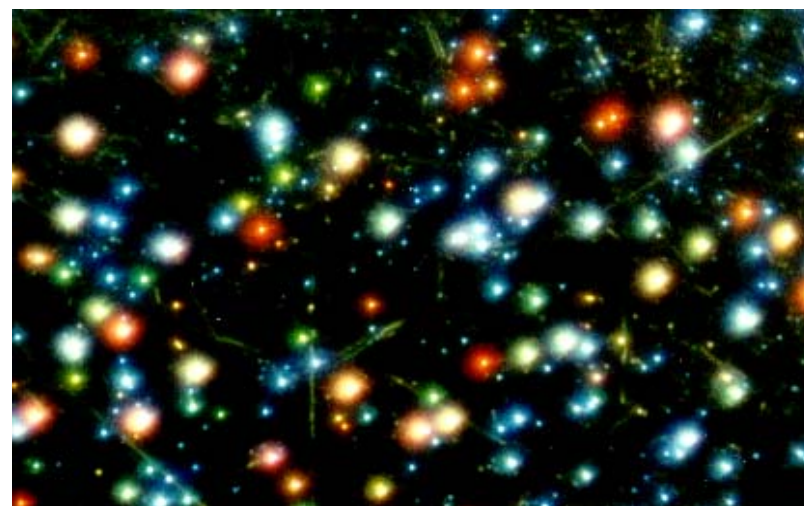


Excited Electronic States of Ag Nanocrystals - “Plasmons”

Lou Brus,
Chemistry Department, Columbia University

- Single molecule Raman Scattering (SERS)
- Chemisorbed Molecules
- Photovoltage: Citrate Photo-oxidation
- Prisms: Light Driven Ostwald Ripening



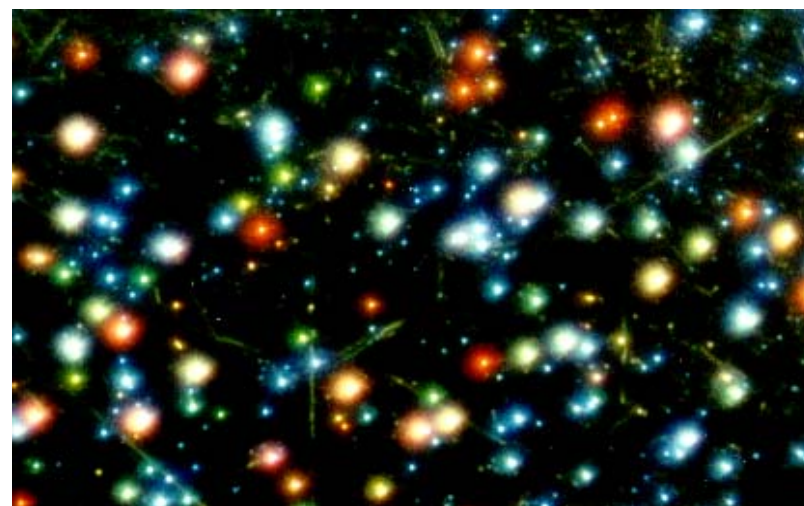
Coworkers: Haitao Liu, Peter Redmond, Xiaomu Wu, Mathieu Maillard, Alex Hallock, Jiang Jiang, Ken Bosnick, Amy Michaels, Manoj Nirmal

Support: DOE Basic Energy Sciences

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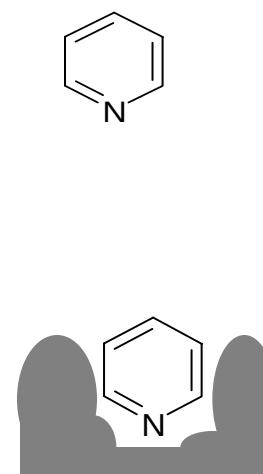
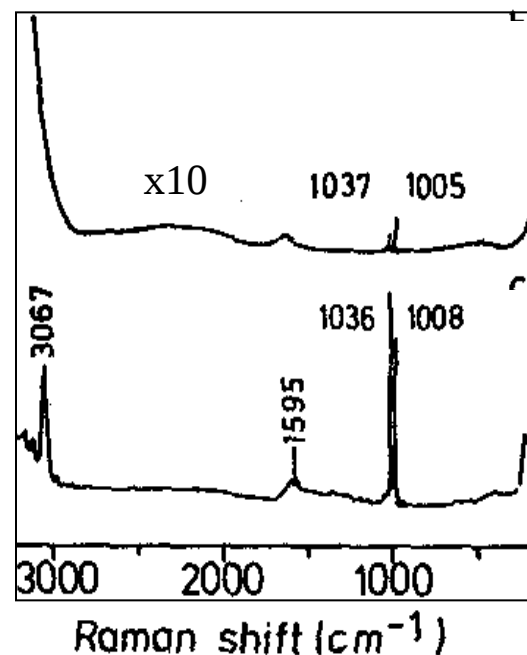
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Surface-Enhanced Raman Spectroscopy (SERS)

Normally Raman spectra are extremely weak
Raman cross section = 10^{-29} cm^2

Dye molecule fluorescence cross section =
 10^{-16} cm^2

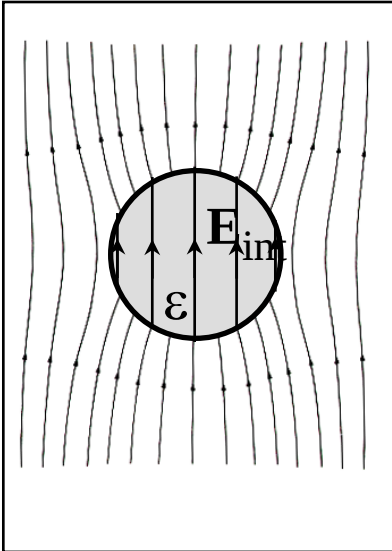


Raman cross sections of molecules adsorbed on rough Ag surfaces or particles are enhanced by 5 or 6 orders of magnitude.

Jeanmaire and Van Duyne, *J. Electroanal. Chem.* **1977**, 84, 1

Albrecht and Creighton, *J. Am. Chem. Soc.* **1977**, 99, 5215

Single Particle, Near-Field Electromagnetic Enhancement “Nano Antenna”



P = COHERENT ac oscillating POLARIZATION Dipole:
Unrelaxed, Hot Electrons

$$\mathbf{P} = 4\pi \left(\frac{\epsilon - 1}{\epsilon + 2} \right) a^3 \mathbf{E}_0$$

P shows
resonance behavior when
 $|\epsilon + 2| = \text{minimum}$

Ag: $\epsilon(380 \text{ nm}) = -2 + i0.2$

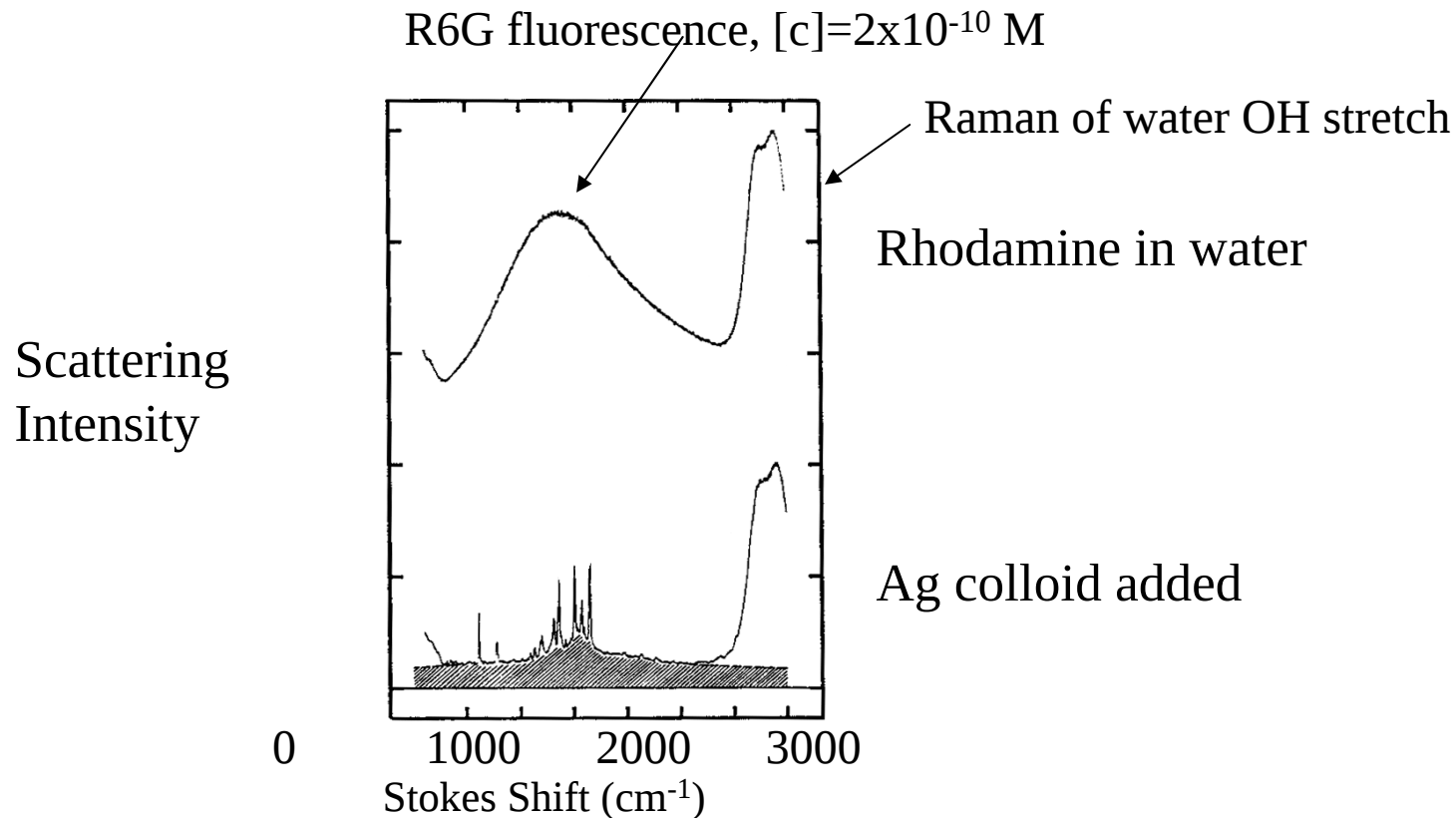
Huge P: Strong Rayleigh (Plasmon) Far Field Scattering and Strong Near Field Intensity -- Oscillator Strength ca. 10^3

Antenna effect at both laser and Raman frequencies

If radius greater than 15 nm, Ag Plasmon scattering cross section larger than optical absorption cross section --- **ideal antenna behavior**

Largest Ensemble SERS Effect: Adsorbed Rhodamine 6G dye in aggregated Ag colloid

Molecular Resonance Raman and SERS combined



B. Pettinger and A. Gerolymatou, Ber.Bunsenges.Phys.Chem. **1984**, 88, 359

❖ 514.5 nm laser excites R6G fluorescence in water. R6G adsorbs on Ag particle $\Rightarrow$ fluorescence quenches. Adsorption produces large increase in Raman scattering, apparent cross section $\sim 10^{-18} \text{ cm}^2$.

Surprise: Single Molecule SERS 1997

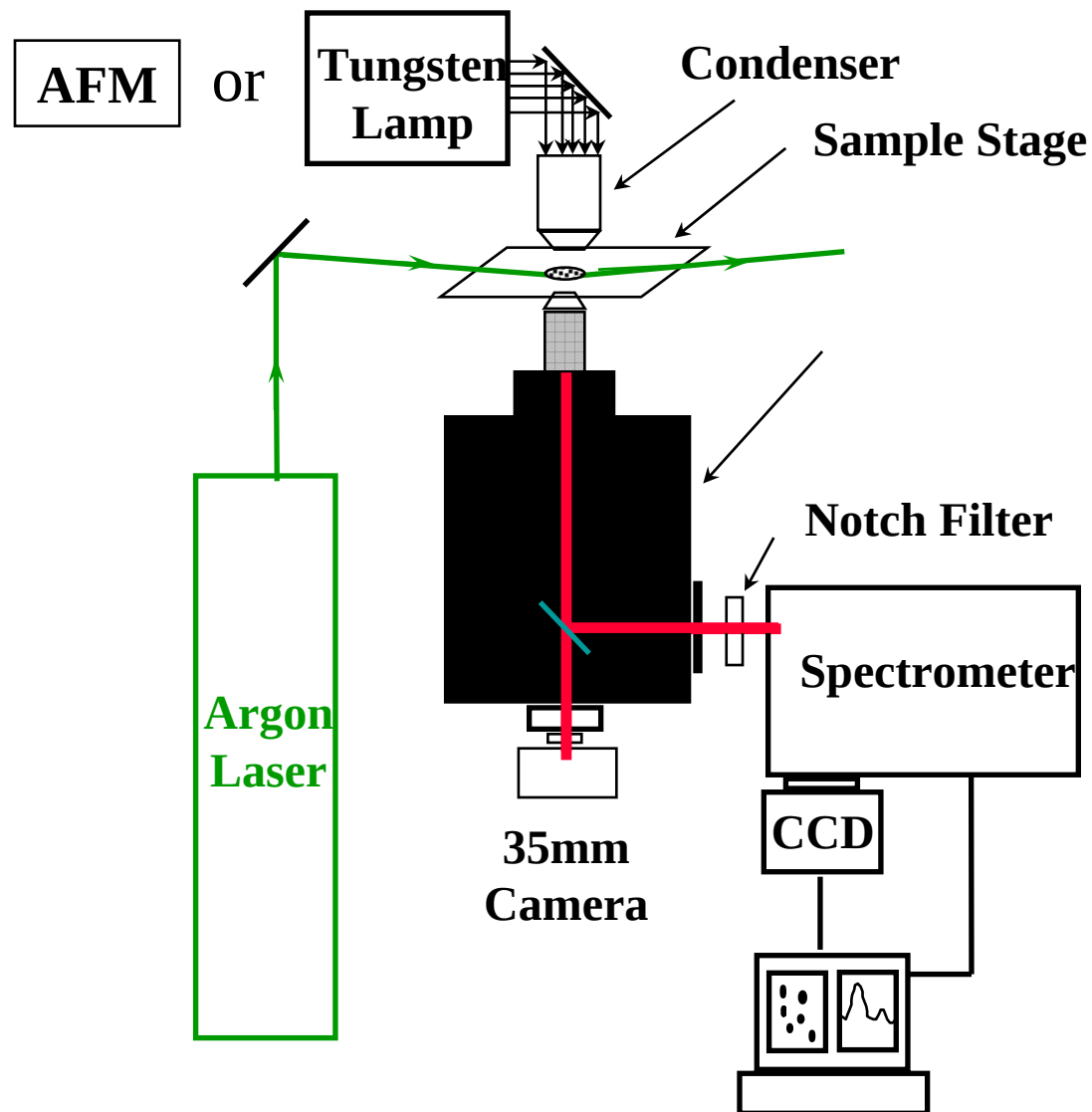
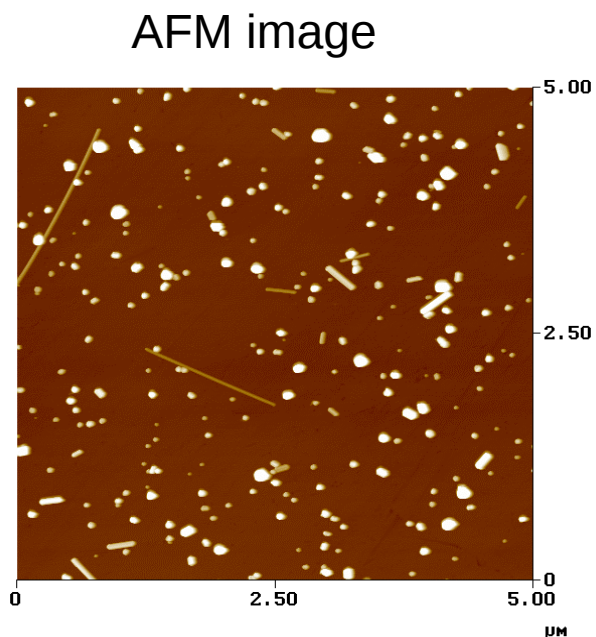
	<i>K n e i p p e t a l .¹</i>	<i>N i e e t a l .²</i>
M o l e c u l e	C r y s t a l V i o l e t	R h o d a m i n e 6 G
M e t a l S u b s t r a t e	A g c o l l o i d	A g c o l l o i d
E x c i t a t i o n λ	8 3 0 n m	5 1 4 . 5 n m
S E R S σ	$1 0^{-17}$ t o $1 0^{-16}$ c m ²	$1 0^{-15}$ c m ²

14 Orders of Magnitude? What is the mechanism?

1. Kneipp et al., *Phys. Rev. Lett.*, **78**, 1667 (1997).
2. Nie and Emory, *Science*, **275**, 1102 (1997).

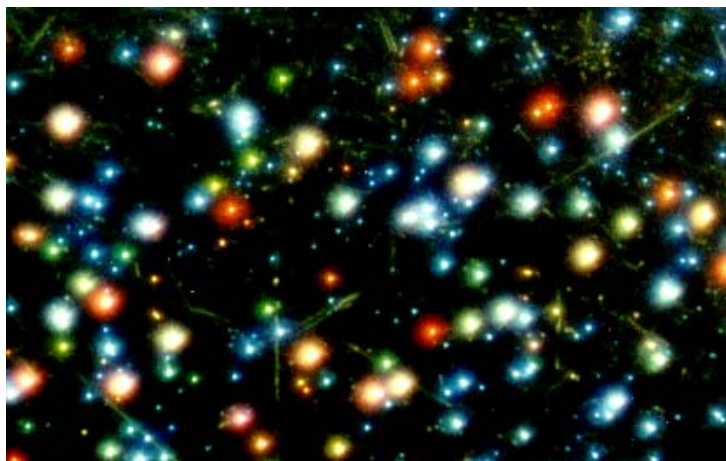
AFM, Raman, and Rayleigh Scattering from a field of Ag Nanocrystals

- Single "particle"/single molecule optical apparatus



White Light, Dark Field Rayleigh Scattering Image

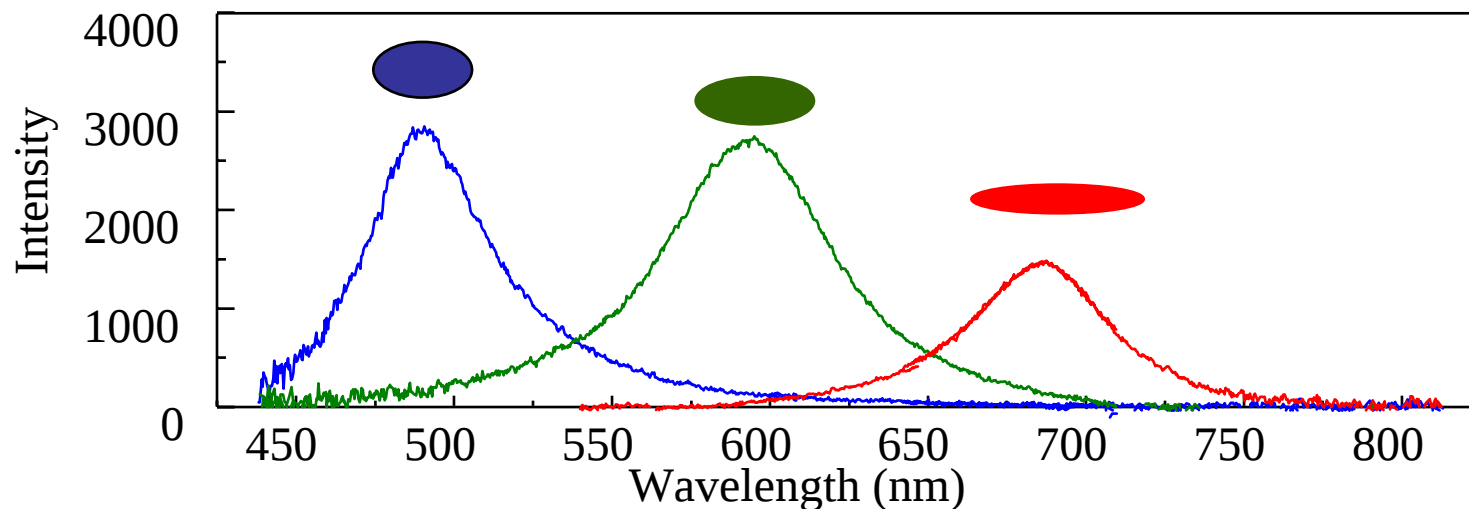
10 μm



Wide variety of particle sizes and shapes
Present in Ag colloid.

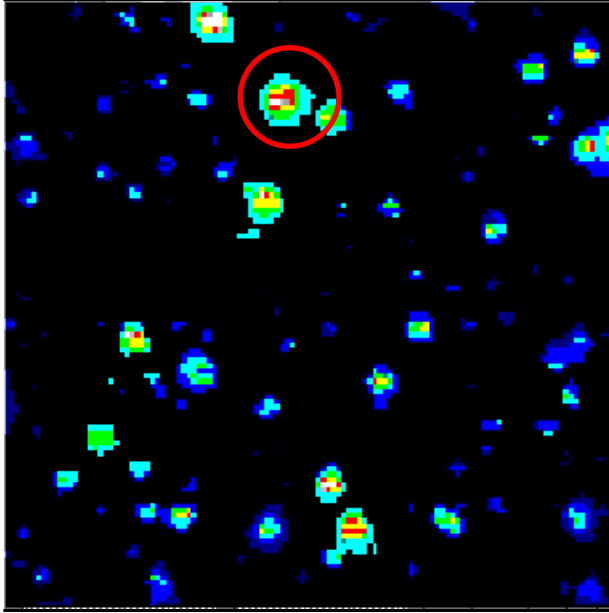
Hypothesis: particles with green
plasmon peak should show intense
SERS with green Laser.

Michaels, Nirmal, Brus JACS 121, 9932 (1999)

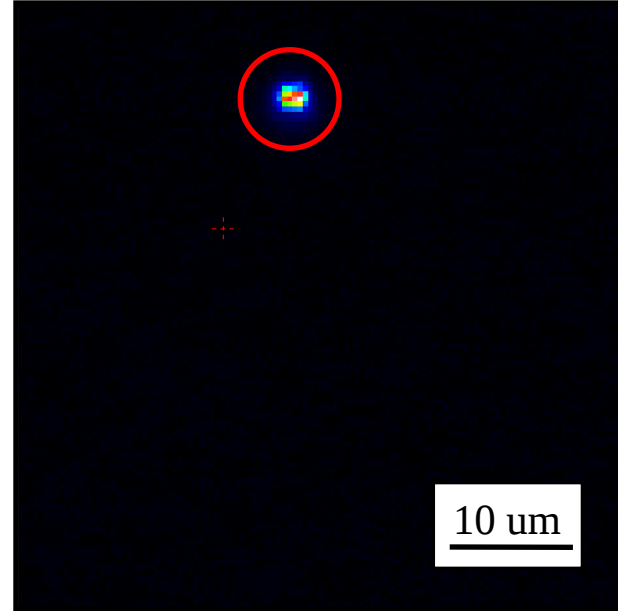


Plasmon scattering spectra depend upon the
geometry of the particle.

SERS Screening



Rayleigh scattering image



Stokes shifted **Raman** image

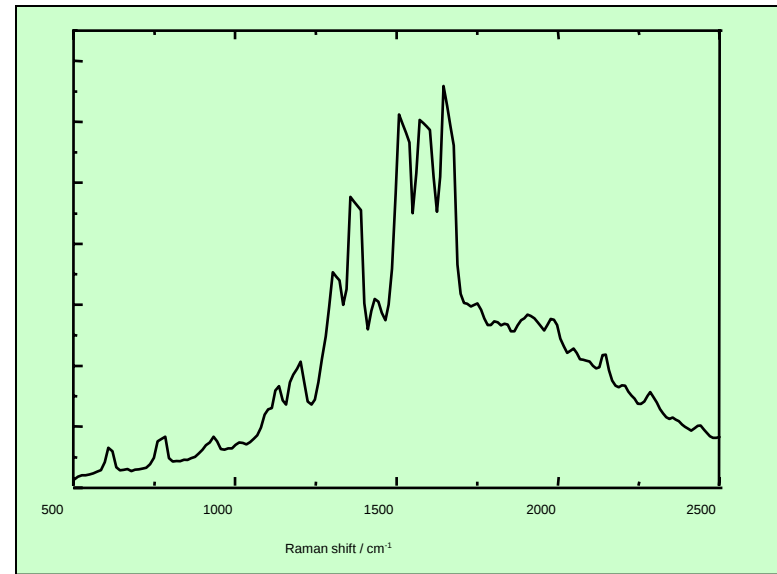
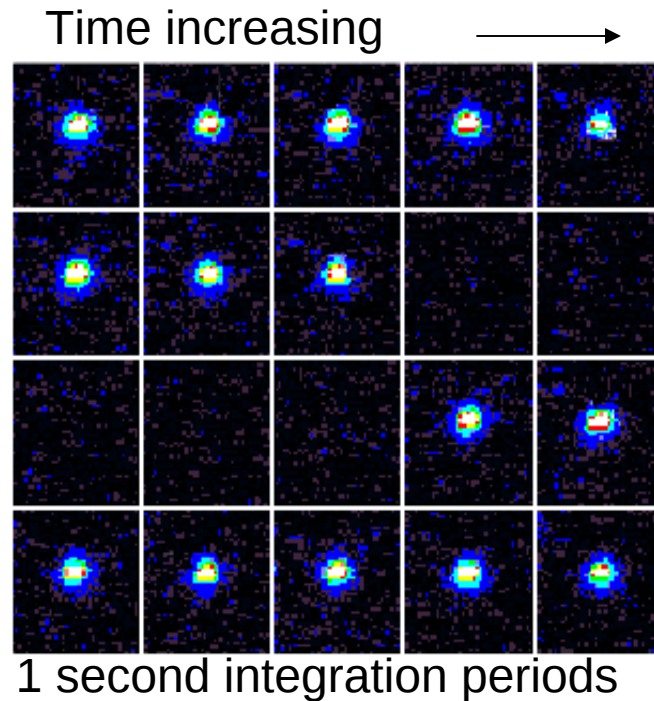
Intense Raman from a few “hot” particles

Our Hypothesis is wrong: Raman signal completely independent of far-field plasmon scattering intensity at laser wavelength

Calibrated SERS cross section – about 100 square Angstroms

Number of active sites saturates

Single Molecules: Blinking of the SERS signal



Stokes shifted Raman spectrum

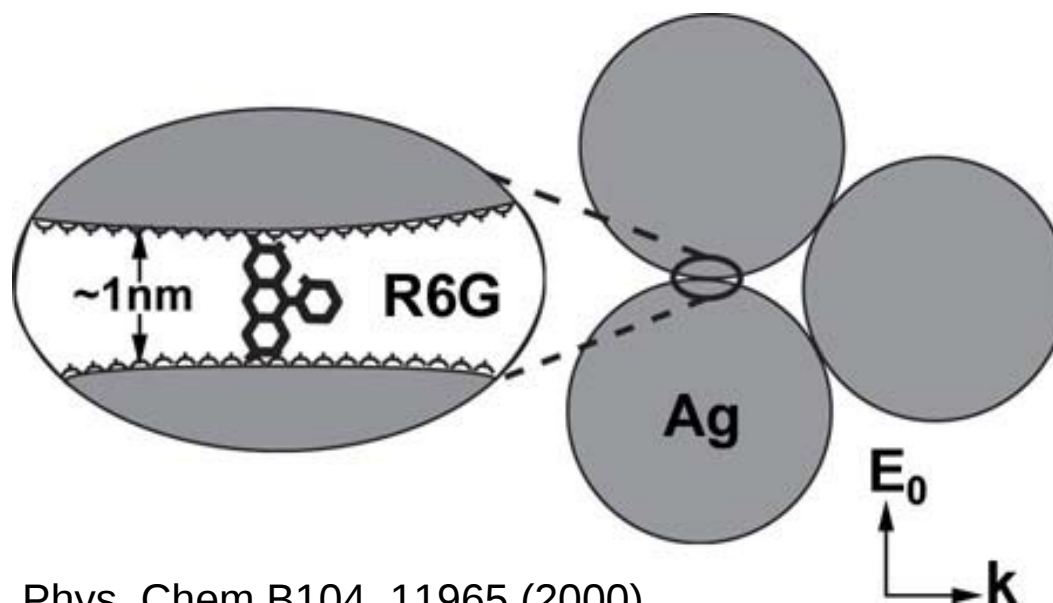
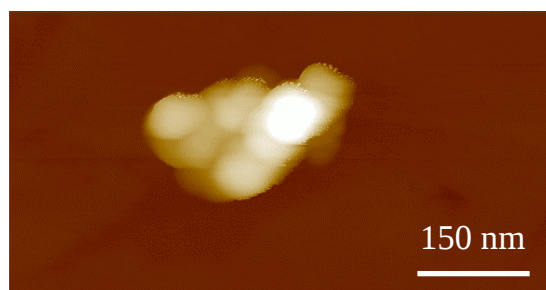
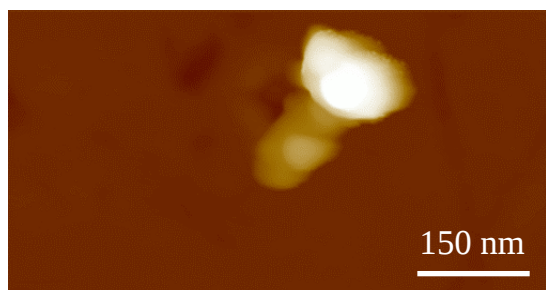
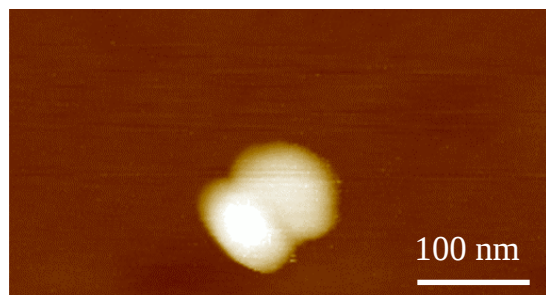
- SERS scattering is dominated by a continuum emission which blinks on and off with the molecular Raman lines.
- Our hypothesis: single adsorbed molecule is an "impurity" turning on both Ag continuum electronic Raman and molecular vibronic Raman.
- Chemisorption of R6G necessary for strong SERS signal; blinking represents adsorption and desorption

AFM Characterization of “hot” particles

all SERS-active particles are compact aggregates consisting of at least two primary silver nanocrystals.

Large single nanocrystals do not show the effect.

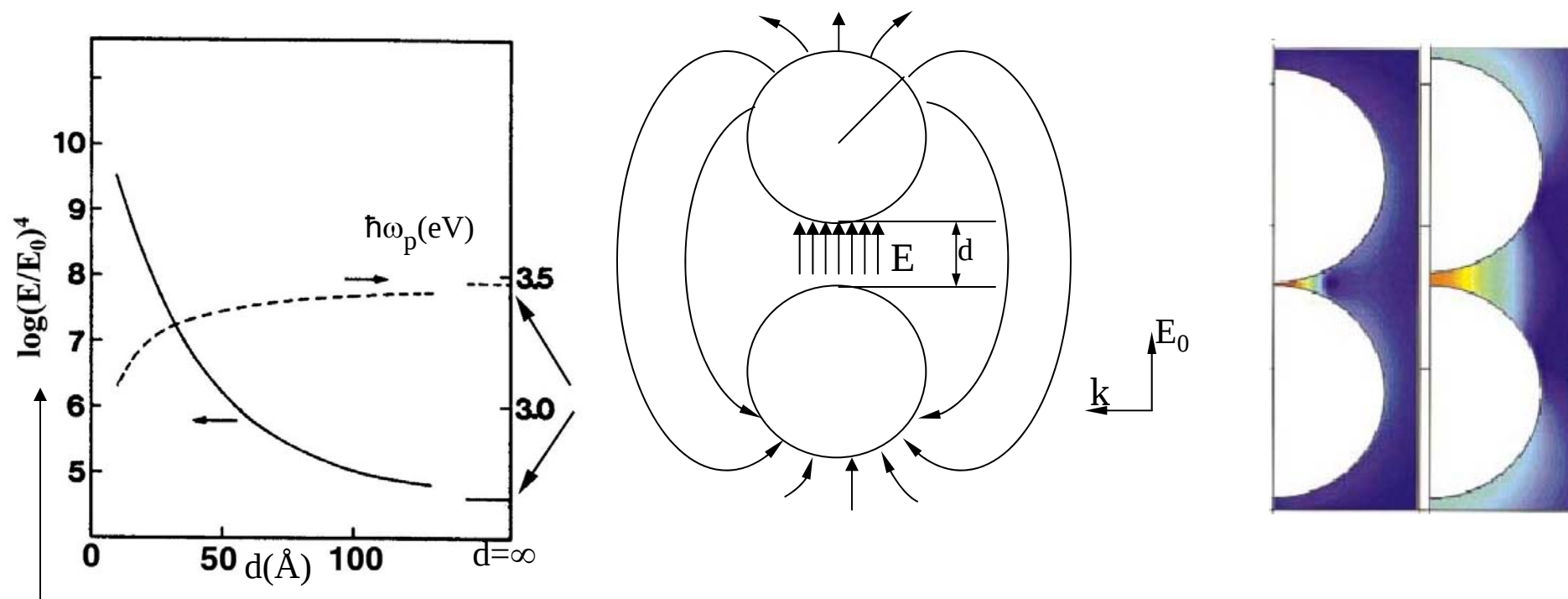
Molecule is at junction of two nanocrystals



Michaels, Jiang, & Brus J. Phys. Chem B104, 11965 (2000)

Exact Electromagnetic Calculation of Field Enhancement Between Two Spherical Ag Particles

Aravind, Nitzan, Metiu. *Surf. Sci.* **1981**, 110, 189
Inoue and Ohtaka. *J. Phys. Soc. Jpn.* **1983**, 52, 3853
Xu et al *Phys. Rev. E*, **2000**, 62, 4318



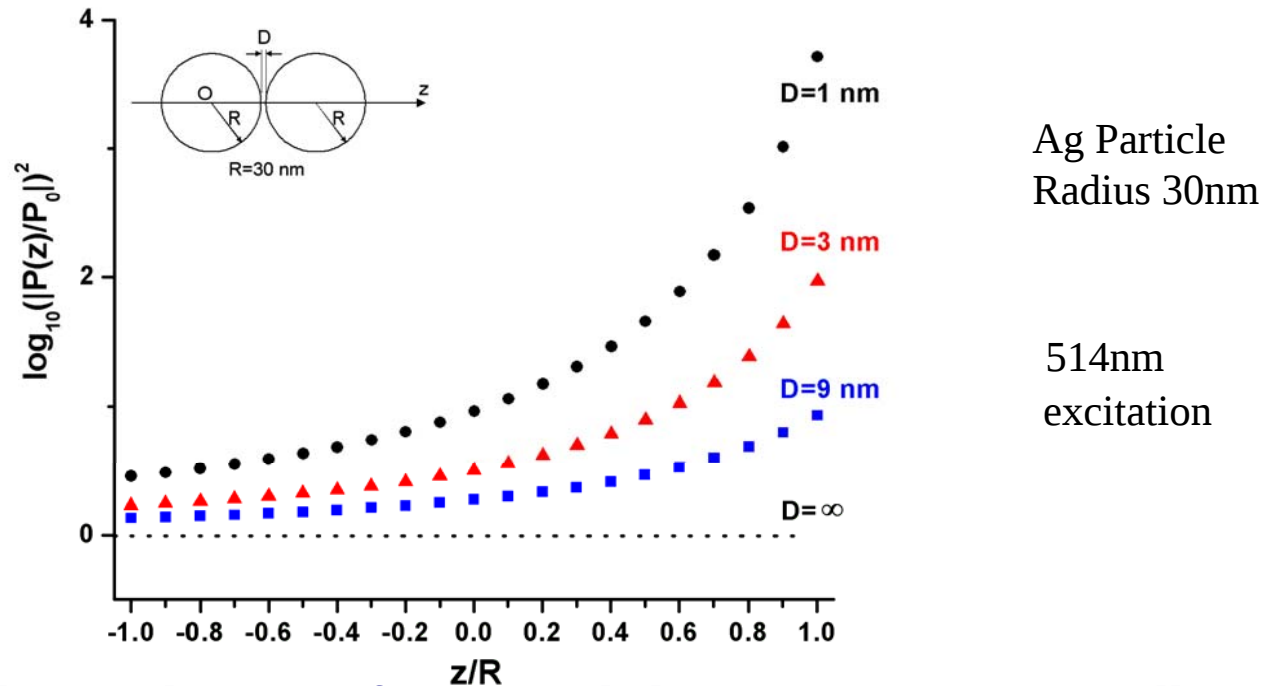
$(E/E_0)^4$ goes to 10(+11) as $d \rightarrow 0$. As volume of space between particles decreases, field enhancement increases.

This is a natural situation for single molecule Raman spectroscopy

Exact Electromagnetic Calculation of Excited Polarization $\mathbf{P}$ inside the Ag metal.

$\mathbf{E}(\mathbf{r})$ and $\mathbf{P}(\mathbf{r})$ (the e-h⁺ pair density) concentrate on metal surface at the particle junction. $\mathbf{P}=(\epsilon-1)\mathbf{E}/4\pi$ inside

This creates the hot spot in the junction above the surface

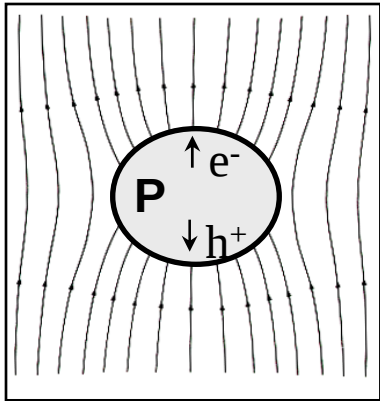


The fundamental nature of an excited electronic state in a metallic particle changes from a volume excitation to a surface excitation as two particles approach each other

Jiang, Bosnick, Maillard & Brus, J. Phys. Chem. B107, 9964 (2003)
Equations from Aravind, Nitzan, Metiu. *Surf. Sci.* **1981**, 110, 189

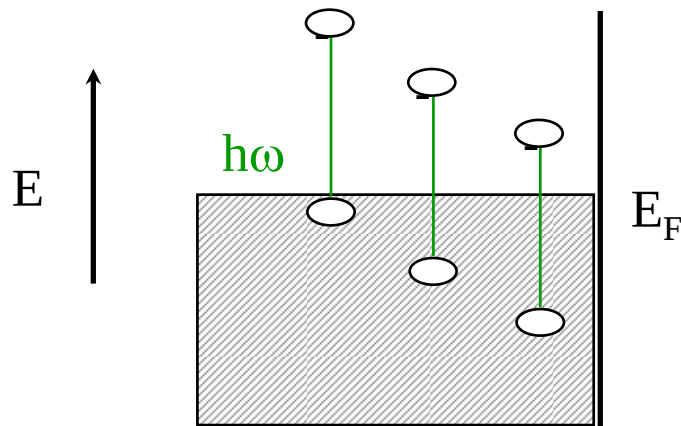
Charge Transfer Photochemistry due to Plasmon Excitation

Dipolar Plasmon of Metal Particles: Coherent Oscillation of Electron-Hole Pairs



$\mathbf{P}(\omega) \equiv$ coherently oscillating polarization at laser frequency ω .

Kubo first expanded $\mathbf{P}(\omega)$ in a coherent infinite sum of e^-h^+ pairs, confined by the shape of the particle.

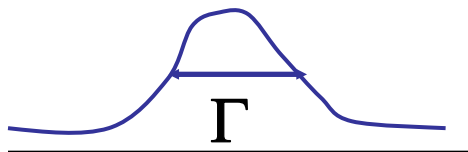


$\mathbf{P}(\omega)$ can either re-radiate (Rayleigh scattering) without loss of energy, or dephase and relax to the Fermi energy (photon absorption).

“Thus, the plasma resonance can be considered as the free carrier absorption which is enhanced by a sort of anti-shielding at the frequency of the plasmon resonance.”

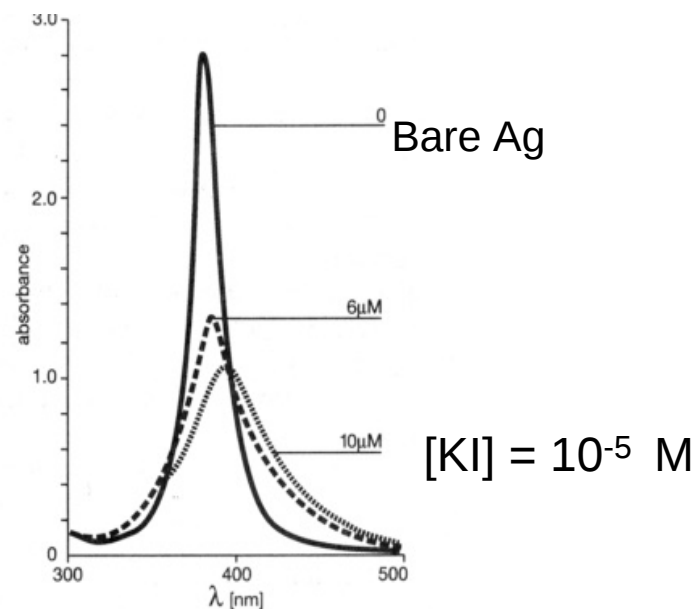
Strong Coupling of Plasmons to Chemisorbed Molecules

- Plasmon width minimum for crystalline Nanoparticles
- Plasmon broadens for smaller radius a --- dephases faster.
- A increases with chemisorbed molecules on surface!!



$$\Gamma = \Gamma_0 + A v_f / 2a$$

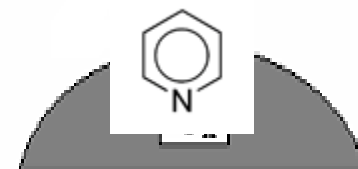
Iodide ion adsorbed on 7 nm Ag nanocrystal



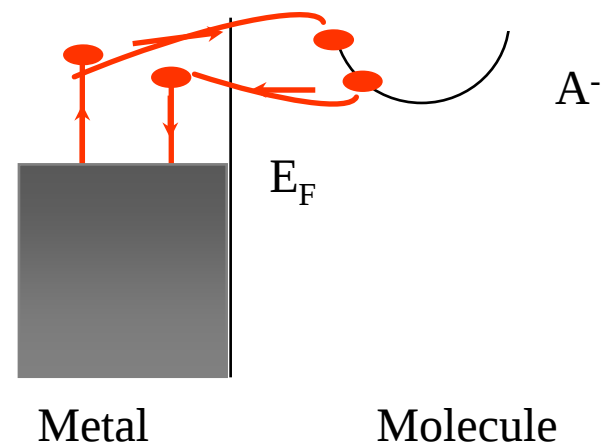
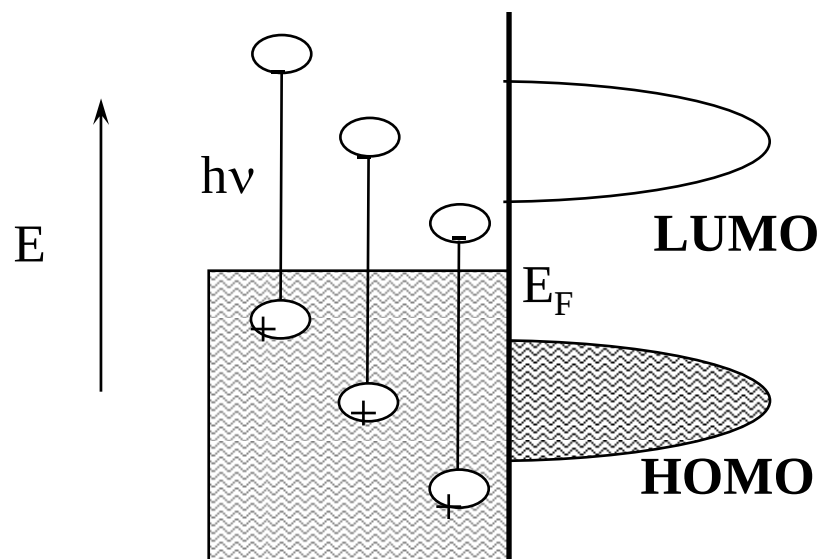
Gutierrez & Henglein, J. Phys. Chem. 1993, 97, 11368

- Quantum yield ca. 1 for hot electron scattering off adsorbed species

Electron exchange coupled SERS



Chemisorbed pyridine on Ag Nanocrystals

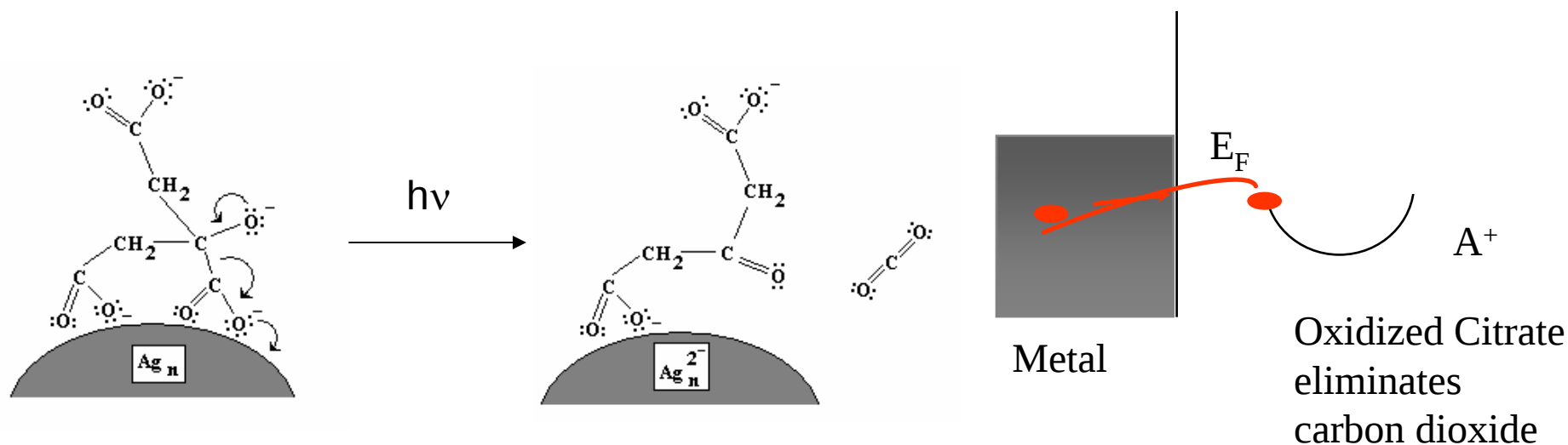


- 1.) Photoexcitation of metal yields hot electrons and holes which scatter off adsorbed pyridine
- 2.) Hot electrons transiently localize on pyridine LUMO
- 3.) Pyridine Anion is stable. Electron return to metal and relaxes to Fermi energy either via radiation or heat.
- 4.) Pyridine SERS cross section high. Water cross section low – LUMO not resonant

Photochemistry: Chemisorbed citrate on aqueous Ag Nanocrystals

Sodium Citrate is an aqueous stabilizing agent

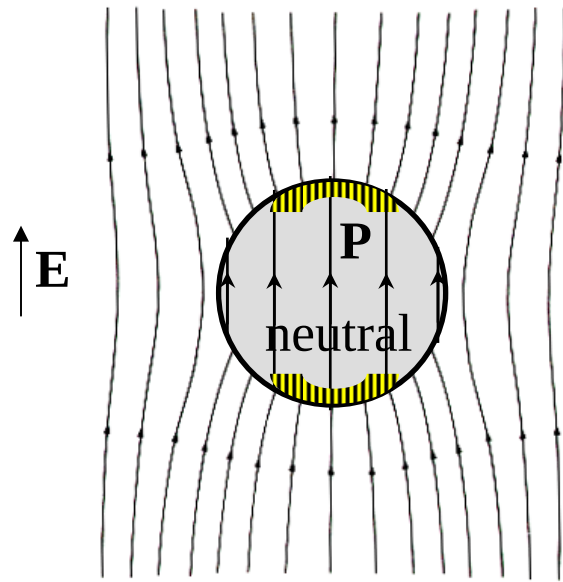
Tunneling of photo-excited hot “hole” from Ag to adsorbed citrate initiates decarboxylation (Kolbe reaction) within femtoseconds.



Oxidized Citrate Anion decomposes irreversibly before hole can return to metal.

Quantum yield for electron transfer photochemistry can be high if molecule quickly decomposes

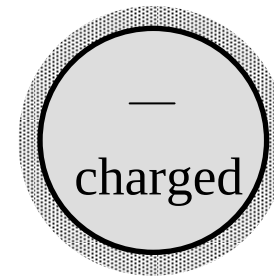
Steady State Photo-voltage created by Citrate Photo-oxidation



Hot electron dipole
$$P = \frac{(\epsilon - 1)}{(\epsilon + 2)} a^3 E$$

Gauss's Law relates hot electron flux to field enhancement above surface $\vec{\nabla} \cdot \vec{E} = 4\pi\rho$

Anisotropic surface citrate oxidation



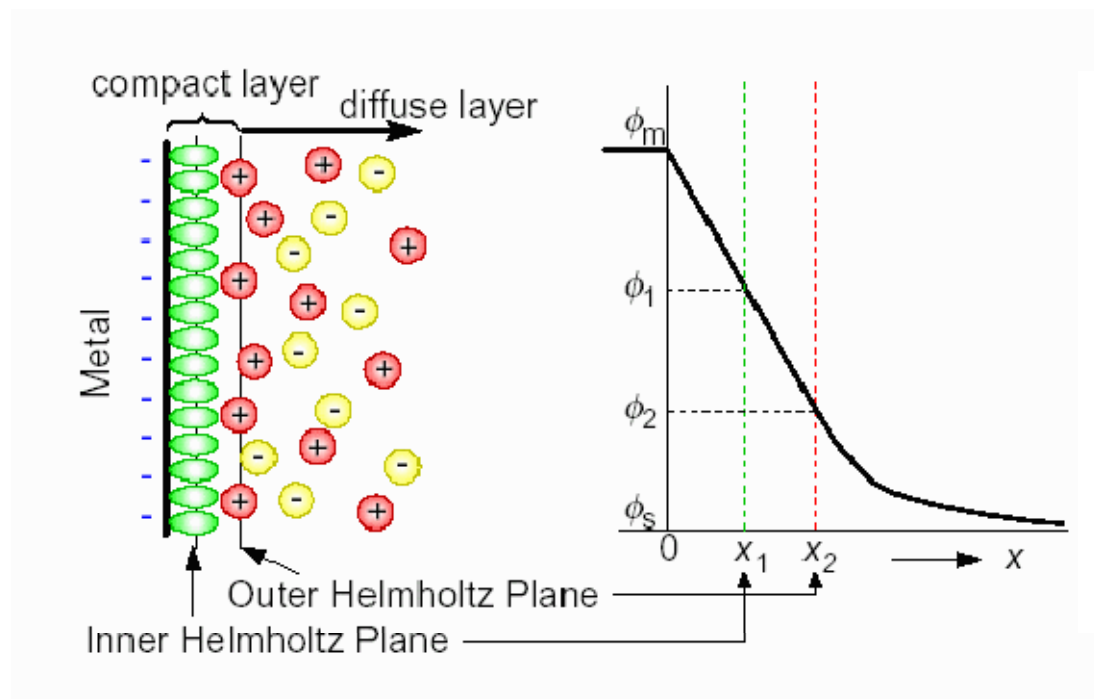
Oxidized citrate

Long lived e^- on Ag for hundreds of seconds. Cathodic Photovoltage develops.

Oxidized adsorbed citrate exchanges with aqueous citrate

If there is Ag^+ in solution, photovoltage reduces Ag ions onto the particle. Particle grows in size

Cathodic Photovoltage is an increase in the citrate double layer potential

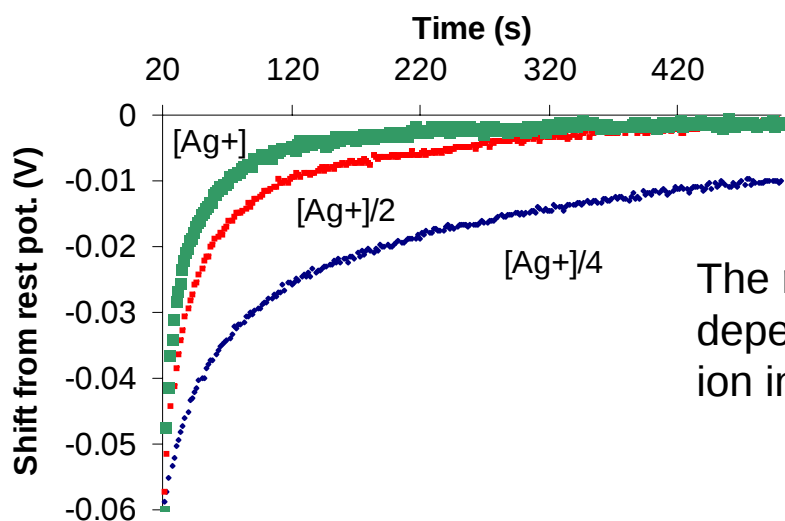
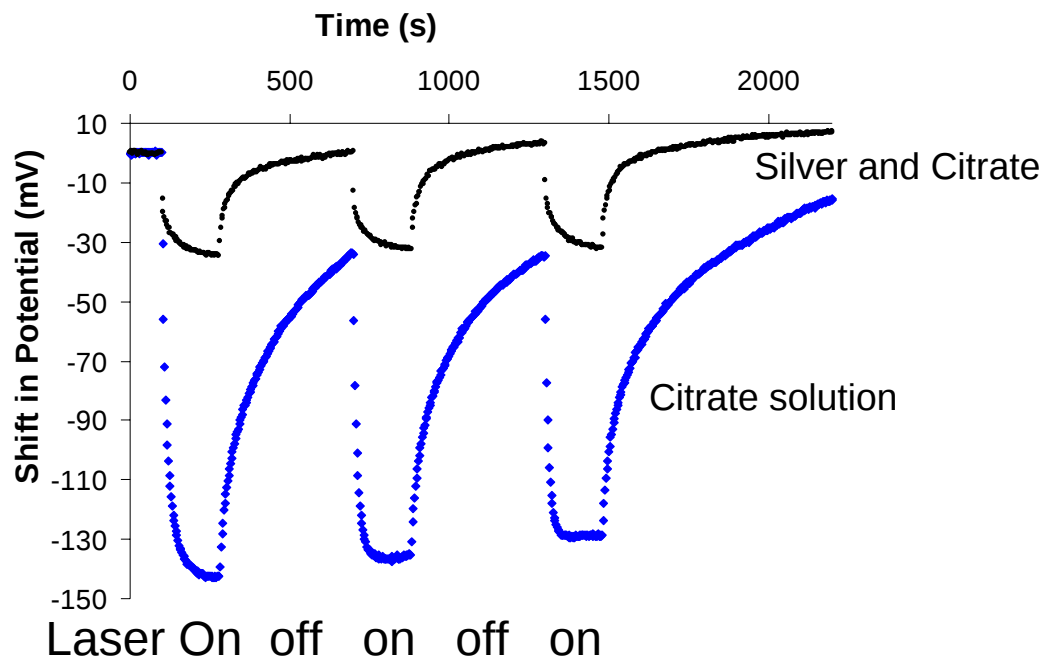


Direct Measurement of Photovoltage for Citrate Stabilized Ag nanocrystals on an ITO electrode

Open Circuit Photovoltage in an electrochemical cell

When the laser is turned off the potential slowly returns to its' original potential.

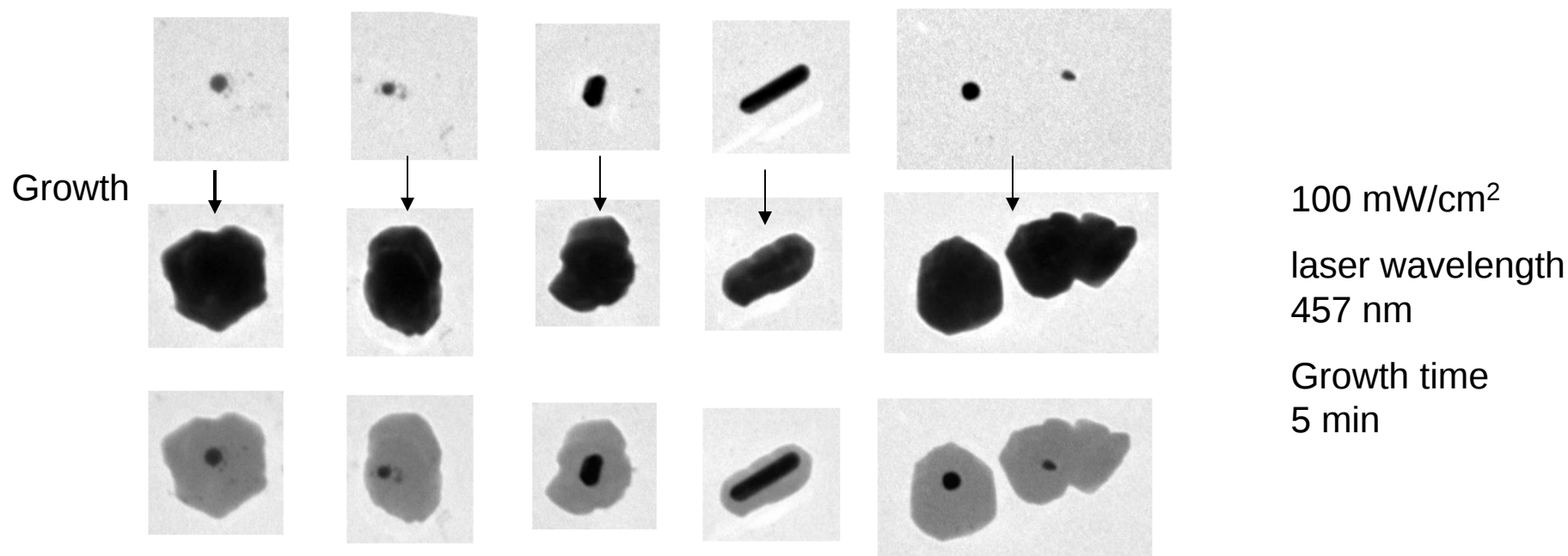
The discharge rate is faster when silver ions are in solution.



The rate of the discharge process is dependent on the concentration of the silver ion in solution.

Individual Nanocrystal growth due to Ag^+ reduction by Photo-voltage

1. Observe dry individual particle on TEM grid
2. Grow particle in aqueous 1.25 mM Ag^+ solution in light
3. Observe same dry individual particle in TEM



200 nm

There is no polarization dependence to the growth of the particles.

Maillard, Huang, Brus, Nano Lett. 2003, 3, 1611
Redmond, Wu, Brus J Phys Chem C 2007, 111, 8942

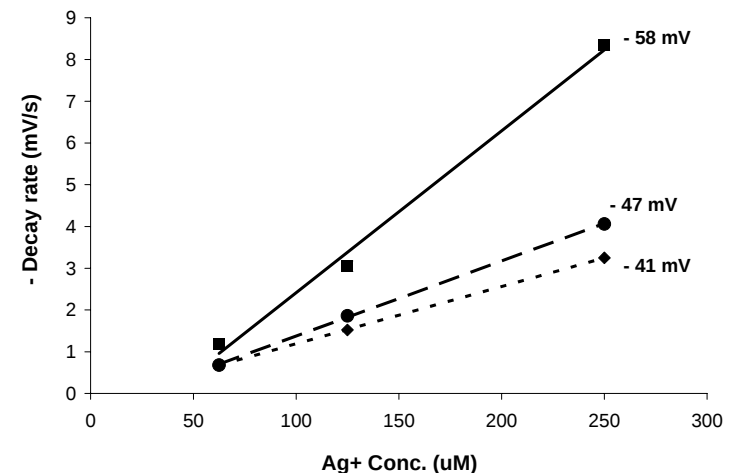
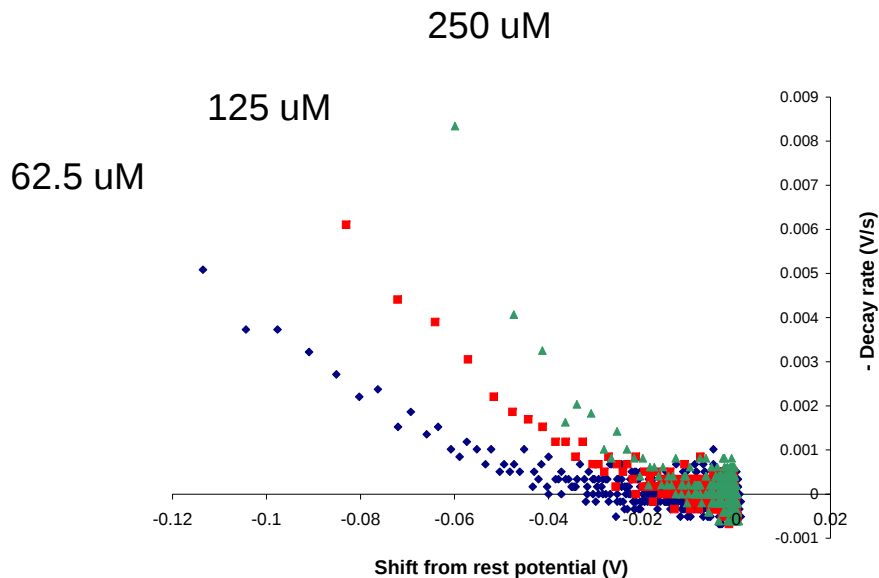
Summary of Photo-Catalyzed Growth

1. Hot holes in Ag oxidize adsorbed citrate, charging Ag particle negatively.
2. Nearby Ag⁺ ion is reduced in a slow thermal reaction. The **Butler-Volmer** equation give the rate of reduction as a function of excess voltage;

$$-\frac{dq}{dt} = nFA [Ag^+] k_0 e^{-(\alpha F / RT)(V - V^0)}$$

3. Reduction rate depends exponentially on the photovoltage.

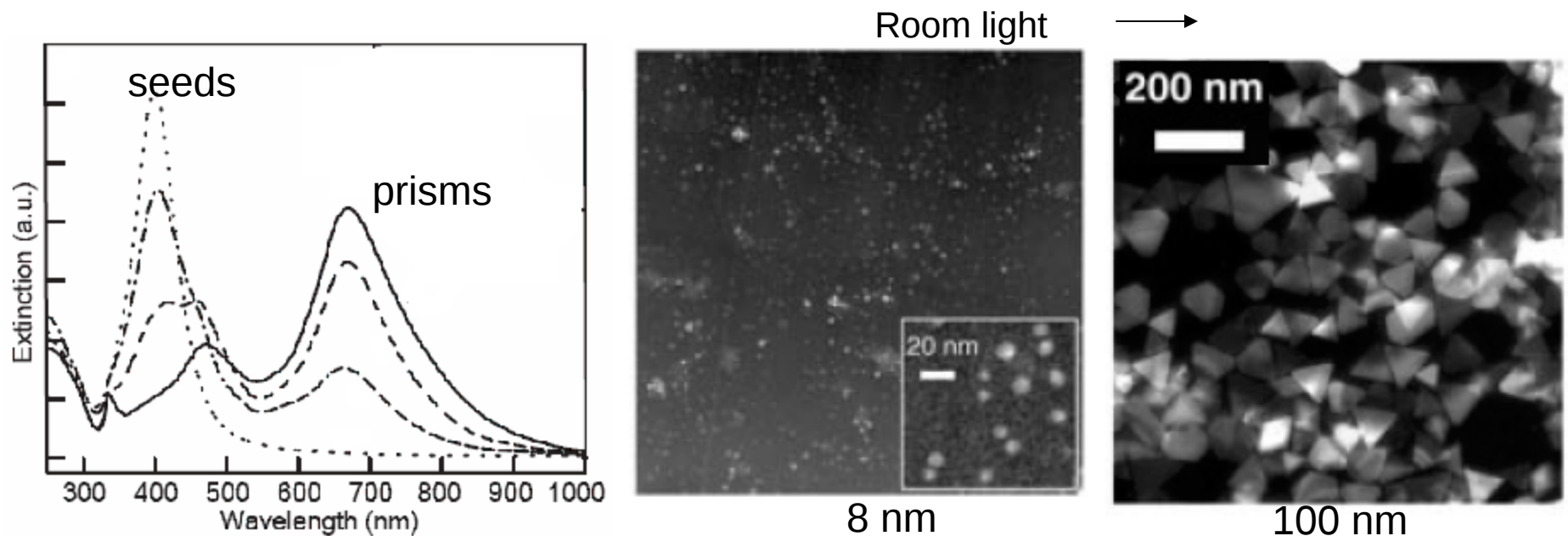
The validity of these rate equations can be tested by plotting the discharge rate as a function of potential with different concentrations of silver ions in solution. The rate at any potential should be linearly dependent on the concentration of silver ions.



Electrochemical exchange current low because of citrate passivation

Application of these ideas: Light driven Ostwald Ripening due to plasmon excitation

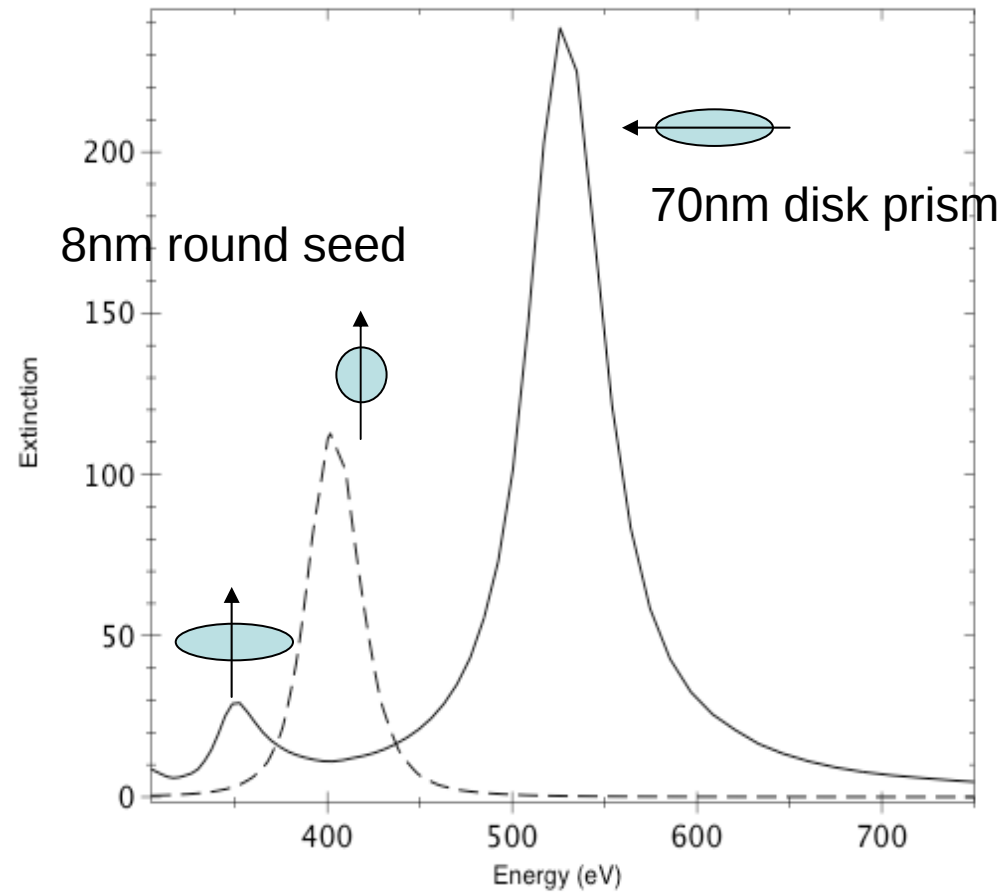
Mirkin discovered that citrate stabilized colloidal 8nm Ag spheres (seeds) irradiated with room light form larger 70nm single crystal Ag prisms over 80 hrs.



The irradiation wavelength determines the lateral prism size.
The conversion appeared to be driven by surface plasmon excitation

R. Jin, Y. Cao, C.A. Mirkin, K. L. Kelly, G.C. Schatz, J.G. Zheng, Science, (2001), 294, 1901

Shape Effect in Ag Nanocrystal Plasmon Spectra and Photovoltage



The irradiation wavelength determines the shape of the nanocrystal that develops photovoltage

Air Oxidation of colloidal metallic Ag



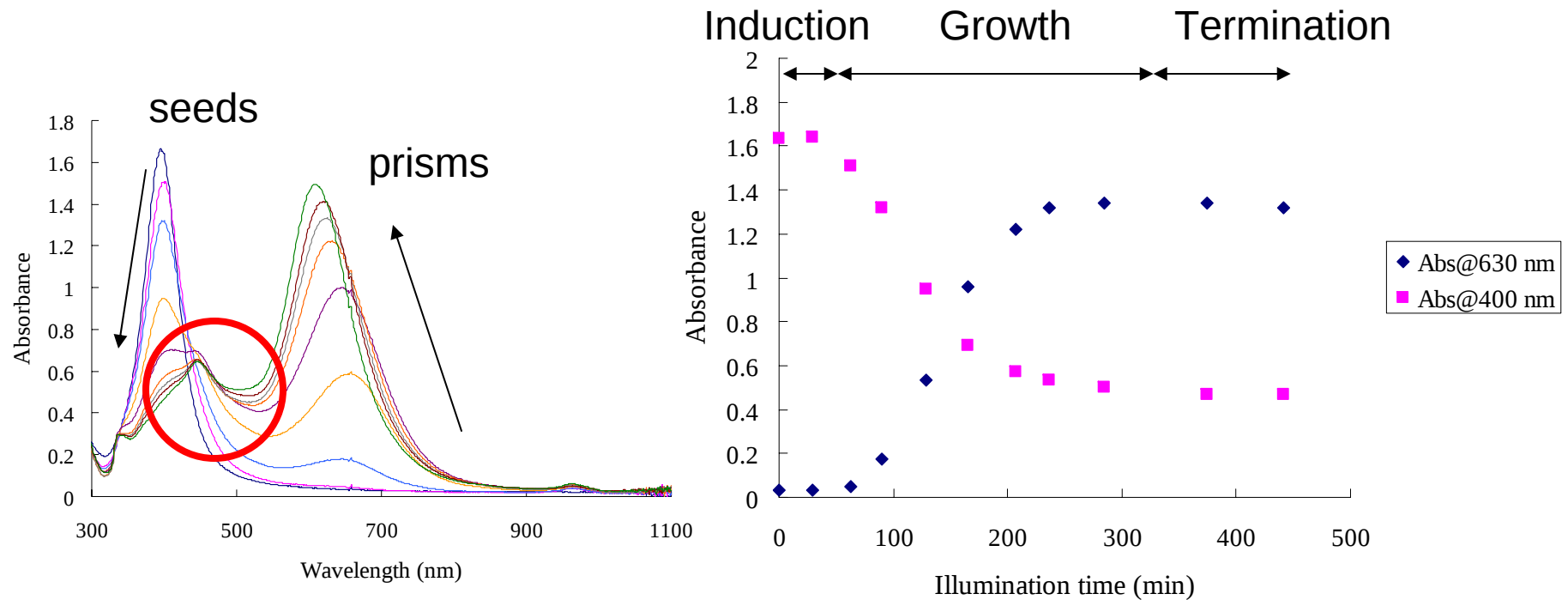
Oxidative etching in aqueous colloidal Ag system produces a low ca. 10^{-8} M equilibrium Ag^+ concentration.

The seeds are acting as a reservoir for aqueous Ag^+ , and as catalyst.

Aqueous Ag^+ reduces on the nanocrystal with the highest photovoltage. Thus, Ag mass transfers from one shape to another.

Tsuji, T. et al. J. Photochemistry and Photobiology a-Chemistry 2006, 183, 297
Wiley, B.; Herricks, T.; Sun, Y. G.; Xia, Y. N. Nano Letters 2004, 4, 2057.
Henglein, A.; Mulvaney, P.; Linnert, T. Faraday Discussions 1991, 31.
Lok, C.-N.; et.al, J Biol Inorg Chem 2007, 12, 527.

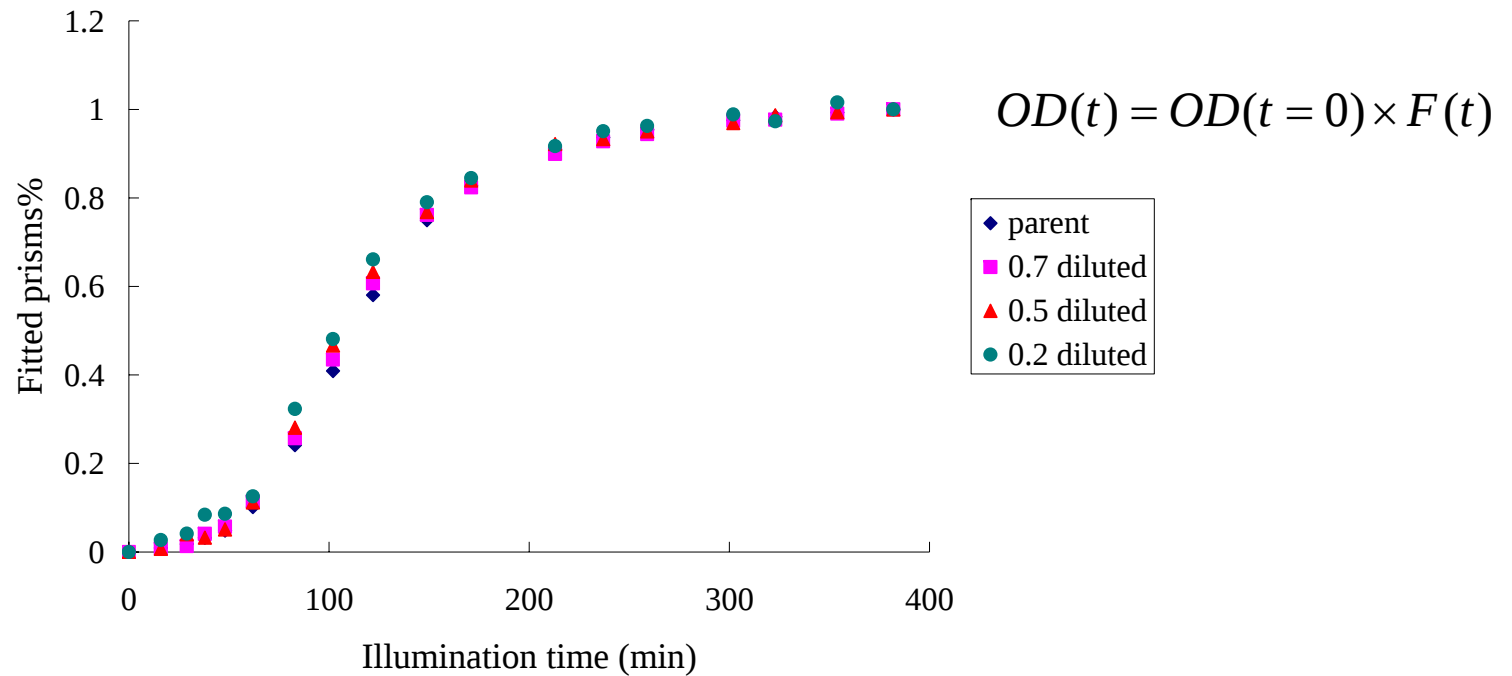
Autocatalytic Kinetics --- illuminated by fluorescence light



A quasi-isosbestic point at approximately 450 nm was observed, indicating that the **concentration of possible intermediates is low**.

Kinetics are autocatalytic – As prisms grow, they absorb more light and reduce Ag^+ faster

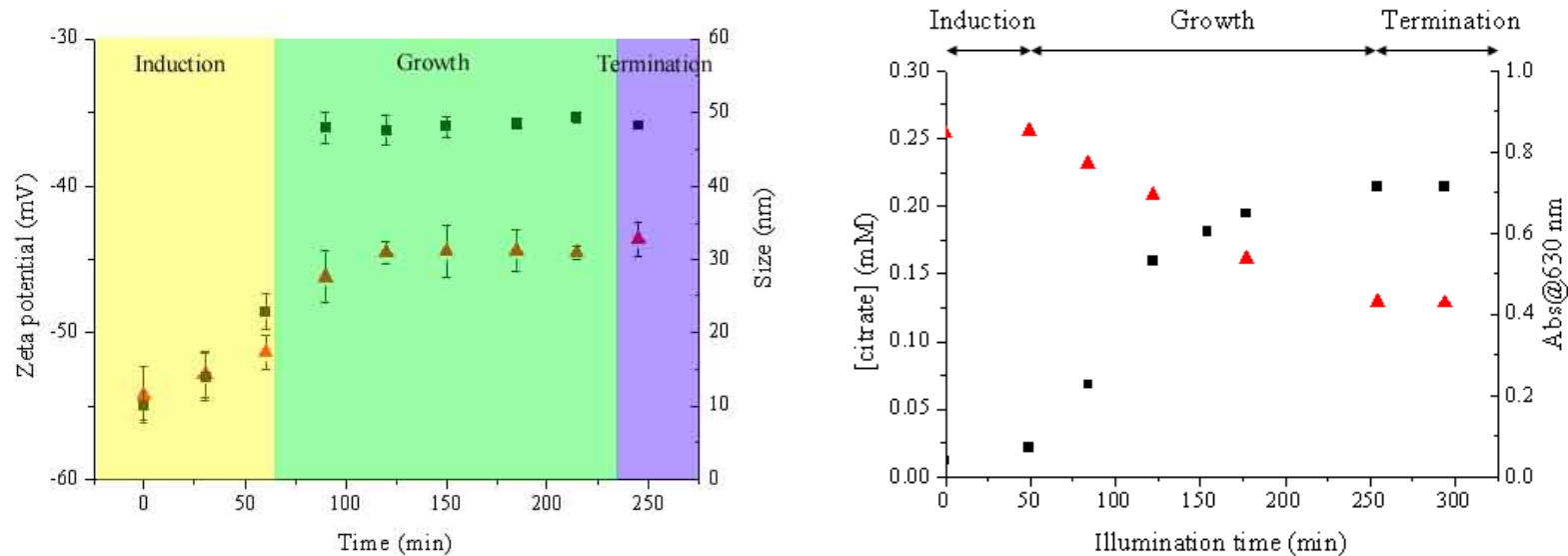
Kinetics are independent of seed concentration



The Ag mass from about 30 seeds must combine to make one triangular disk.

Thermodynamic Ag^+ concentration should be independent of seed concentration

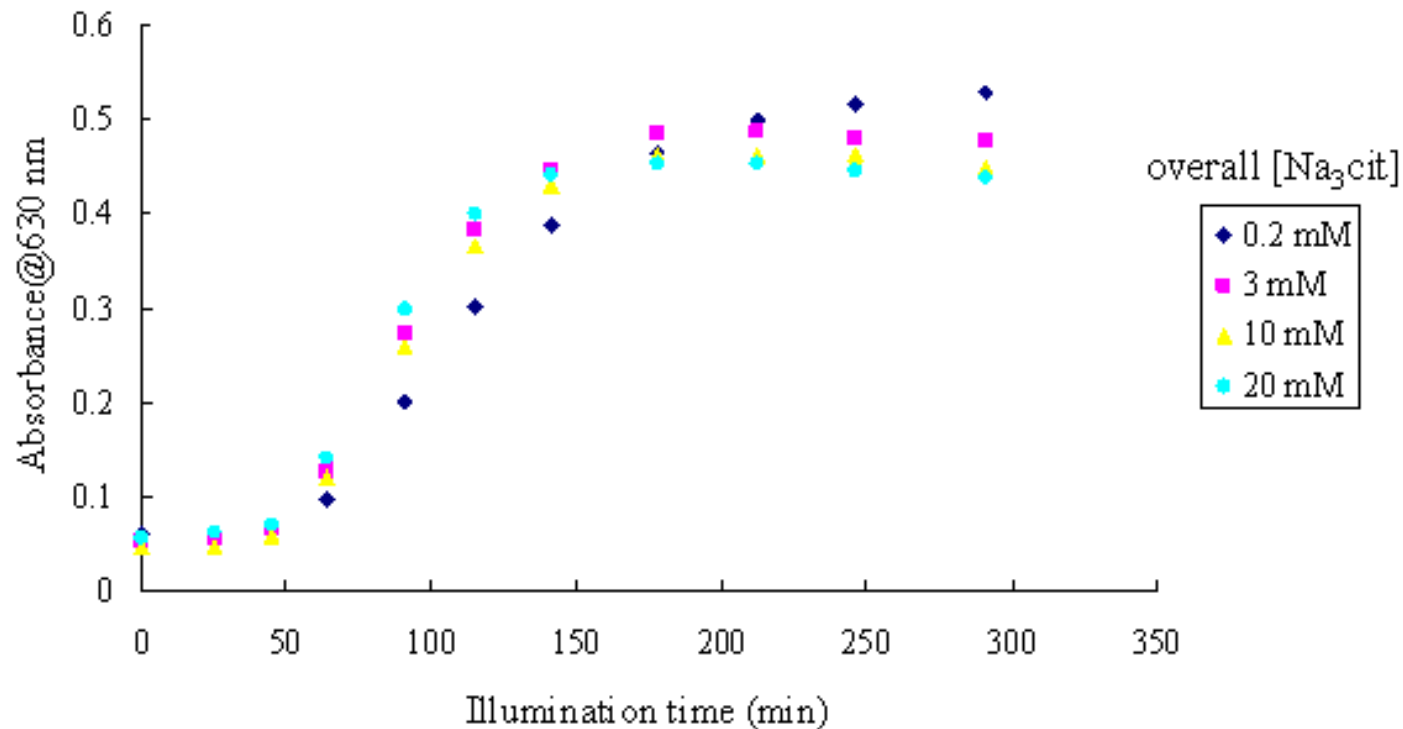
Citrate is consumed as photoconversion proceeds



NMR confirmed the aqueous citrate concentration drops from 0.25 to 0.13 mM in the presence of light. Summing estimated adsorbed and aqueous citrate, we have 0.26 and 0.13 mM total citrate before and after the conversion.

The unrelaxed, ballistic "hot holes" created in Ag plasmon excitation oxidize adsorbed citrate molecules.

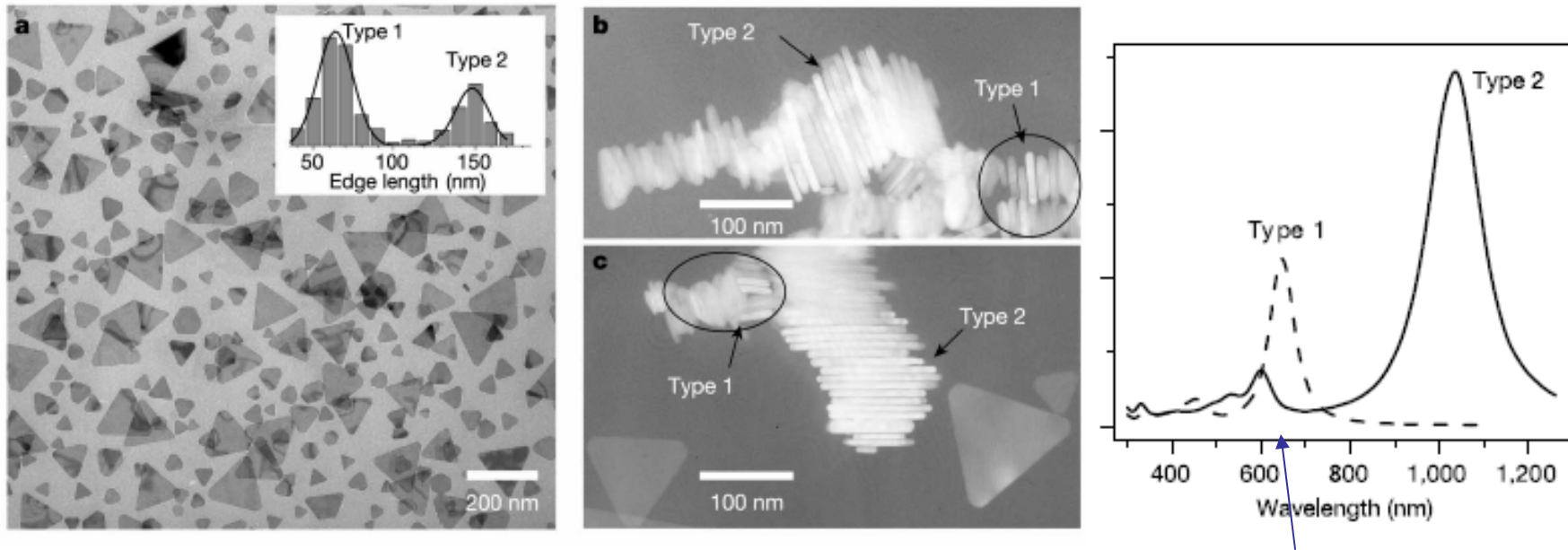
Citrate is essential for the photoconversion,
yet rate is independent of citrate concentration



The photoconversion kinetics and yield are essentially unchanged in the range 0.27mM to 20mM citrate concentration. These results imply that **above 0.27 mM we have a complete citrate monolayer on the seeds and prisms.**

Flocculation does not occur; there is an excess of aqueous citrate.

Growth of two discrete prism sizes – 70nm and 150nm



Jin, R. C. et al Nature 2003, 425, 487

Excitation Wavelength 5500 Angstroms

spherical particle	small prism (70 nm)				big prism (150 nm)	
	in-plane dipole	in-plane quadrupole	out-of-plane quadrupole	out-of-plane dipole	dipole	quadrupole
400	640	450	340	(410)	1065	(340, 600)

5500 Angstrom excitation in resonance with in-plane dipole transition of small prism and quadrupole transition of large prism

mass transport flux of Ag^+ onto surface of prism

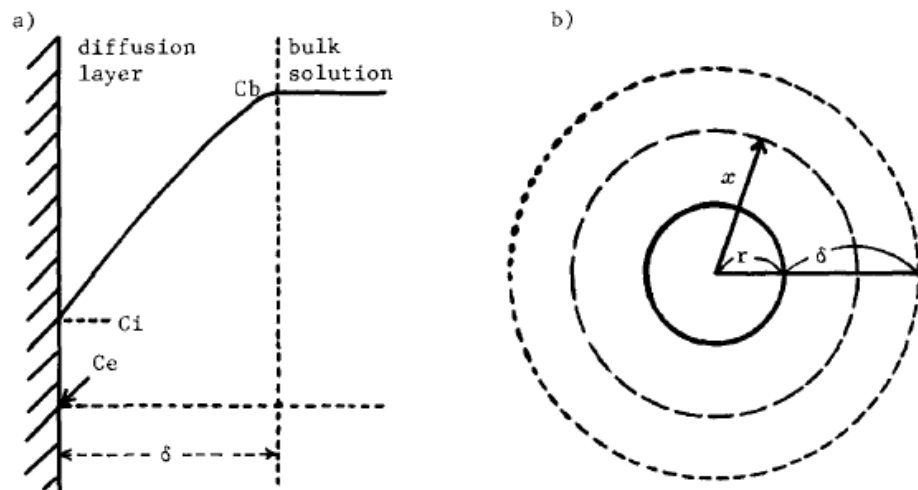


Fig. 2. (a) The profile of solute concentration in a diffusion layer. (b) The diffusion layer around a spherical particle.

Sugimoto diffusion-controlled mass transfer model

$$J = \frac{4\pi D r (r + \delta)}{\delta} (C_b - C_e)$$

$$D_{\text{Ag}^+} = 1.65 \times 10^{-5} \text{ cm}^2/\text{s}$$

The time averaged growth rate over 5 hours using the 514 nm laser line at 10 mW/cm² is about 62 silver atoms per prism per second. We calculate the experimental growth rate would equal the mass transfer rate if $[\text{Ag}^+] \sim 3 \times 10^{-10} \text{ M}$.

In the low intensity linear regime, the growth rate is a lower limit for the Ag^+ mass transfer rate, which varies linearly with $[\text{Ag}^+]$. As irradiation intensity increases, the kinetics will enter the second regime when the growth rate equals the Ag^+ mass transfer rate.

Sugimoto, T. *Adv. Colloid Interface Sci.* **1987**, 28, 65-108.

Furukawa, K.; Takahashi, Y.; Sato, H. *Geochim. Cosmochim. Acta* **2007**, 71, 4416-4424.

Conclusions:

- Single molecule Raman possible at junctions if molecule also optically resonant. Localization of the plasmon to the junction creates a hot spot in the field enhancement. Chemisorption causes exchange coupling to excited state metallic electrons. Blinking from adsorption and desorption. Not well understood.
- Hot holes from plasmon excitation oxidize adsorbed citrate molecules. This creates a cathodic photovoltage, which can reduce Ag^+ ions in solution. Thus plasmon excitation can photo-catalyze particle growth and shape reformulation. The kinetics are quite slow and can be modeled with the Butler-Volmer equation.
- 70 NM single crystal prisms grow from 8nm round seeds under room lights, due to light induced Oswald ripening. Illumination wavelength determines shape which develops photovoltage and thus grows. First order in seed concentration, zero order in citrate concentration

Thanks to the DOE for support of this work