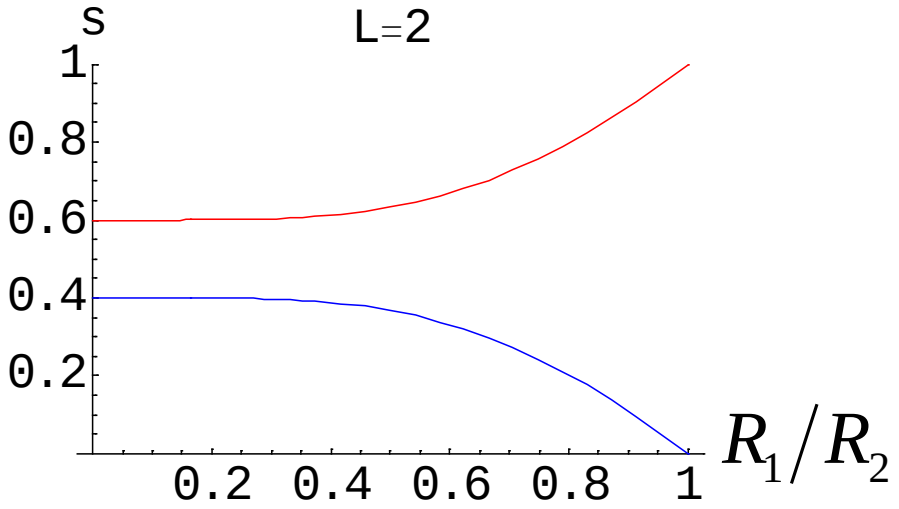
Eigenvalues of plasmon eigenmodes (resonances) (Material independent)

$$s_{L\pm} = \frac{1}{2}\left[1 \pm \frac{1}{2L+1}\sqrt{1+4L(L+1)\left(\frac{R_1}{R_2}\right)^{2L+1}}\right]$$





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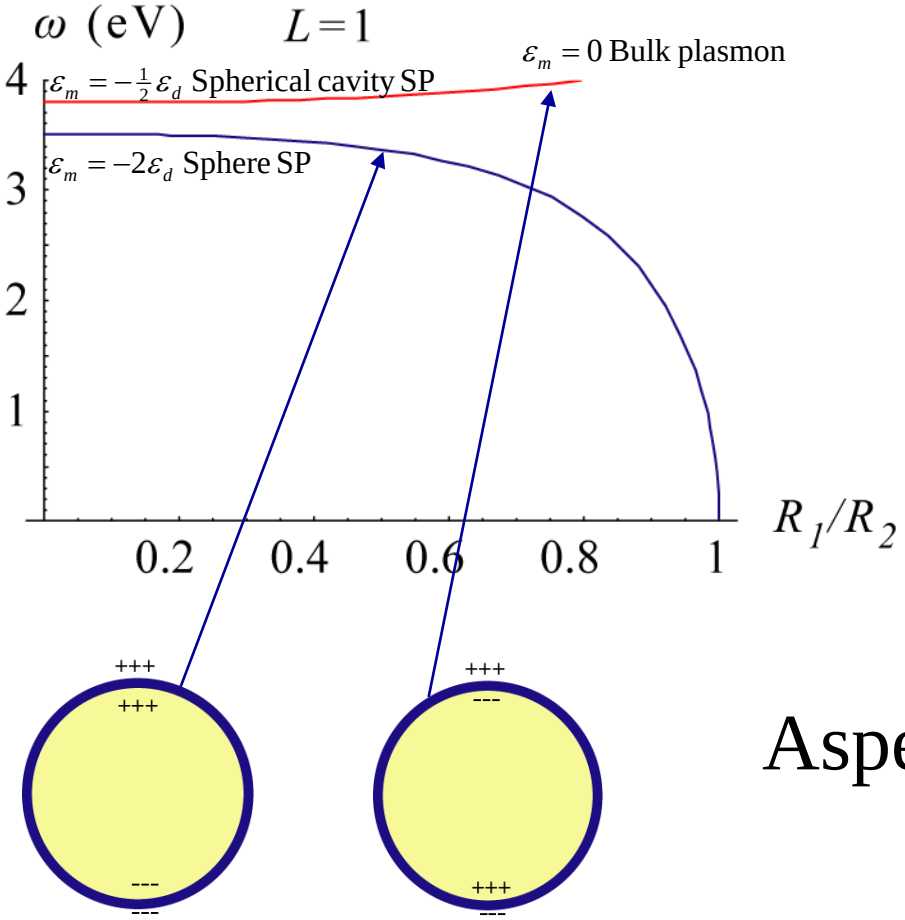
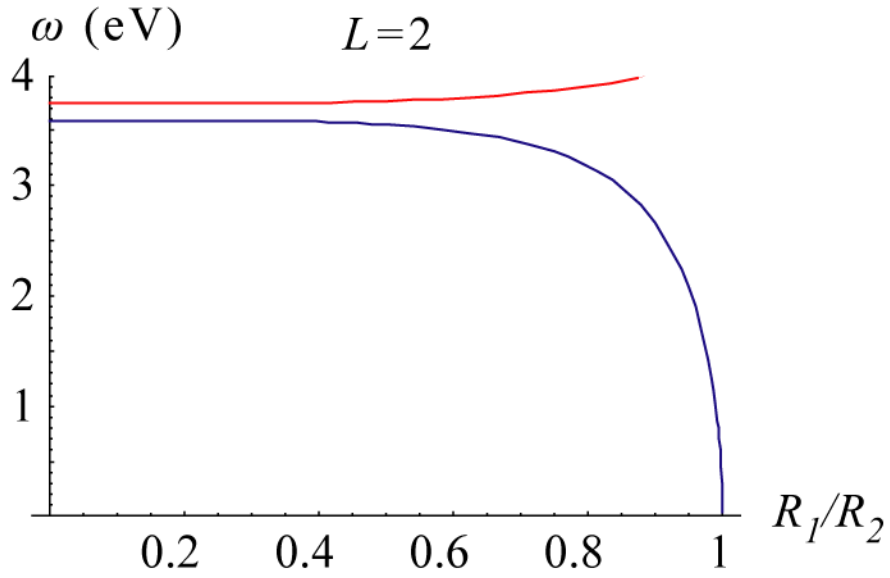
Eigenfrequencies of Surface Plasmons for Silver





Aspect ratio: R_1 / R_2

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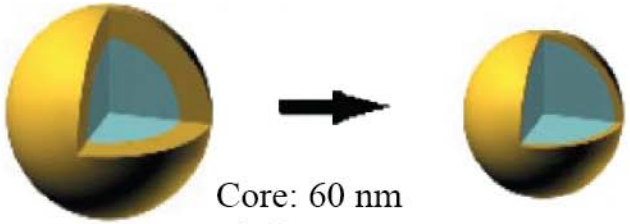
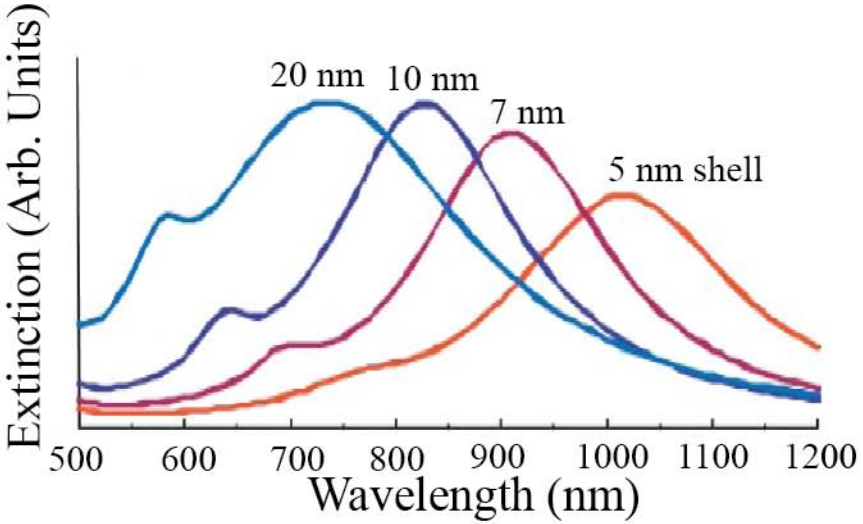
J. L. West and N. J. Halas, *Engineered Nanomaterials for Biophotonics Applications: Improving Sensing, Imaging, and Therapeutics*, Annu. Rev. Biomed. Eng, 5, 285-292 (2003).

Nanoshell Spectral Properties





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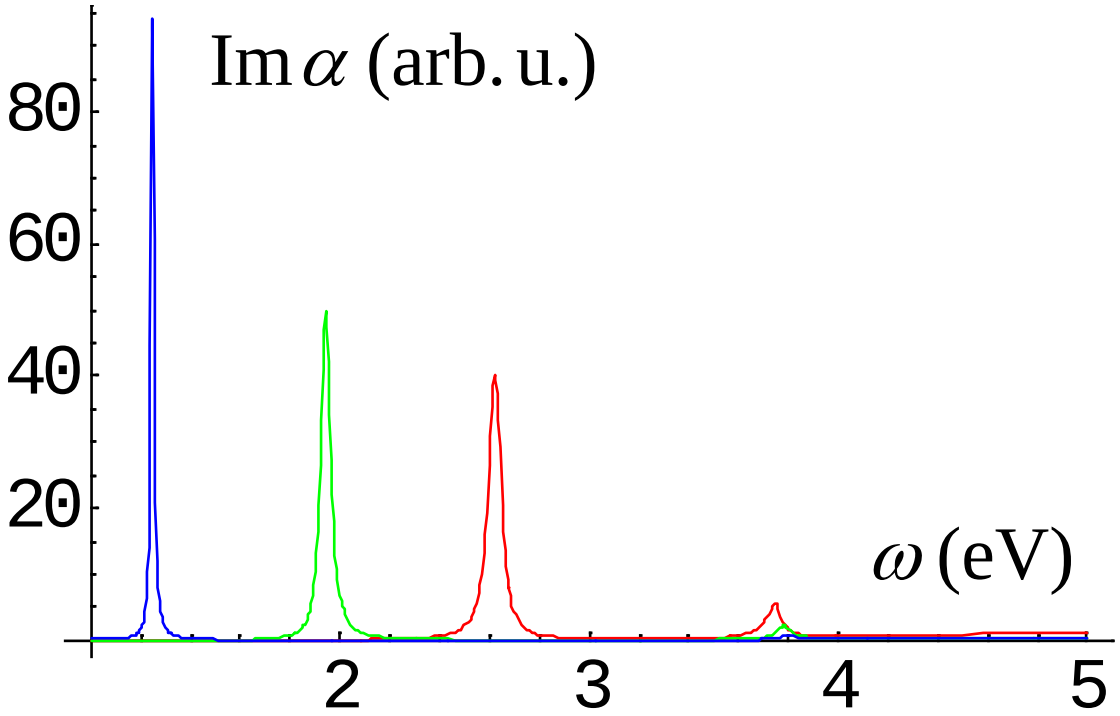
Absorption Cross Section of Silver Nanoshells

$$\sigma = 2\pi \frac{\omega}{c} \mathrm{Im}\,\alpha$$

$R_1:R_2$=20:30, 25:30, 28:30



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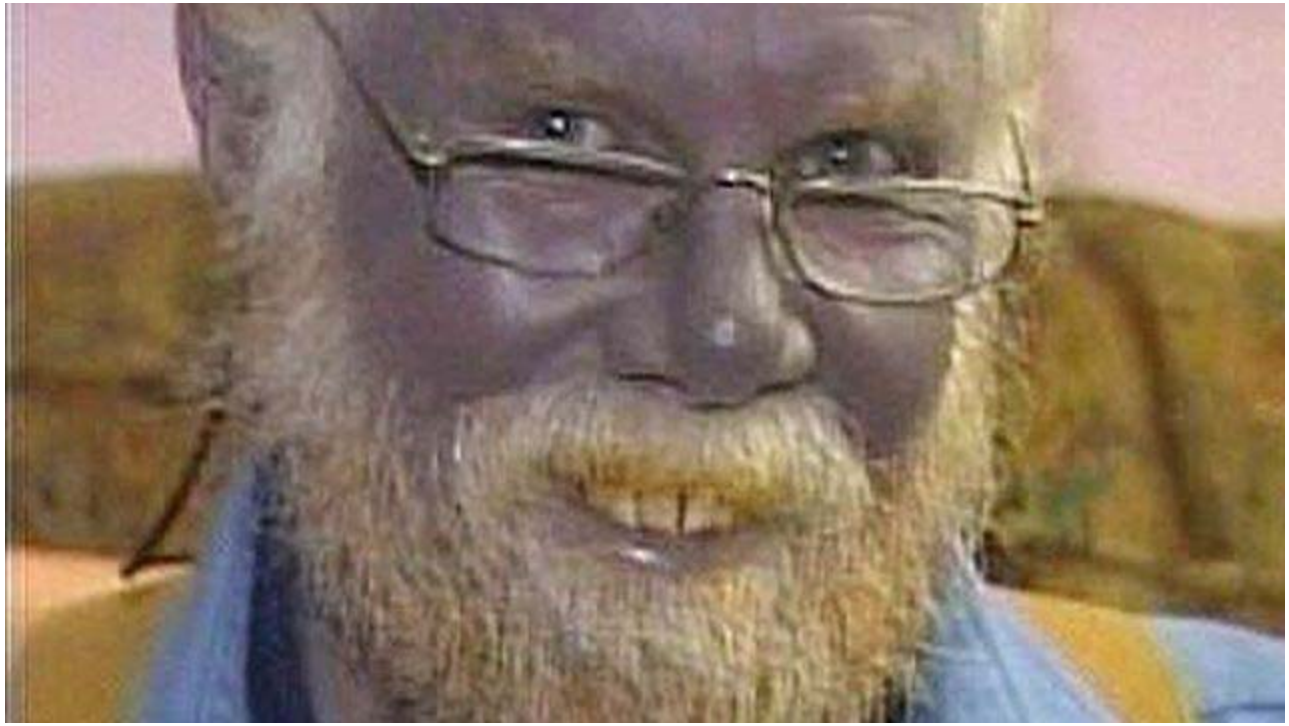
Gold is biologically inert. Colloidal gold can be consumed in macroscopic amounts without long-time damage.

In contrast, colloidal silver is very and irreversibly toxic.

This man drank colloidal silver. He is dead at 61.



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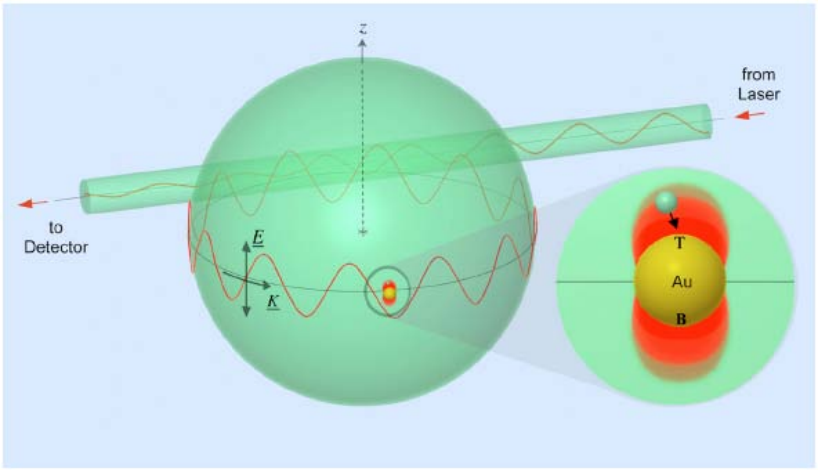
Plasmonic detection of a single virus using a nanoshell in a hybrid device

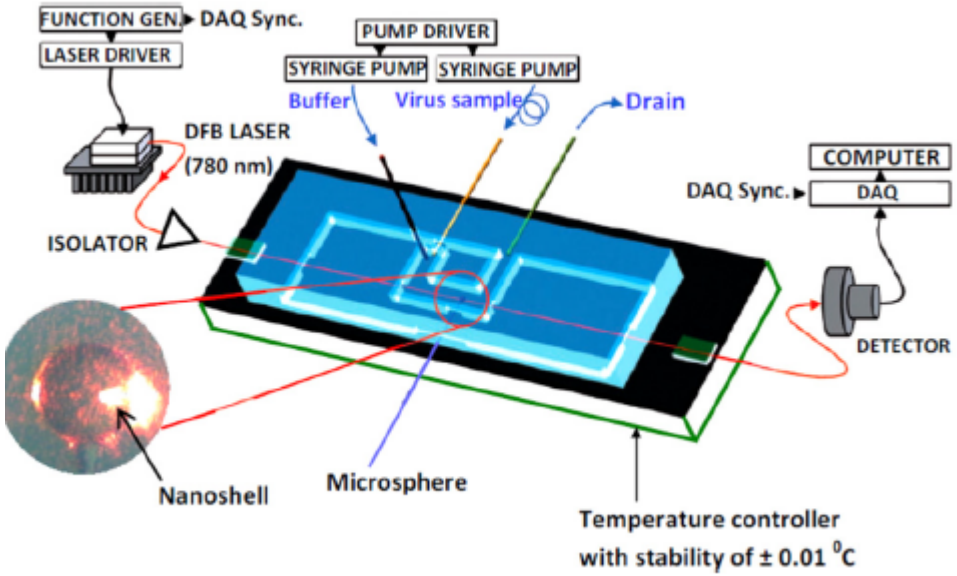
APPLIED PHYSICS LETTERS **101**, 043704 (2012)

Taking whispering gallery-mode single virus detection and sizing to the limit

V. R. Dantham,[1] S. Holler,[1,2] V. Kolchenko,[3] Z. Wan,[4] and S. Arnold[1,a)]
[1]*Microparticle Photophysics Lab, Polytechnic Institute of NYU, Brooklyn, New York 11201, USA*

We report the label-free detection and sizing by a microcavity of the smallest individual RNA virus, MS2, with a mass only ~1% of InfluenzaA (6 vs. 512 ag). Although detection of such a small bio-nano-particle has been beyond the reach of a bare spherical microcavity, it was accomplished with ease (S/N = 8, $Q = 4 \times 10^5$) using a single dipole stimulated plasmonic-nanoshell as a microcavity wavelength shift enhancer, providing an enhancement of ~70×, in agreement with theory. Unique wavelength shift statistics are recorded consistent with an ultra-uniform genetically programmed substance that is drawn to the plasmonic hot spots by light-forces. © *2012 American Institute of Physics.* [http://dx.doi.org/10.1063/1.4739473]





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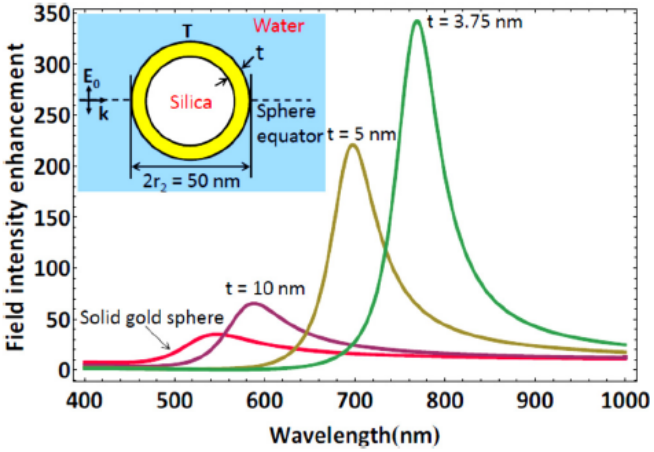
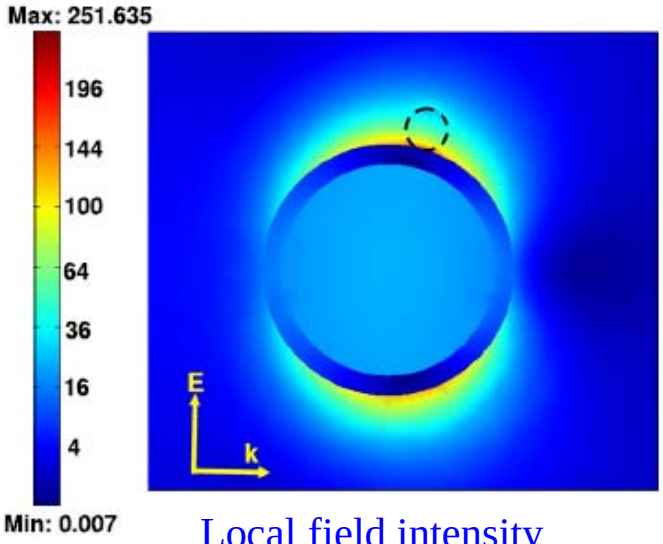


Nanoshell spectra



Local field intensity

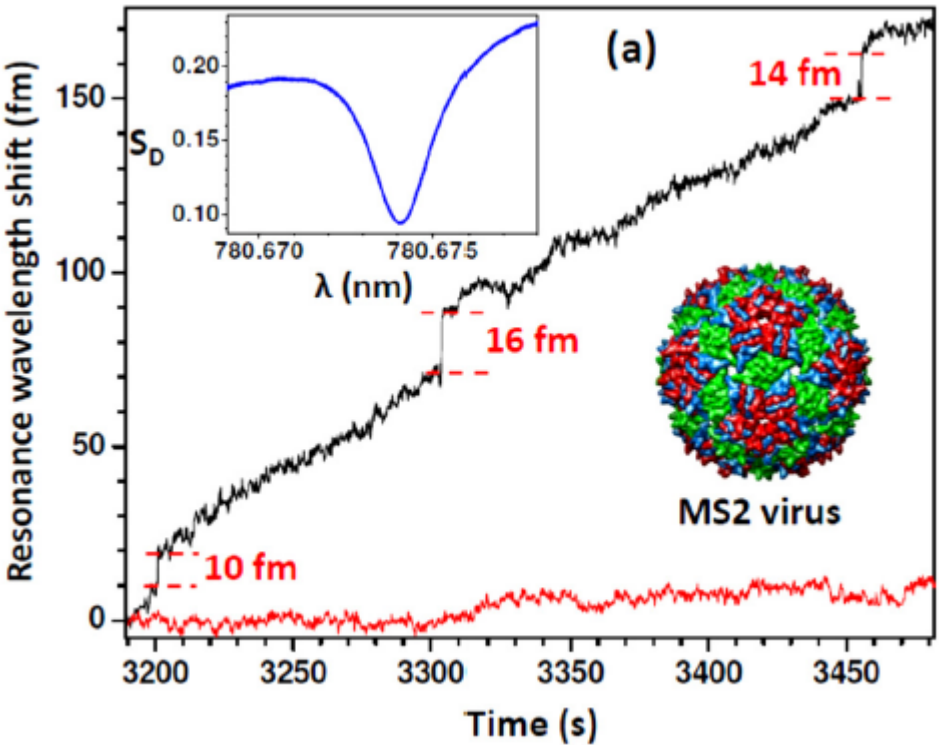


FIG. 3. (a) Shift of resonance wavelength above 780.674 nm of a WGM resonator $R = 45\,\mu$m having a gold nanoshell attached at its equator due to the adsorption of MS2 viruses (upper trace). The lower trace shows the background without MS2 or the gold nanoshell (r.m.s. noise 2 fm). Insets show the recorded spectrum S_D for the hybrid resonator ($Q \sim 4 \times 10^5$) and an illustration of MS2 virus (radius $a \sim 13.6$ nm). (b) Step number statistics for all

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Localization of Surface Plasmons

Any Anderson-localized (or, strongly localized) mode is dark.

Consequently:

It is impossible that all surface-plasmon modes of any system are Anderson-localized (or, strongly localized).

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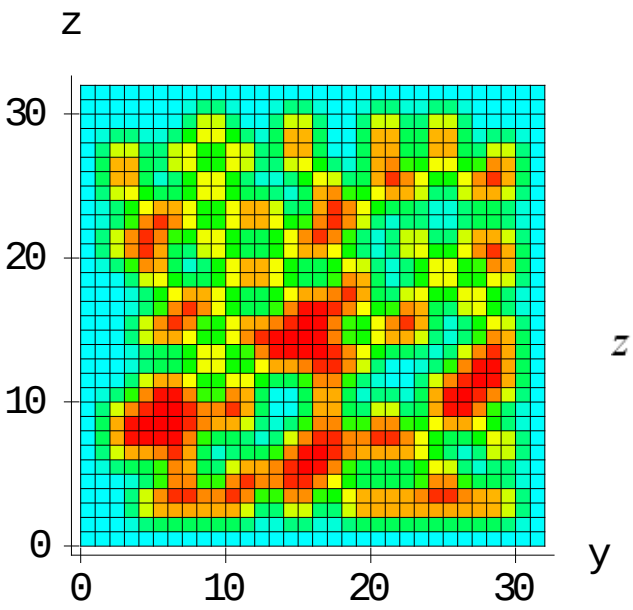
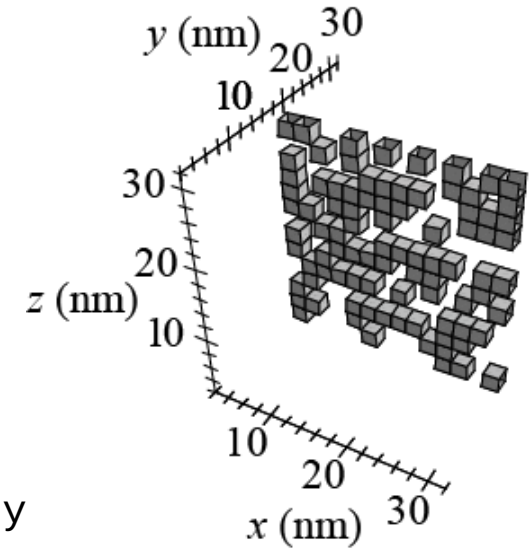
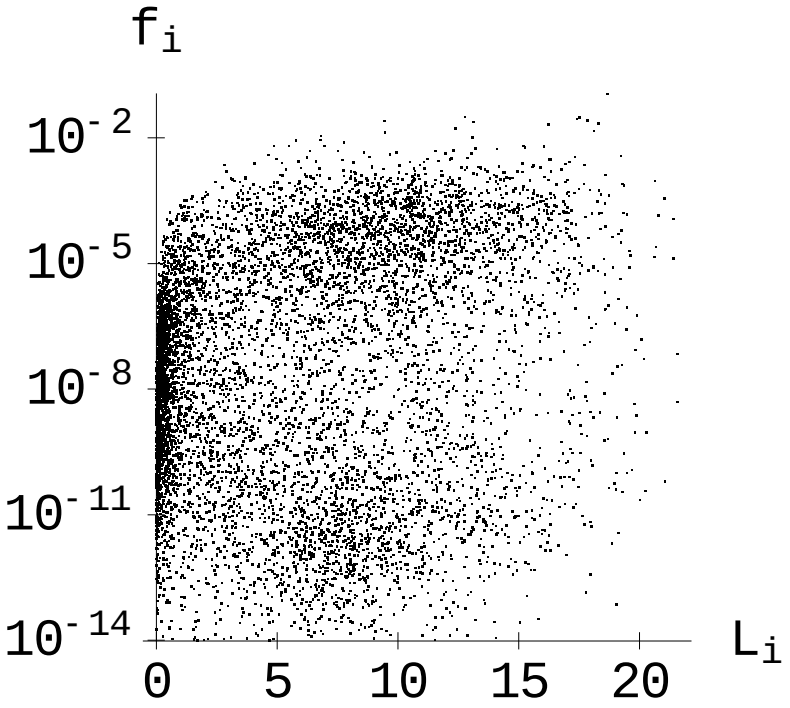




Geometry of Random Planar Composite



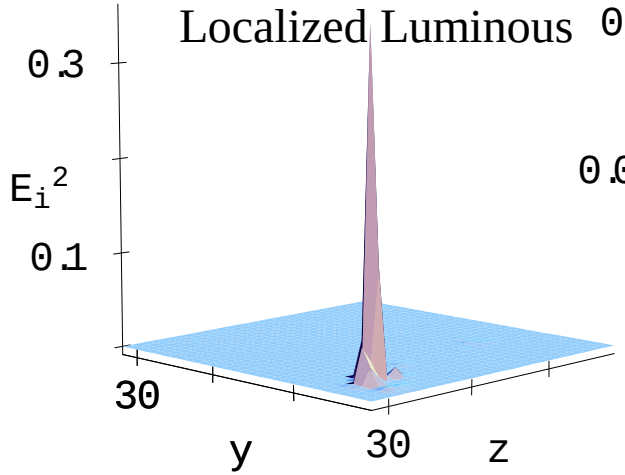
Distribution of Eigenmodes over their Oscillator Strength f_i and Localization Radius L_i

Phys. Rev. Lett. **87**, 167401 (2001).

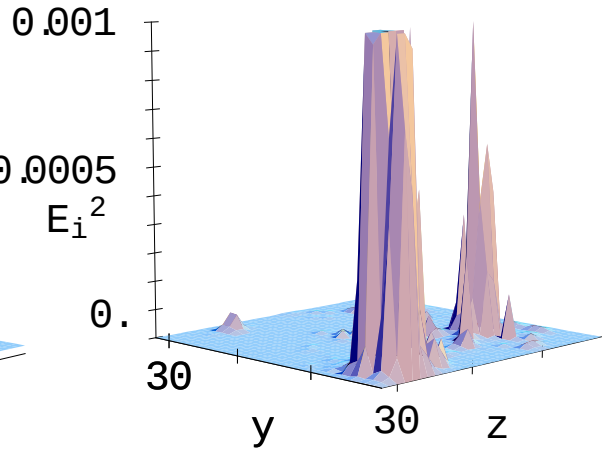
Local Field Intensities for Four Eigenmodes Representative of Each Class of Eigenmodes

s_i=0.1995 , L_i=2.1

Localized Luminous

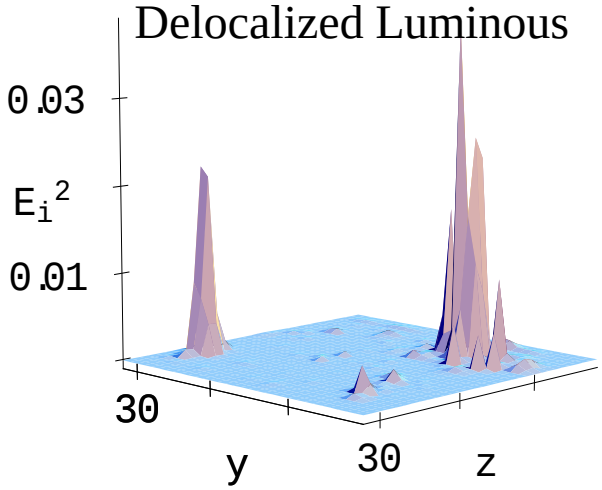


s_i=0.1995 , L_i=2.1



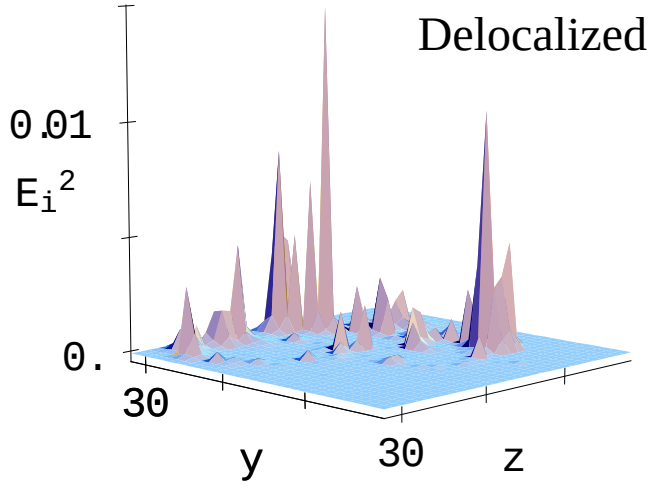
s_i=0.2 , L_i=11.2

Delocalized Luminous



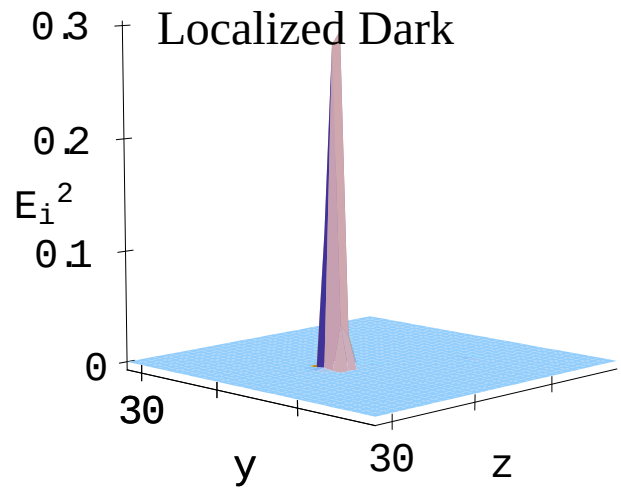
s_i=0.201 , L_i=9.6

Delocalized Dark



s_i=0.2015 , L_i=1.

Localized Dark



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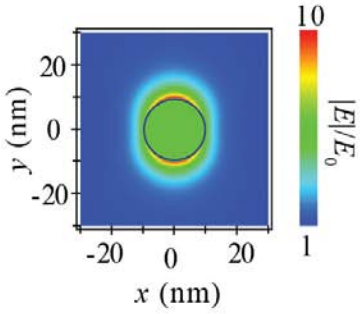
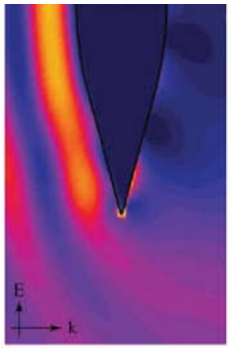
Plasmonic Near-Field **Hot Spots:** Happy 16th Anniversary!

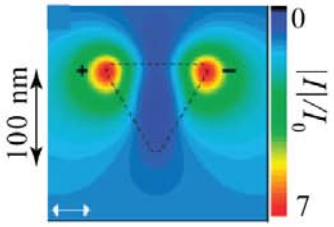
•M. I. Stockman et al., *Phys. Rev. Lett.* **75**, 2450 (1995)



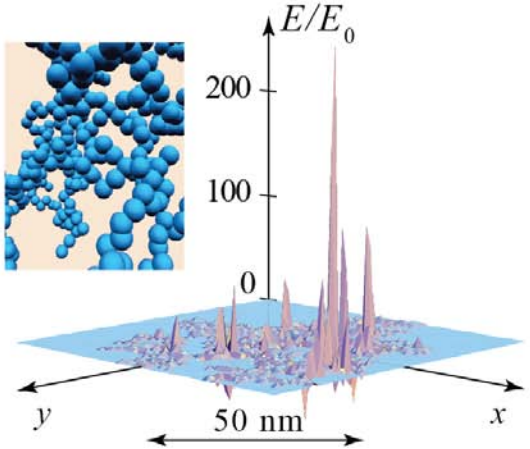
Silver nanosphere



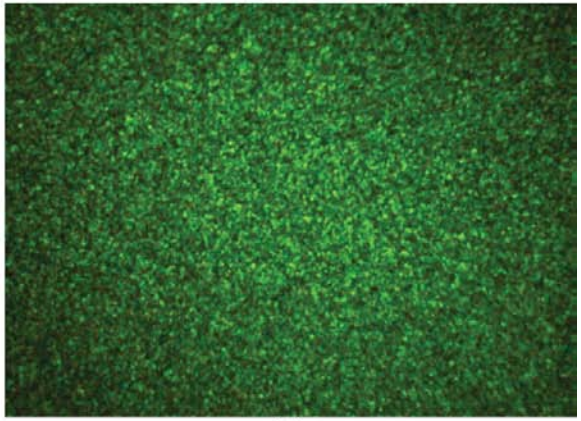
Metal tip: L. Novotny and S. J. Stranick, Annual Rev. Phys. Chem. **57**, 303-331 (2006)



Nano-pyramid: M. Rang et al., Nano Lett. **8**, 3357 (2008)



Fractal cluster of silver: M. I. Stockman, L. N. Pandey, and T. F. George, Phys. Rev. B **53**, 2183-2186 (1996)



Optical counterpart: laser speckles on a screen

$$R_{Speckle} \sim \frac{\lambda\!\!\!^{-}}{A} L$$

$R_{Speckle}$ is speckle size

$\lambda\!\!\!^{-} \sim 100$ nm is reduced wave length

A is laser spot size,

L is distance to the screen

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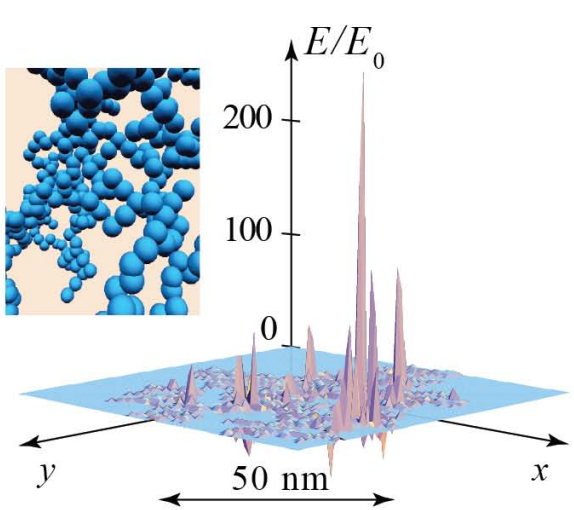
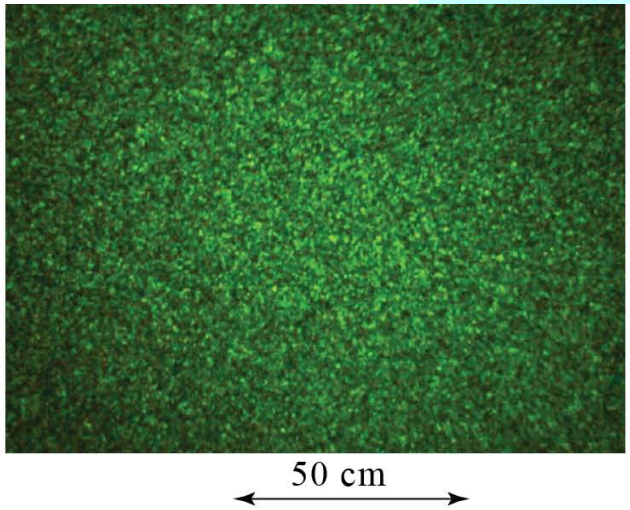
Plasmonic Near-Field **Hot Spots:** Happy 20th Anniversary!

•D. P. Tsai et al., Phys. Rev. Lett. **72**, 4149 (1994).
•M. I. Stockman et al., *Phys. Rev. Lett.* **75**, 2450 (1995)
•M. I. Stockman, L. N. Pandey, and T. F. George, Phys. Rev. B **53**, 2183 (1996)



M. I. Stockman, L. N. Pandey, and T. F. George, Phys. Rev. B 53, 2183 (1996).



Random scattering speckles

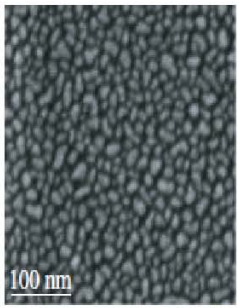
$$R_{Speckle} \sim \frac{\lambda\!\!\!^{-}}{A} L$$

$R_{Speckle}$ is speckle size

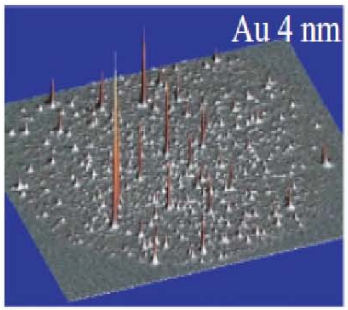
$\lambda\!\!\!^{-} \sim 100$ nm is reduced wave length

A is laser spot size,

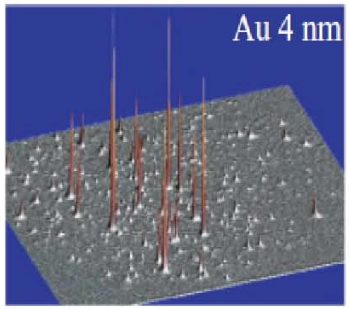
L is distance to the screen



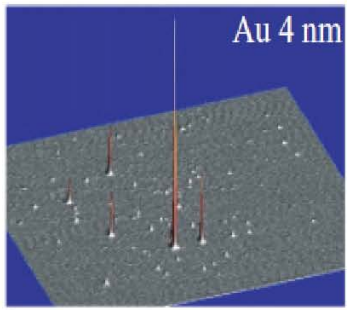
Au 4 nm, f = 0.53



λ = 800 nm, Hot Spots Nb = 617



λ = 930 nm, Hot Spots Nb = 453



λ = 970 nm, Hot Spots Nb = 402

C. Awada, G. Barbillon, F. Charra, L. Douillard, and J. J. Greffet, Phys. Rev. B **85**, 045438 (2012).

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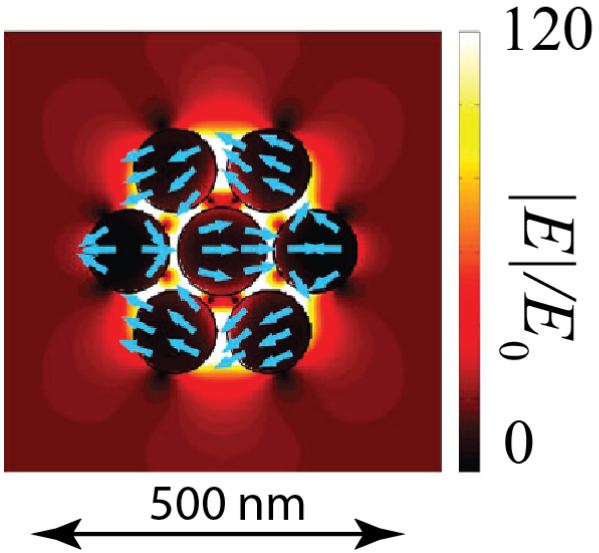
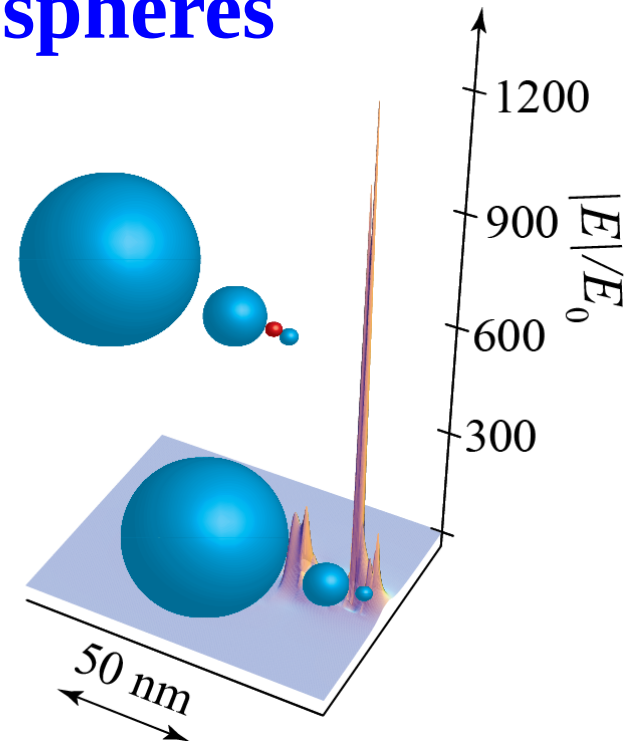
Engineered Nanoplasmonic Hot Spots in Small Clusters of Nanospheres





Fano resonance in a nanosphere cluster:
- J. A. Fan et al., Science **328**, 1135 (2010)
- M. Hentschel et al., Nano Lett. **10**, 2721 (2010)

Self-similar nanosphere nanolens: K. Li, M. I. Stockman, and D. J. Bergman, Phys. Rev. Lett. **91**, 227402 (2003)

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Giant Raman Scattering in Complex Natural and Engineered Nanosystems

Theory of SERS (Surface Enhanced Raman Scattering)

1. M. I. Stockman, V. M. Shalaev, M. Moskovits, R. Botet, and T. F. George, *Enhanced Raman Scattering by Fractal Clusters: Scale Invariant Theory*, Phys. Rev. B **46**(5), 2821-2830 (1992).

2. M. I. Stockman, *Electromagnetic Theory of SERS*, in: Springer Series Topics in Applied Physics, edited by K. Kneipp, M. Moskovits and H. Kneipp, *Surface Enhanced Raman Scattering – Physics and Applications* (Springer-Verlag, Heidelberg New York Tokyo, 2006).

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Discovery of Surface Enhanced Raman Scattering (SERS)

1. M. Fleischmann, P. J. Hendra, and A. J. McQuillan, *Raman Spectra of Pyridine Adsorbed at a Silver Electrode*, Chem. Phys. Lett. **26**, 163-166 (1974).
2. D. L. Jeanmaire and R. P. Van Duyne, *Surface Raman Spectroelectrochemistry Part I. Heterocyclic, Aromatic, and Aliphatic Amines Adsorbed on the Anodized Silver Electrode*, J. Electroanal. Chem. **84**, 1-20 (1977).
3. M. G. Albrecht and J. A. Creighton, *Anomalously Intense Raman Spectra of Pyridine at a Silver Electrode*, J. Amer. Chem. Soc. **99**, 5215 - 5217 (1977).

Raman scattering from molecules absorbed on clusters of colloidal silver or rough silver surfaces enhanced by a factor of $G^{RS}\sim 10^4$-10^6 with respect to the same molecules free in solution

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SERS Enhanced by factor of $\sim 10^{12} - 10^{14}$

Observation of Single-molecule Surface-Enhanced Raman Scattering:

•K. Kneipp, Y. Wang, H. Kneipp, L. T. Perelman, I. Itzkan, R. Dasari, and M. S. Feld, *Single Molecule Detection Using Surface-Enhanced Raman Scattering (SERS)*, Phys. Rev. Lett. **78**, 1667-1670 (1997).

•S. M. Nie and S. R. Emery, *Probing Single Molecules and Single Nanoparticles by Surface-Enhanced Raman Scattering*, Science **275**, 1102-1106 (1997).

See also: Z. J. Wang, S. L. Pan, T. D. Krauss, H. Du, and L. J. Rothberg, *The Structural Basis for Giant Enhancement Enabling Single-Molecule Raman Scattering*, Proc. Natl. Acad. Sci. USA **100**, 8638-8643 (2003).

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SERS enhanced by a factor 10^{12} - 10^{14}

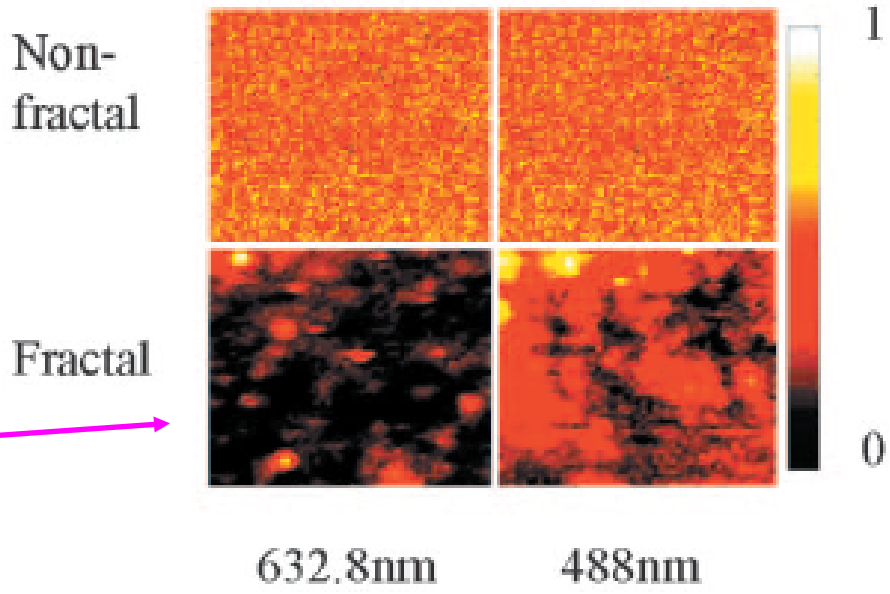

Fig. 6. Raman images of a single area on selected fractal and nonfractal surfaces for different excitation wavelengths. (*Upper*) The Raman images of immersion oil on the 100-nm-thick silver film. (*Lower*) The Raman images of 4-mercaptopyridine adsorbed on cluster–cluster aggregated films. The size of each image is 5 μm × 5 μm. Note that each image is internally normalized to its maximum so that relative intensities between images cannot be compared. In particular, the hot spots on fractal surfaces have orders of magnitude more Raman scattering than counterparts of similar color on nonfractal surfaces.

PNAS | July 22, 2003 | vol. 100 | no. 15 | 8641

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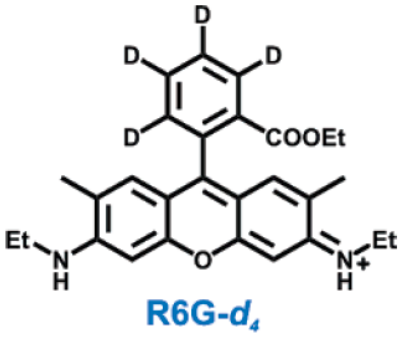
A Frequency Domain Existence Proof of Single-Molecule Surface-Enhanced Raman Spectroscopy

Jon A. Dieringer, Robert B. Lettan II, Karl A. Scheidt, and Richard P. Van Duyne*

Northwestern University, Department of Chemistry, 2145 Sheridan Road, Evanston. Illinois 60208

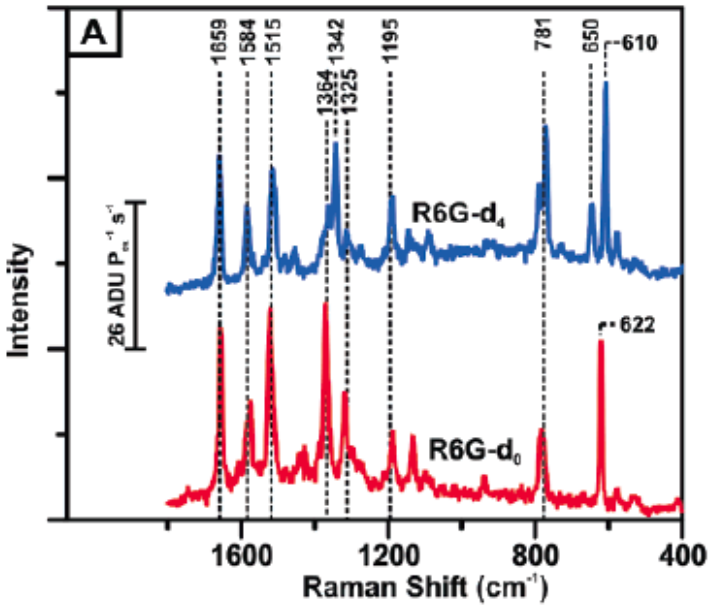
J. AM. CHEM. SOC. 2007, *129*, 16249–16256

Scheme 1. Chemical Structure of the Two Isotopologues, R6G-d_4 and R6G-d_0



R6G-d_4

R6G-d_0



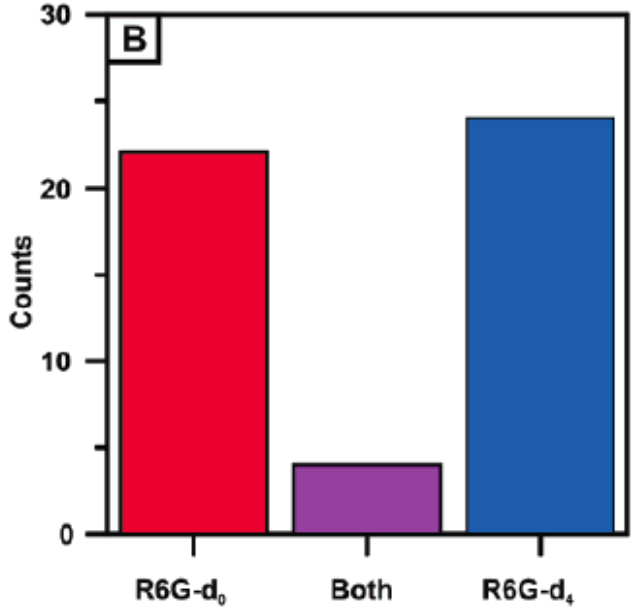


Figure 2. (A) Two representative spectra from the single-molecule results where one contains uniquely R6G-d_0 (red line) and the other uniquely R6G-d_4 (blue line) vibrational character. (λ_{ex} = 532 nm, t_{aq} = 10 s, P_{ex} = 2.4 W/cm^2, grazing incidence) (B) Histogram detailing the frequency with which only R6G-d_0, only R6G-d_4 and both R6G-d_0 and R6G-d_4 vibrational modes were observed with low adsorbate concentration under dry N_2 environment.

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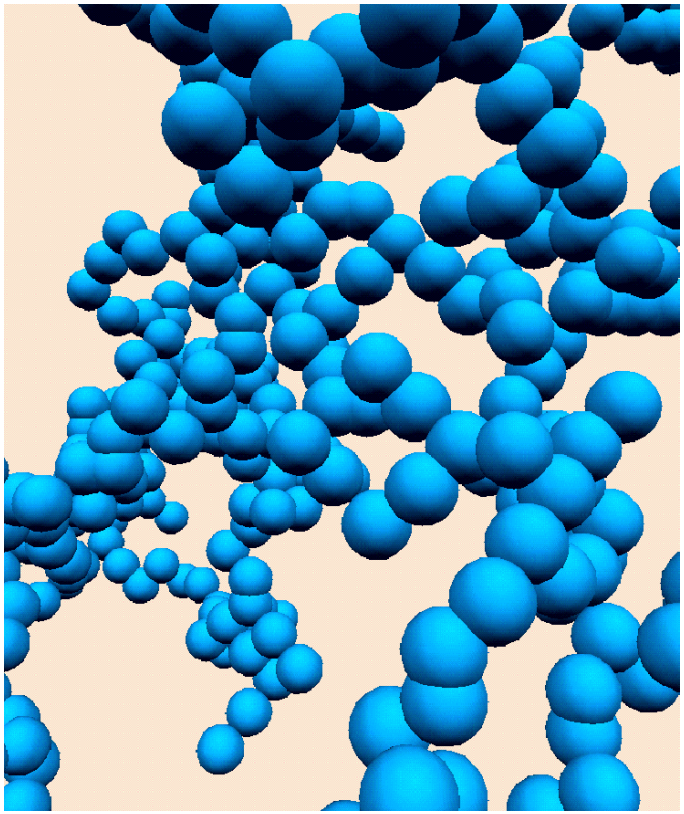
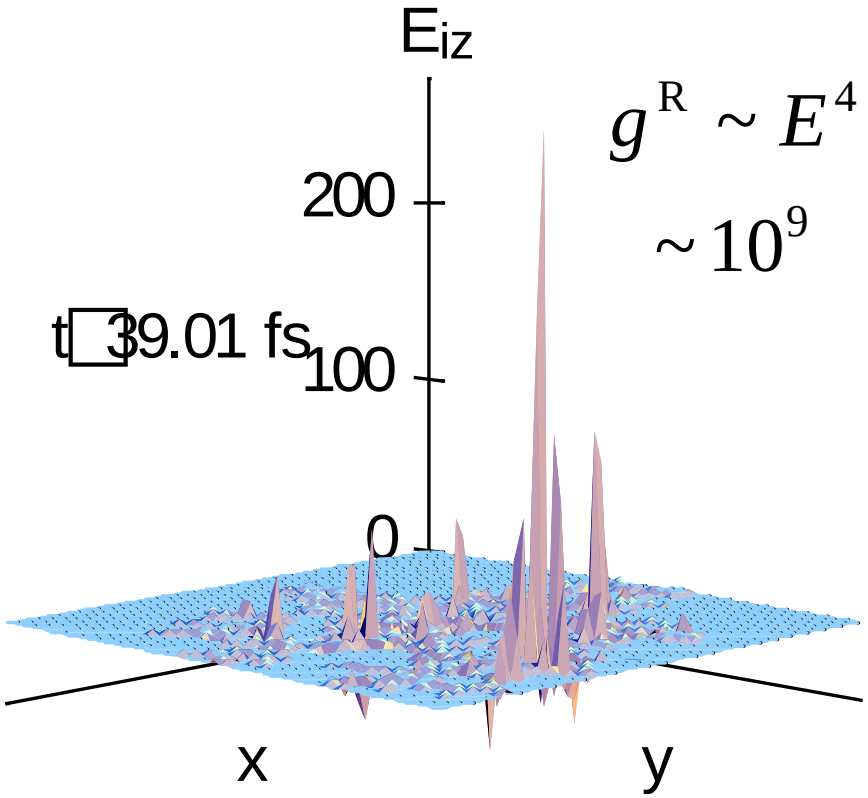
Enhancement of Optical Responses in Fractals



Self-similar fractal geometry



$g^{R} \sim E^{4}$

$\sim 10^{9}$

Local optical fields in fractal cluster [MIS, Phys. Rev. Lett. **84**, 1011 (2000)].

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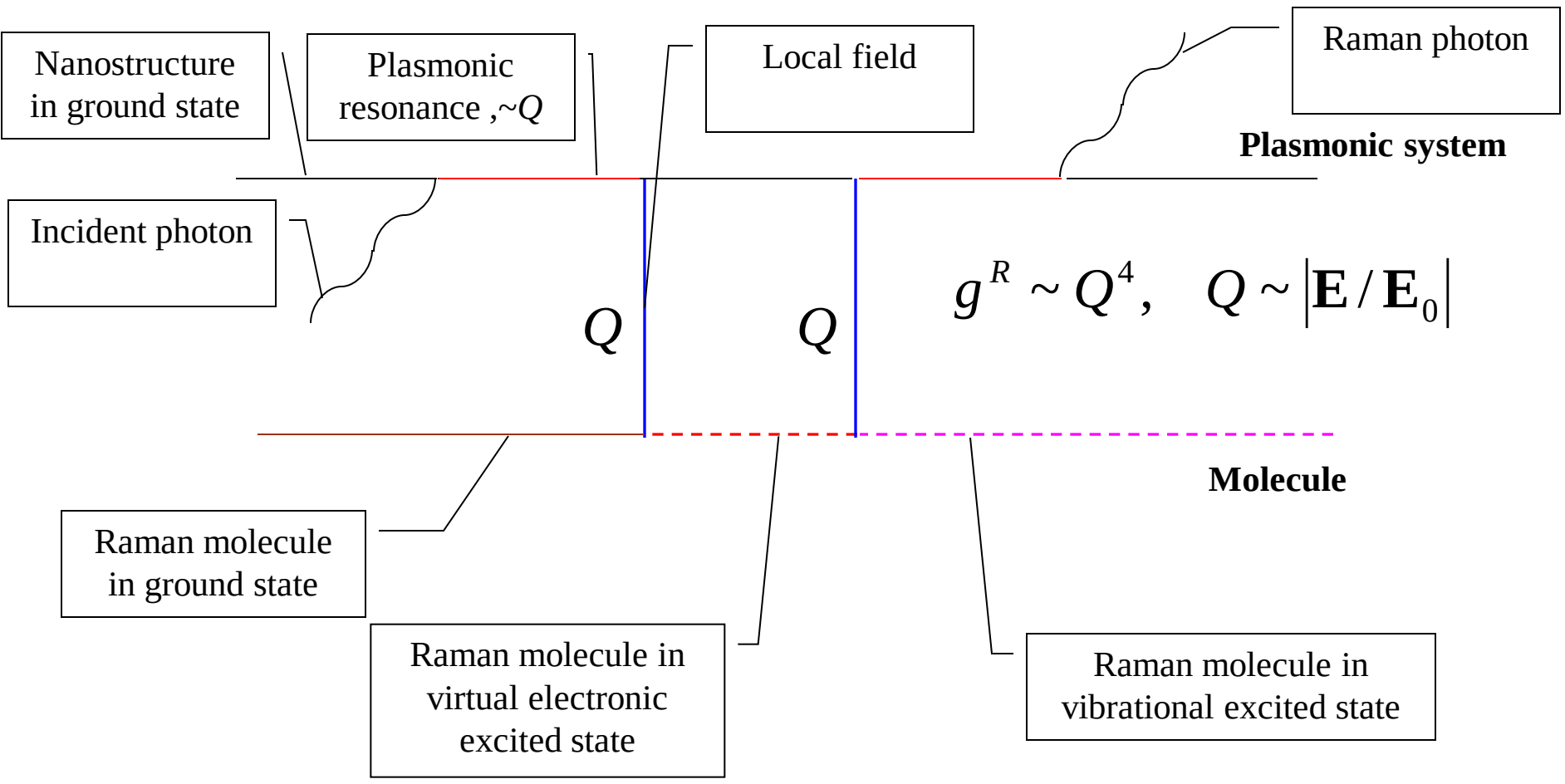
Amplitude of the Leading SERS Process



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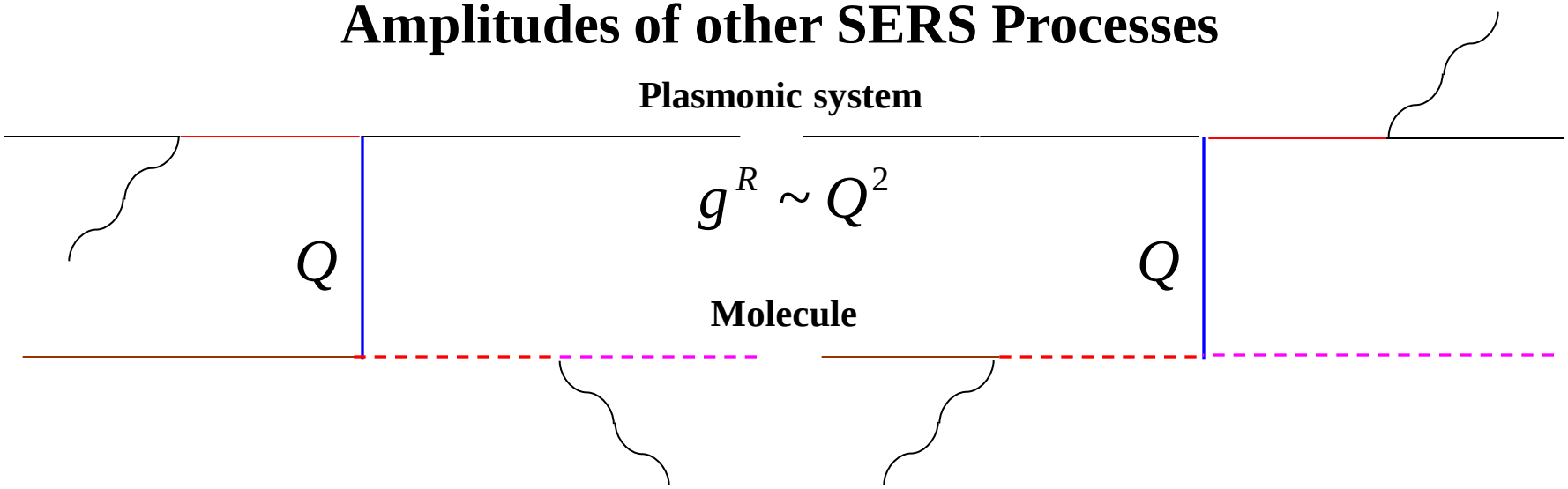
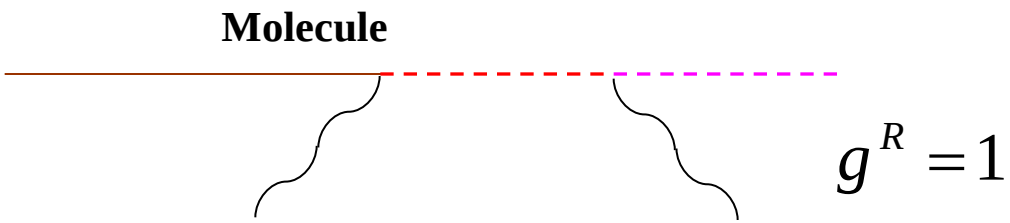
Amplitudes of other SERS Processes





M.I. Stockman, *Nanoplasmonics Theory*, in Springer Series Topics in Applied Physics, edited by K. Kneipp, M. Moskovits and H. Kneipp, *Surface Enhanced Raman Scattering – Physics and Applications* (Springer-Verlag, Heidelberg New York Tokyo, 2006), p. 47-66.

Enhancement coefficient of SERS for a molecule at a point $\mathbf{r}_0$

$$g^R = \frac{1}{|s(\omega_R)|^2} \sum_{\alpha=x,y,z} \left| \sum_{\beta=x,y,z} g_{\beta\alpha}(\mathbf{r}_0;\omega^R) g_{\beta z}(\mathbf{r}_0,\omega) \right|^2$$

$$g^R \sim Q^4$$

where the local field enhancement factor is expressed in terms of dyadic Green's function

$$g_{\alpha\beta}(\mathbf{r},\omega) = \int_V G^r_{\alpha\beta}(\mathbf{r},\mathbf{r}';\omega)\Theta(\mathbf{r}')\,\mathrm{d}^3 r'$$

$$G^r_{\alpha\beta}(\mathbf{r},\mathbf{r}';\omega) = \frac{\partial^2}{\partial r_\alpha \partial r_\beta} G^r(\mathbf{r},\mathbf{r}';\omega)$$

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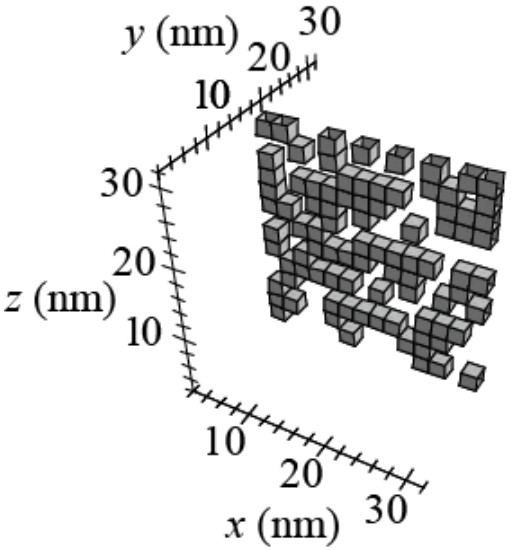
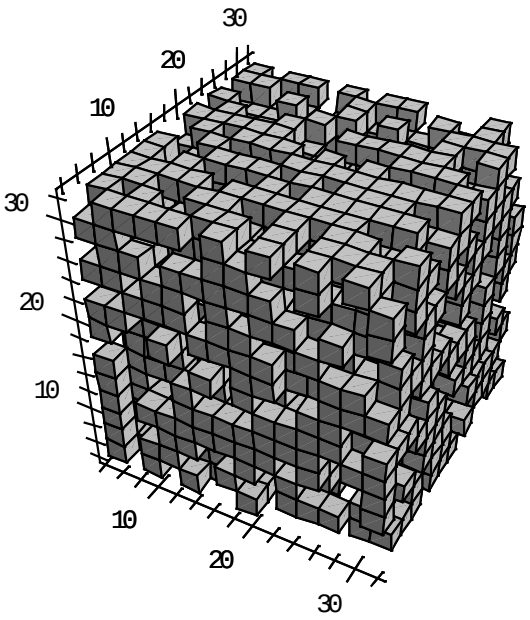
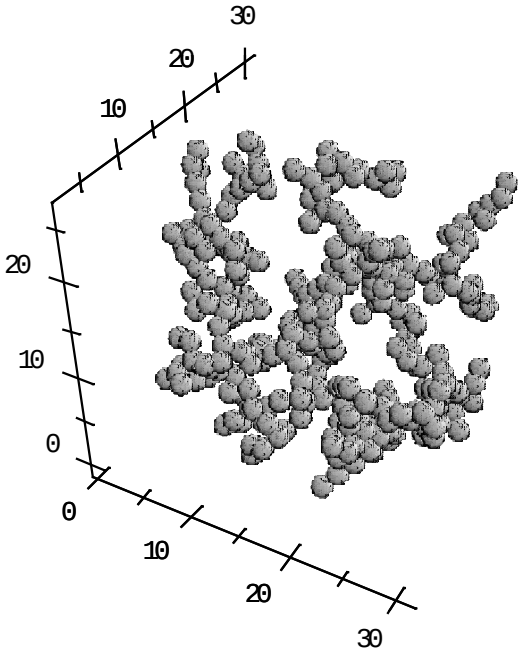
Types of Systems



Random Planar Composite



Random Bulk Composite



Fractal Cluster (Cluster-Cluster Aggregate)

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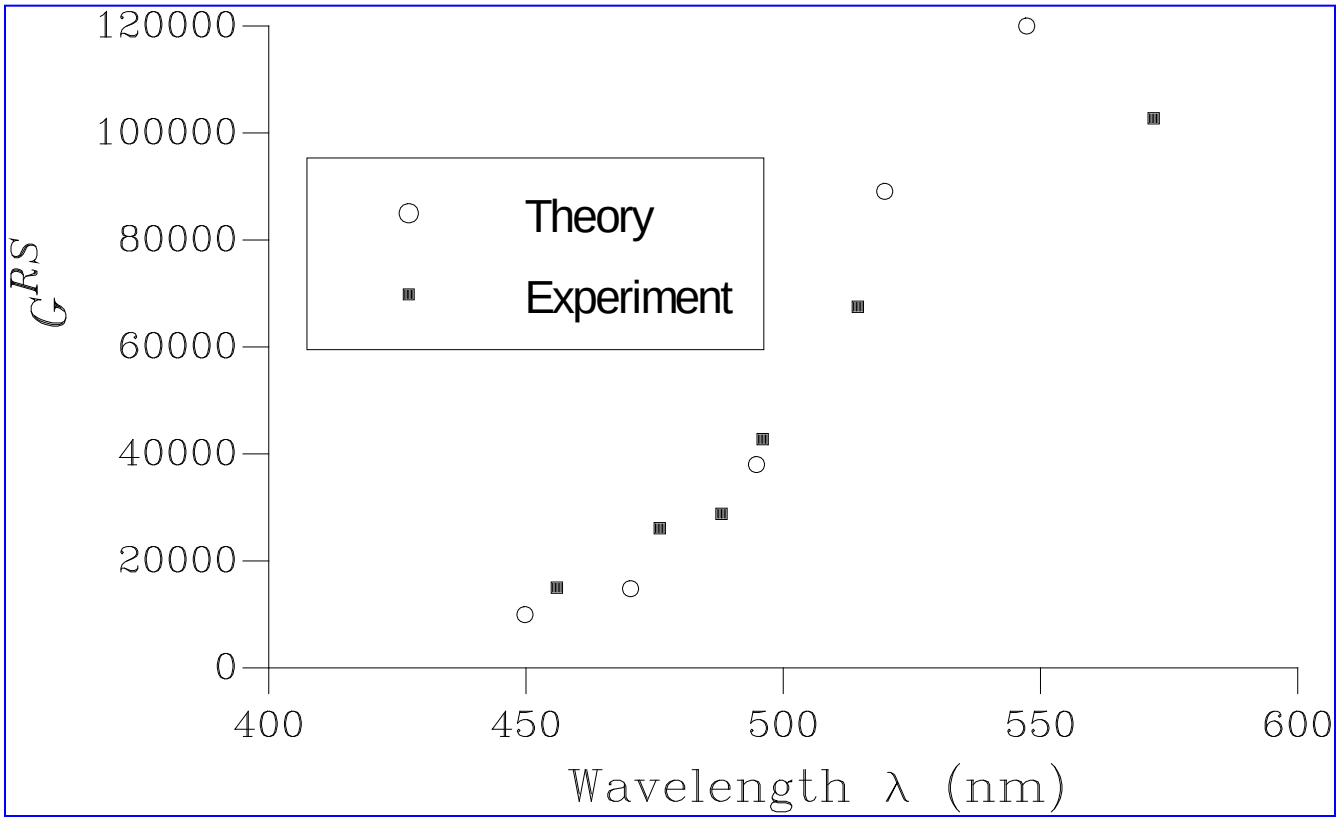
Surface Enhanced Raman Scattering (SERS)



Comparison of theoretical predictions and experimental data for the SERS enhancement coefficient from silver colloid clusters [M. I. Stockman, V. M. Shalaev, M. Moskovits, R. Botet, and T. F. George, *Enhanced Raman-Scattering by Fractal Clusters - Scale-Invariant Theory*, Phys. Rev. B **46**, 2821-2830 (1992)].

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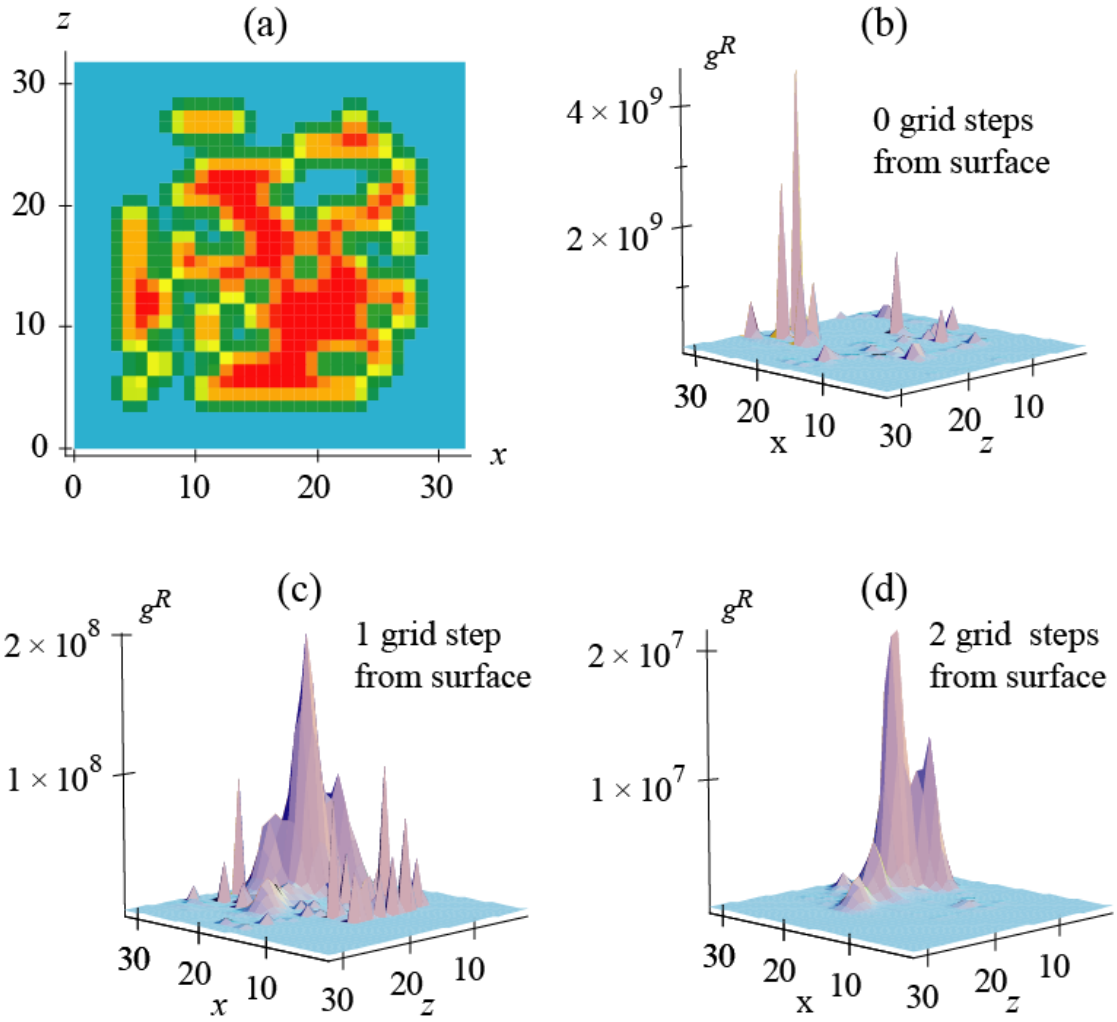
Theory: Single molecule SERS enhancement for different distances from rough silver surface

Random Planar Composite



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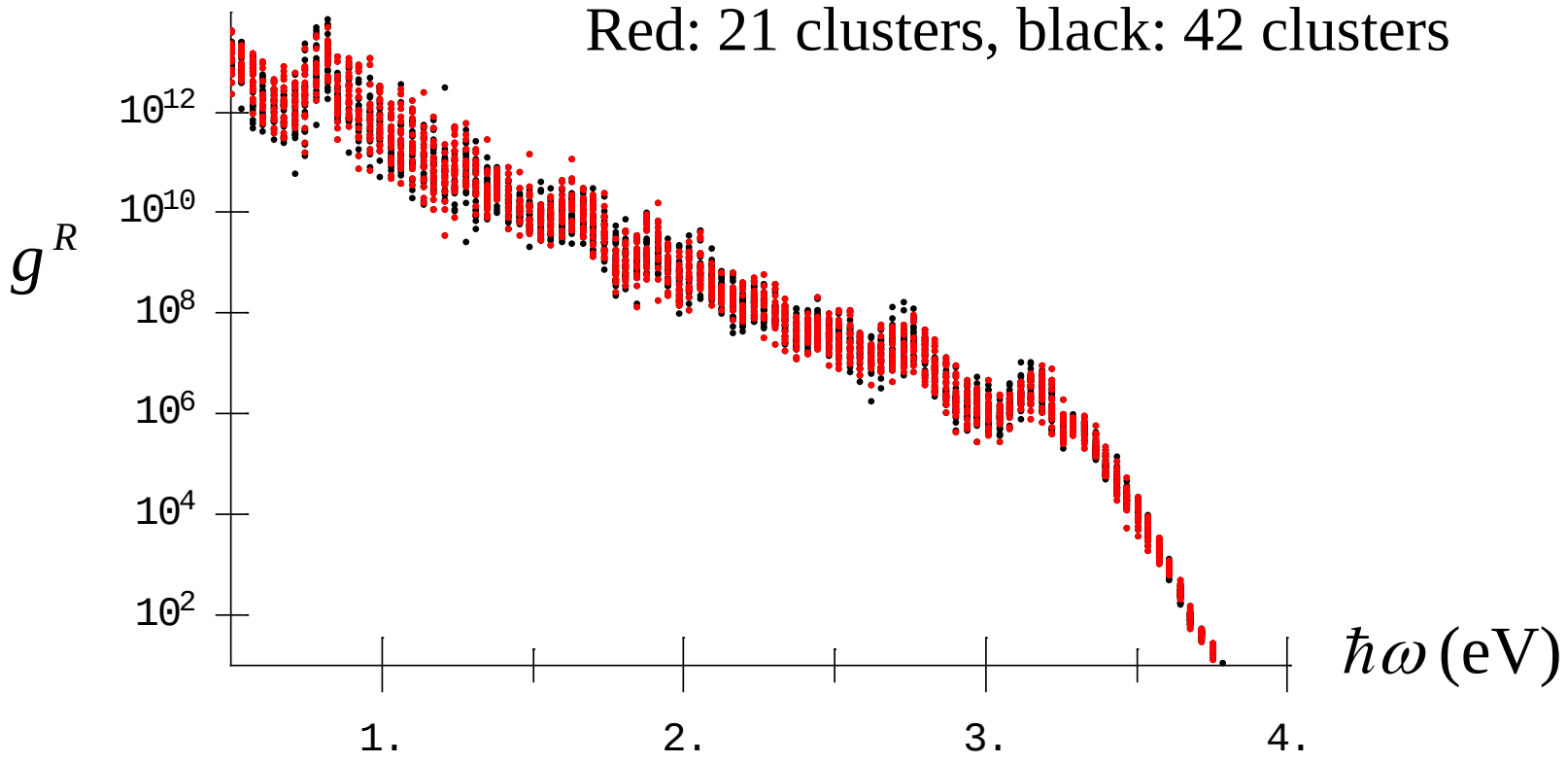
Theory: Spectrum of SERS enhancement for a single molecule at silver surface at the "hottest spot" obtained from a large ensemble of systems



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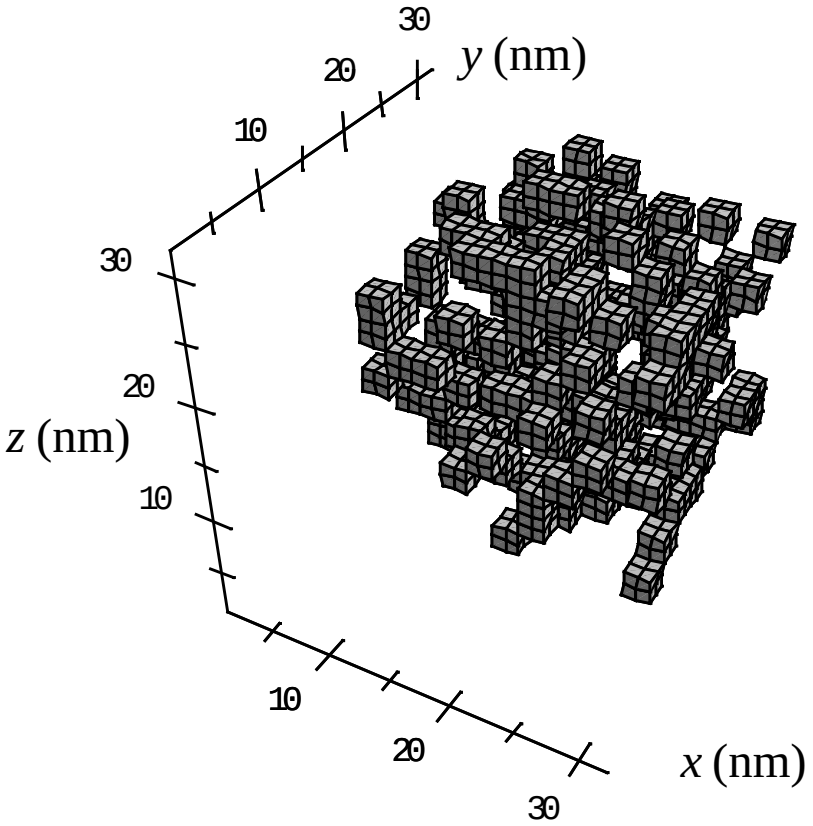
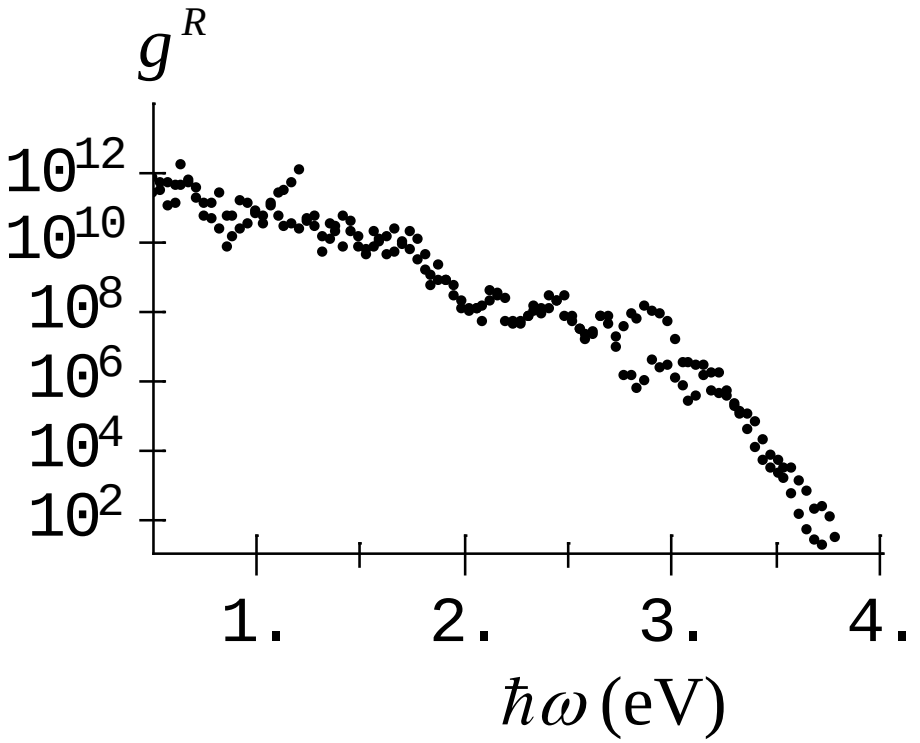
Fractal Cluster (Cluster-Cluster Aggregate)





NANO LETTERS
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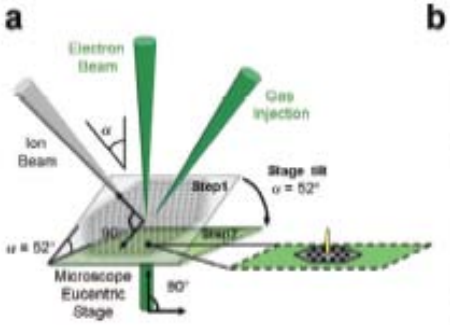
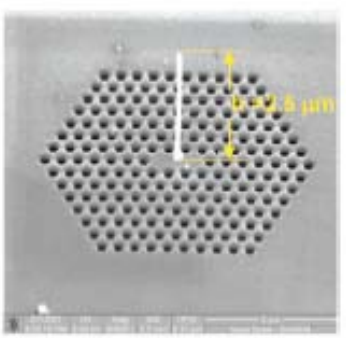
A Hybrid Plasmonic−Photonic Nanodevice for Label-Free Detection of a Few Molecules

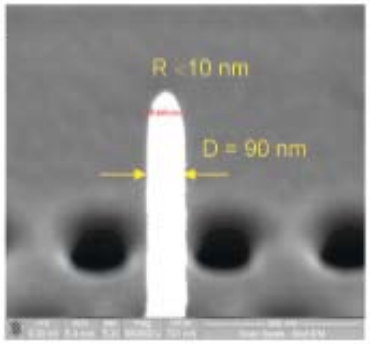
Francesco De Angelis,[†,‡] Maddalena Patrini,[§] Gobind Das,[†,‡] Ivan Maksymov,[§] Matteo Galli,[§] Luca Businaro,[∥] Lucio Claudio Andreani,[§] and Enzo Di Fabrizio*[,†,‡,⊥]

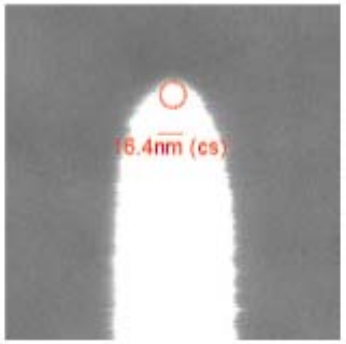
BIONEM laboratory, University of Magna Graecia, Campus S. Venuta, Germaneto, viale Europa, 88100 Catanzaro, Italy, CNISM and Department of Physics "A. Volta", University of Pavia, via Bassi 6, 27100 Pavia, Italy, TASC National Laboratory, CNR-INFM, Area Science Park, Basovizza, 34012 Trieste, Italy, and CalMED s.r.l., Campus S. Venuta, Germaneto, viale Europa, 88100 Catanzaro, Italy

Received April 18, 2008; Revised Manuscript Received June 6, 2008









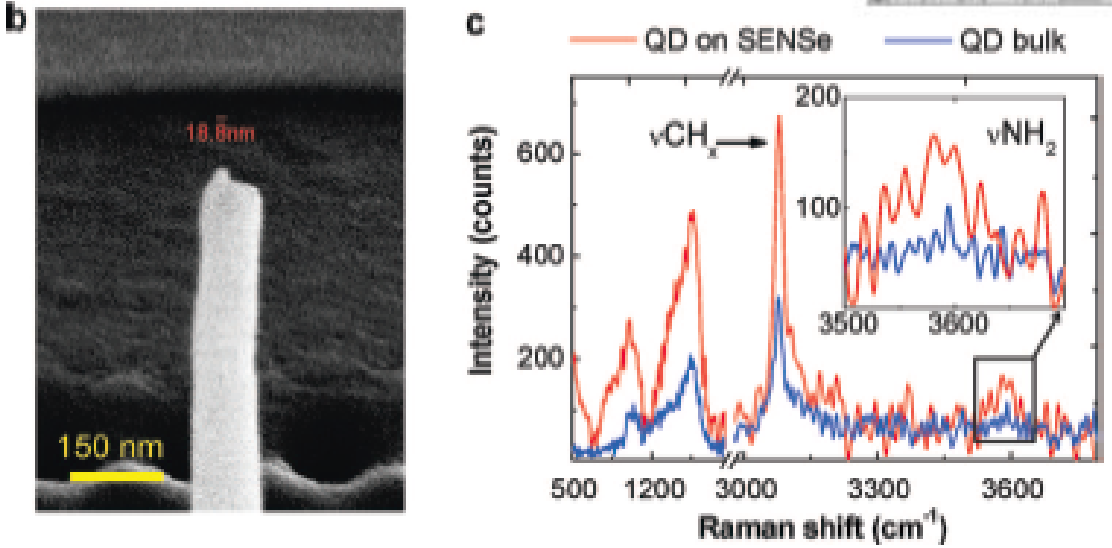


Figure 4. Single quantum dot deposition on the nanoantenna. (a) SEM images arranged in progressive magnification (from top left to bottom right) to show the deposition technique of QDs from the manipulator tip to the nanoantenna. (b) SEM image of a single core−shell ZnS/CdSe QD deposited at the SENSe tip. (c) Raman scattering spectra (λ_{exc} = 514 nm, P = 0.18 mW, T_{int} = 150 s) taken from the single QD (red line) as compared to that of a QD bulk sample (blue line). In the inset the asymmetric stretching vibration, ν-NH_2, at 3580 cm^{-1} is reported in the range between 3400 and 3800 cm^{-1}.

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Conclusions

•Electromagnetic theory of SERS predicts enhancement at 2 eV (600 nm) on order or less than 10^9- 10^{10}, which is three to four orders of magnitude less than experimentally observed

•Theory for random composites and fractal clusters predicts approximately the same magnitude of enhancement\

•Adiabatic concentration in nanoplasmonic tapers provide an alternative and very efficient way to SERS, including SERS nanoscopy

•Other factors must contribute to SERS:

Chemical enhancement? J. Jiang, K. Bosnick, M. Maillard, and L. Brus, *Single Molecule Raman Spectroscopy at the Junctions of Large Ag Nanocrystals*, J. Phys. Chem. B **107**, 9964-9972 (2003)

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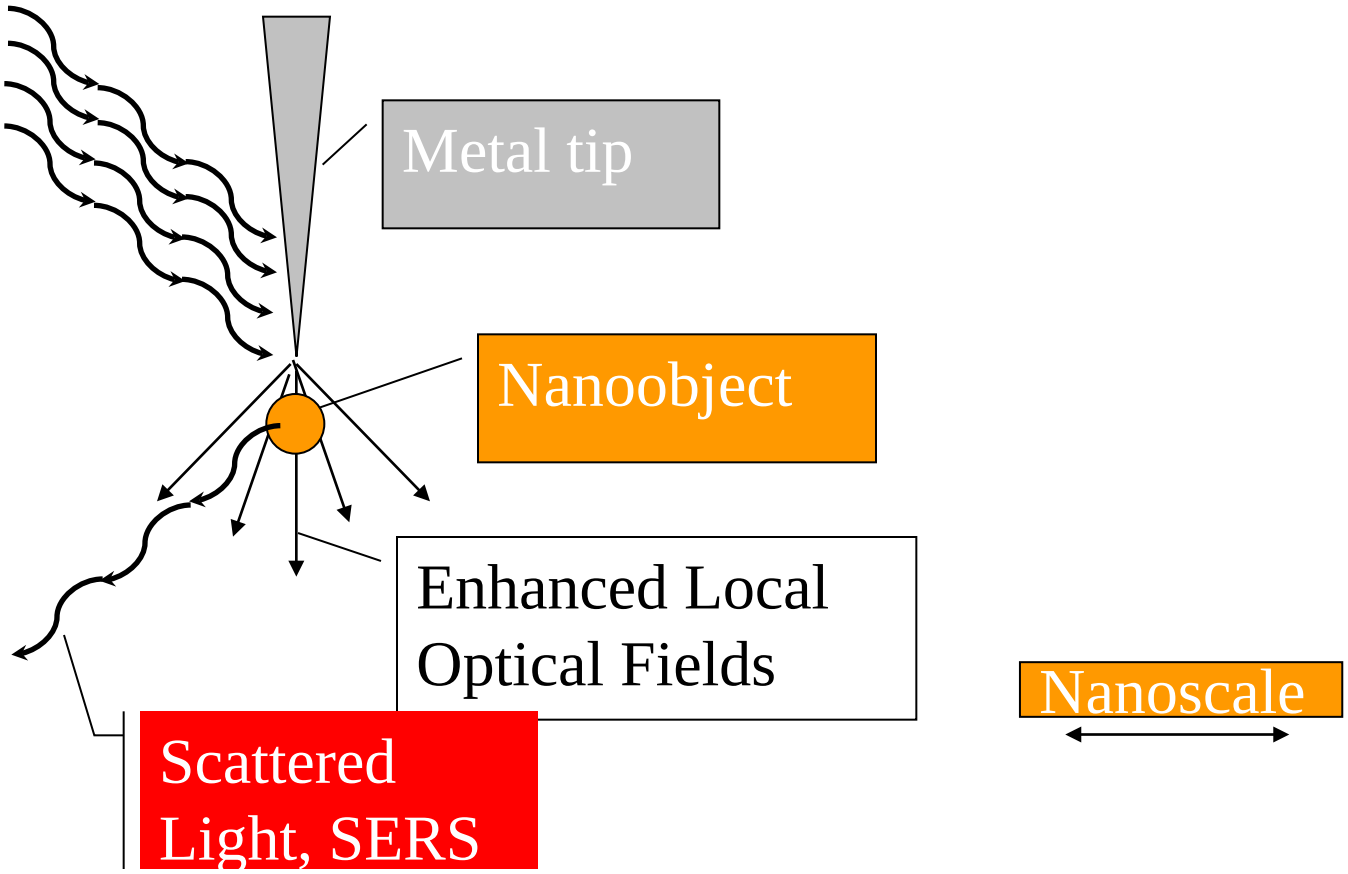
Applications of Plasmonics: Nanoscopy



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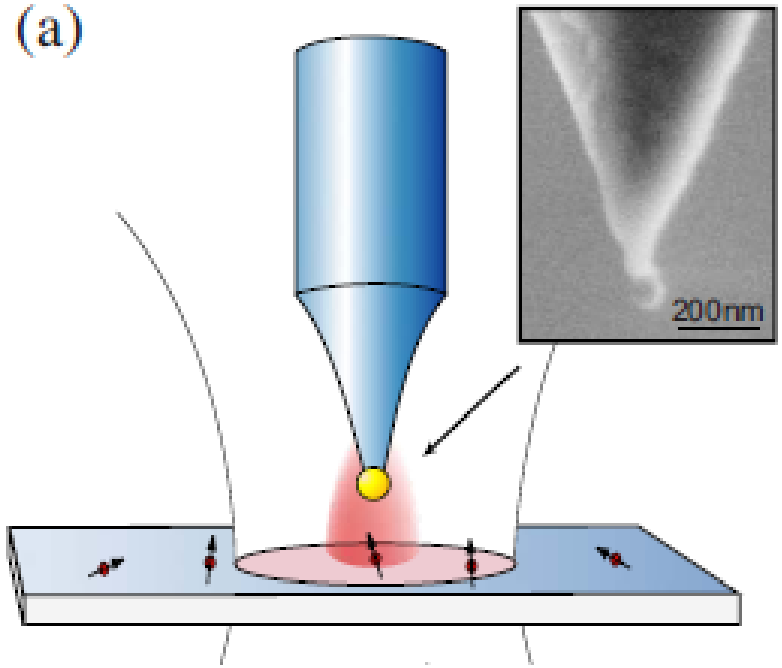
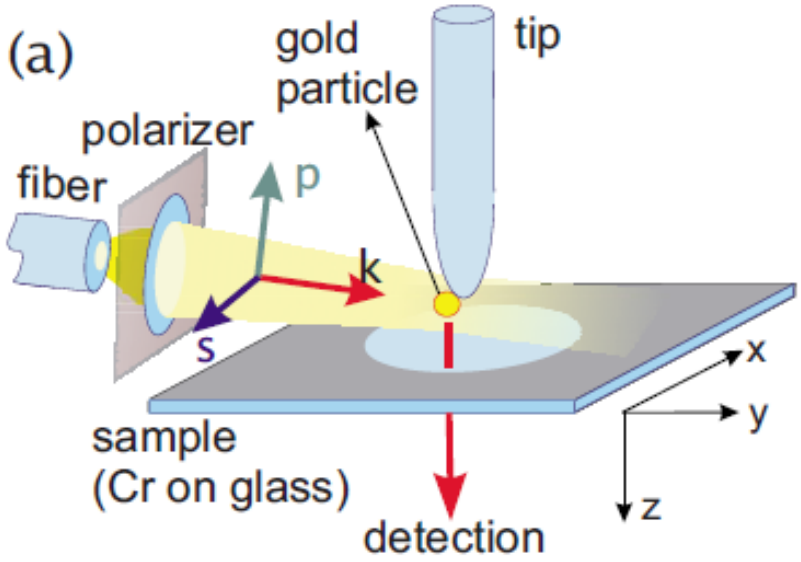
Metal Nanosphere as an Optical Antenna in Scanning Near-Field Optical Microscope (SNOM)

P. Bharadwaj, B. Deutsch, and L. Novotny, *Optical Antennas*, Advances in Optics and Photonics **1**, 438–483 (2009)





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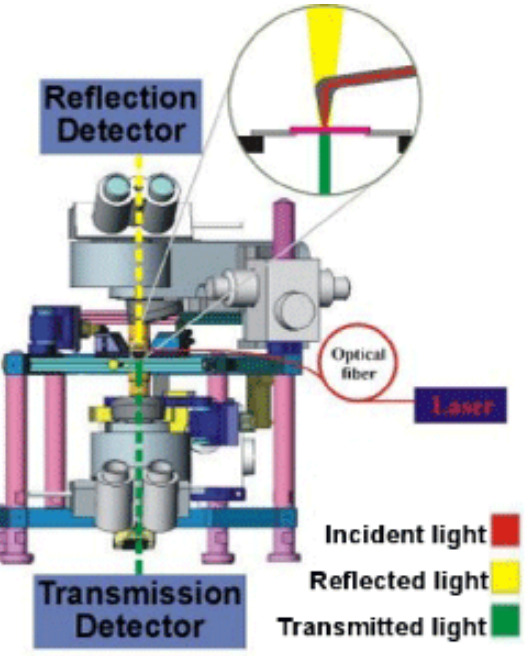
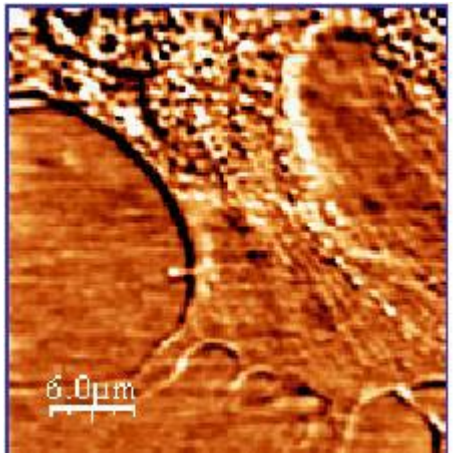
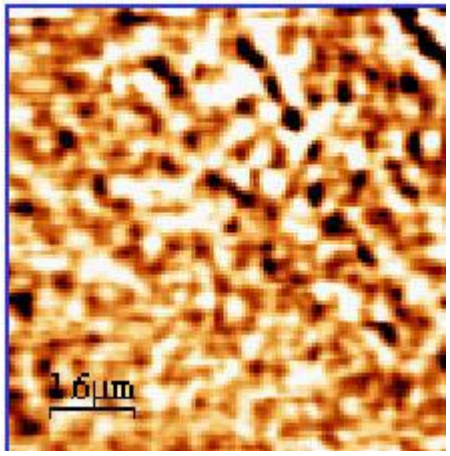
NANONICS IMAGING Ltd.

NSOM images of healthy human dermal fibroblasts in liquid obtained in transmission mode with a Nanonics cantilevered tip with a gold nanosphere







Repeating slide to remind

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L. Novotny and S. J. Stranick, *Near-Field Optical Microscopy and Spectroscopy with Pointed Probes*, Annual Rev. Phys. Chem. **57**, 303-331 (2006)

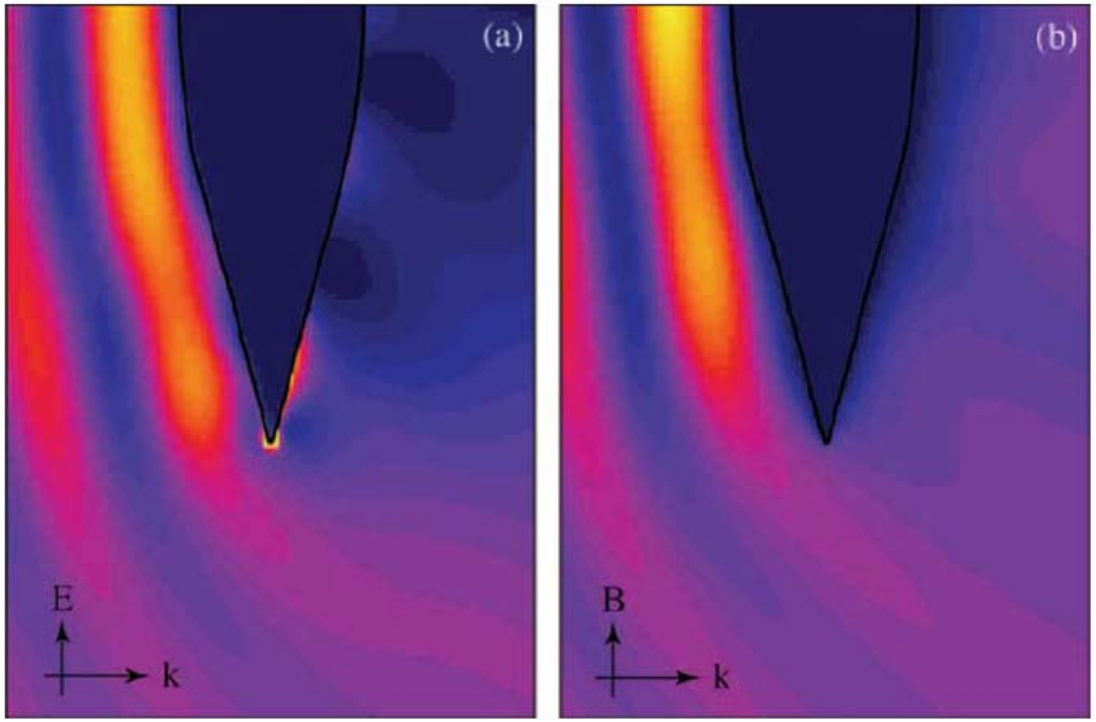

Figure 6 Calculated intensity distribution near a laser-irradiated gold tip. The exciting wave is incident from the left and forms a standing wave pattern as it interferes with the reflected field from the tip shaft, and at the end of the tip, the wave diffracts. Two different excitation polarizations are used. The field-enhancement effect is observed only if the incident wave is polarized along the tip axis (*a*). In the case of an incident wave polarized perpendicular to the tip axis, the field near the tip is attenuated (*b*).

Neil Anderson, Achim Hartschuh, and Lukas Novotny, *Chirality Changes in Carbon Nanotubes Studied with Near-Field Raman Spectroscopy* Nano Lett. 577 – 582 (2007)

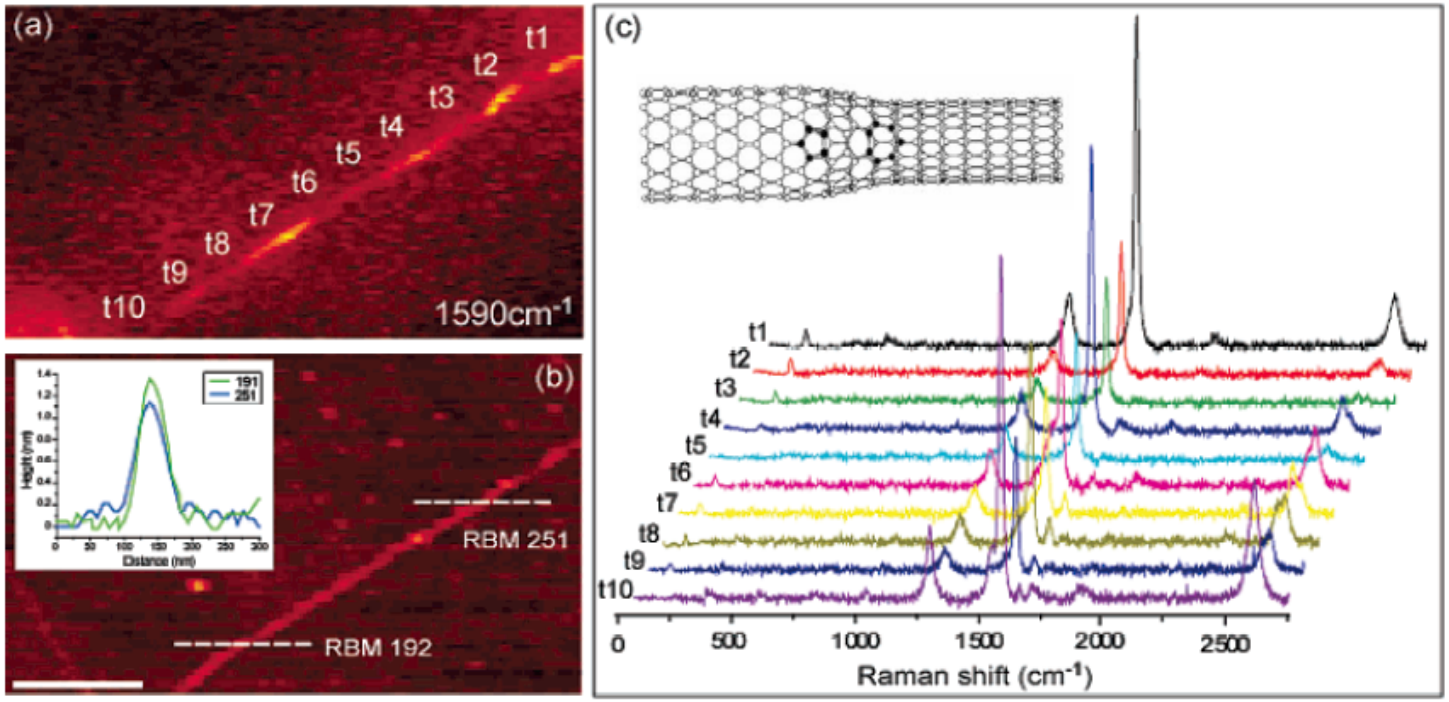

Figure 1. Near-field Raman imaging and spectroscopy: near-field Raman image (a) and corresponding topography image (b) of an isolated SWNT, where the optical resolution was determined to be 40 nm (fwhm). Also shown are a series of tip-enhanced Raman spectra (c) acquired along the length of the SWNT. From the recorded spectra, two resonant RBM phonons are detected. One RBM phonon frequency is detected at 251 cm^{-1}, from which we assign a semiconducting chirality. The second RBM phonon frequency recorded from the lower section of the SWNT is centered at 192 cm^{-1}, from which we assign a metallic chirality. See main text for details. The inset of (b) displays two cross-sectional profiles acquired from both the upper and lower sections, respectively, revealing that the expected diameter change occurs as the SWNT undergoes the transition from a semiconducting to metallic chirality. Scale bar denotes 200 nm and is valid for both (a) and (b).

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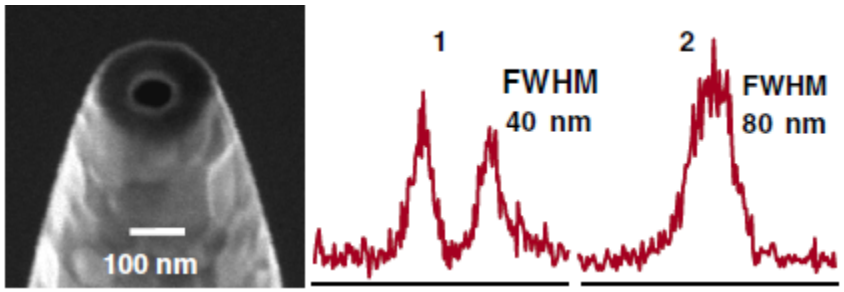
T. H. Taminiau, F. B. Segerink, R. J. Moerland, L. Kuipers, and N. F. van Hulst, *Near-Field Driving of an Optical Monopole Antenna*, Journal of Optics a-Pure and Applied Optics **9**, S315-S321 (2007).



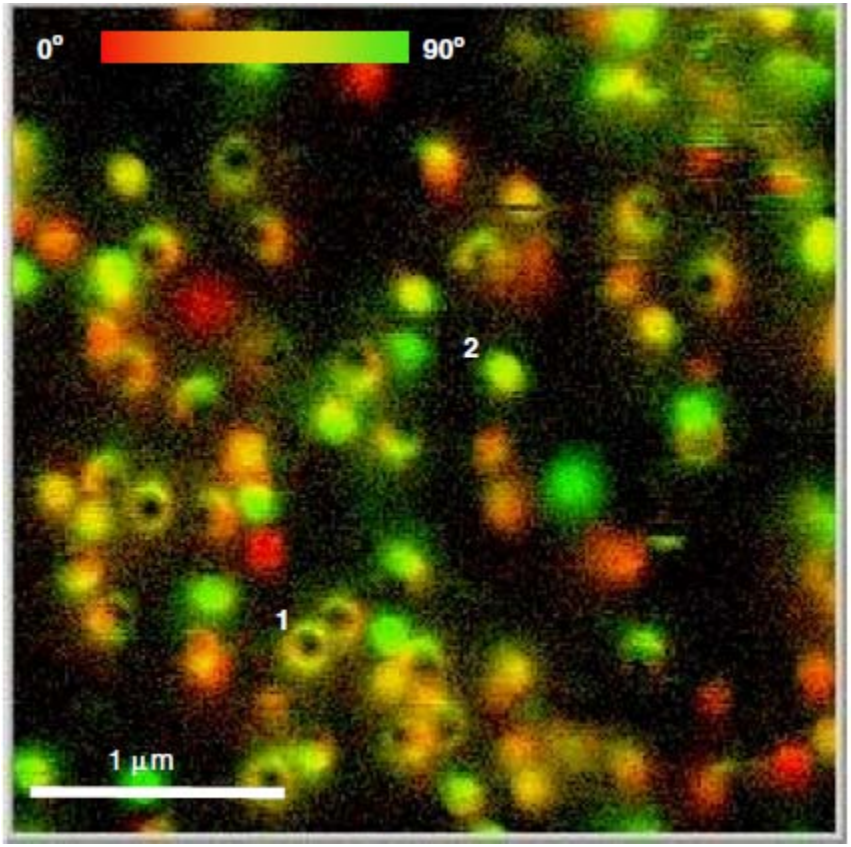
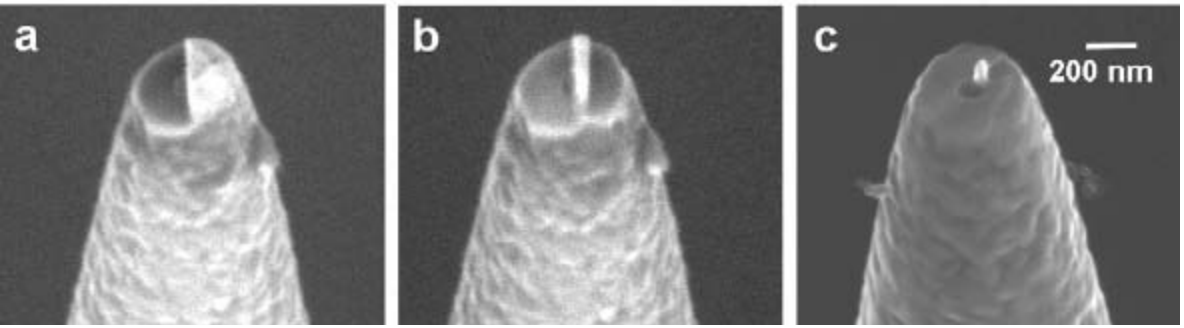
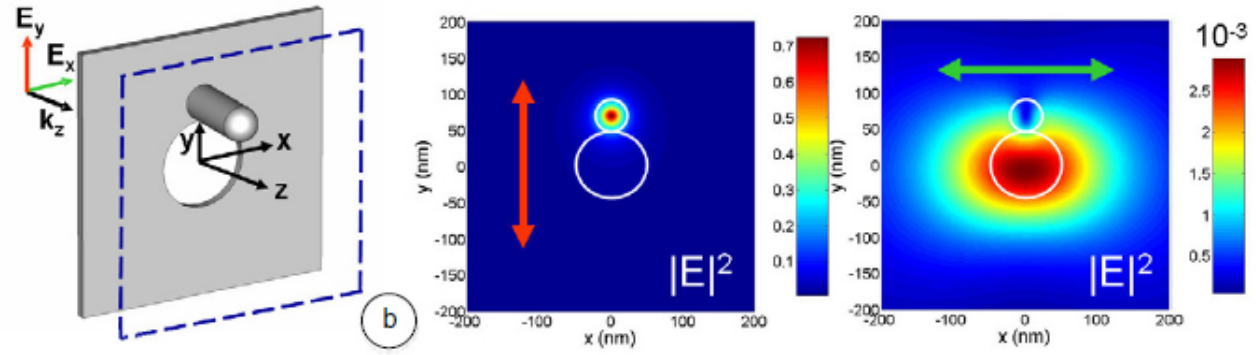
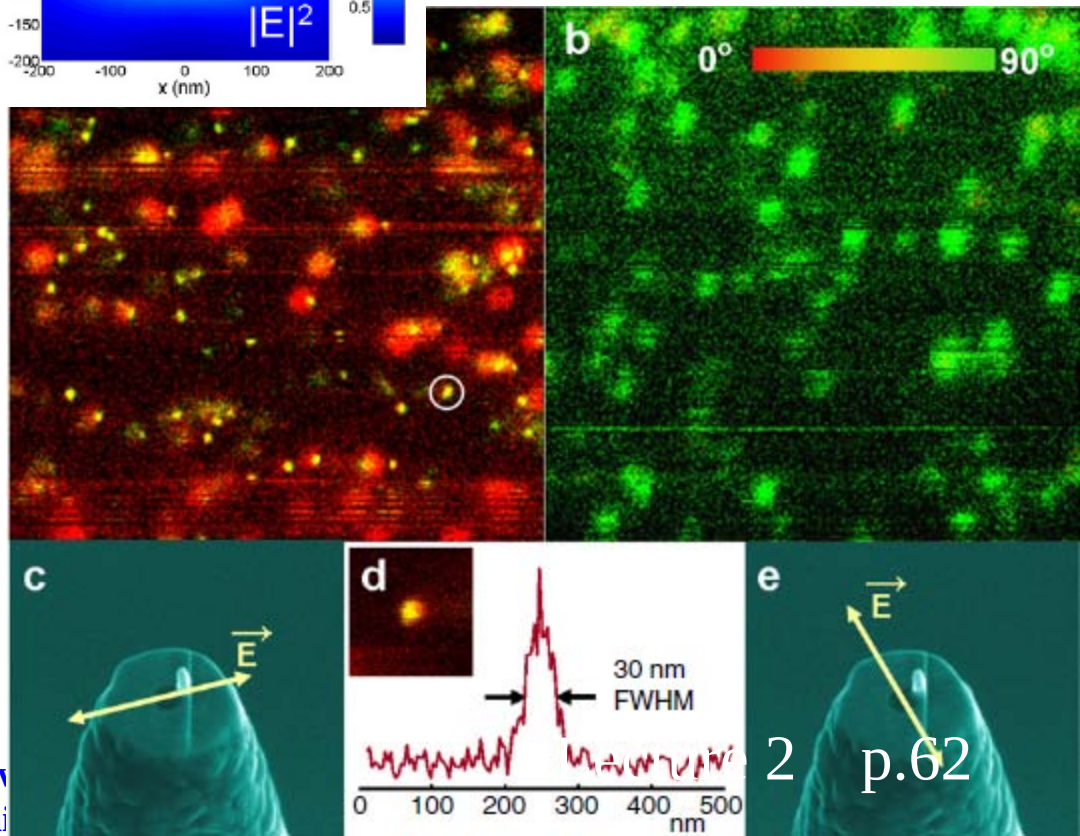


Figure 2. Near-field image showing the spatial fluorescence profile of several single molecules (DiI in PMMA) excited by an aperture probe. The signal is colour-coded according to the polarization of the fluorescence (red horizontal, green vertical). The inset shows a 75 nm aperture probe fabricated by FIB milling and typical fluorescence line traces for selected molecules oriented out of plane (1) and in plane (2).





Single fluorescent DiI molecules excited by the antenna probe, for two directions of incident linear polarization. Two features appear: sharp spots (~30 nm) showing molecules excited by the local monopole antenna and large spots (~150 nm) associated with molecules excited by the aperture. The sharp spots only occur in (a) for the polarization that drives the antenna. ((c), (e)) Excitation polarization with respect to the position of the antenna. (d) Fluorescence line trace for a selected molecule excited by the monopole, demonstrating the localized antenna field with 30 nm FWHM at the position of the molecule.



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Next generation of scanning near-field optical microscopy (SNOM) with chemical mapping:

Adiabatic concentration of optical energy and giant surface-enhanced Raman scattering (SERS)

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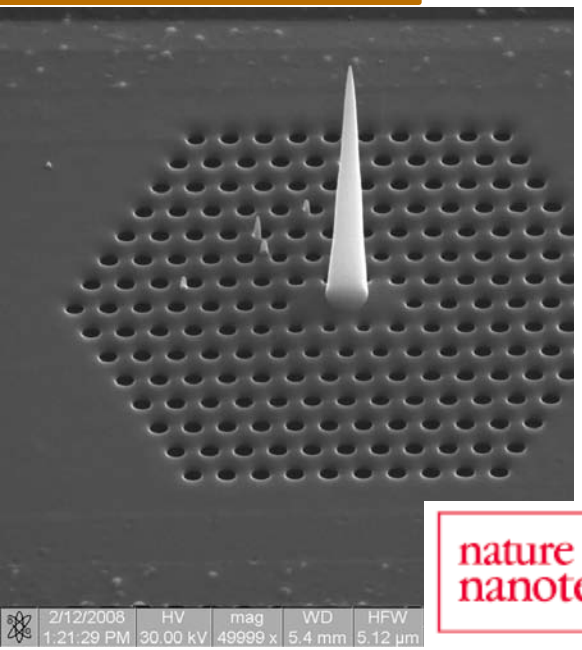
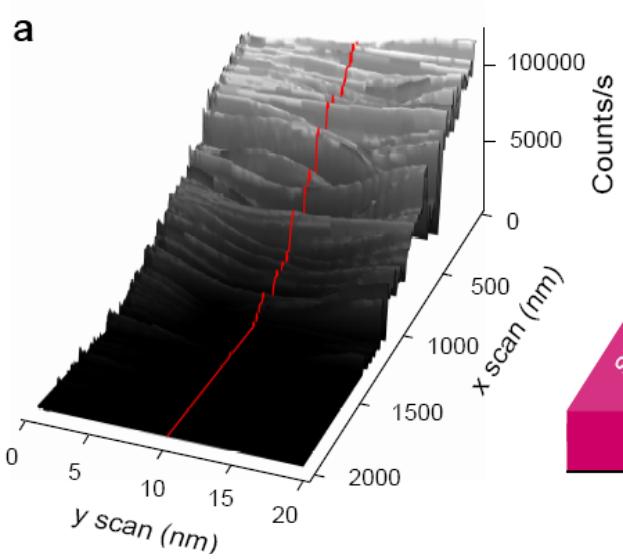
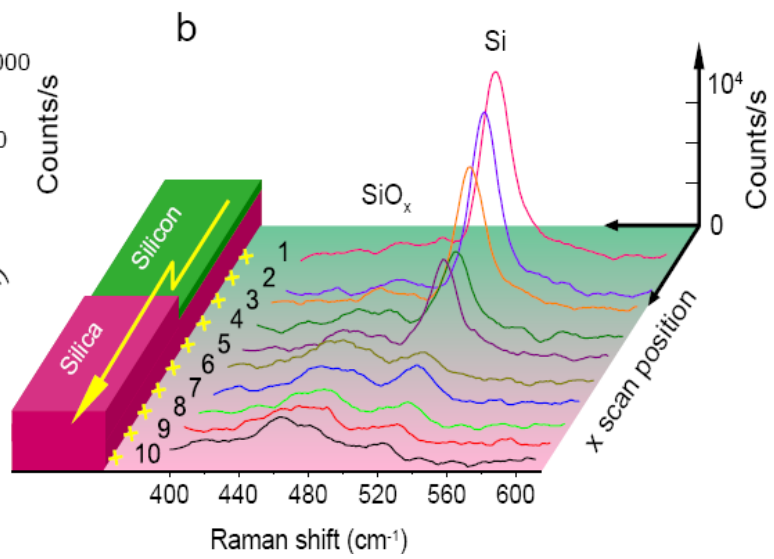
Di Fabrizio, E., *et. al*, Italian patent n. TO2008A000693 23.09.2008

5 nm radius







nature nanotechnology
ARTICLES
PUBLISHED ONLINE: 22 NOVEMBER 2009 | DOI: 10.1038/NNANO.2009.348

Nanoscale chemical mapping using three-dimensional adiabatic compression of surface plasmon polaritons

Francesco De Angelis[1,2], Gobind Das[1], Patrizio Candeloro[2], Maddalena Patrini[3], Matteo Galli[3], Alpan Bek[4], Marco Lazzarino[4,5], Ivan Maksymov[3], Carlo Liberale[2], Lucio Claudio Andreani[3] and Enzo Di Fabrizio[1,2]*

Probing the Magnetic Field of Light at Optical Frequencies

M. Burresi,[1]* D. van Oosten,[1] T. Kampfrath,[1] H. Schoenmaker,[1]
R. Heideman,[2] A. Leinse,[2] L. Kuipers[1]

Science **326**, 550 (2009);
DOI: 10.1126/science.1177096

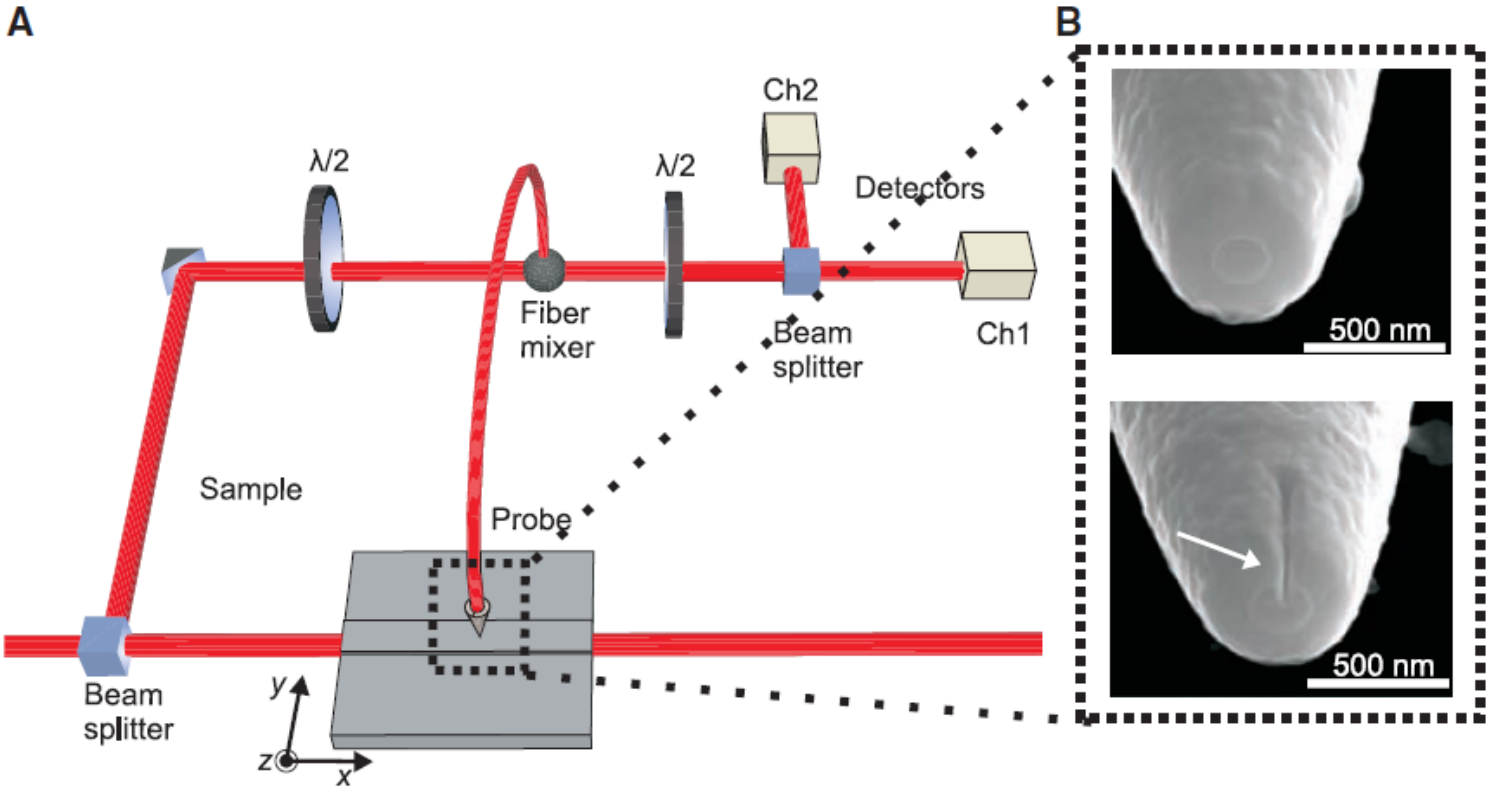


Fig. 1. (**A**) Schematic of the phase-sensitive near-field microscope. The near-field probe, indicated by the dashed box, is scanned 20 nm above the sample and collects the evanescent field of the light inside the waveguide. The light is mixed with light from a reference branch. The resulting

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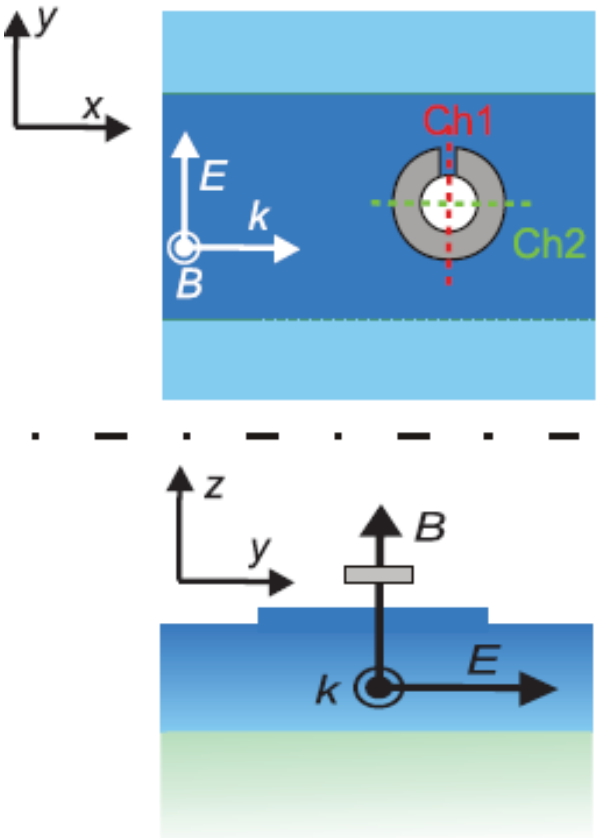
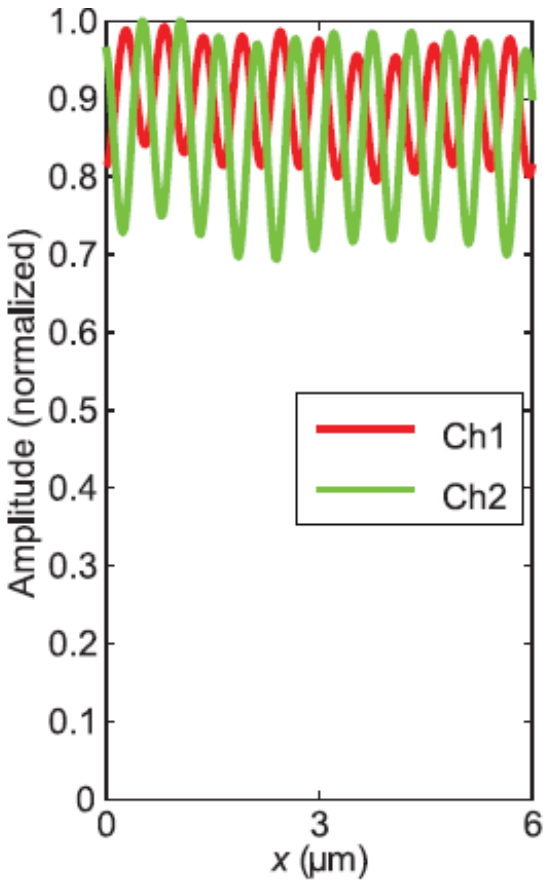
M. Burresi, D. van Oosten, T. Kampfrath, H. Schoenmaker, R. Heideman, A. Leinse, and L. Kuipers, *Probing the Magnetic Field of Light at Optical Frequencies*, Science **326**, 550-553 (2009).





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CONCLUSIONS: Nanoscopy

- Nanoscopy is performed with near-field probes generating nanolocalized hot spots
- There are different near-field probes: nanoparticles, pointed probes (tips) with external excitation, nanophotonic-nanoplasmonic tapered fibers, and adiabatic nanoplasmonic tapers
- The most efficient probe is an adiabatic nanoplasmonic taper that allows for SERS nanoscopy with resolution ~5 nm
- There is a possibility to record polarization, phase, and electrical and magnetic components of the nanolocalized fields

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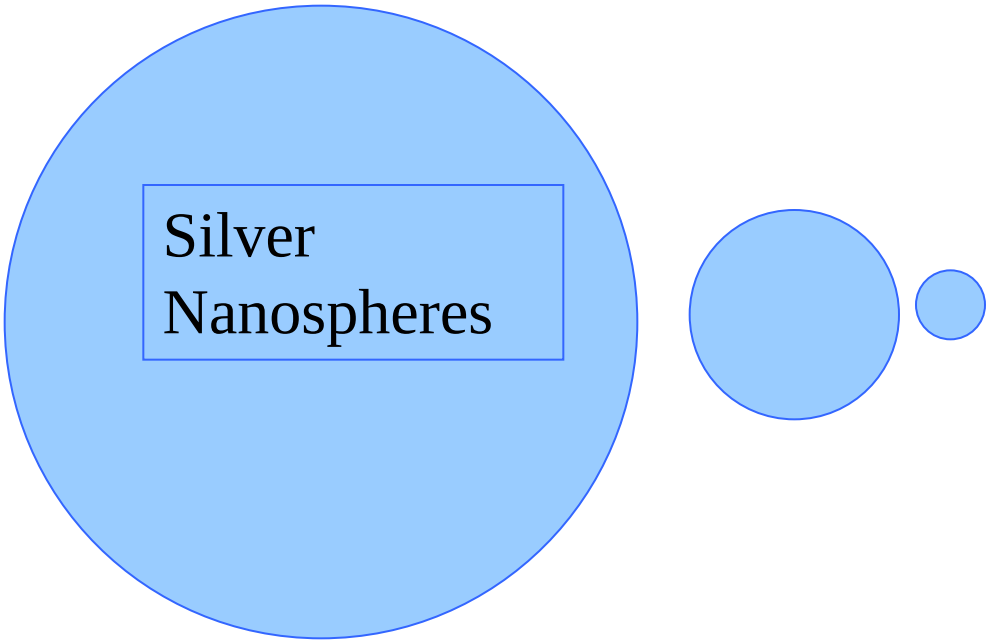
Efficient Self-Similar Nanolens of Nanospheres

K. Li, M. I. Stockman, and D. J. Bergman, *Self-Similar Chain of Metal Nanospheres as an Efficient Nanolens*, Phys. Rev. Lett. **91**, 227402 (2003).



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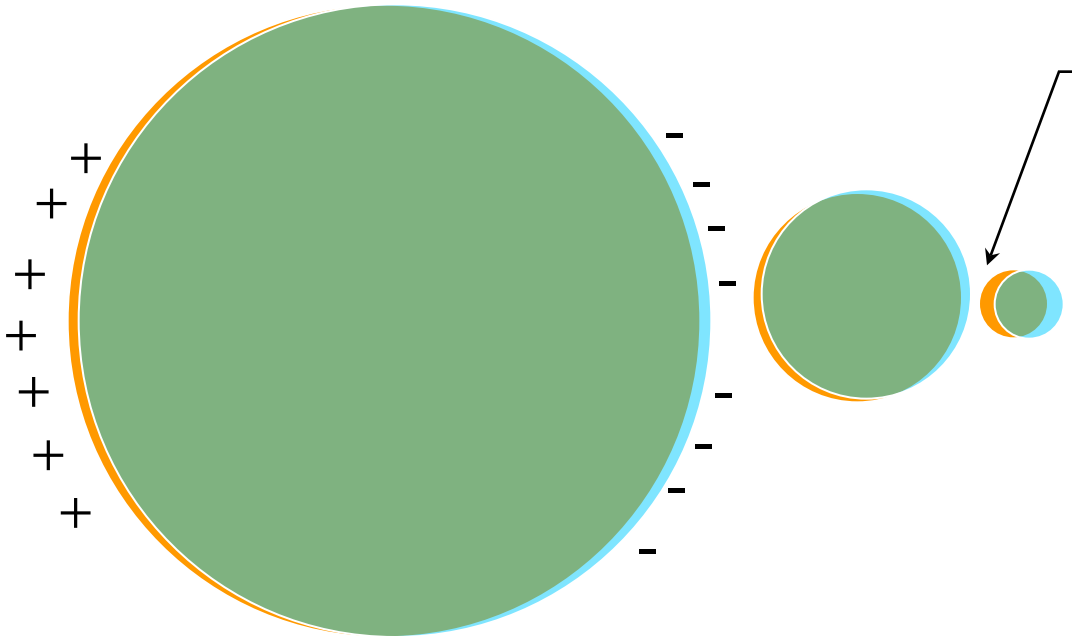
Underlying physics of local field enhancement in efficient nanolens: Cascade enhancement



Giant local fields in the minimum gap: Nanoscale localization of optical energy

Optical Electric Field

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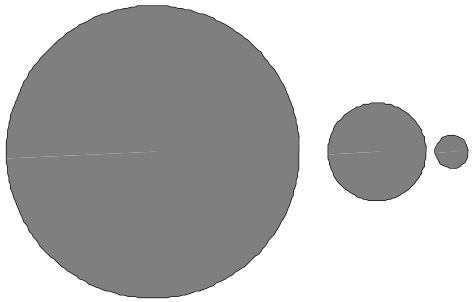
Giant Local Field Enhancement in Nanolens

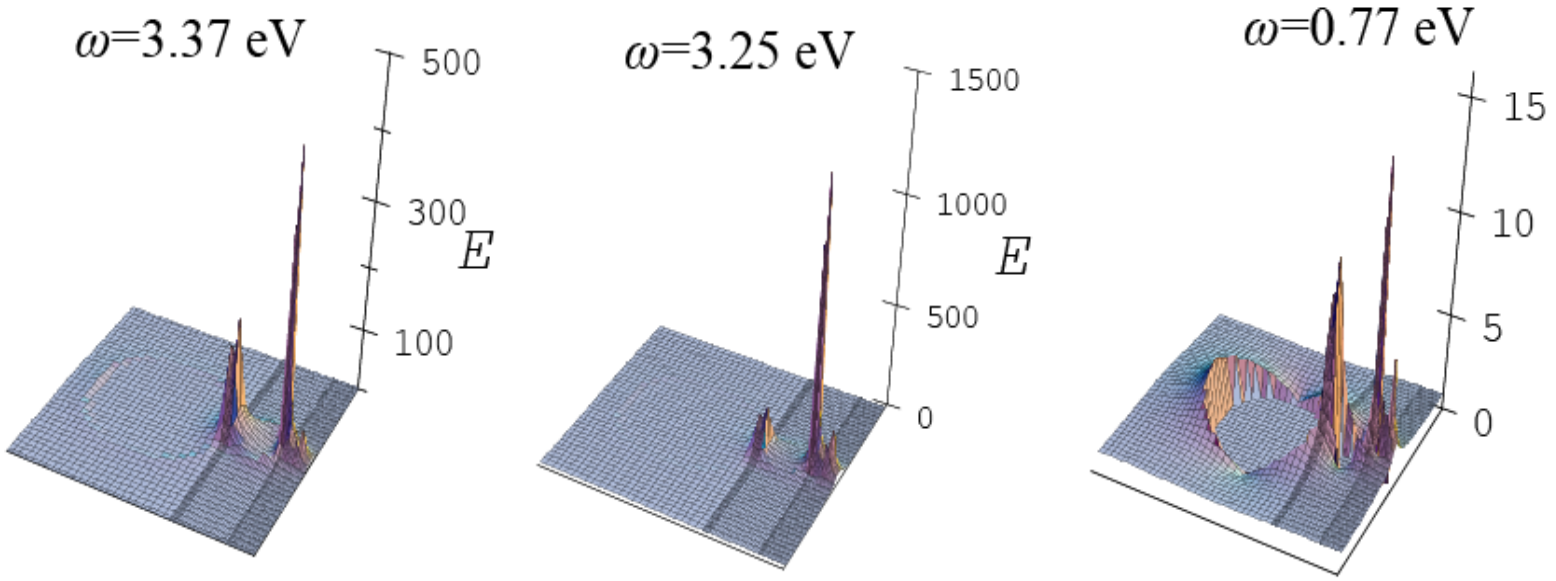
d=0.3R

Local Fields for Silver 3-Sphere Nanolens



K. Li, M. I. Stockman, and D. J. Bergman, *Self-Similar Chain of Metal Nanospheres as an Efficient Nanolens*, Phys. Rev. Lett. **91**, 227402 (2003).

Raman enhancement ~ E^4 ~ 10^{13}



Anal. Chem. 2008, 80, 4247–4251

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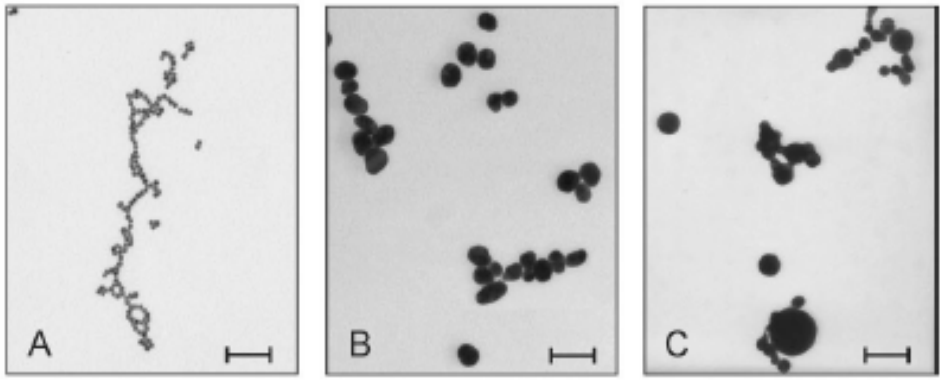
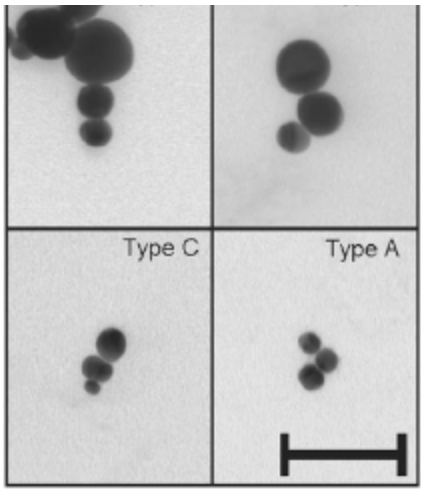
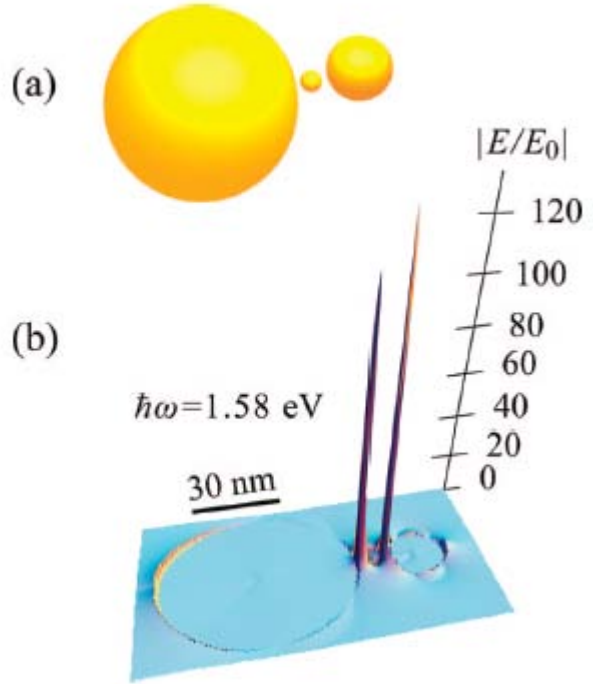
Gold Nanolenses Generated by Laser Ablation-Efficient Enhancing Structure for Surface Enhanced Raman Scattering Analytics and Sensing

Janina Kneipp,*,†,‡ Xiangting Li,§ Margaret Sherwood,† Ulrich Panne,‡ Harald Kneipp,† Mark I. Stockman,§ and Katrin Kneipp†,||







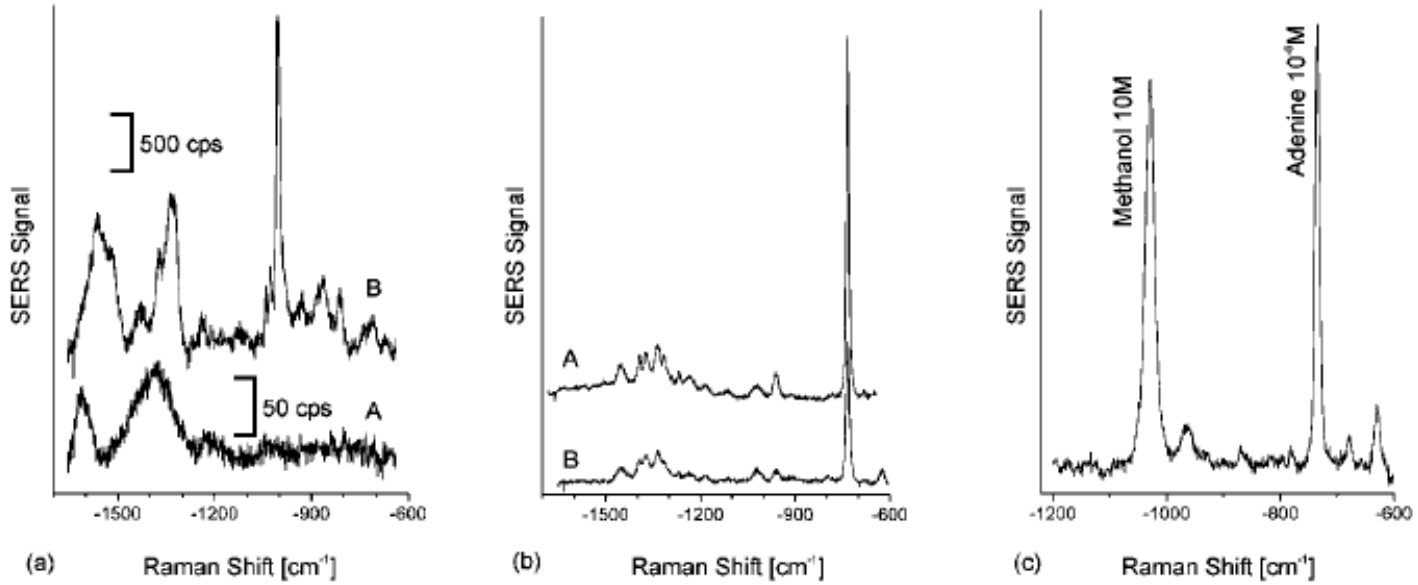


Figure 3. Comparison of SERS using gold nanolenses made by ablation and chemically prepared nanoaggregates as enhancing nanostructures. (a) Raman spectra measured from aqueous solutions of gold nanoaggregates without any analyte to compare background signals. The chemically prepared gold nanoparticles (spectrum B) display surface enhanced Raman lines, resulting from impurities introduced during the preparation process of this particular batch of colloids, such as the line at ~1000 cm^{-1}. The bands around 1500 cm^{-1} in the spectrum of the ablation nanoaggregates can be assigned to carbonate complexes.[18] Spectra were measured at 50 mW at 785 nm excitation in 10 s (spectrum A) and 1 s (spectrum B) collection times. Abbreviation: cps, counts per second. (b) SERS signals of adenine measured in solutions of ablation aggregates (spectrum A) and chemically prepared nanoaggregates (spectrum B) using 10 mW at 785 nm excitation. (c) Comparison of the Raman signal of 10^{-8} M adenine and 10 M methanol measured in aqueous solutions of nanoaggregates.

Self-Similar Gold-Nanoparticle Antennas for a Cascaded Enhancement of the Optical Field

Christiane Höppener,[1,2] Zachary J. Lapin,[1] Palash Bharadwaj,[1] and Lukas Novotny[1,*]
[1]*Institute of Optics, University of Rochester, Rochester, New York 14627, USA*
[2]*Institute of Physics, University of Münster, 48149 Münster, Germany*

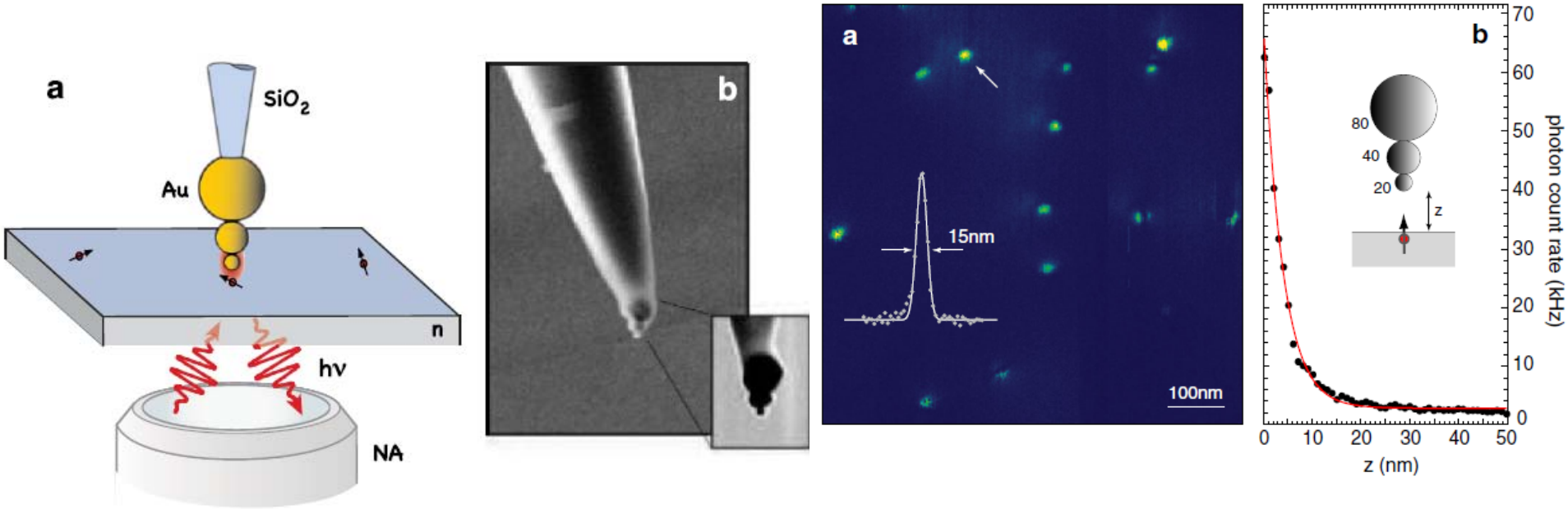


FIG. 4 (color online). Excitation of single-molecule fluorescence with a trimer antenna consisting of 80, 40, and 20 nm gold nanoparticles. (a) Fluorescence image of the single-molecule sample. Inset: Line cut through the single fluorescence spot marked by the arrow. (b) Fluorescence from a single z-oriented molecule recorded as a function of distance from a trimer antenna. The steep rise of fluorescence counts for separations smaller than 15 nm is due to strong field localization along the z axis at the apex of the trimer antenna.

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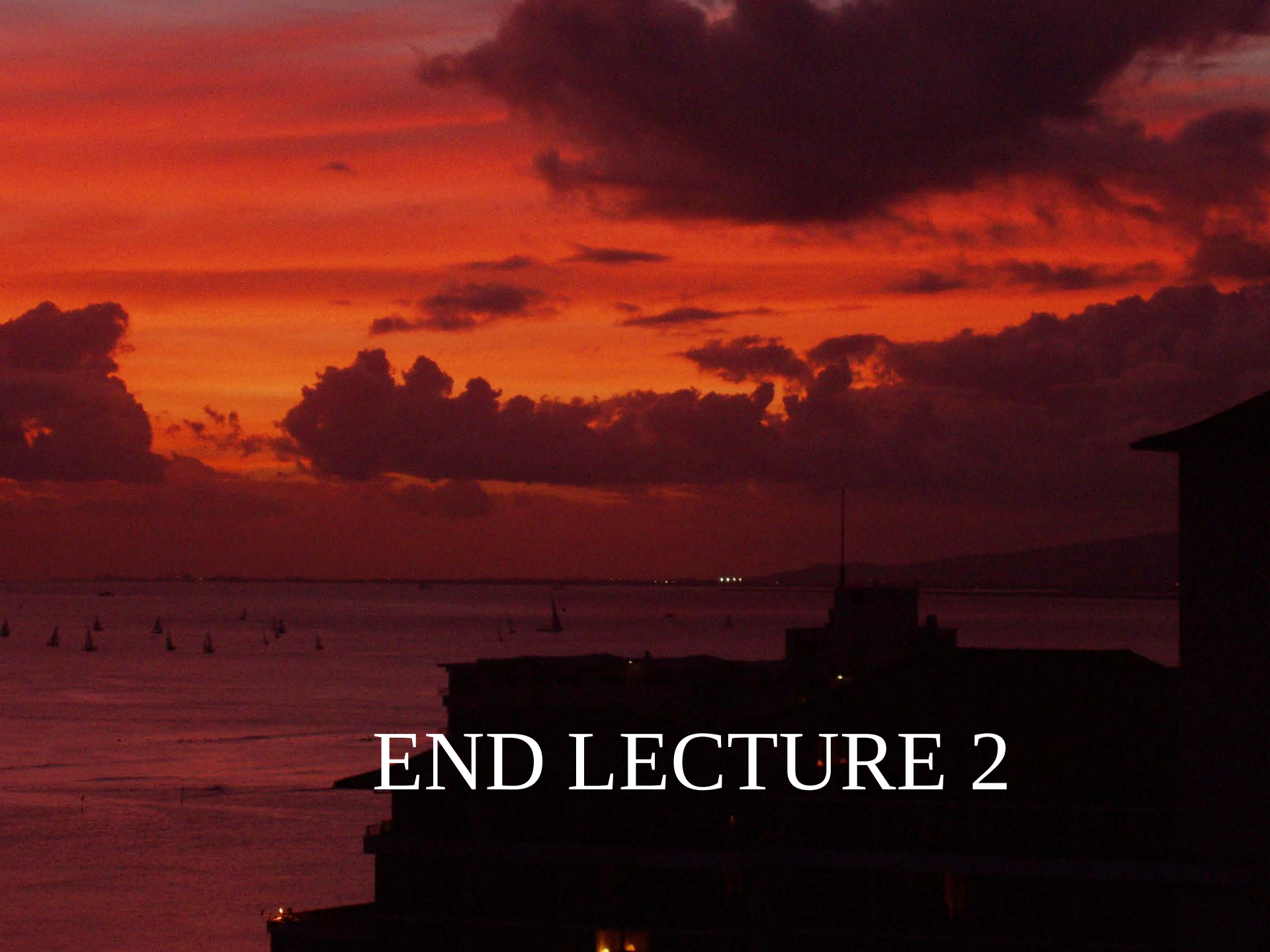
CONCLUSIONS

- A self-similar chain of metal nanospheres makes an efficient nanolens focusing energy of optical field, concentrating it a nanoscale gap between the smallest nanospheres
- The optical field in the nanofocus is enhanced by more then three orders of magnitude
- A molecule adsorbed in this nanofocus will exhibit Raman scattering enhanced by a factor on order or greater than 10^{13}
- Using the nanolens at a tip of a SNOM renders unprecedented field concentration and spatial resolution


END LECTURE 2