SuNMaG

The Supramolecular Nano-Materials Group

Metal Nanoparticles and Self-Assembled Monolayer

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DMSE

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Outline

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- History
- Metal Nanoparticles Synthesis
- Electrical Double Layer
  - Solubility
- Self-Assembly and Self-Assembled Monolayer
- Ligand Coated Metal Nanoparticles
  - Solubility
  - Mixed Ligands

Nanoscale Materials

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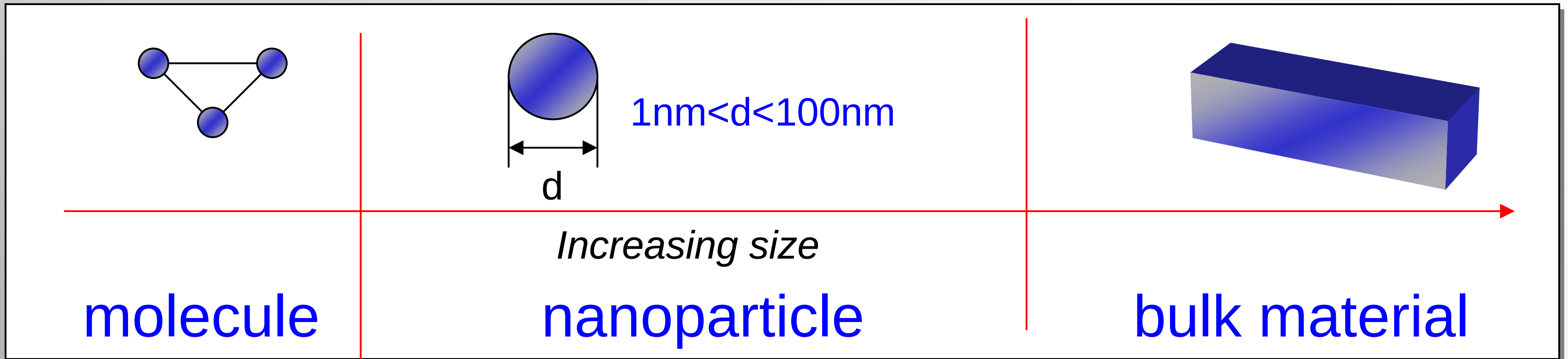
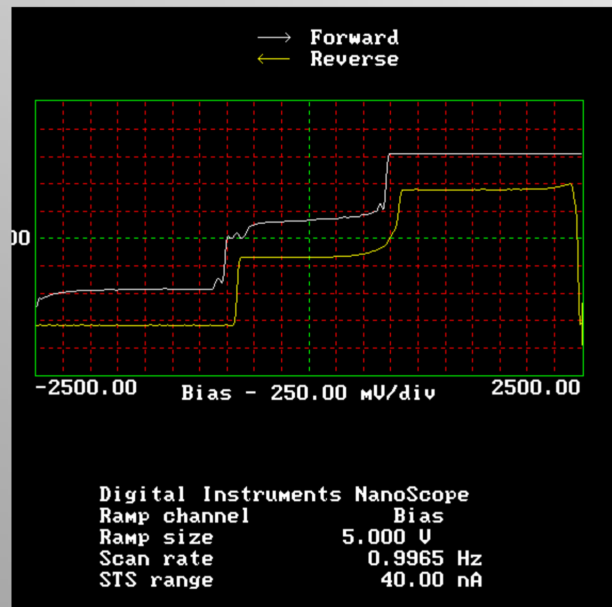


Milan - Duomo



Single Electron Transistor

*Andres et al., **Science**, 1323, 1996*

Florence - S. Croce

What are they?

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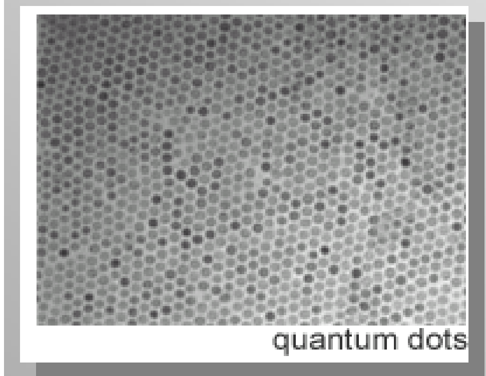
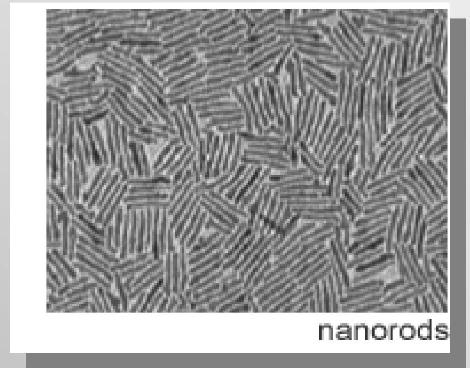
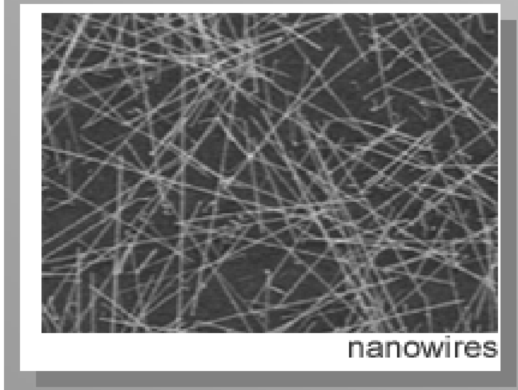


Nanoparticles

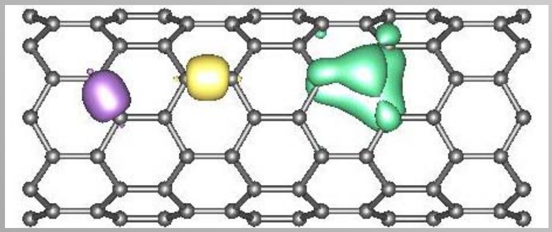


Nanorods

0 dimensional nanomaterials:
unique properties due to quantum confinement and very high surface/volume ratio



Nanowires



Nanotubes

1 dimensional nanomaterials:
extremely efficient classical properties

More Specifically

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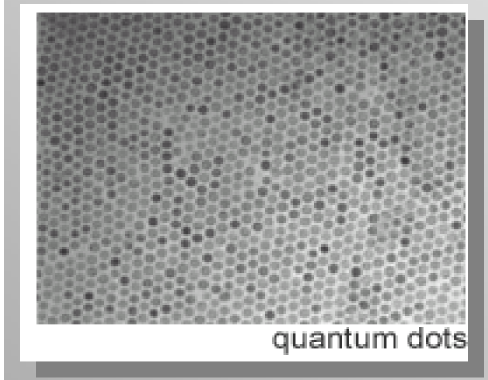
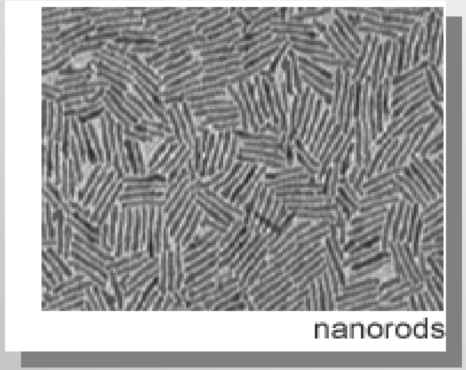
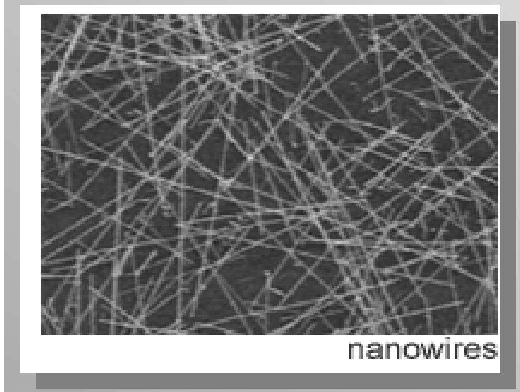


Nanoparticles

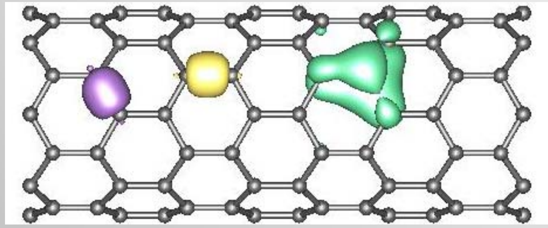


Nanorods

0 dimensional nanomaterials:
unique properties due to quantum confinement and very high surface/volume ratio



Nanowires



Nanotubes

1 dimensional nanomaterials:
extremely efficient
classical properties

Properties of Metal Nanoparticles

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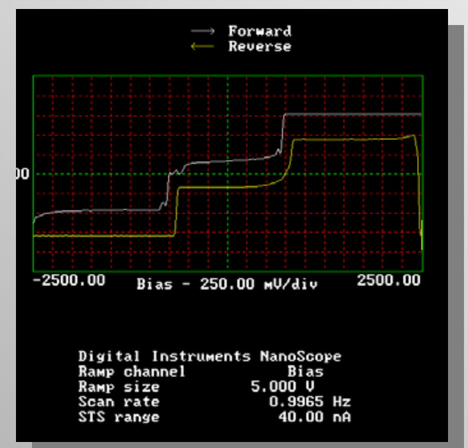
Optical Properties

Electronic Properties



Nanoscale Materials Have Different Properties when compared to their bulk counterparts!

A brief historical Background

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- the extraction of gold started in the 5th millennium B.C. near Varna (Bulgaria) and reached10 tons per year in Egypt around 1200-1300 B.C.when the marvelous statue of Touthankamon was constructed.

- it is probable that “soluble” gold appeared around the 5th or 4th century B.C. in Egypt and China.

- the Lycurgus Cup that was manufactured in the 5th to 4th century B.C. It is ruby red in transmitted light and green in reflected light, due to the presence of gold colloids.

- **The reputation of soluble gold until the Middle Ages was to disclose fabulous curative powers for various diseases, such as heart and venereal problems, dysentery, epilepsy, and tumors, and for diagnosis of syphilis.**
- **the first book on colloidal gold, published by the philosopher and medical doctor Francisci Antonii in 1618. This book includes considerable information on the formationof colloidal gold sols and their medical uses, including successful practical cases.**
- **In 1676, the German chemist Johann Kunckels published another book, whose chapter 7 concerned “drinkable gold that contains metallic gold in a neutral, slightly pink solution that exert curative properties for several diseases”. He concluded that “gold must be present in such a degree of communition that it is not visible to the human eye”.**

- **A colorant in glasses, "Purple of Cassius", is a colloid resulting from the heterocoagulation of gold particles and tin dioxide, and it was popular in the 17th century.**
- **A complete treatise on colloidal gold was published in 1718 by Hans Heinrich Helcher. In this treatise, this philosopher and doctor stated that the use of boiled starch in its drinkable gold preparation noticeably enhanced its stability.**
- **These ideas were common in the 18th century, as indicated in a French dictionary, dated 1769, under the heading "or potable", where it was said that "drinkable gold contained gold in its elementary form but under extreme sub-division suspended in a liquid".**
- **In 1794, Mrs. Fuhlame reported in a book that she had dyed silk with colloidal gold.**
- **In 1818, Jeremias Benjamin Richters suggested an explanation for the differences in color shown by various preparation of drinkable gold: pink or purple solutions contain gold in the finest degree of subdivision, whereas yellow solutions are found when the fine particles have aggregated.**

- **In 1857, Faraday reported the formation of deep red solutions of colloidal gold by reduction of an aqueous solution of chloroaurate ($AuCl_4^-$) using phosphorus in CS_2 (a two-phase system) in a well known work.**

- **He investigated the optical properties of thin films prepared from dried colloidal solutions and observed reversible color changes of the films upon mechanical compression (from bluish-purple to green upon pressurizing).**

- **The term “colloid” (from the French, *colle*) was coined shortly thereafter by Graham.**

Marie-Christine Daniel and Didier Astruc, *Chem. Rev.* **2004,** *104,* 293-346

Synthesis of Metal Nanoparticles

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The citrate method

•It is easy
•It requires only water

•It requires skills
•Has reproducibility issues

What is on the surface?

The electrical double layer

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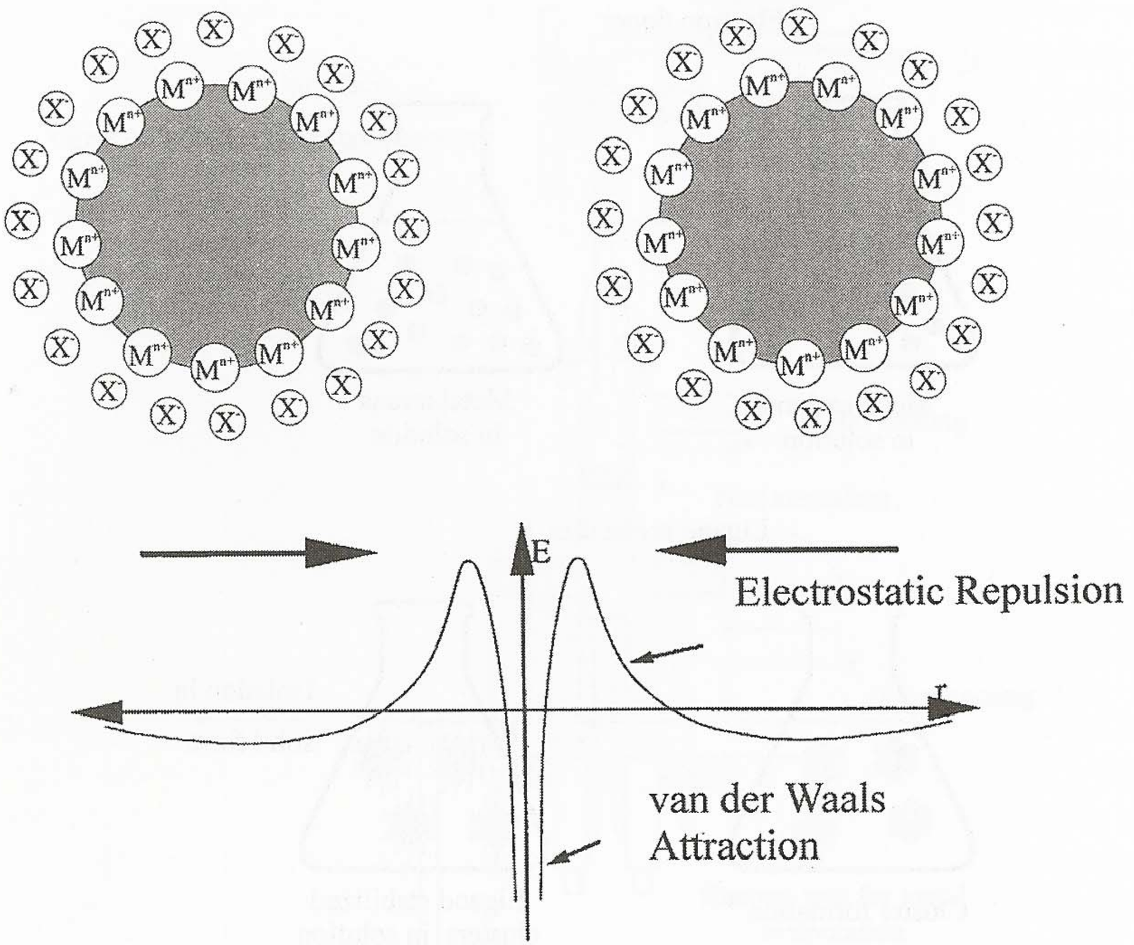

FIGURE 2.24 Electrostatic stabilization of metal colloids. Van der Waals attraction and electrostatic repulsion compete with each other.[27]

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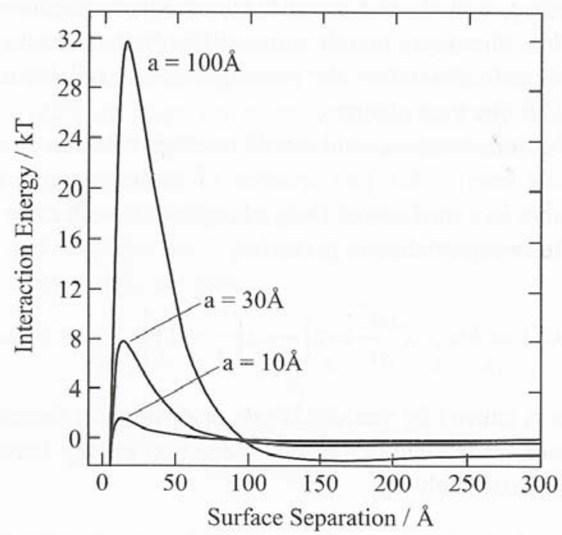


FIGURE 5.4 Plot of the interaction energy between two spherical gold particles in aqueous solution as a function of the particle separation, for several particle radii. Hamaker constant $= 25 \times 10^{-20}$ J, $I = 1$ mM, $\psi_0 = 0.10$ V, $a = 1.0$ nm, 3.0 nm, and 10.0 nm, Debye length $= 10$ nm. Note that the secondary minimum is negligible for nanoparticles, but becomes important above 10 nm.

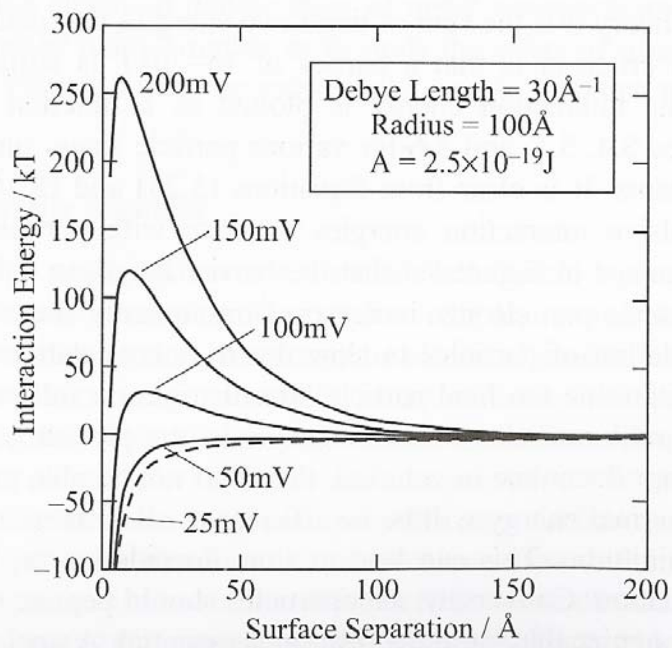
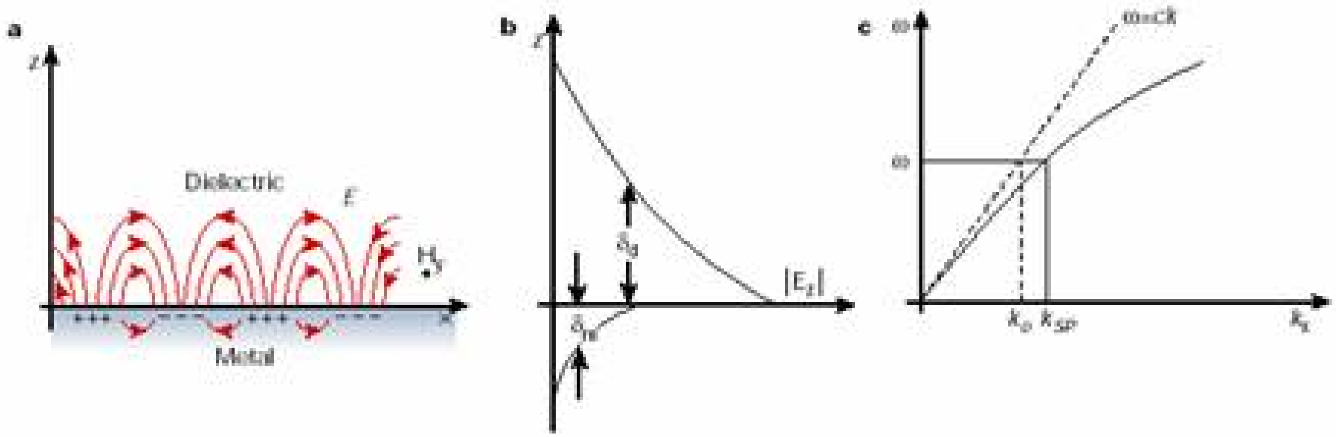


FIGURE 5.5 Plot of the interaction energy between two spherical gold particles in aqueous solution as a function of the particle separation for several surface potentials. Hamaker constant = 25×10^{-20} J, $I = 10$ mM, $a = 10$ nm, Debye length = 3 nm. Note that a zeta potential, $|\zeta| > 50$ mV, is necessary for colloid stability because of the high Hamaker constant.

What are the limitations?

Plasmons

Box 1
Surface plasmon basics



SPs at the interface between a metal and a dielectric material have a combined electromagnetic wave and surface charge character as shown in **a**. They are transverse magnetic in character (**H** is in the y direction), and the generation of surface charge requires an electric field normal to the surface. This combined character also leads to the field component perpendicular to the surface being enhanced near the surface and decaying exponentially with distance away from it (**b**). The field in this perpendicular direction is said to be evanescent, reflecting the bound, non-radiative nature of SPs, and prevents power from propagating away from the surface. In the dielectric medium above the metal, typically air or glass, the decay length of the field, δ_d, is of the order of half the wavelength of light involved, whereas the decay length into the metal, δ_m, is determined by the skin depth. **c**, The dispersion curve for a SP mode shows the momentum mismatch problem that must be overcome in order to couple light and SP modes together, with the SP mode always lying beyond the light line, that is, it has greater momentum ($\hbar k_{sp}$) than a free space photon ($\hbar k_0$) of the same frequency ω.

Optical Properties

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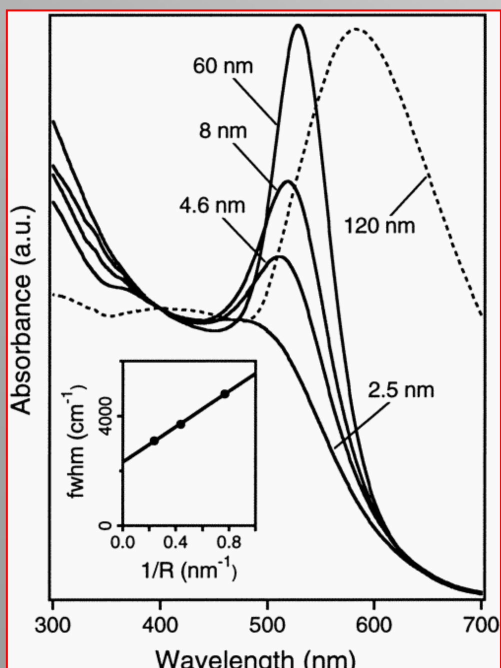
Mie Theory(1908)

$$\sigma_{abs}(\omega) = \frac{9\omega V_0 \varepsilon_m^{3/2}}{c} \frac{\varepsilon_2}{(\varepsilon_1 + 2\varepsilon_m)^2 + \varepsilon_2^2}$$

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$$



*J.H. Hodak, et al. ; **J. Phys Chem. B**, 104(43), 9954, **2000**.*

Drude free electron model

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 - i\gamma\omega}$$

Empirically

$$\gamma(r) = \gamma_0 + \frac{a}{r}$$

Surface Plasmon Resonance is invariant with respect to the size on the nanoparticle.

The FWHM scales with the radius of the particles.

- **Assumes spherical particle**
- **Particle diameter << λ/10**

Plasmon on nanoparticles

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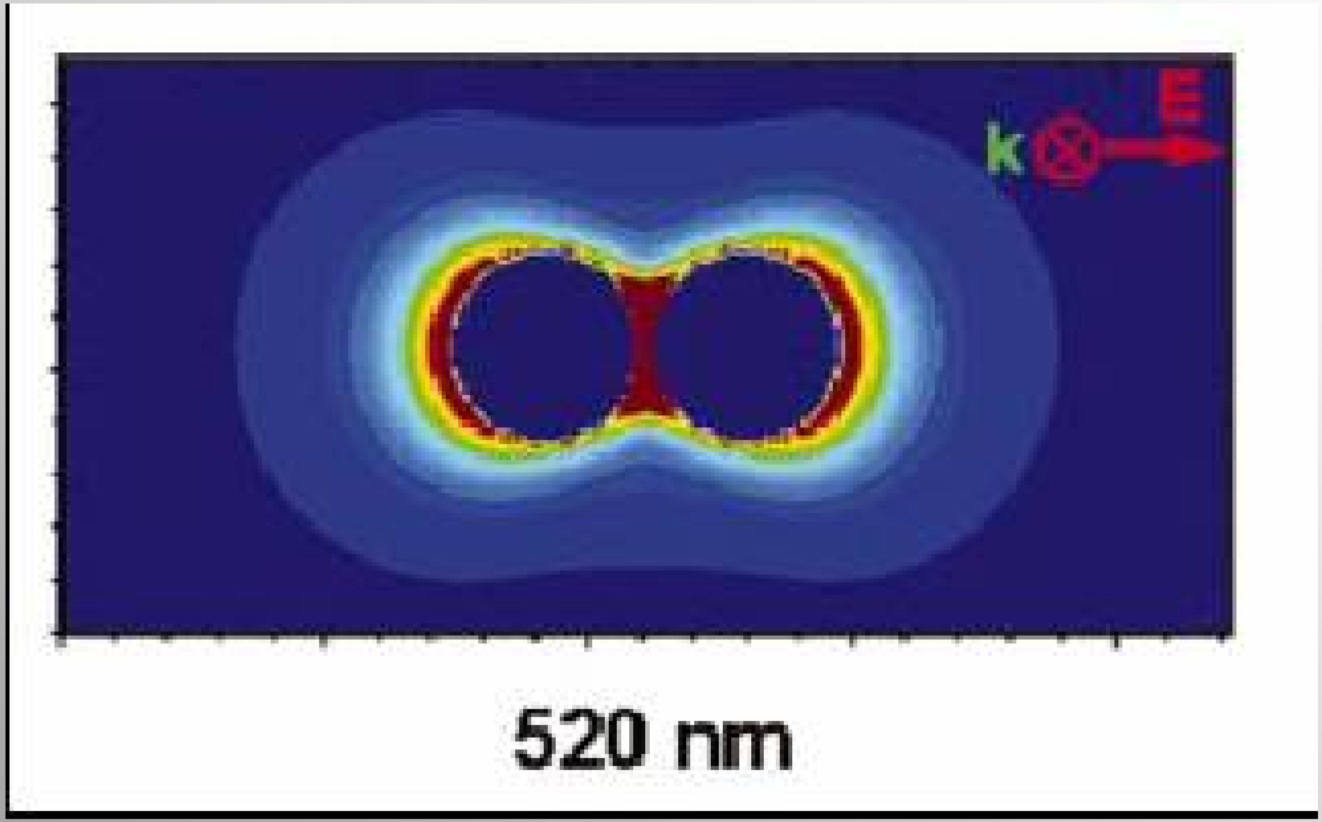

Funny shapes

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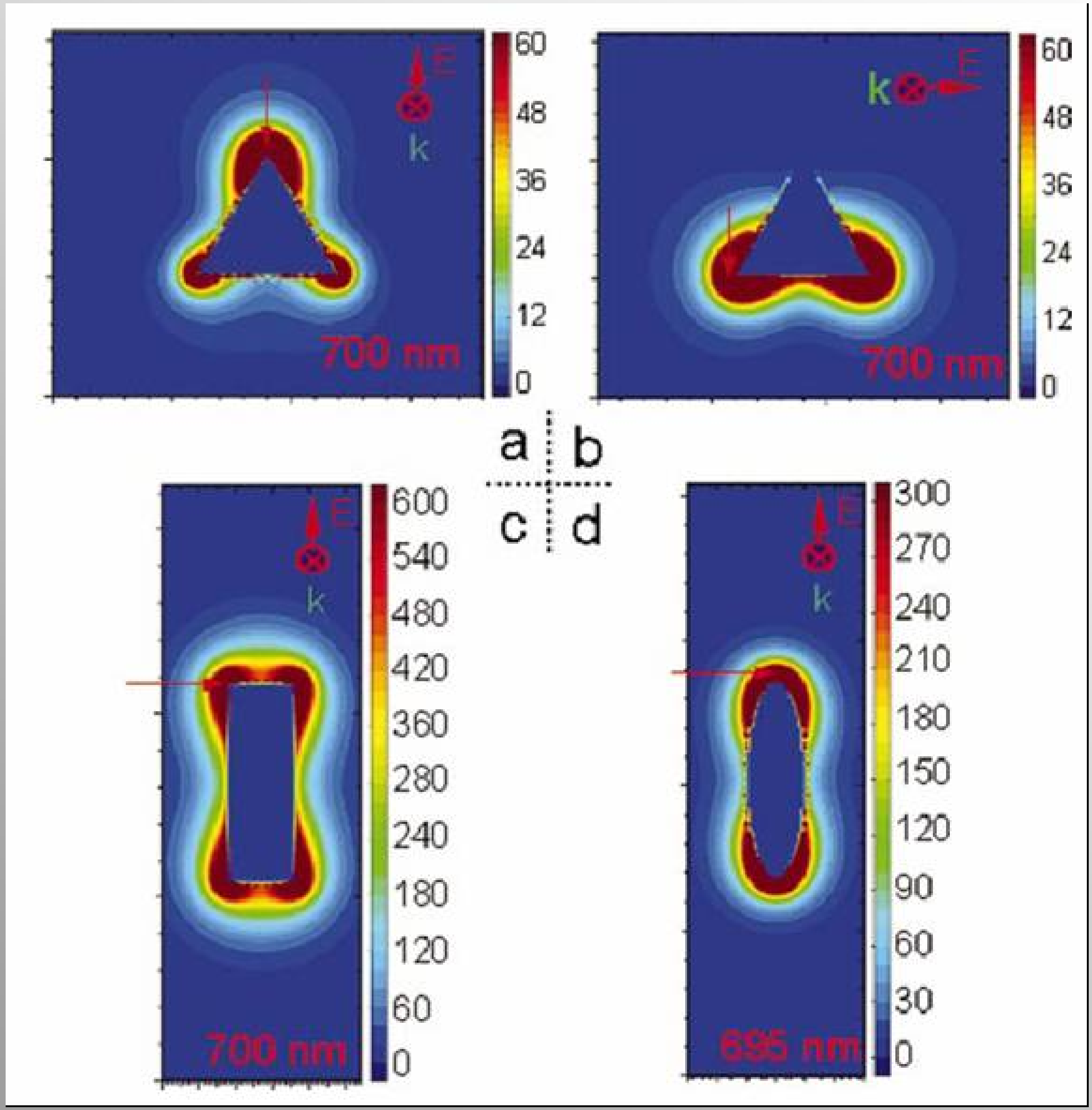

Surface Enhanced Raman Scattering

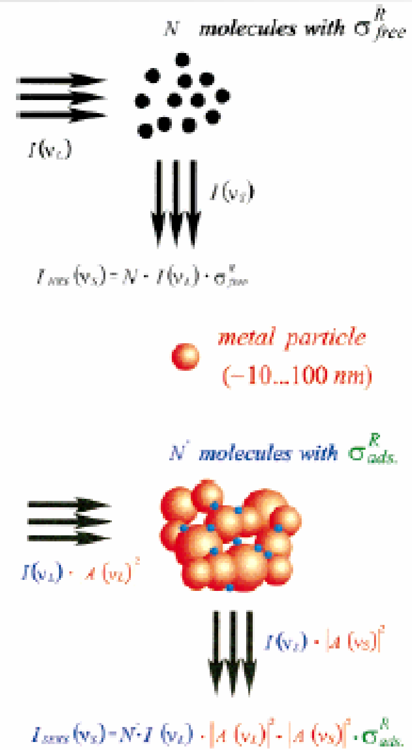

Figure 1. Comparison of "normal" (top) and surface-enhanced (bottom) Raman scattering. In Figure 1a, the conversion of laser light I_L into Stokes scattered light I_{NRS} is proportional to the Raman cross section $\sigma^R{}_{free}$, the excitation laser intensity I_L, and the number of target molecules N in the probed volume. Figure 1b displays a schematic of a SERS experiment. $\sigma^R{}_{ads}$ describes the increased Raman cross section of the adsorbed molecule ("chemical" enhancement); $A(\nu_L)$ and $A(\nu_S)$ are the field enhancement factors at the laser and Stokes frequency, respectively; N' is the number of molecules involved in the SERS process.

Local Field Enhancement

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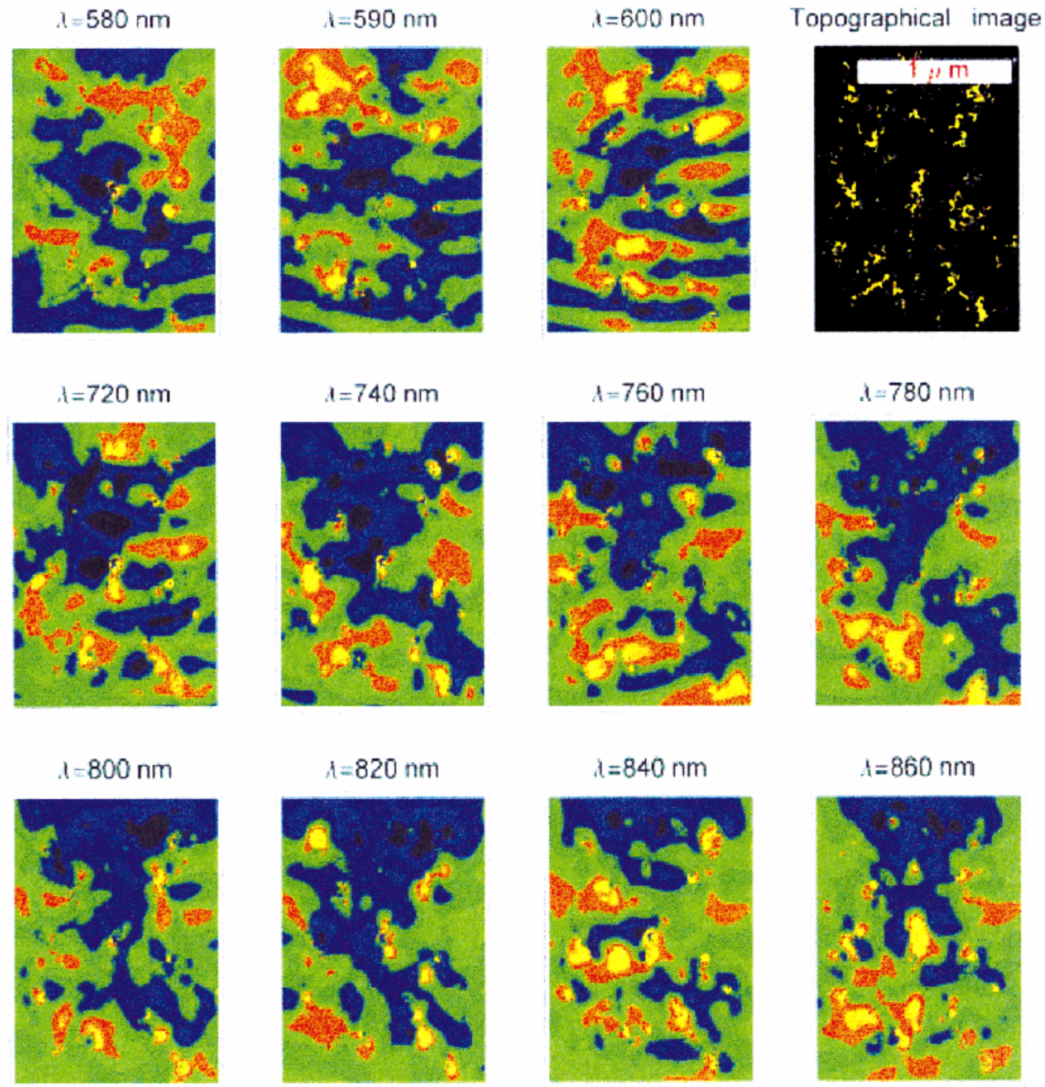

Figure 3. Calculated near-field false-color images computed 100 nm above the topographical silver cluster image shown in the upper right-hand corner. Maximum intensity is shown as yellow and the minimum is black; the intensity range covers approximately a factor 4. (Reprinted with permission from ref 62. Copyright 1999 American Institute of Physics.)

Concentration Dependence

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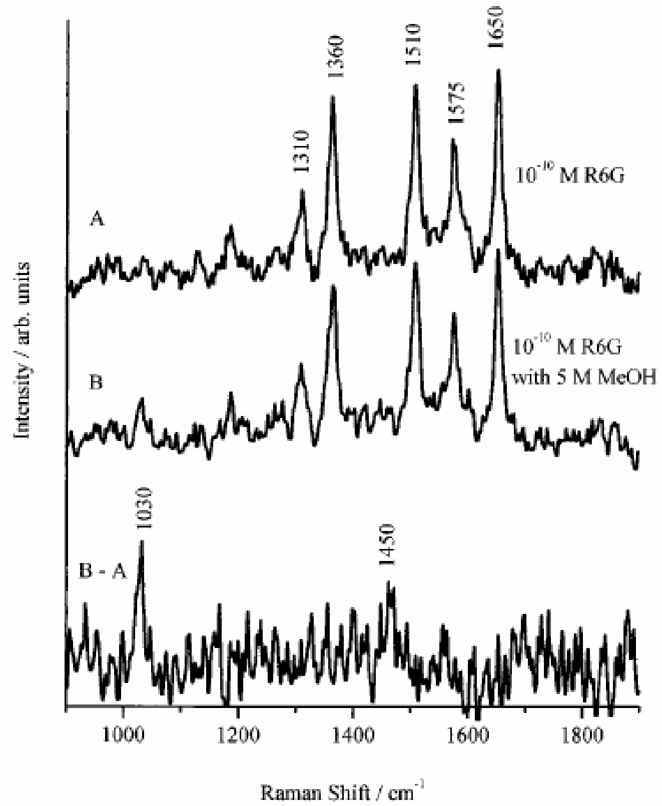

Figure 4. SERRS spectrum from 8×10^{-11} M rhodamine 6G in silver colloidal solution (top), with addition of 5 M methanol (middle). Spectra were measured using 514.5 nm resonant excitation; laser intensity was ca. 10^3 W/cm^2. No fluorescence was obtained at such low concentration because all dye molecules can find a place on the colloidal silver particles where the fluorescence is quenched. The bottom curve depicts the exact subtraction of the top curve from the middle one and shows only the methanol lines. The methanol Raman signal is not enhanced on colloidal silver and shows a Raman cross section on the order of 10^{-30} cm^2/molecule.[133]

Resonances

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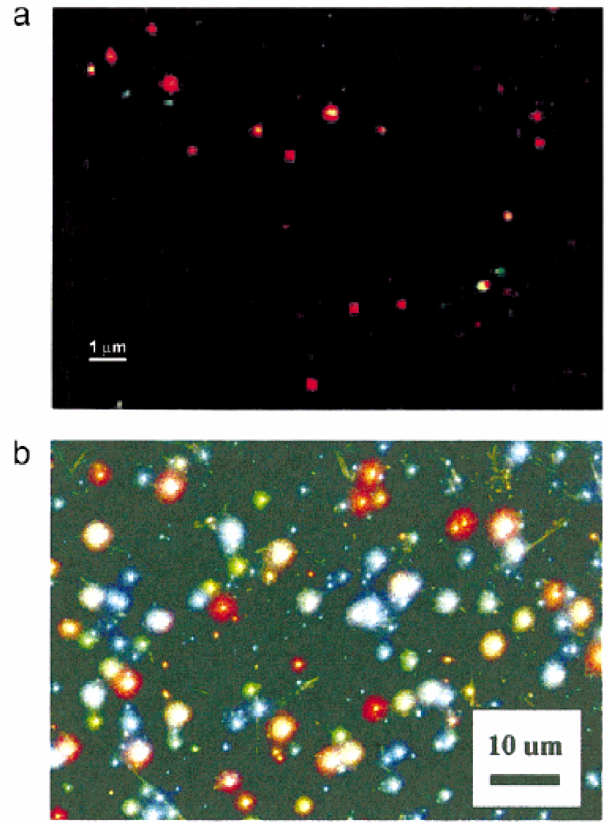

Figure 8. (a) Multicolor Raman image of Ag nanoparticles excited with a mercury lamp at 490 and 570 nm. The probe molecule is bis(4-bipyridyl)ethylene (BPE). The green, red, and yellow signals correspond to 70 nm particles (excited at 490 nm), 140 nm particles (excited at 570 nm), and intermediate-sized particles or nanoaggregates (excited at both 490 and 570 nm), respectively. (b) Multicolor Rayleigh image of Ag nanoparticles excited with a tungsten lamp. For rough orientation, the blue particles correspond to spherical Ag particles with a size of approximately 50 nm or to smaller nonspherical particles and red images come from particles with very high axial ratios, such as rods. (Reprinted with permission from refs 85 and 87. Copyright 1998 American Chemical Society.)

Hemoglobin

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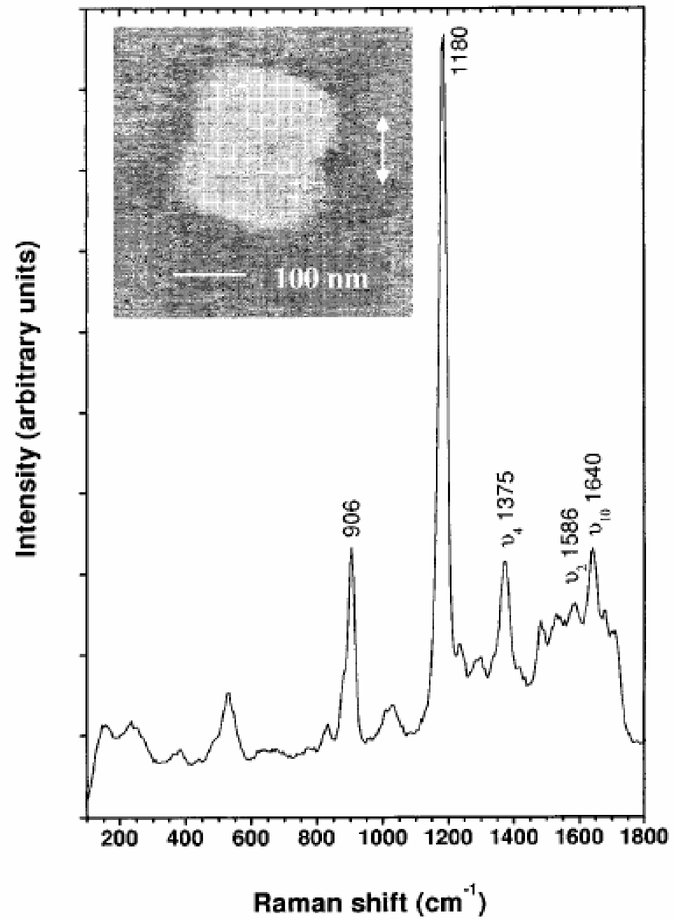

Figure 14. SERS spectrum of a single Hemoglobin molecule on an optically "hot" silver nanoparticle (see inset). A 100× microscope objective was used to illuminate this pair and also to collect the scattered light. The laser wavelength was 514.5 nm, laser power was ~20 μW, laser focus radius was ~1 μm, and integration time was 200 s. (Reprinted with permission from ref 86.)

Metal Nanoparticles Fractal Clusters

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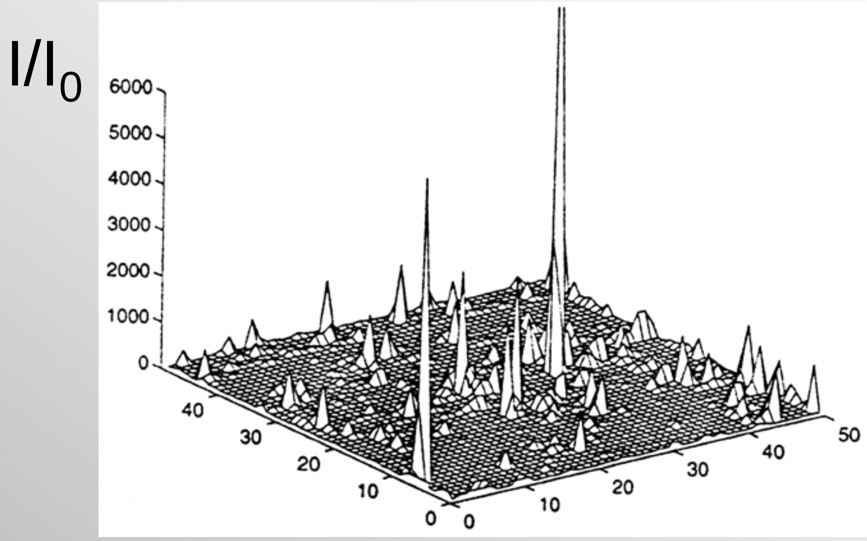
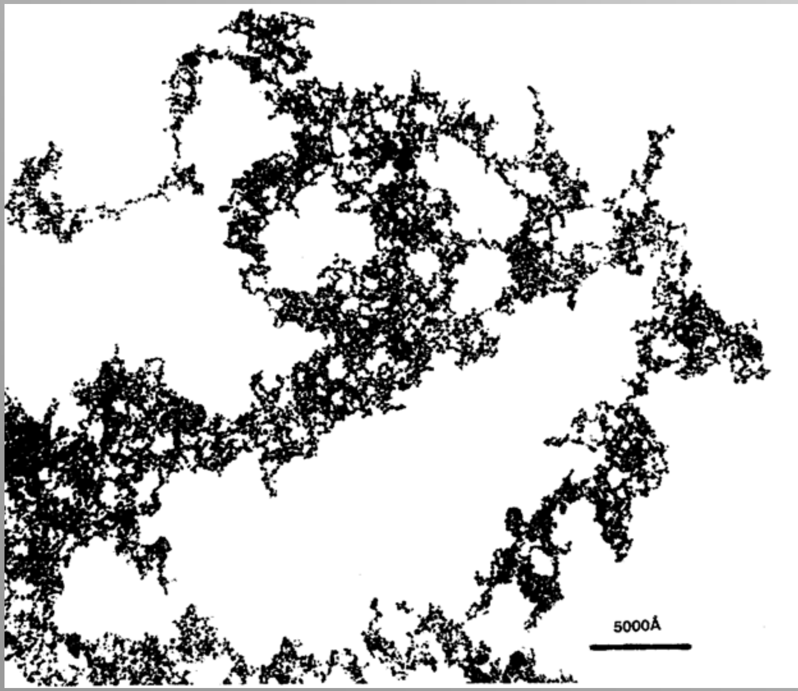
- Metal nanoparticle fractal clusters
  → Collective surface plasmon modes
    - strongly localized
    - resonate at VIS/NIR frequencies

Theoretical simulation by Shalaev *et al*., PRB 1997





- Enhancement of optical processes:
  Raman scattering, Lasing, DFWM, TPA

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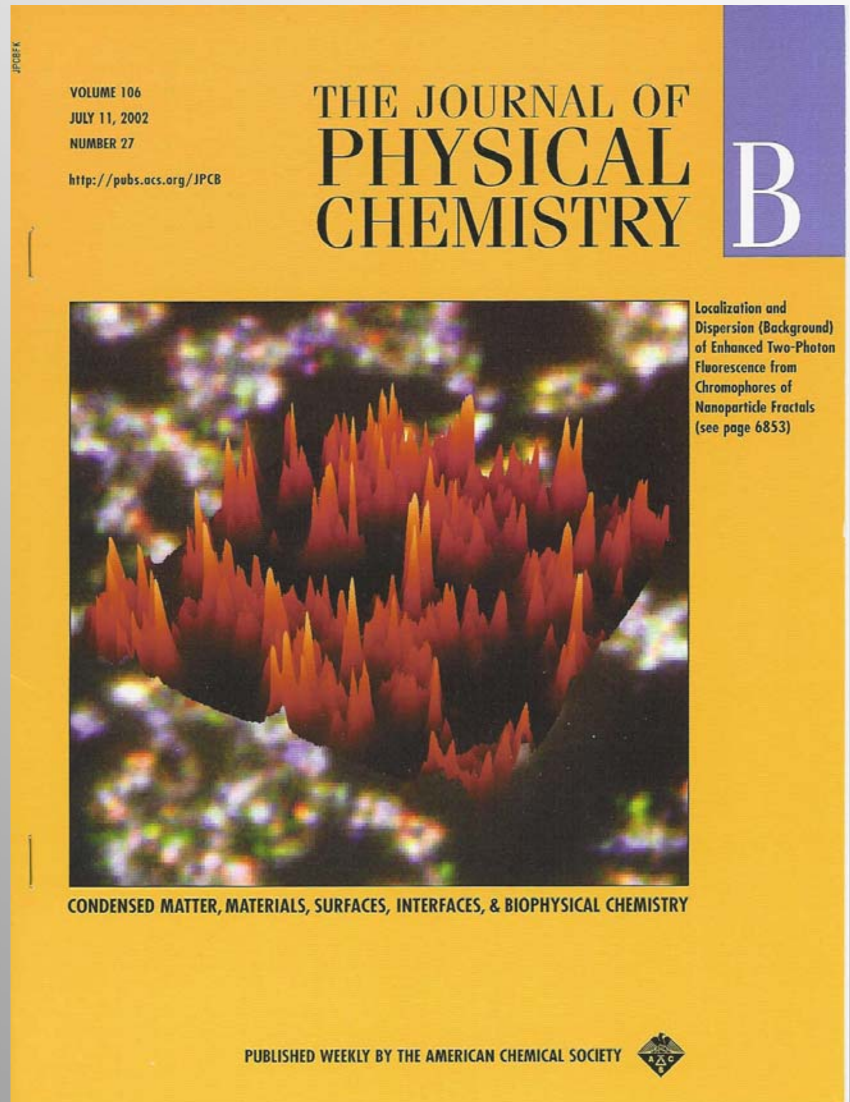
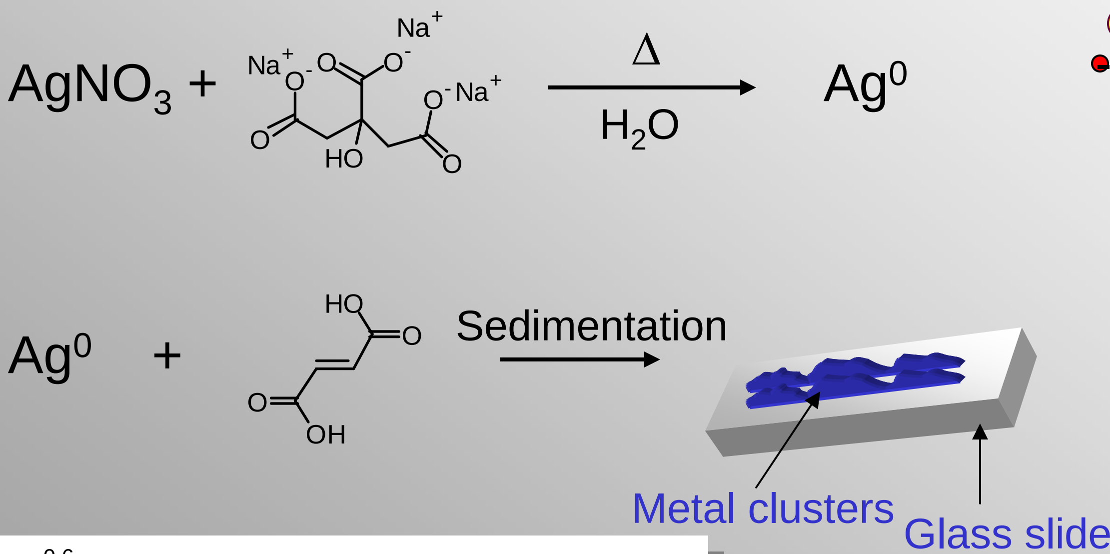
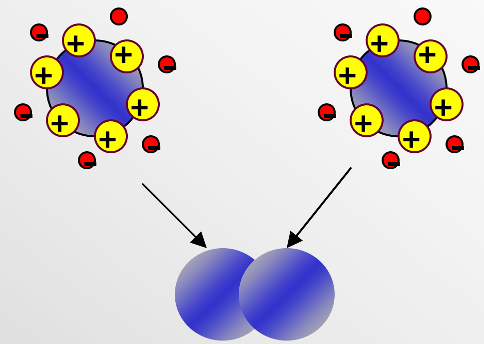
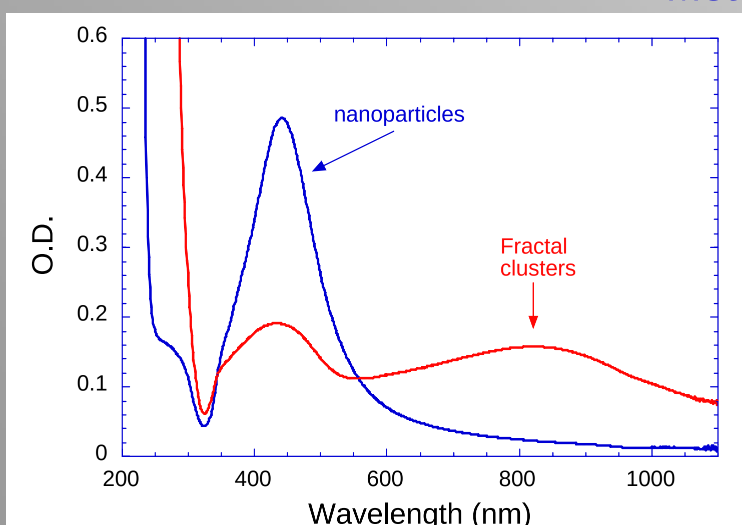


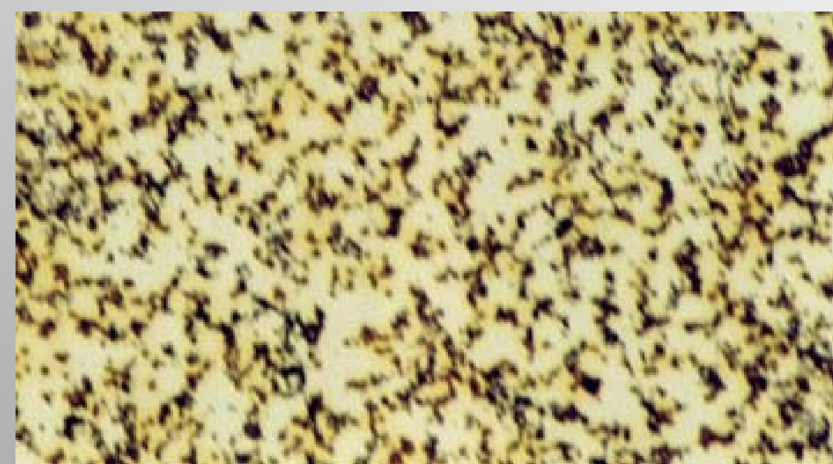
VOLUME 106
JULY 11, 2002
NUMBER 27
http://pubs.acs.org/JPCB
THE JOURNAL OF PHYSICAL CHEMISTRY B
Localization and Dispersion (Background) of Enhanced Two-Photon Fluorescence from Chromophores of Nanoparticle Fractals (see page 6853)
CONDENSED MATTER, MATERIALS, SURFACES, INTERFACES, & BIOPHYSICAL CHEMISTRY
PUBLISHED WEEKLY BY THE AMERICAN CHEMICAL SOCIETY

Sample Preparation









TPA Enhancement

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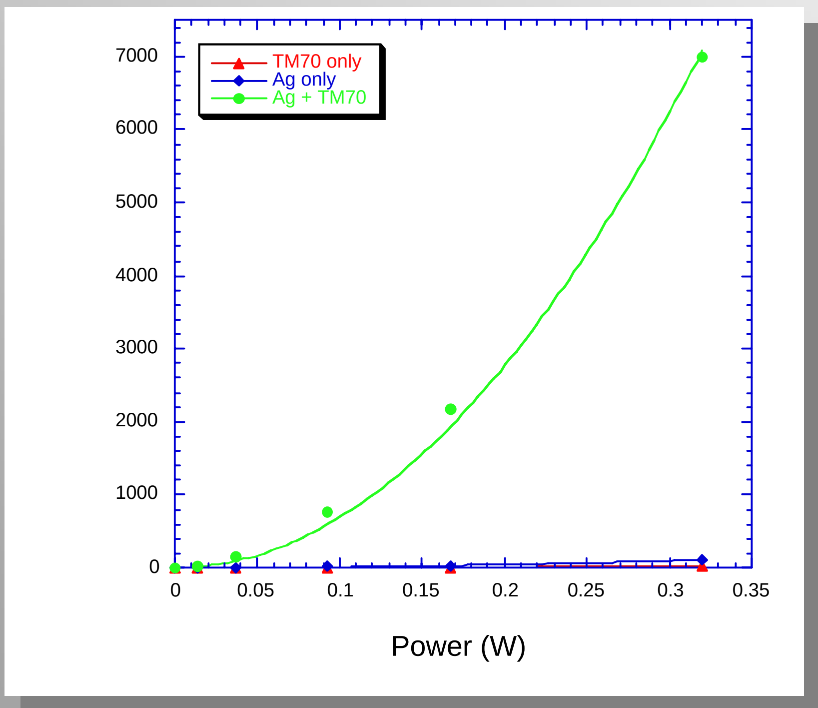

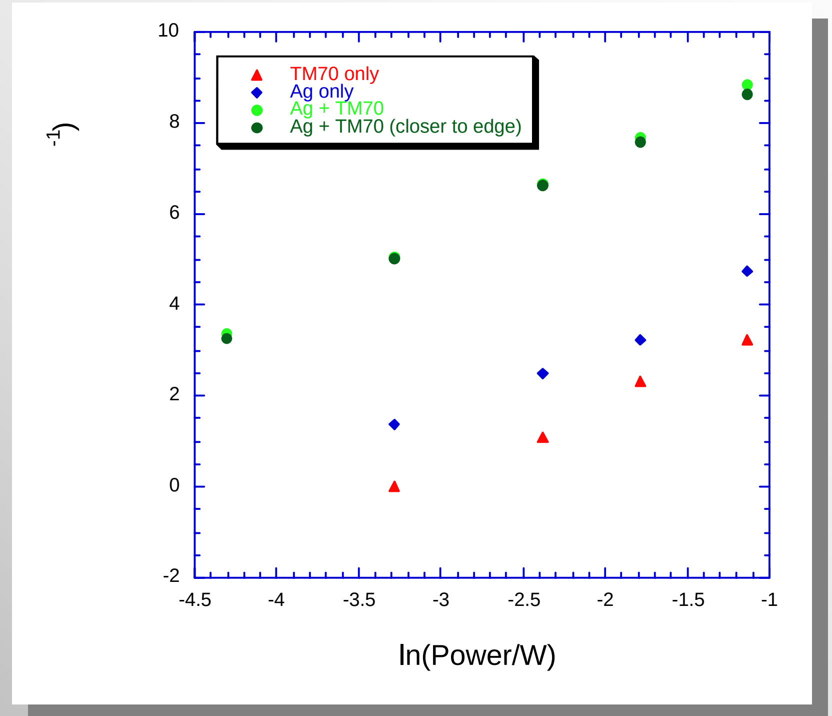

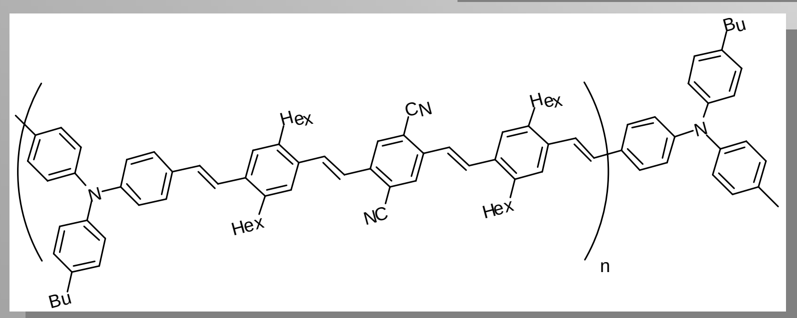

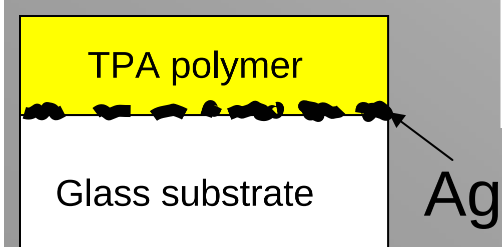

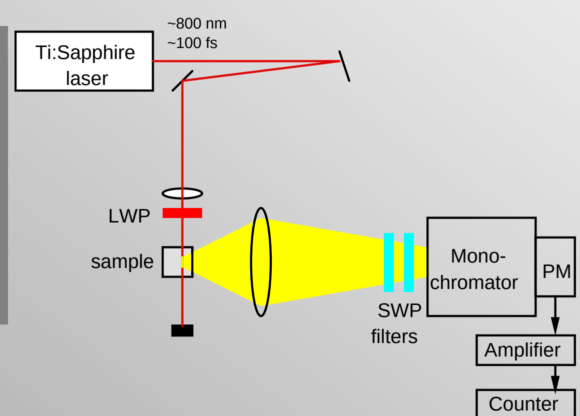

Spatial Inhomogeneity

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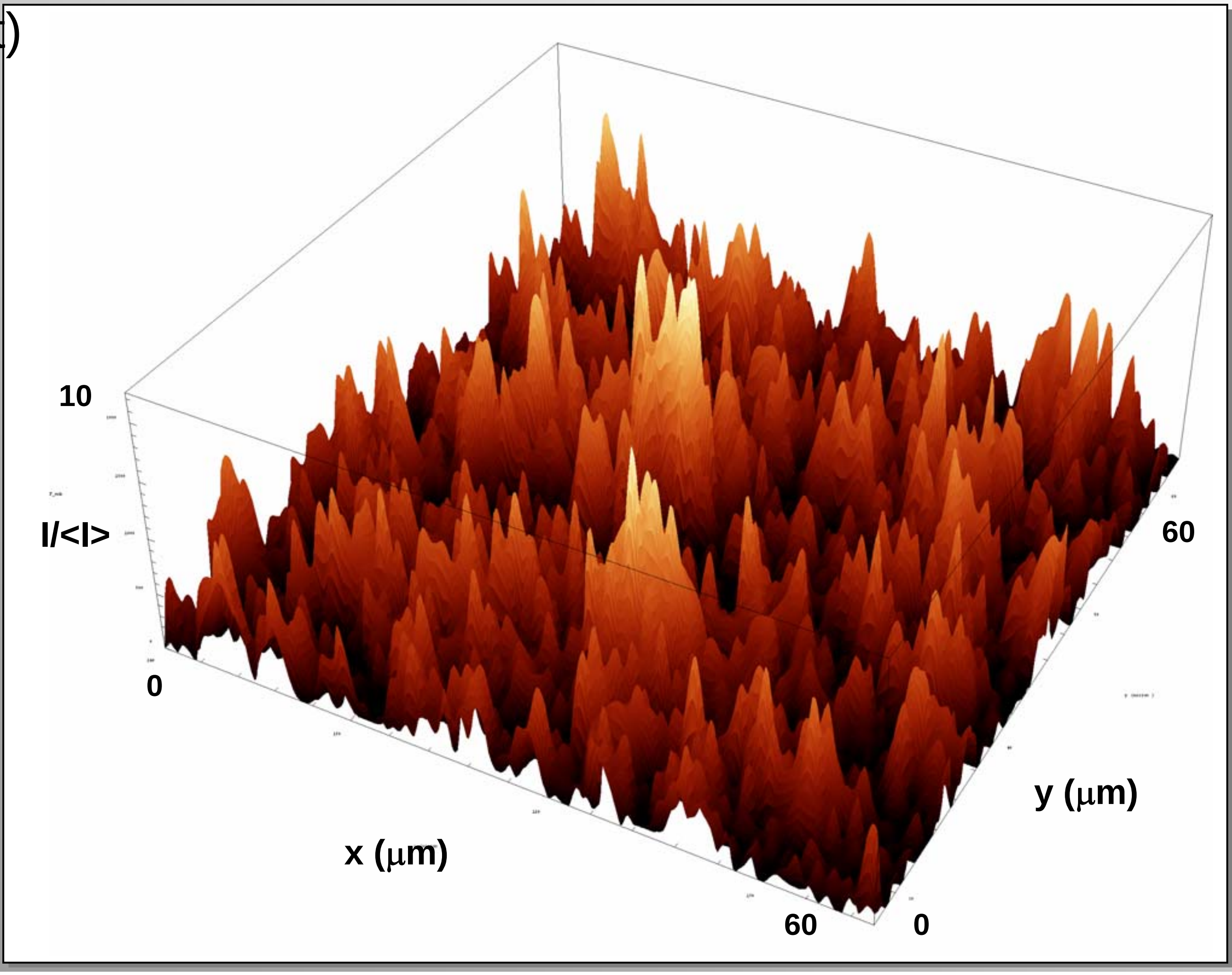
- TPF *vs*. position: very inhomogeneous as expected

Average enhancement factor ~ 235==> Peak enhancement factor >2000 (lower limit)

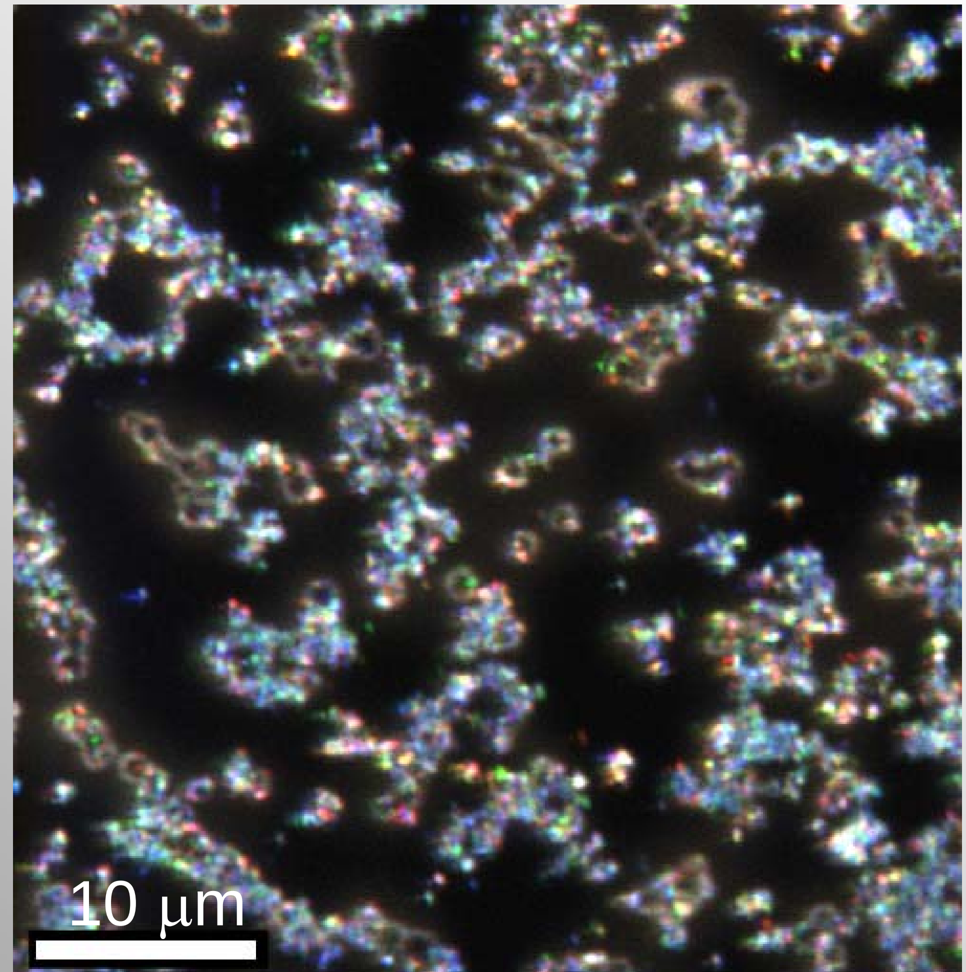


Frequency Dependence

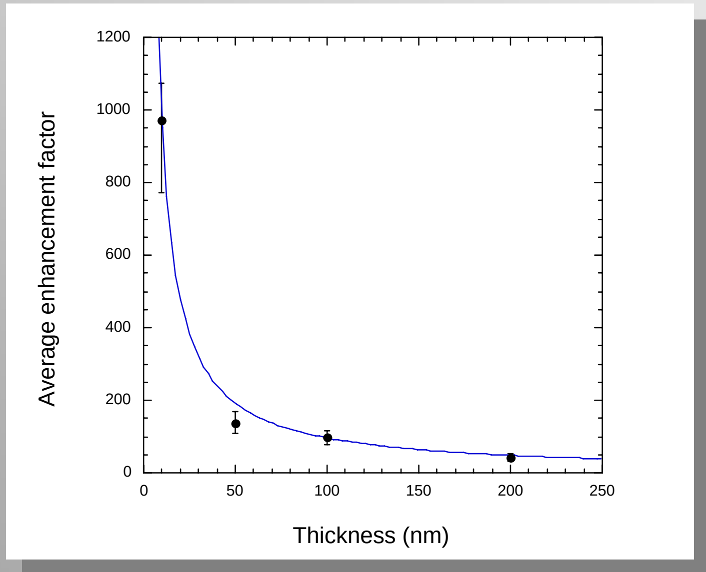
- Excitation wavelength dependence:

λ_{exc} = 720 nm
820 nm
890 nm

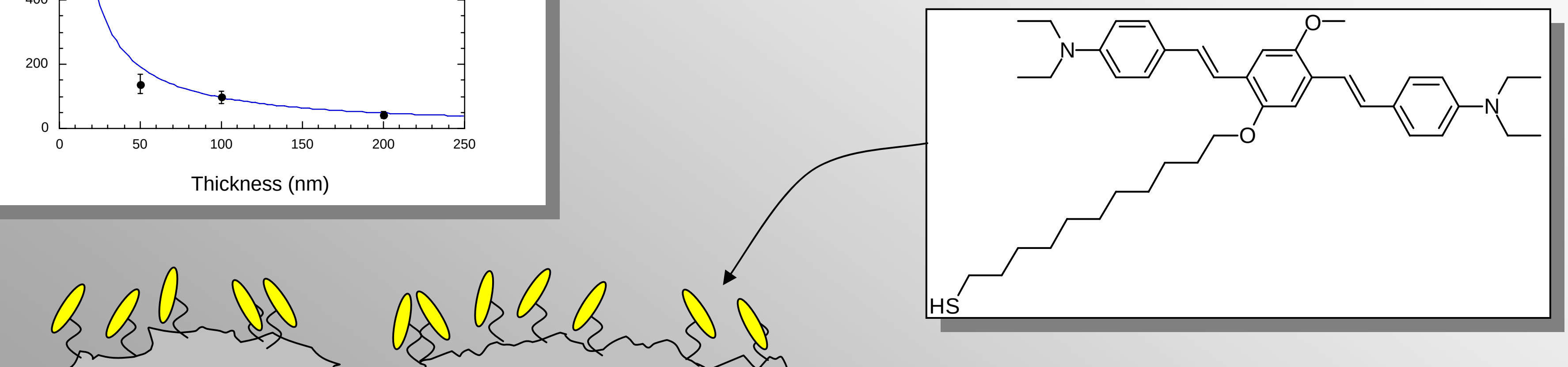
False Color Overlay



Sub-monolayers on MNFC



Thickness dependence



•Spatially averaged TPF enhancement factor ~ 20000 (referenced against one-photon fluorescence)

•Peak TPF enhancement factor > 160000

Morphology Effect

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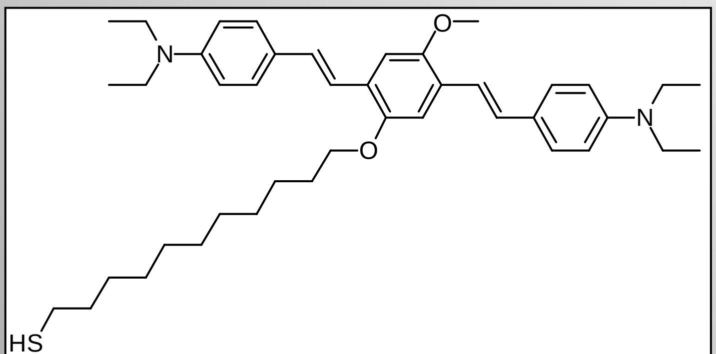
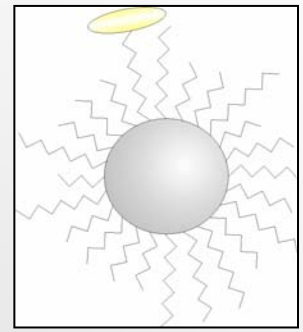
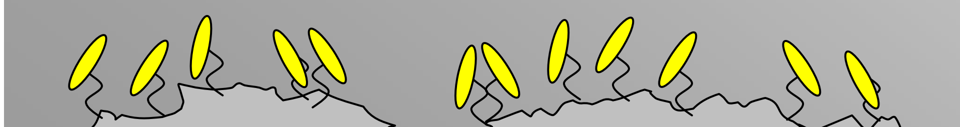


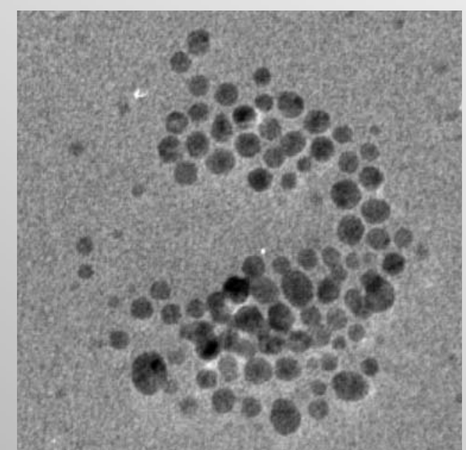
Enhancement factor: 1



Enhancement factor: 10^4

Enhancement factor: 5





Metal Nanoparticles Synthesis

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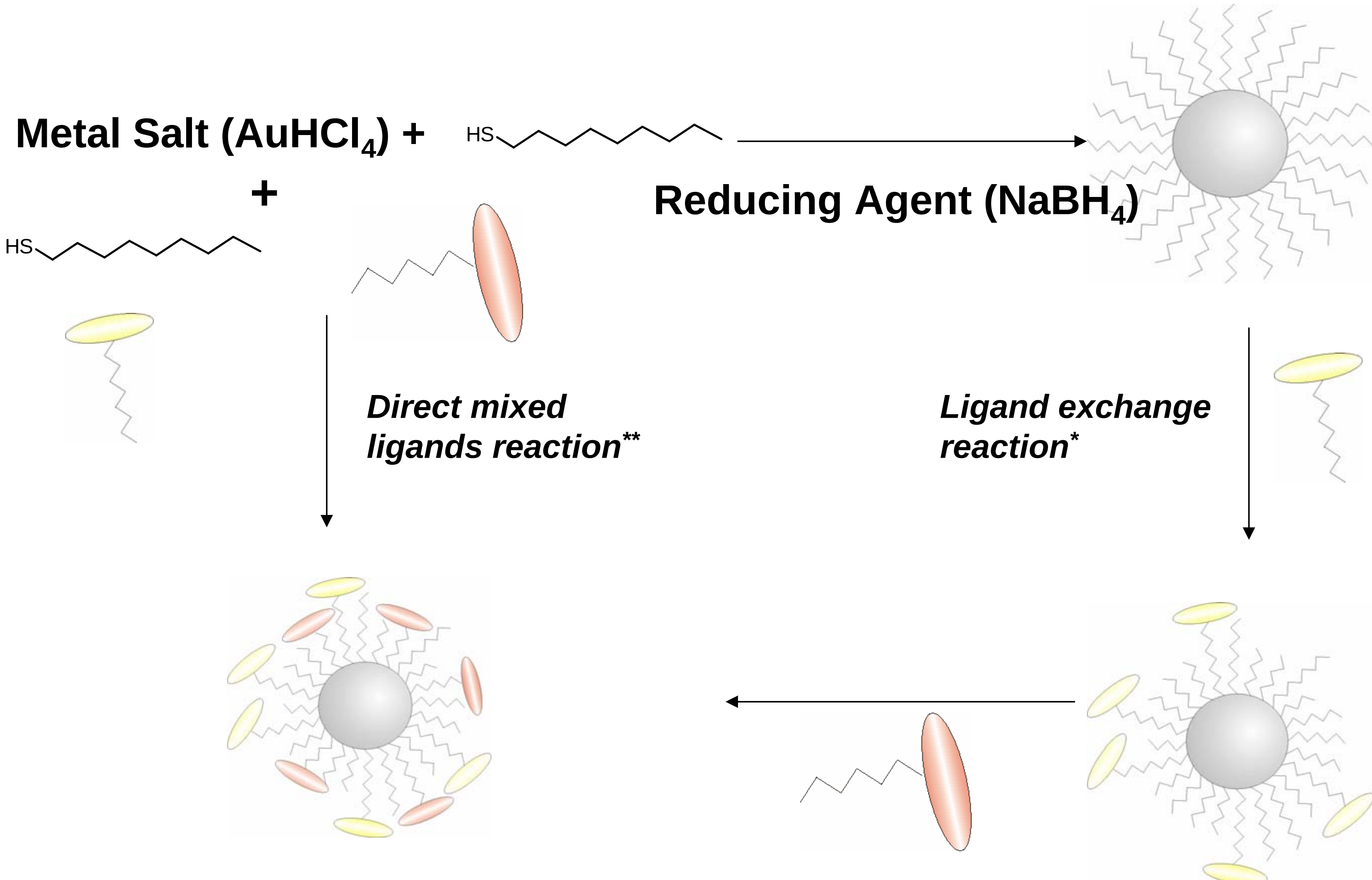

F. Stellacci, et al. *Adv. Mat.* **2002**, 14, 194

A. C. Templeton, M. P. Wuelfing and R. W. Murray, *Accounts Chem. Res.* **2000**, 33, 27

Synthesis Mechanism

Synthesis Procedure

Place Exchange Reactions

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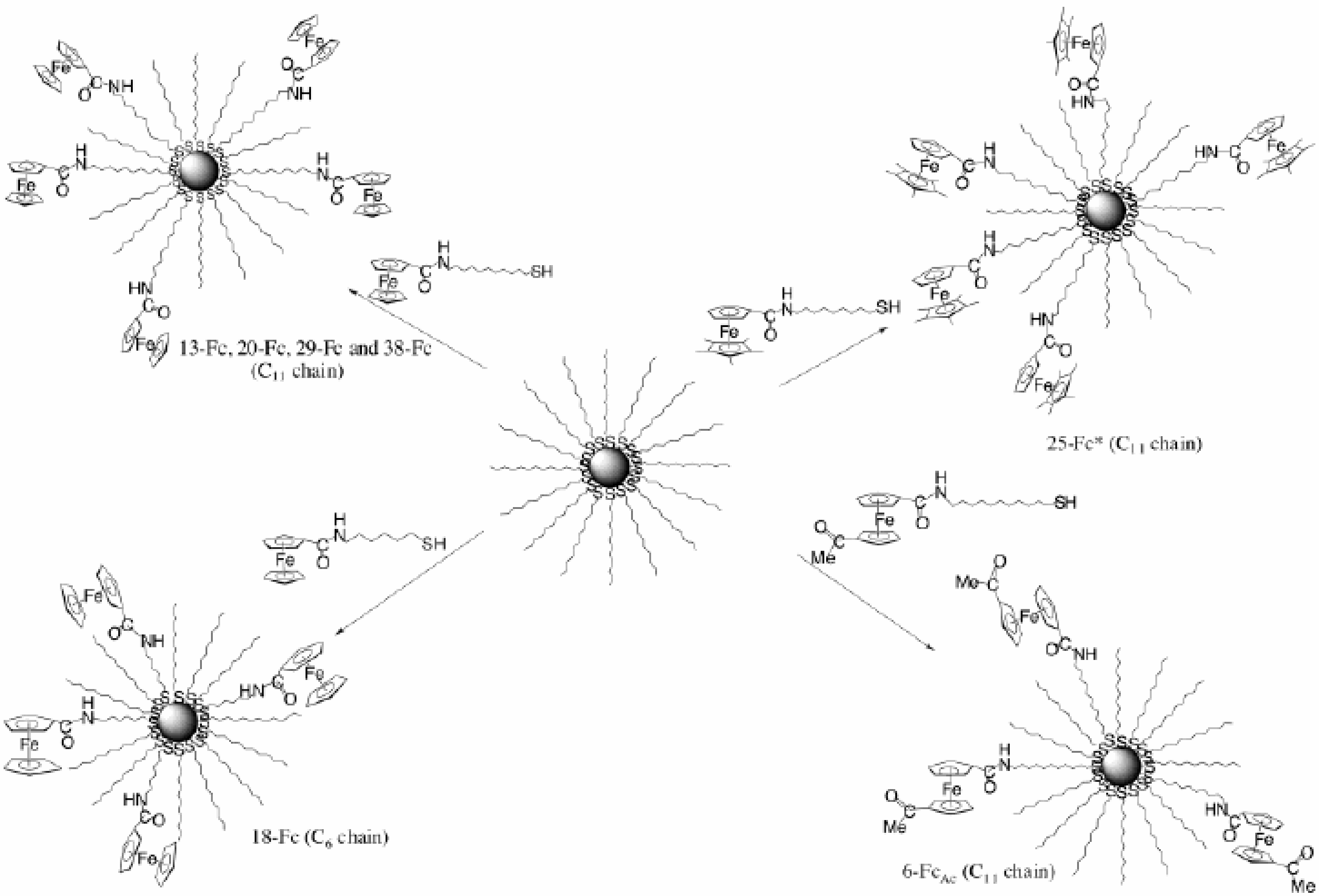


Figure 5. Ligand substitution reactions (CH_2Cl_2, 2 d, room temperature) for the syntheses of the AuNPs containing mixed dodecanethiol and (amidoferrocenyl) alkanethiol-type ligands with variation of the chain length (C_{11} vs C_6) and ring structure of the ferrocenyl motif (Cp, Cp*, C_5H_4COMe). Reprinted with permission from ref 140 (Astruc's group). Copyright 2002 American Chemical Society.

Galvanic Exchange

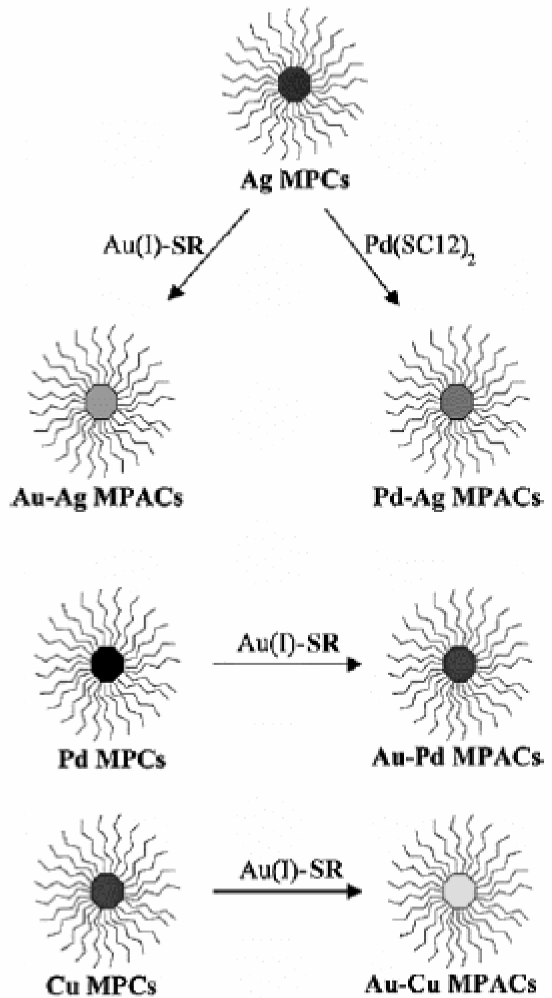


Figure 16. Cartoon diagram of core metal galvanic exchange reactions. MPC, monolayer-protected cluster; MPAC, monolayer-protected alloy cluster; SC12, $S(CH_2)_{11}$-CH_3. Reprinted with permission from ref 166a (Murray's group). Copyright 2002 American Chemical Society.

Solid State Photo-Patterning

S u N M a G

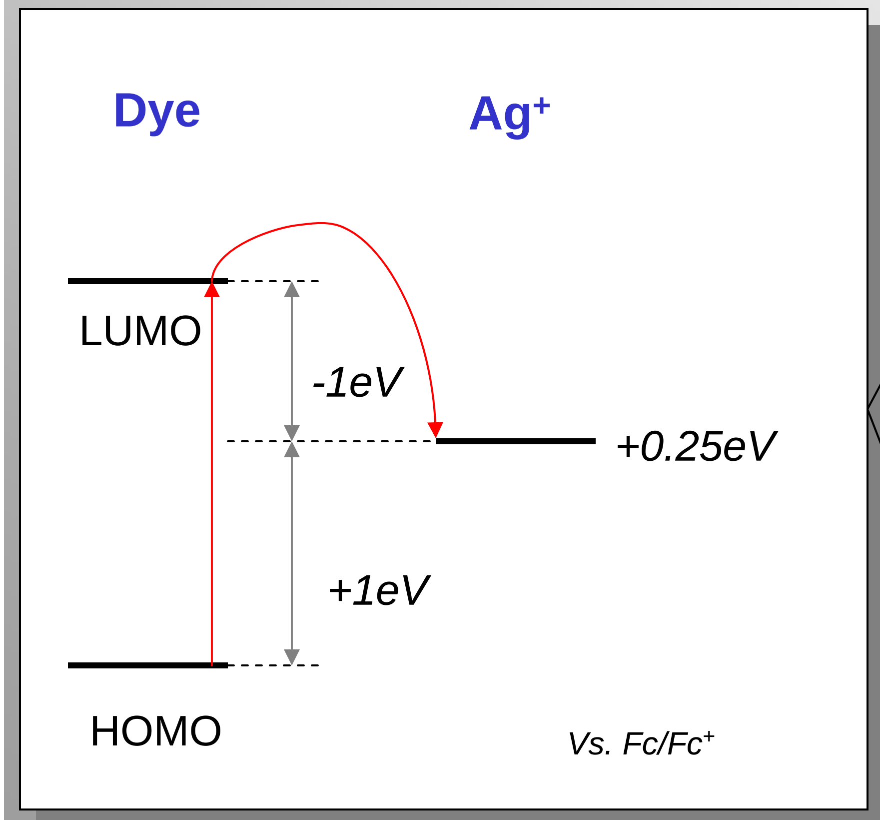
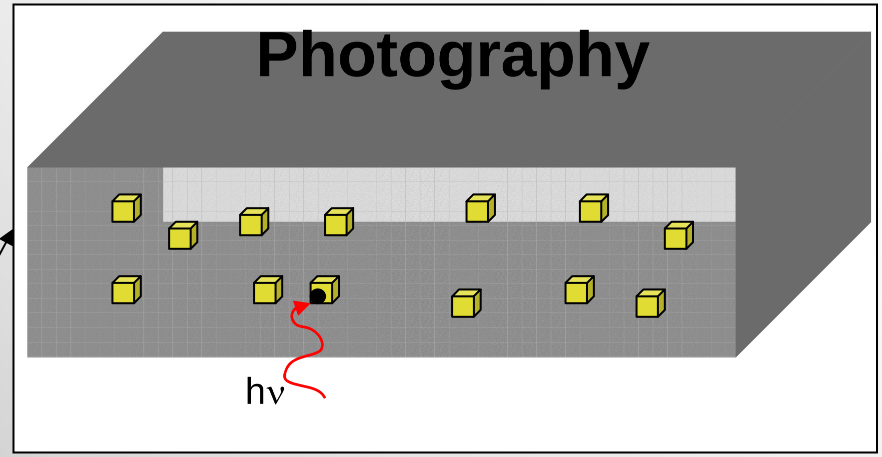
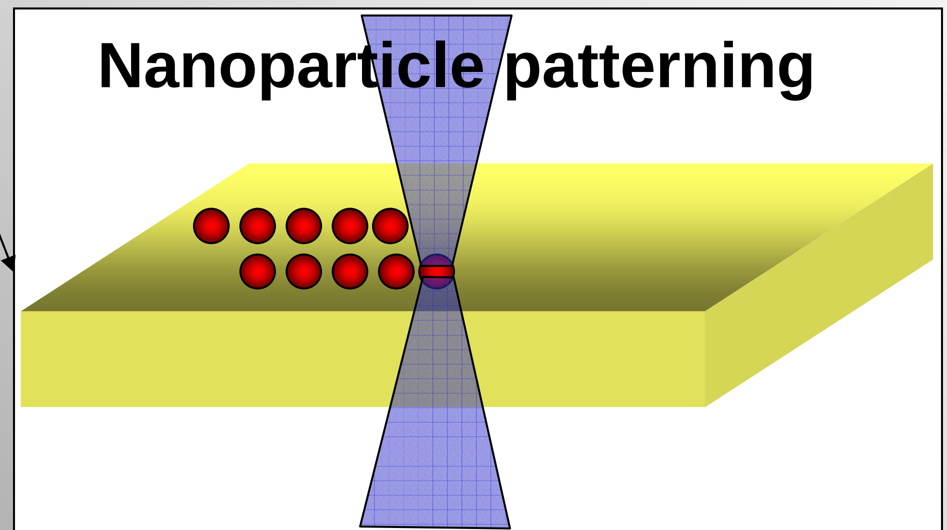


Photo-reduction



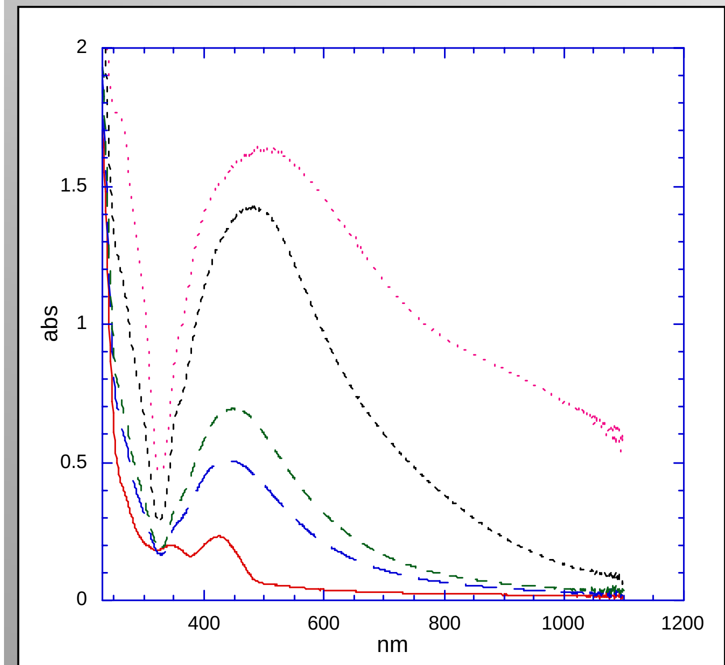


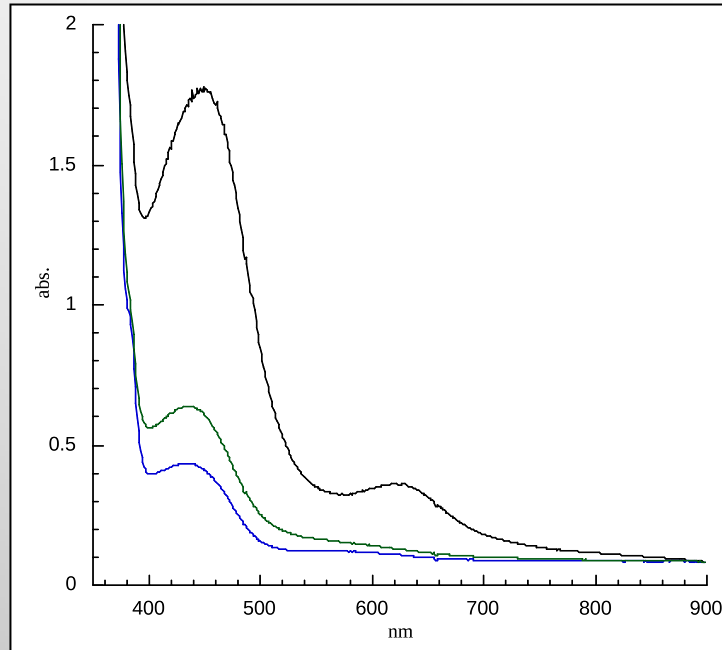
In solution: *Huang et al.*, ***Langmuir***, *12 (4),909,1996*

Nanoparticle Generation

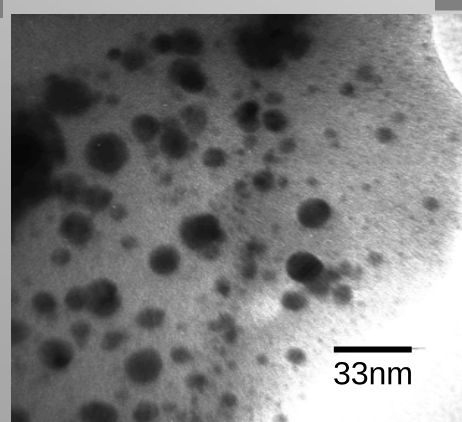
S u N M a G

Dye and $AgBF_4$ in a 1:1 molar ratio irradiated @ 488nm





In Acetonitrile

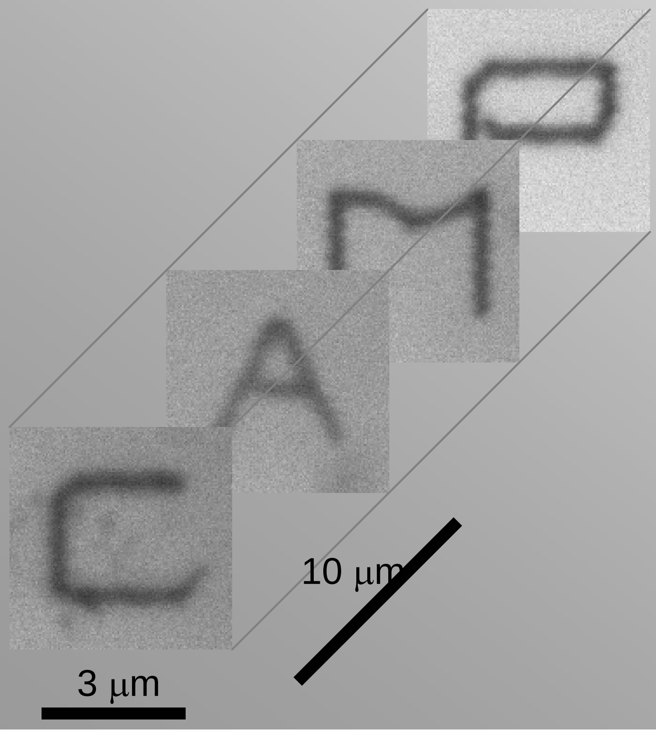


In PVK

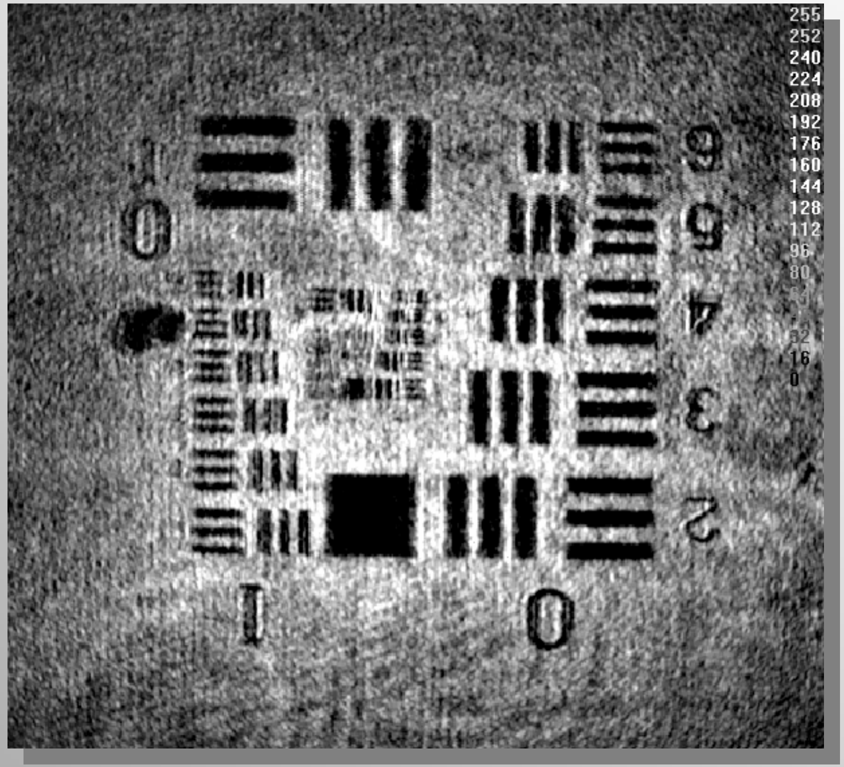
Applications for Nanoparticles Patterns

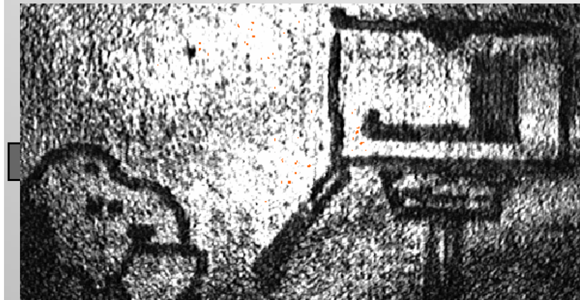
S u N M a G

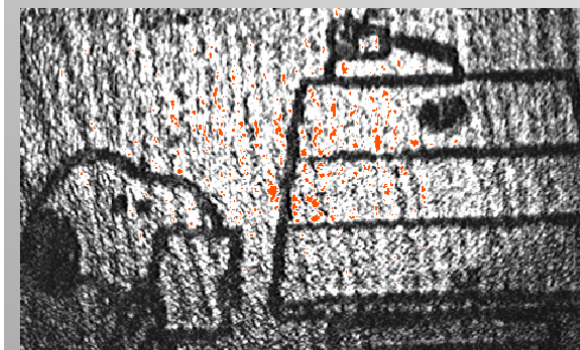
3D Optical Memories with fluorescence-based and refractive index-based readout

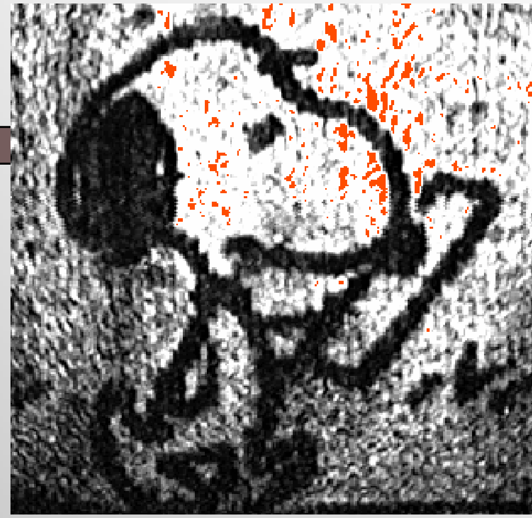


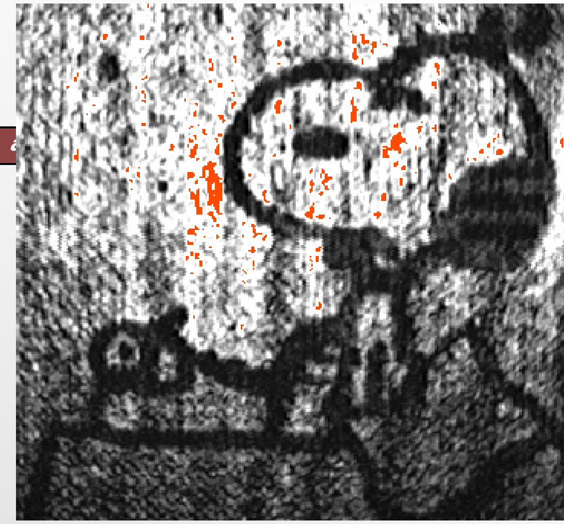
Holographic Data Storage



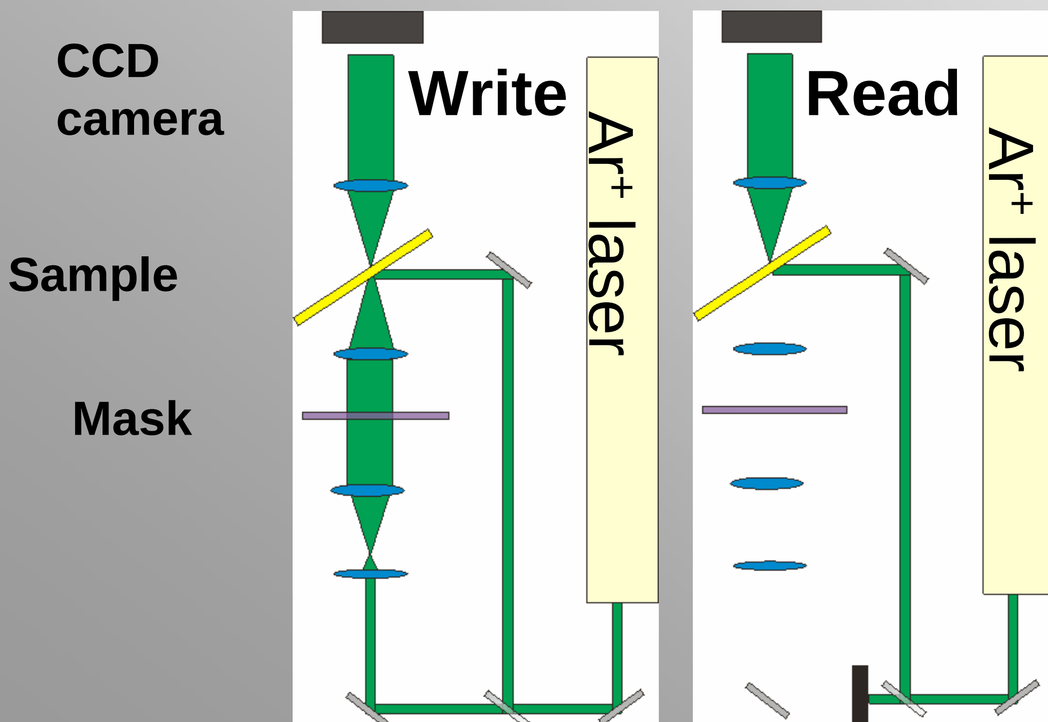


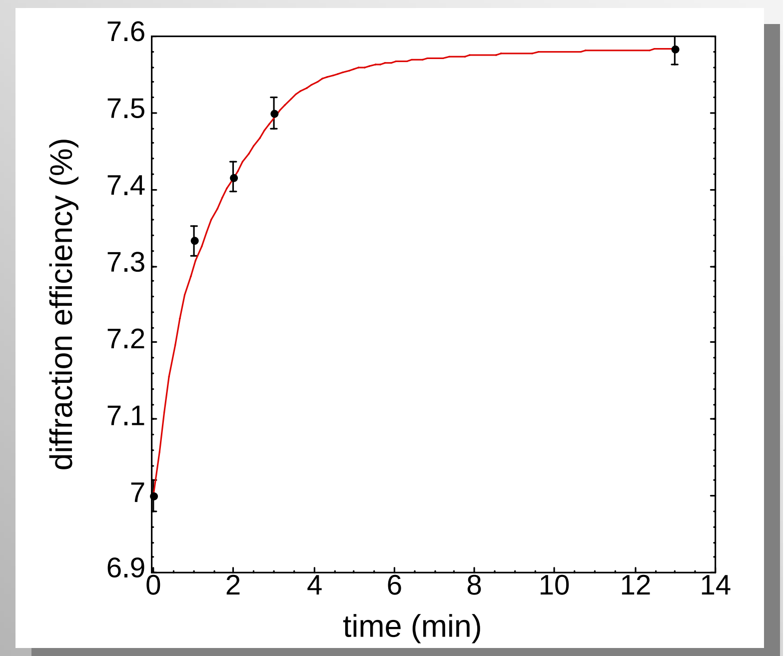






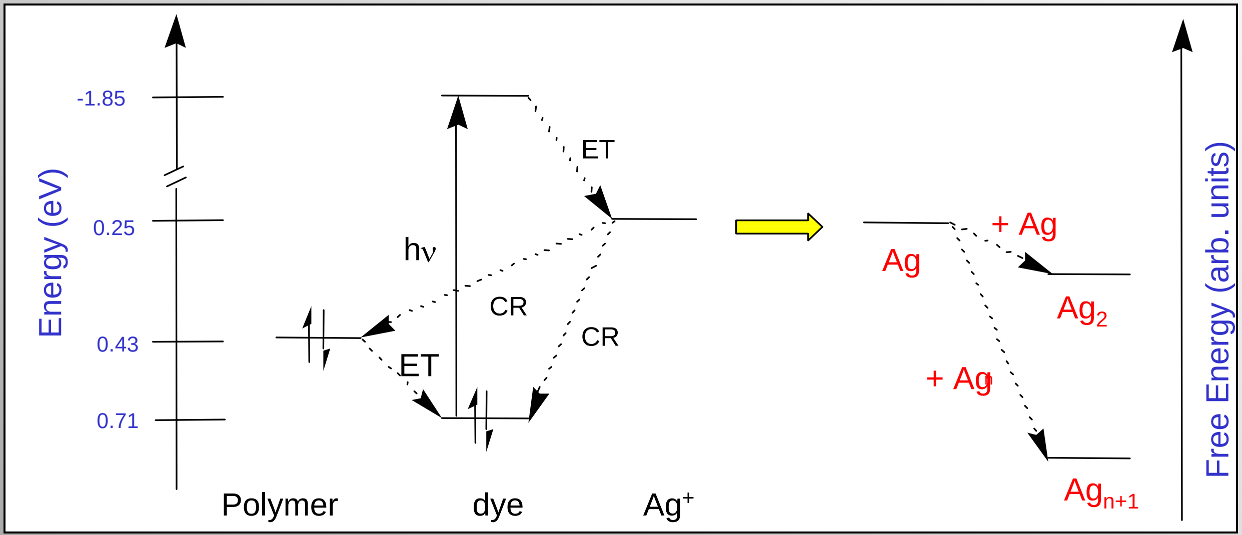
All the images were saved on the same spot spaced of 7^0

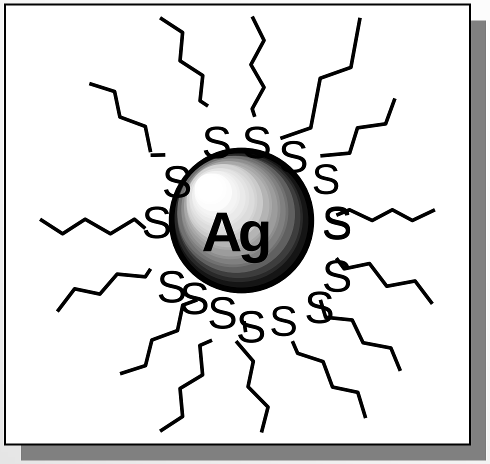


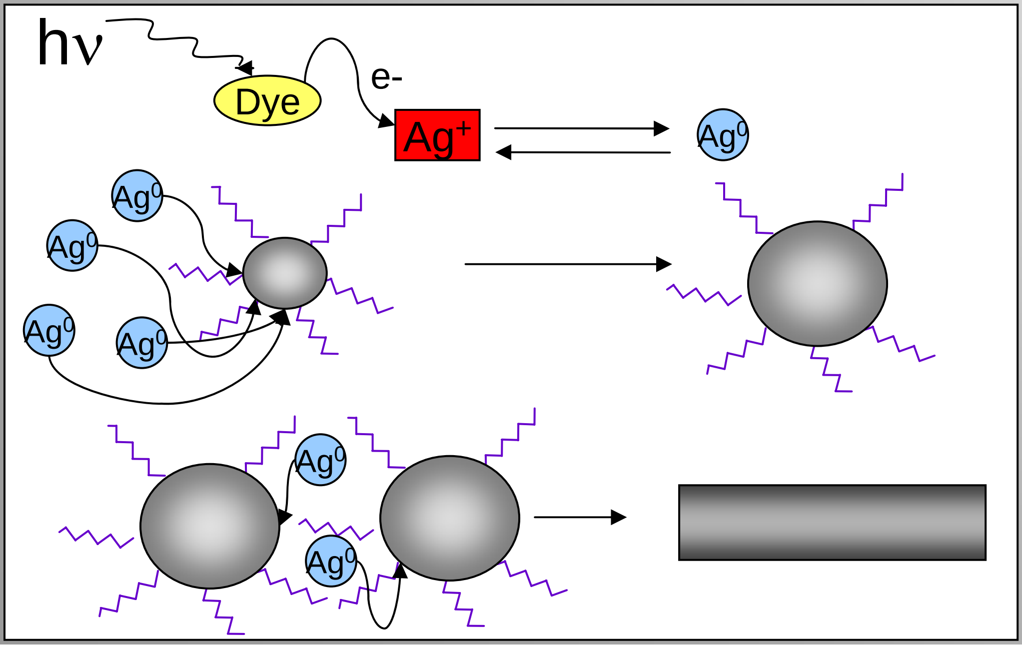


General Concept

S u N M a G







1. Photo-reduction

2. Growth

3. Coalescence

Silver Nanoparticles Synthesis

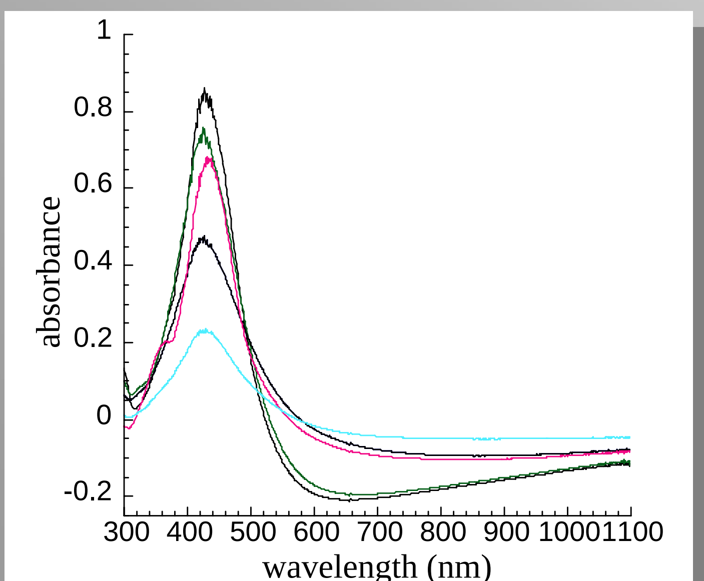
$$Ag^+ + RSH \longrightarrow (RSAg)_n$$

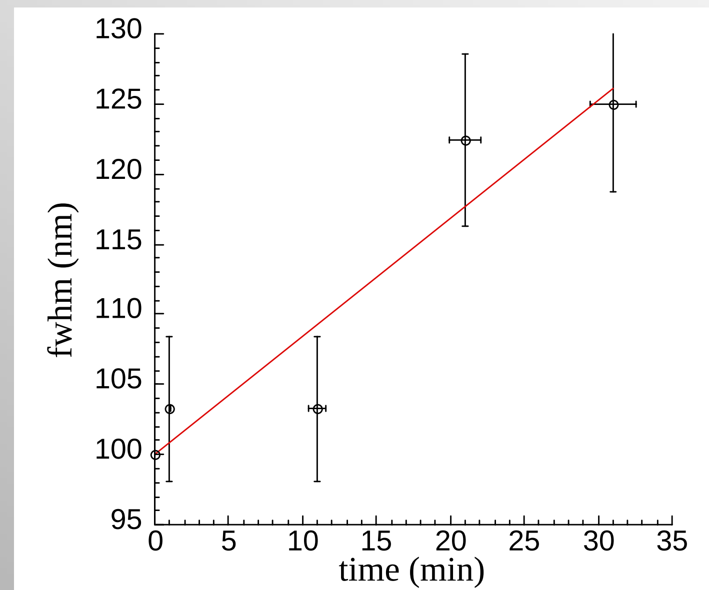
$$(RSAg)_n + Ag^+ \xrightarrow{NaBH_4} (RS)_n\, Ag_{m'}$$

$m' > n$

$$(RS)_n\, Ag_{m'} + Ag^+ \xrightarrow[h\nu]{Dye} (RS)_n\, Ag_{m''}$$

$m'' > m'$



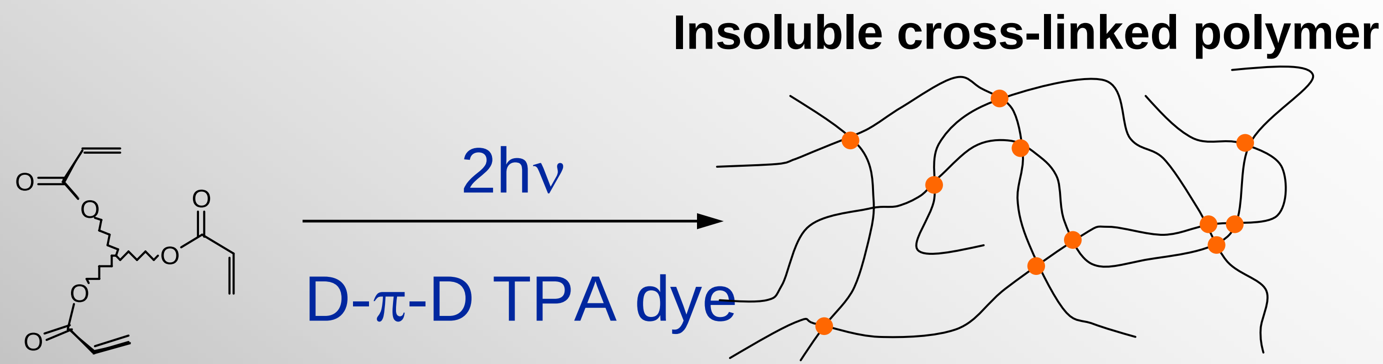


Brust,et. al. ***Chem Commun.****, 1655, 1995.*

Kim et al., ***Langmuir*** *14,226, 1998*

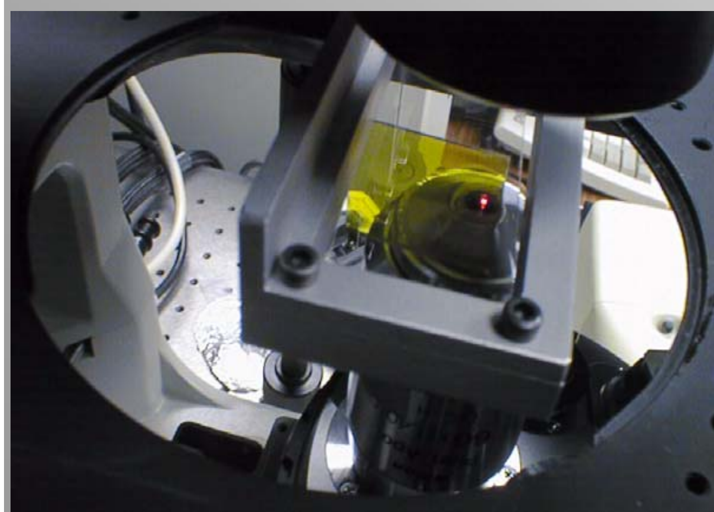
TPA induced Microfabrication

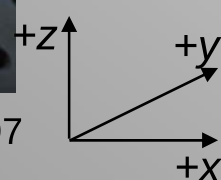
S u N M a G

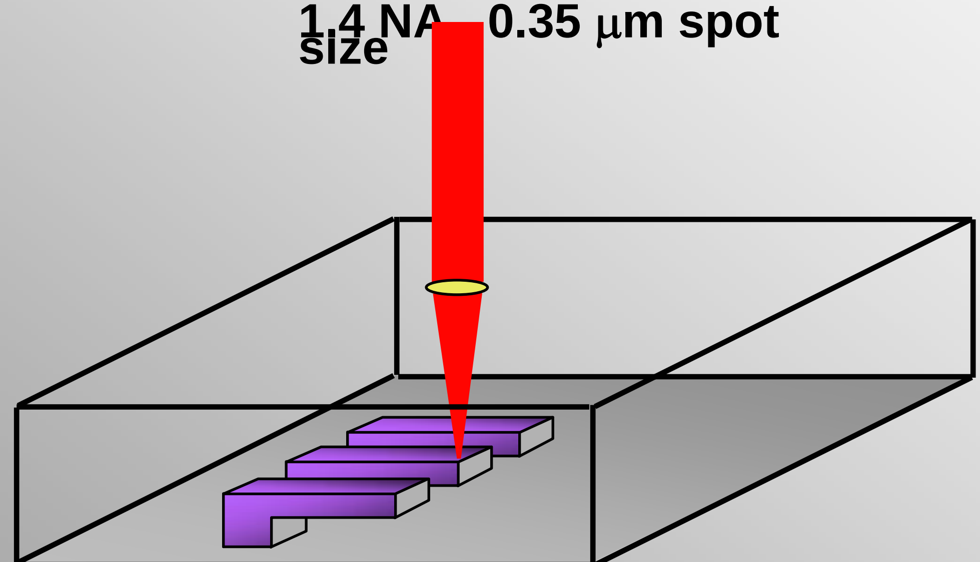


100 fs pulses 700 - 800 nm

1.4 NA, 0.35 μm spot size



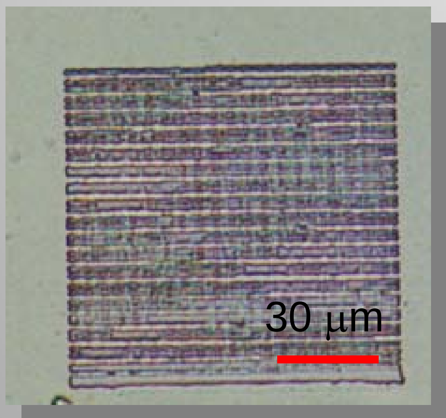




Maruo, Nakamura, Kawata, *Opt.Lett.* 1997
Wu, Webb *et al., Proc. SPIE* 1992

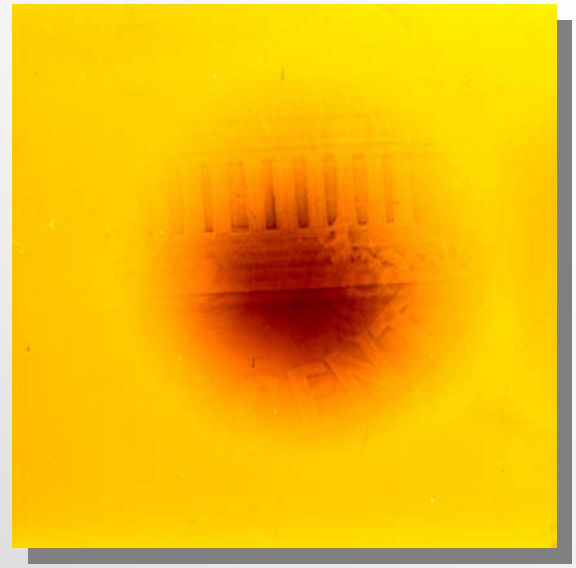
Silver Patterns

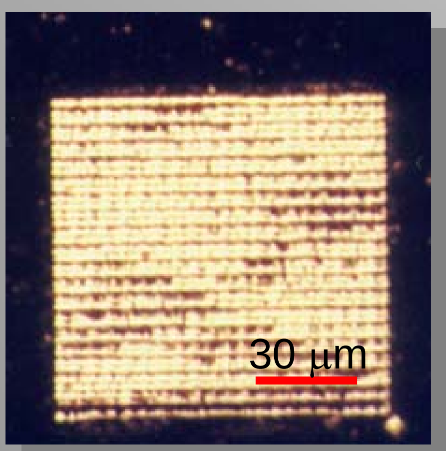
S u N M a G



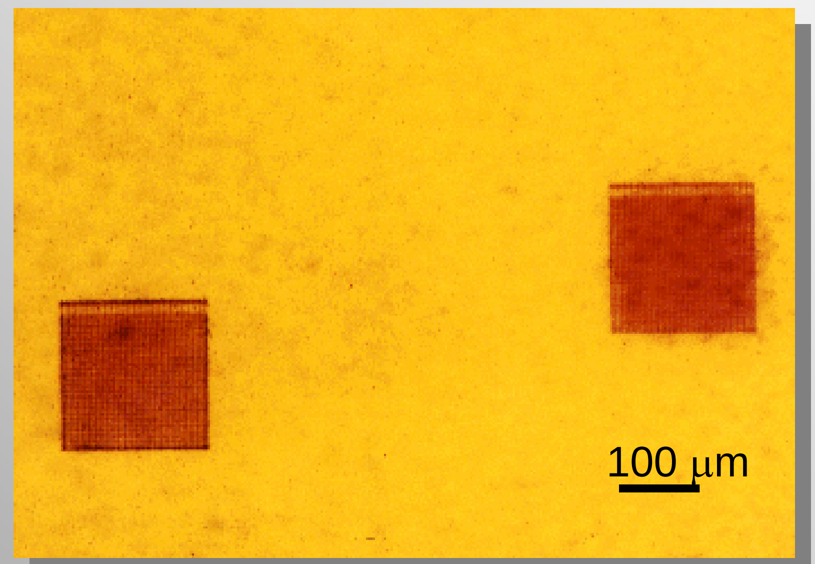
Transmission Image

Wavelength: 488 nm
Average Power: 3 mW
Writing Speed: 25 μm/s





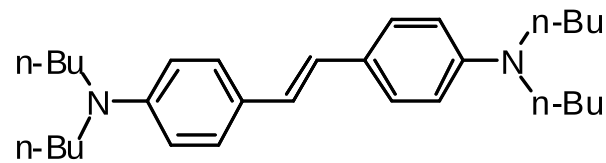
Reflection Image

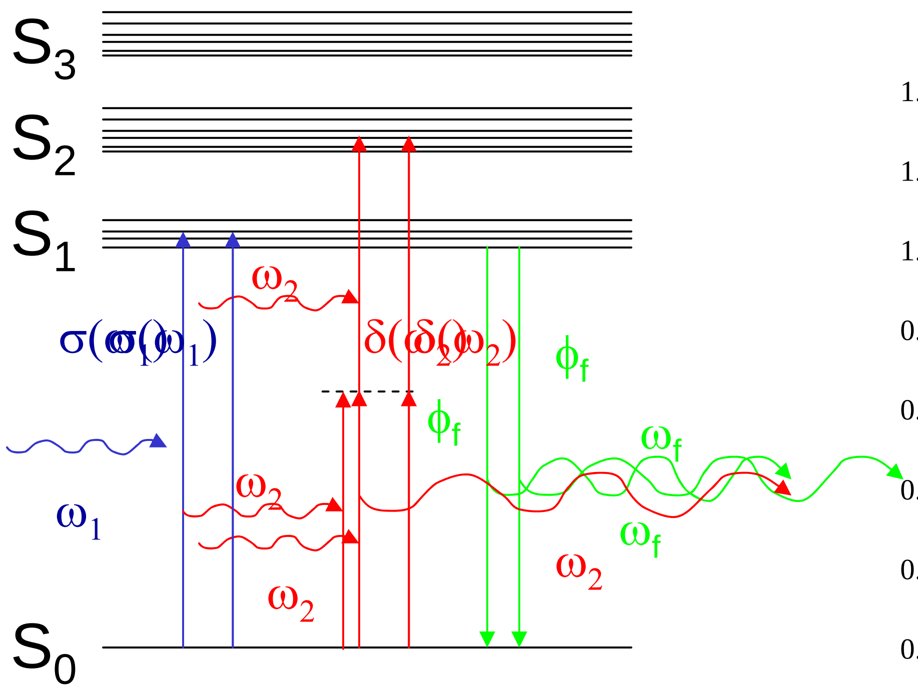


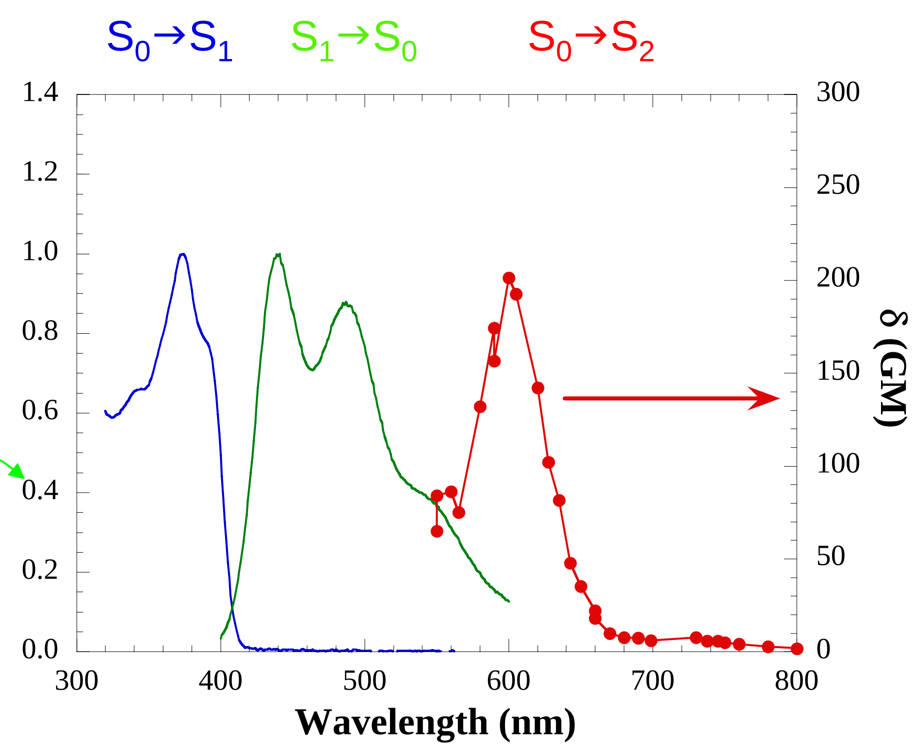
Two-Photon Absorption (TPA)

σ one-photon cross section --> cm^2 molecule^{-1}

δ two-photon cross section --> cm^4 s photon^{-1} molecule^{-1}





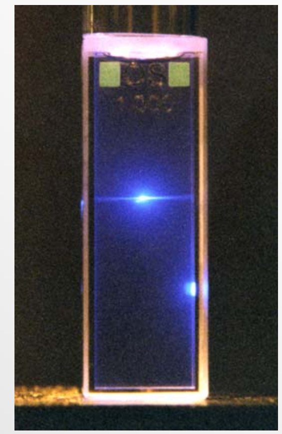


Albota *et al*. ***Science*** 281, 1653, 1998 Rumi et al., ***JACS*** 122, 9500,2000

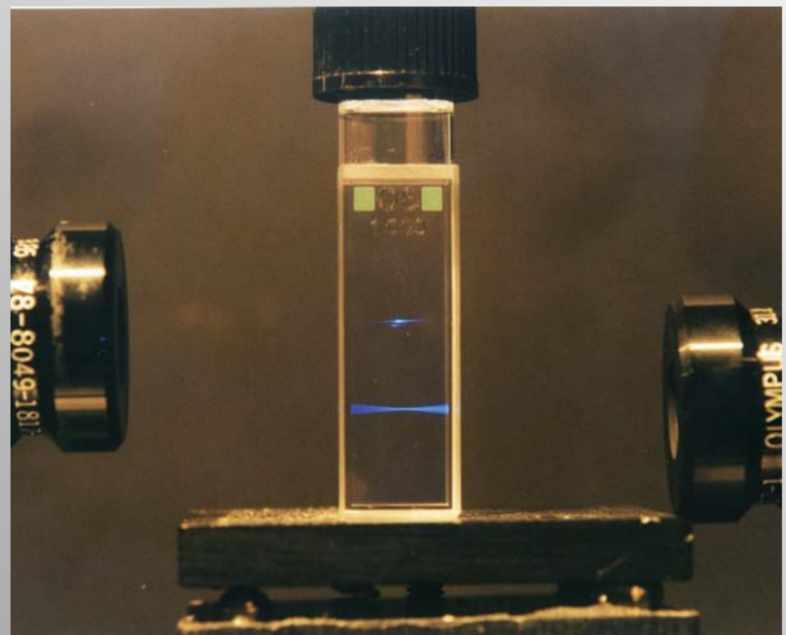
TPA Properties

S u N M a G

- *3D confinement*
- *Depth penetration*



Two-photon excitation



One-photon excitation

$$\text{TPA} \propto \delta I^2$$

$$I \sim \frac{1}{z^2}$$

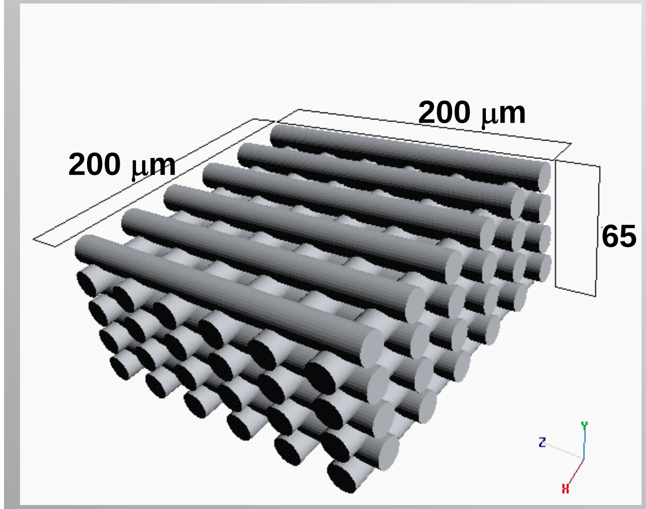
$$\Rightarrow TPA \sim \frac{1}{z^4}$$

Excited volume as small as ~ 0.05 μm^3

3D Metal Structures

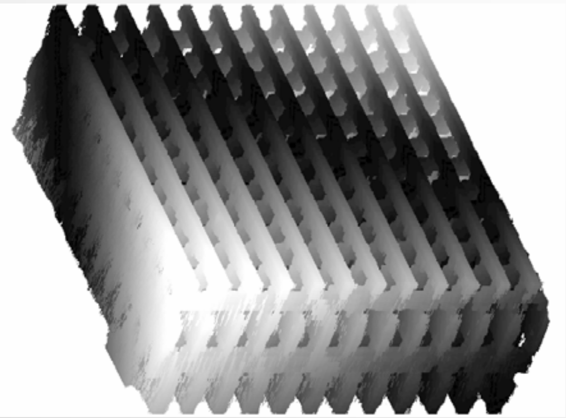
S u N M a G

Schematic Drawing

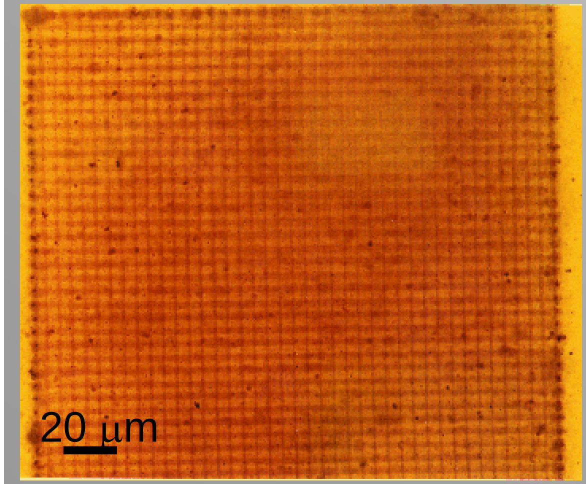


Wavelength: 730 nm
Pulse duration: 120 fs
Average Power: 15 mW
Writing Speed: 25 μm/s

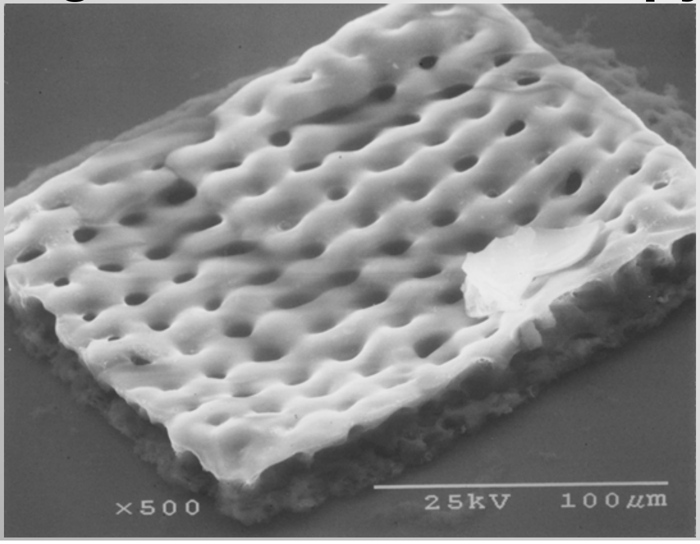
Two-Photon Microscopy



Transmission Optical Microscopy

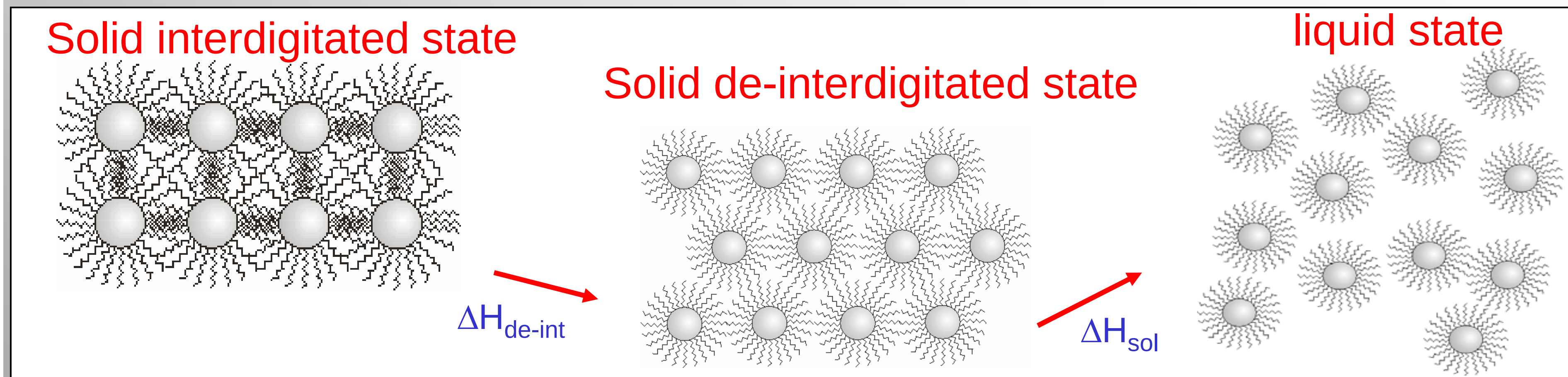


Scanning Electron Microscopy



Solubility Issue

S u N M a G

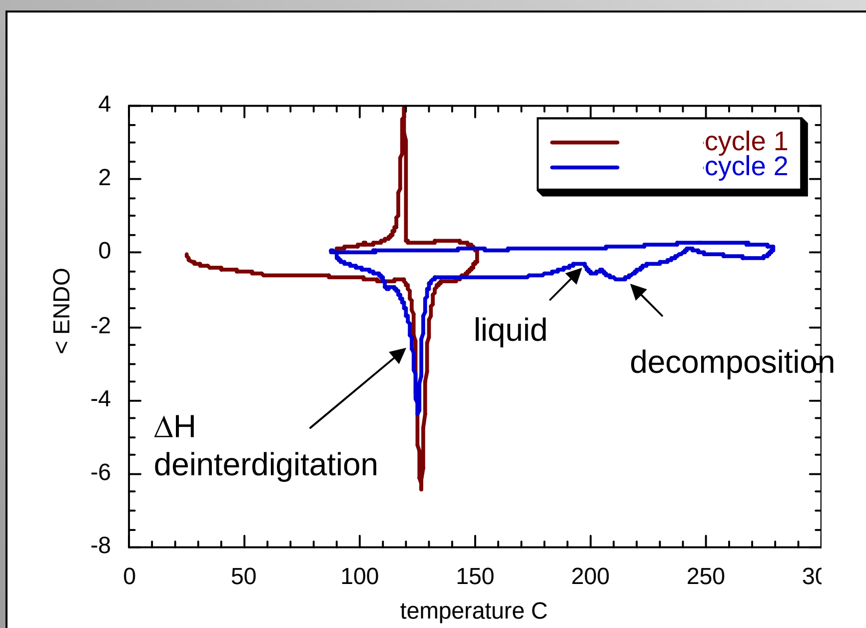


DSC-

Differential

Scanning

Calorimetry



*Pradeep et al, **Phys. Rev. B**, 2(62), R739,2000.*

*Badia et. al. **Chem. Europ. J.**, 2(3), 359,1996.*

Ligand Length Effect

S u N M a G

Sample	ligand	ΔH(kJ/mol organic)	Temp(K)
d = 5 nm	octadecanethiol	-42.3	402
d = 5 nm	dodecanethiol	-35.5	402
d = 5 nm	octanethiol	-20.7	401

↑ increasing length

Result-
The shorter the ligand the smaller the interdigitation enthalpy

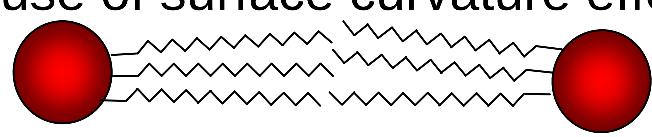
Nanoparticle Size Effect

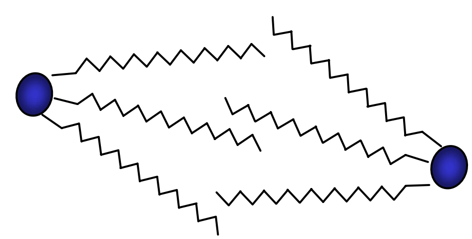
S u N M a G

Sample	ligand	relative ligand amount	ΔH(kJ/mol org)	Temp(K)
d = 5 nm	octanethiol	1	-20.7	401
larger				
d = 7 nm		1/3	-13.5	401
d = 5 nm	3:1 oct/dod	1	-20.7	382
larger				
d = 8 nm		1/2	-5.7	377

Result-

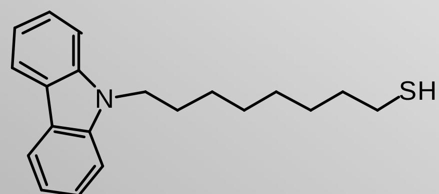
The larger the nanoparticle the smaller the interdigitation enthalpy, probably because of surface curvature effect





Mixed Ligands Effect

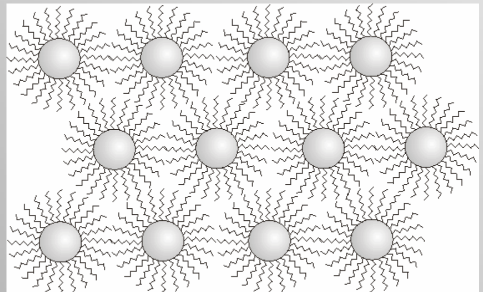
S u N M a G

Sample	ligand	ΔH(kJ/mol org)	Temp(K)
d = 7 nm	3:1 oct/dod	-5.7	377
d = 5 nm	 1:3 carbazolethiol/oct	-6.0	384
d = 5 nm	1:1:1 oct/hep/dod	-9.5	380
d = 5 nm	1:1 octadecane/dodecane	-20.6	420
d = 5 nm	3:1 hep/dod	14.1	384

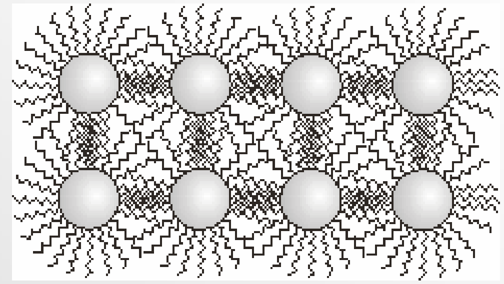
Result-
Mixture of ligands lower the interdigitation enthalpy

Order/Disorder Transition

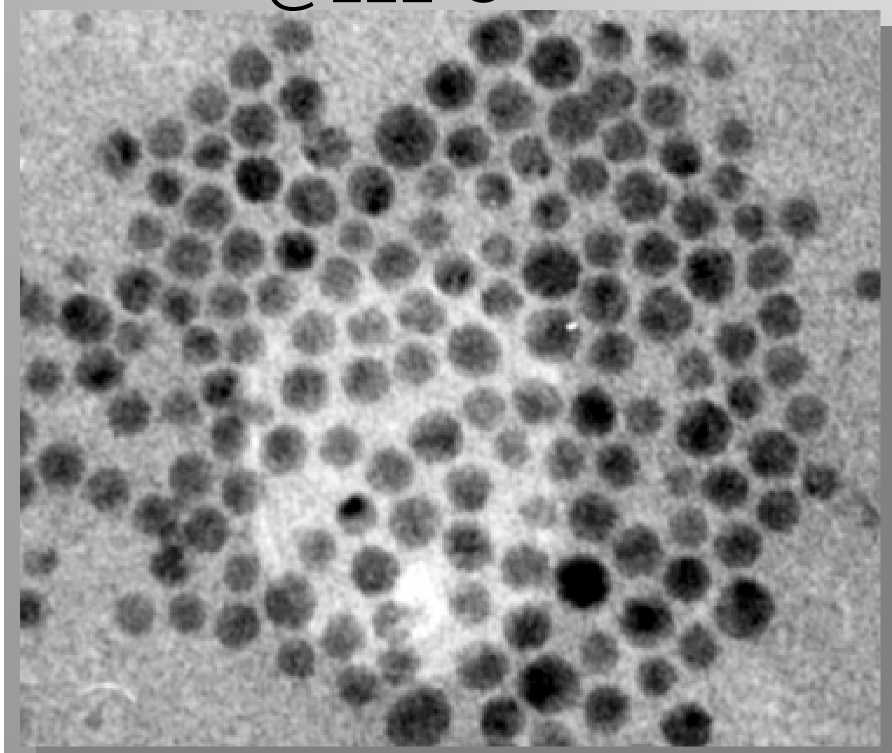
S u N M a G

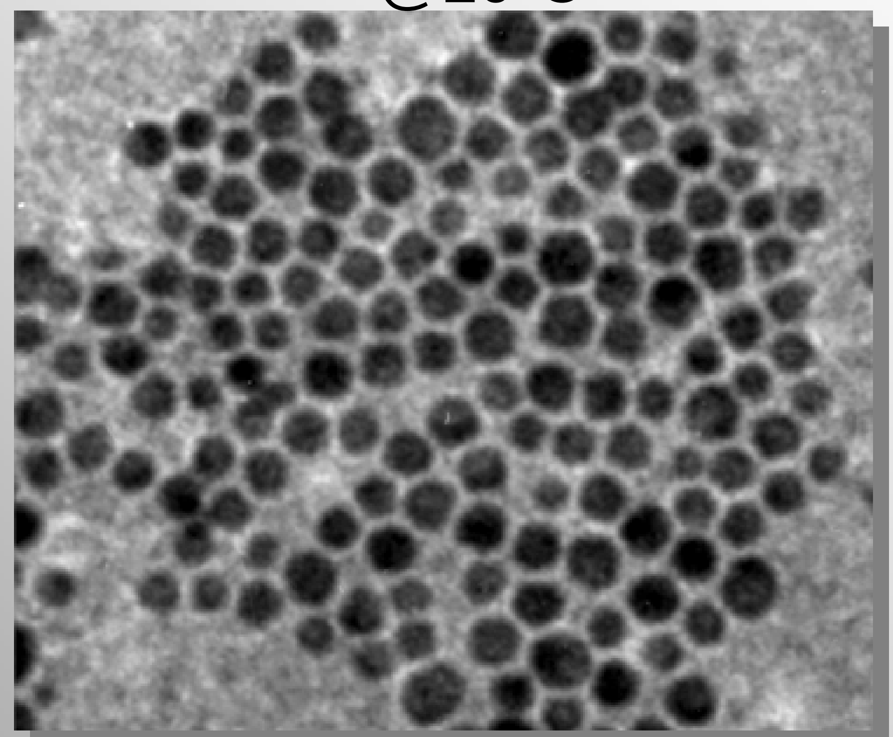


@122^{0}C



@20^{0}C





10nm

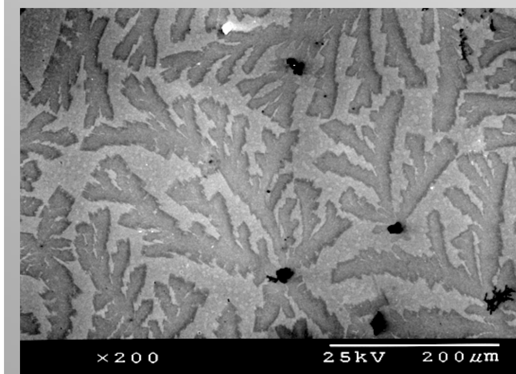
Deinterdigitated

Interdigitated

Thermal Annealing Evidences

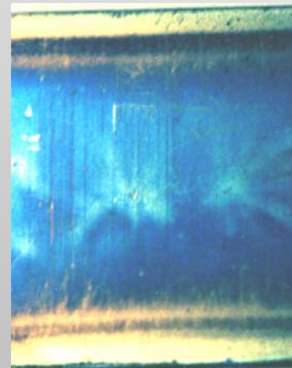
S u N M a G

SEM

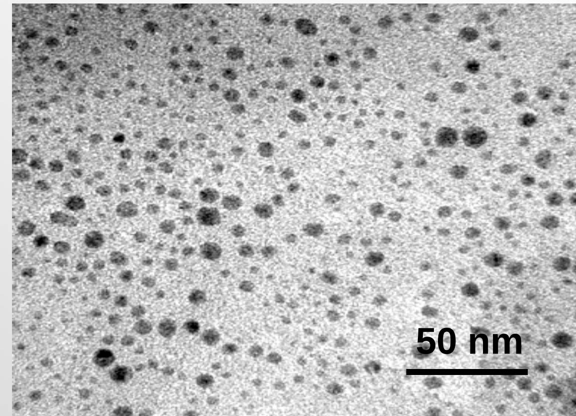


Pristine Film with a thickness of ~ 20nm

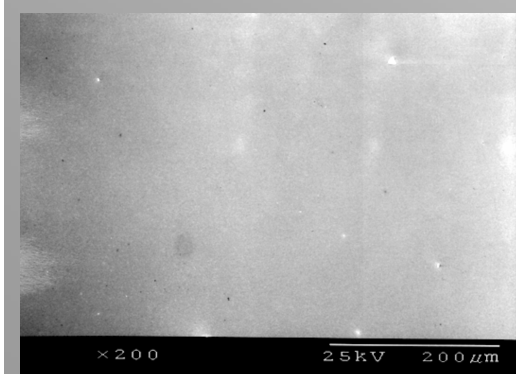
Thick annealed film



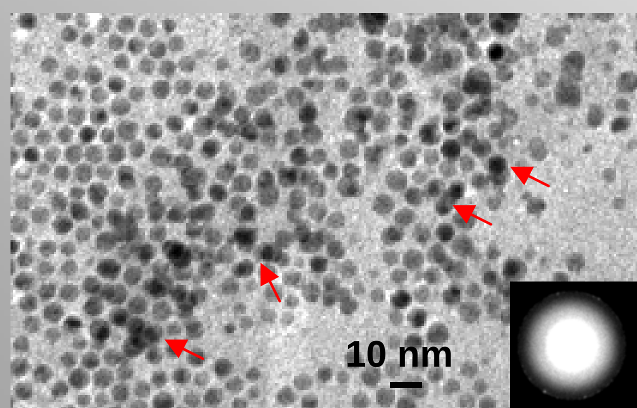
TEM



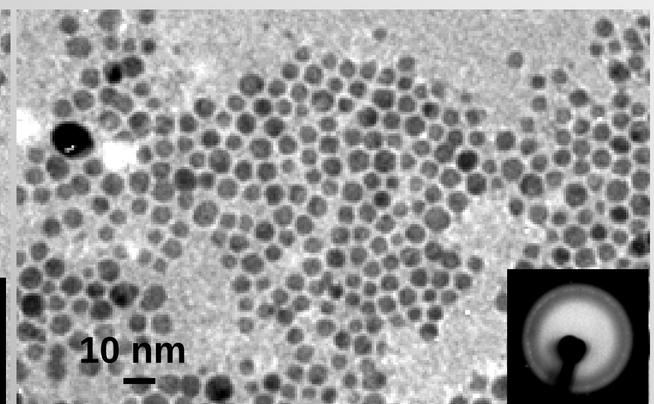
Submonolayer



After 1 thermal cycle



After 4 thermal cycles



After 5 thermal cycles

Ligands on Nanoparticles

S u N M a G

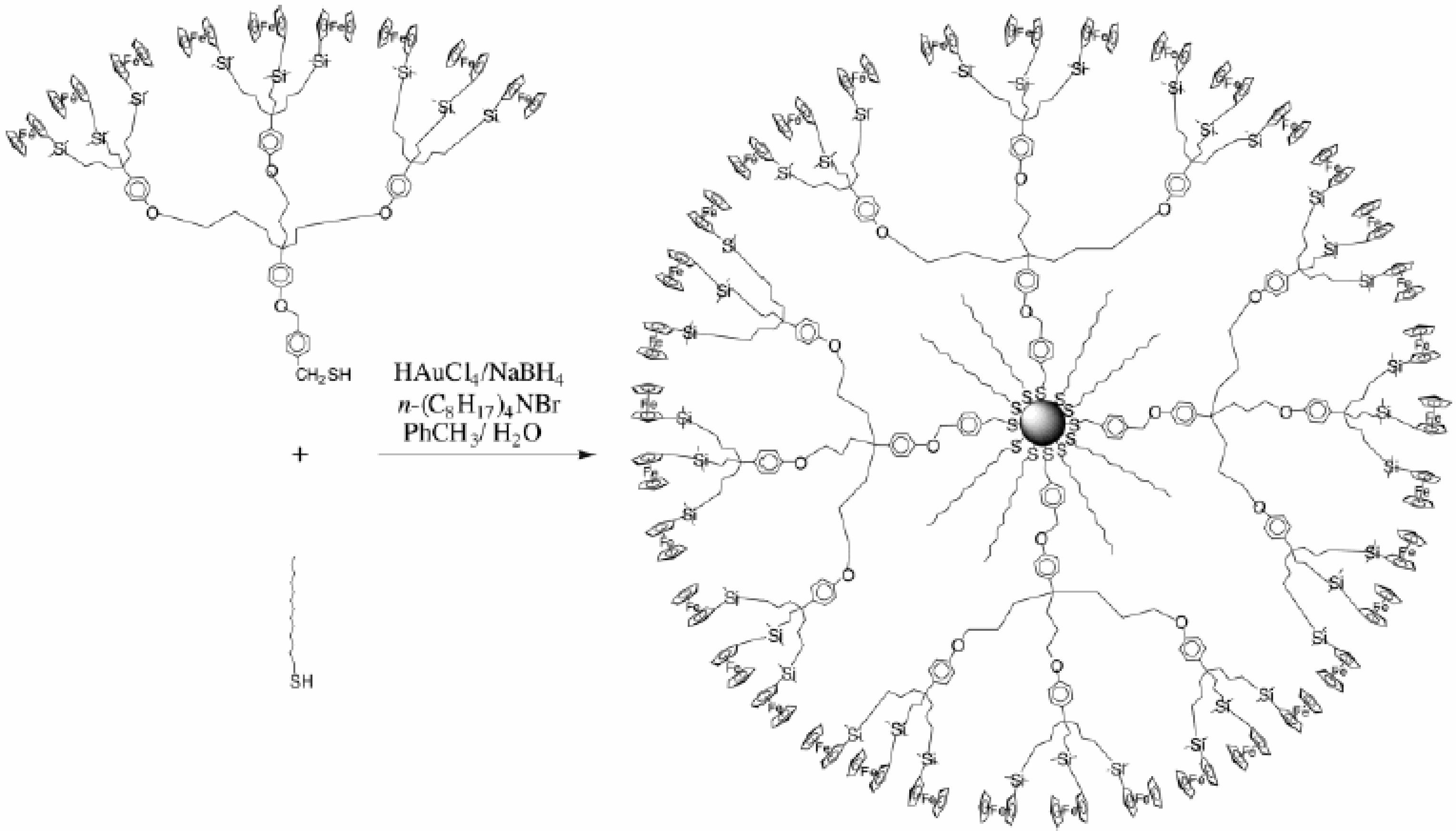
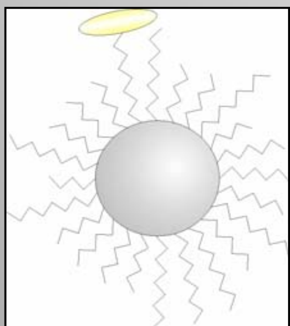


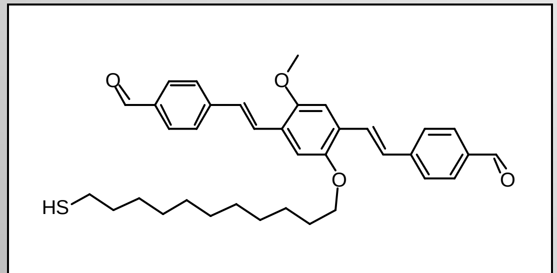
Figure 25. Direct syntheses of dendronized AuNPs containing a nonaferrocenyl thiol dendron (about 180 ferrocenyl groups). Reprinted with permission from ref 251 (Astruc's group). Copyright 2003 American Chemical Society.

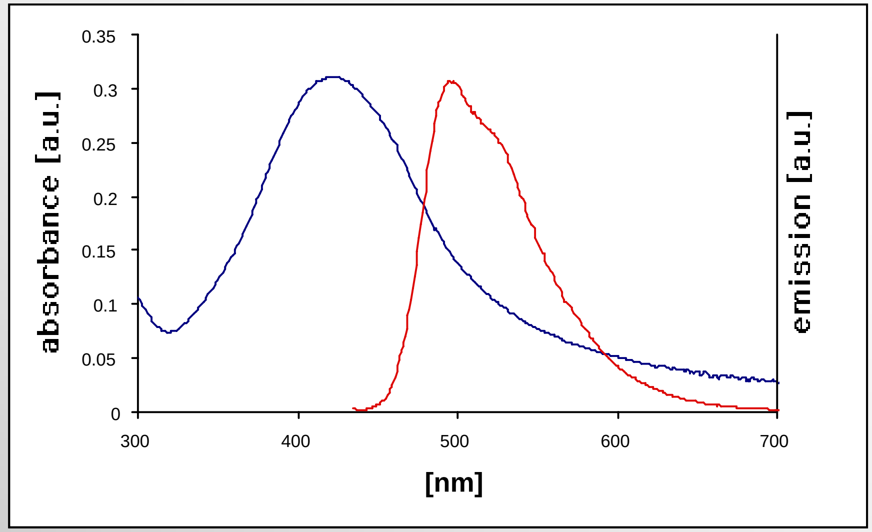
Fluorescent Nanoparticles

S u N M a G

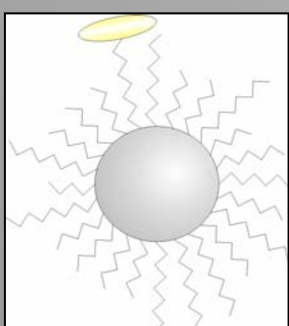
Nanoparticles synthesized by place exchange reactions

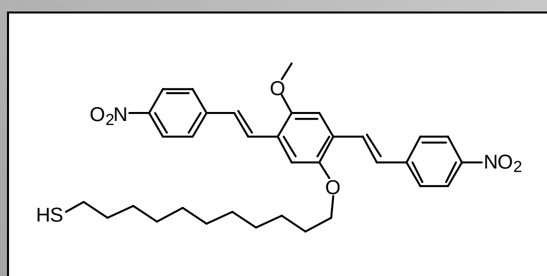


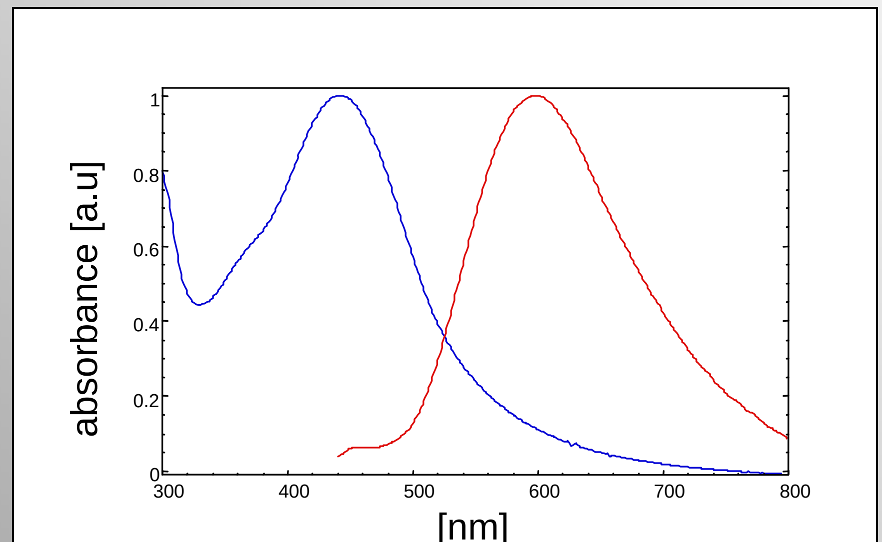




~ 10 dyes per nanoparticles

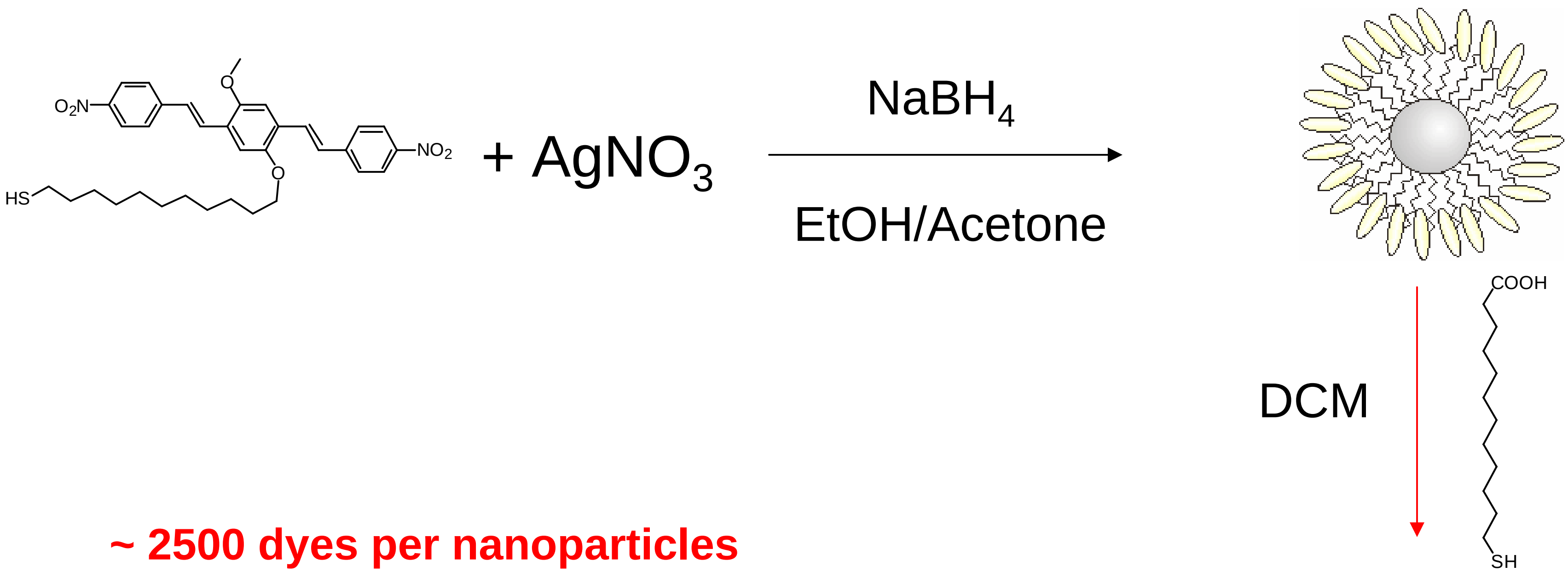






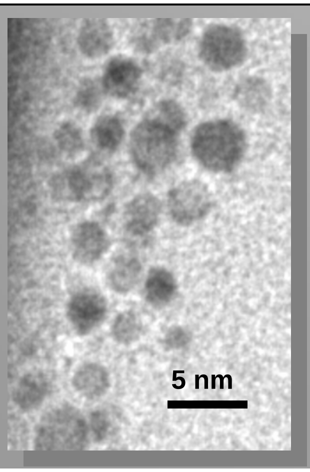
~ 60 dyes per nanoparticles

All Dye Coated Nanoparticles



~ 2500 dyes per nanoparticles

Water Soluble

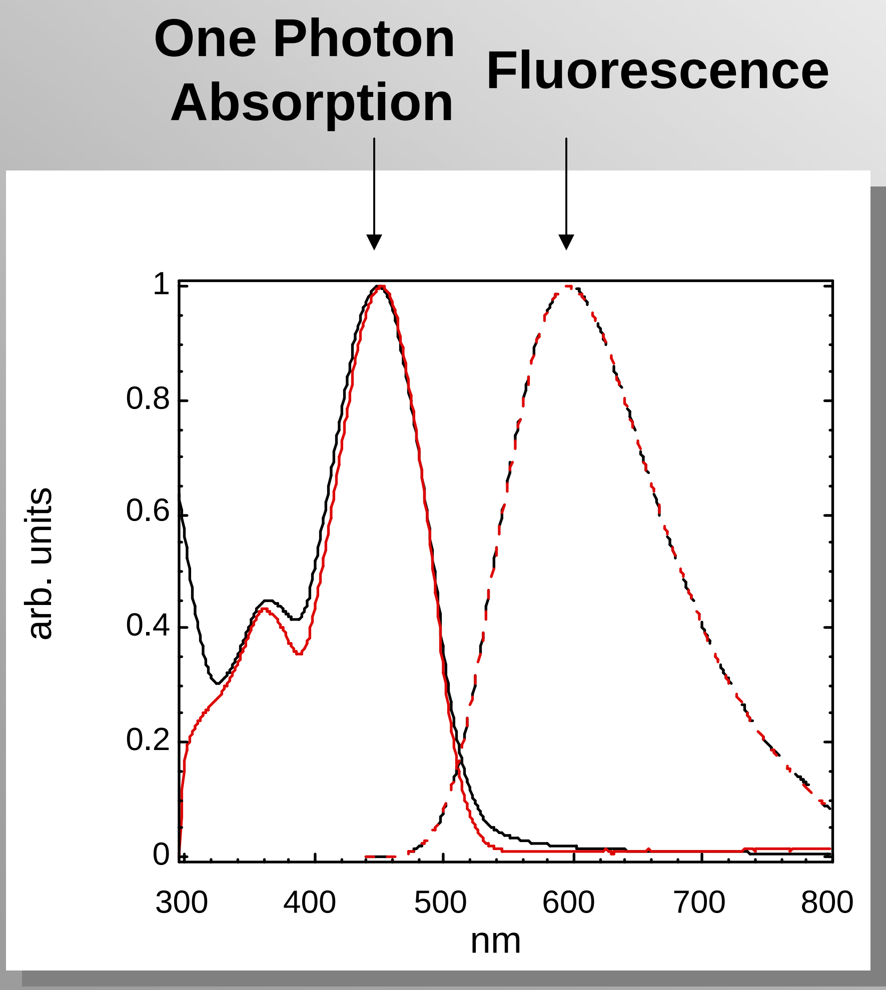


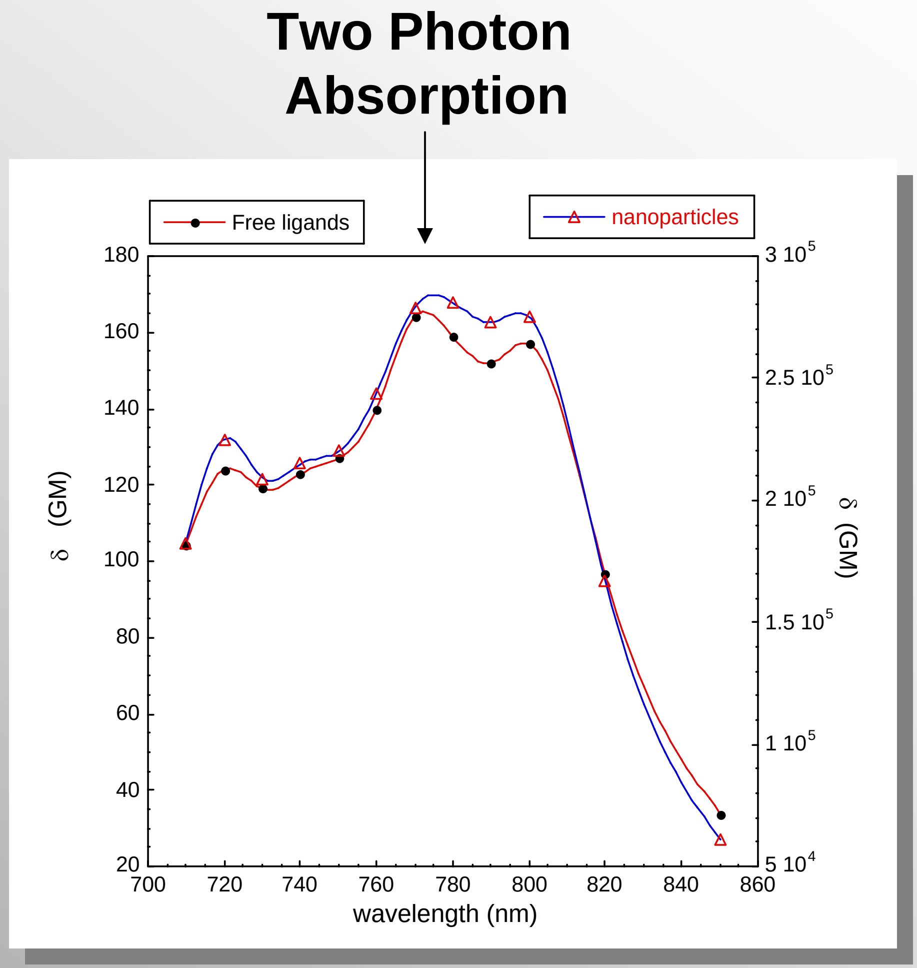
Fluorescence Quantum Yield (η) of the:

Free Dye	**48% (2.2 ns)**
Dye on the particle	**33% (1.8 ns)**

Optical Spectroscopy

S u N M a G





•Two-Photon Cross Section per Nanoparticle δ: 3 10^5 GM