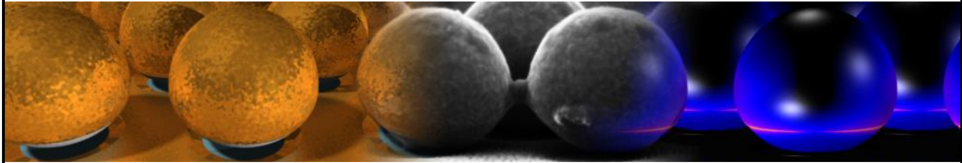
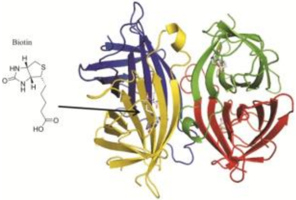
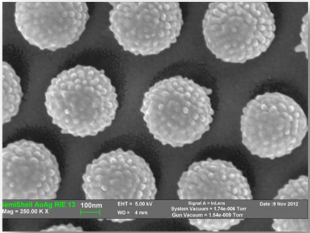


Biosensing

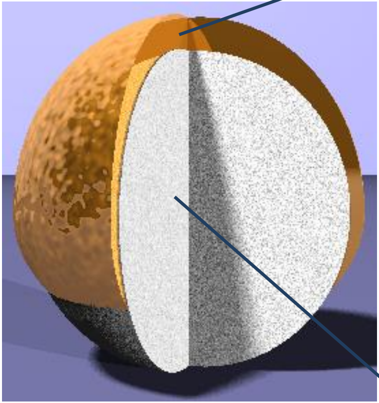

Biotin

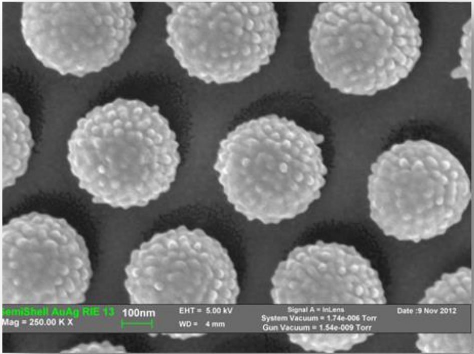

emiShell AuAg RIE 13
Mag = 250.00 K X
100nm
EHT = 5.00 kV
WD = 4 mm
Signal A = InLens
System Vacuum = 1.74e-006 Torr
Gun Vacuum = 1.54e-009 Torr
Date :9 Nov 2012

Semi-NanoShell

(noble) metallic shell: Au,Ag, AuAg, Ni, Al, …

CORE - SHELL



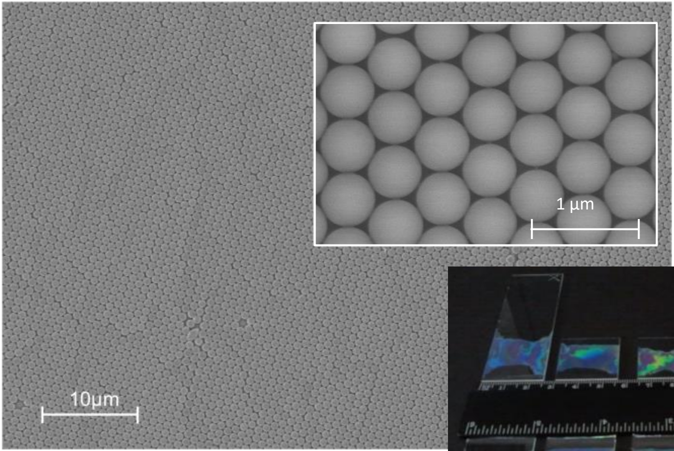


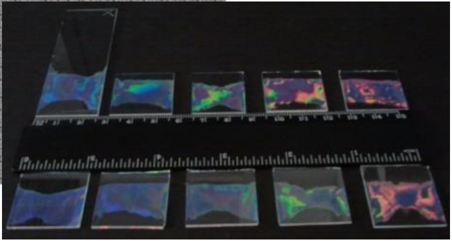
dielectric core: PS, SiO_2

Semi-nanoshell array nanolaser:
fabrication steps

1. NanoSphere Lithography

PS NS (300-1500 nm)



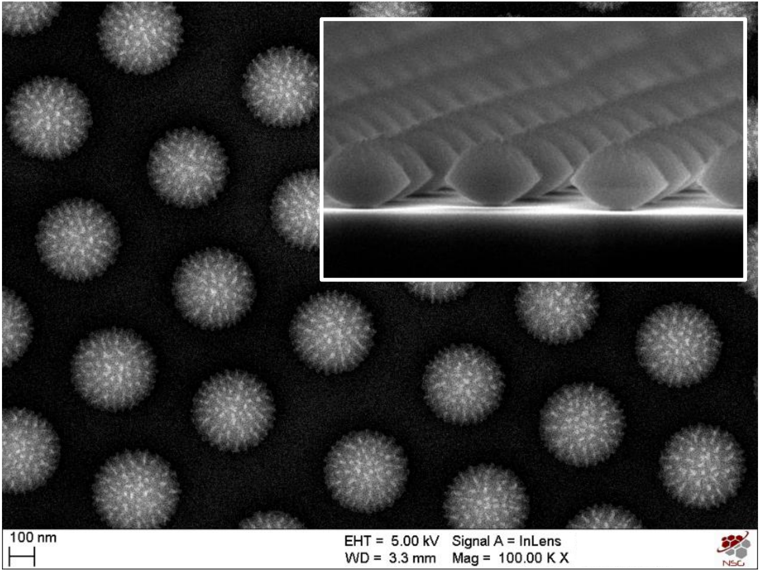


D.Piccotti et al, (submitted 2017)

Semi-nanoshell array:
fabrication steps

2.

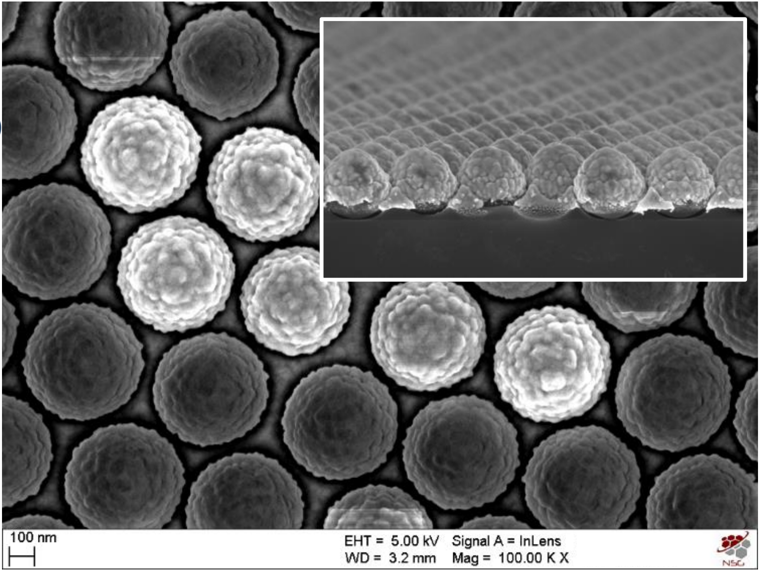
Reactive Ion Etching ($Ar+O_2$)



Semi-nanoshell array
fabrication steps

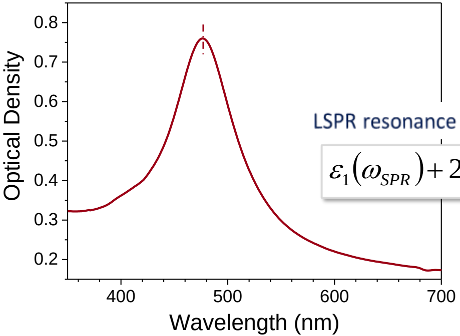
3.

SNSA
(Au depo.)



LSPR sensors

Noble metal nanoparticle



LSPR resonance condition

$$\varepsilon_1(\omega_{SPR}) + 2\varepsilon_m = 0$$

λ_{SPR} depends on:

- metal: $\varepsilon_1(\omega)$
- shape
- morphology
- interaction
- surrounding medium: $\varepsilon_m(\omega)$

LSPR sensors

Noble metal nanoparticle

Dielectric shell

ε_m changes

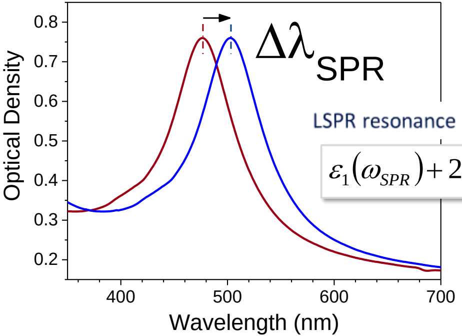
↓

LSPR resonance changes

↓

$\Delta\lambda_{SPR}$

SENSOR OUTPUT SIGNAL



LSPR resonance condition

$$\varepsilon_1(\omega_{SPR}) + 2\varepsilon_m = 0$$

λ_{SPR} depends on:

- metal: $\varepsilon_1(\omega)$
- shape
- morphology
- interaction
- surrounding medium: $\varepsilon_m(\omega)$

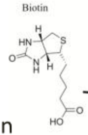
Biomolecules

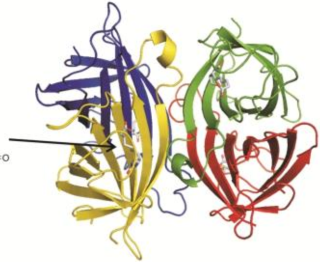
Receptor

Biotin

Biotin is a small vitamin

MW = 244 g/mol





Analyte

Streptavidin (SA)

Bacterial tetrameric protein

MW = 60.000 g/mol

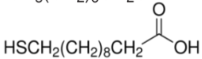
Model system

- ❑ Very high binding affinity;
- ❑ The biotin can be linked to alkylthiolate molecules, Polyethylene Glycol (PEG), PEG-Amine, proteins, antibodies and others;
- ❑ The bond stands to many conditions of temperature, pH or organic solvents.

Biofunctionalization

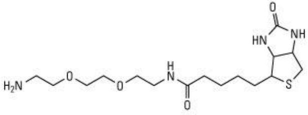
1. Self Assembled Monolayer of thiols (SAM)

- 1-Octanethiol — $CH_3(CH_2)_6CH_2SH$
- 11-Mercaptoundecanoic acid

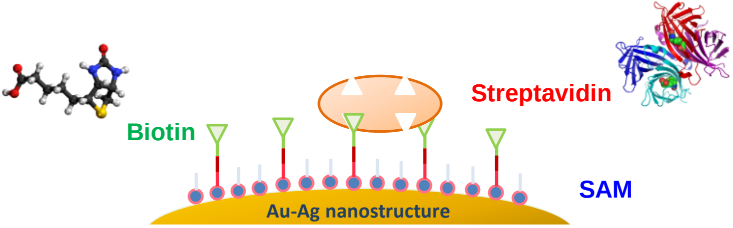


2. Receptor layer (Biotin)

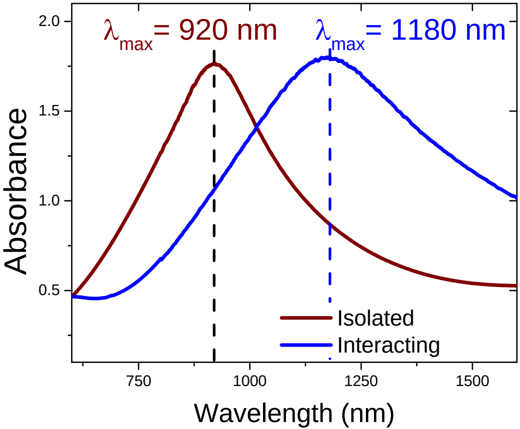
- Amine-PEG$_2$-Biotin

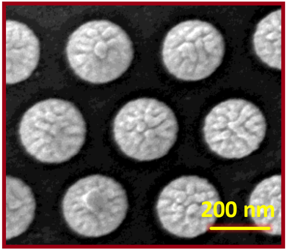


3. Analyte layer (Streptavidin)



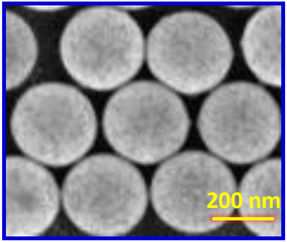
Semi-NanoShell Array (SNSA)





Low Int.

D = 195 nm
h_{metal}= 30 nm

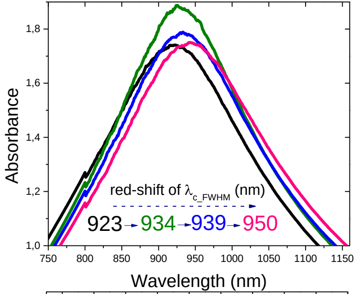


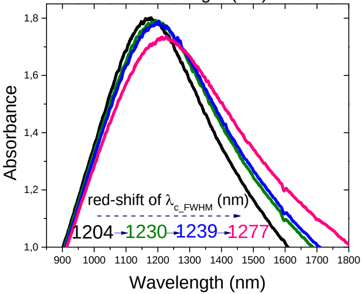
High Int.

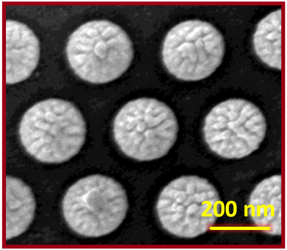
D = 270 nm
h_{metal}= 30 nm

Russo, V. *et al.* Gold–silver alloy semi-nanoshell arrays for label-free plasmonic biosensors. *Nanoscale* **9**, 10117–10125 (2017).

Semi-NanoShell Array (SNSA)

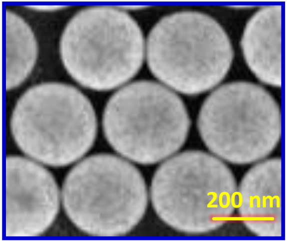






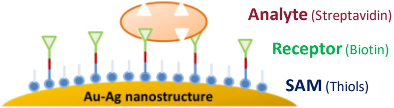
Low Int.

D = 195 nm
h_{metal}= 30 nm



High Int.

D = 270 nm
h_{metal}= 30 nm

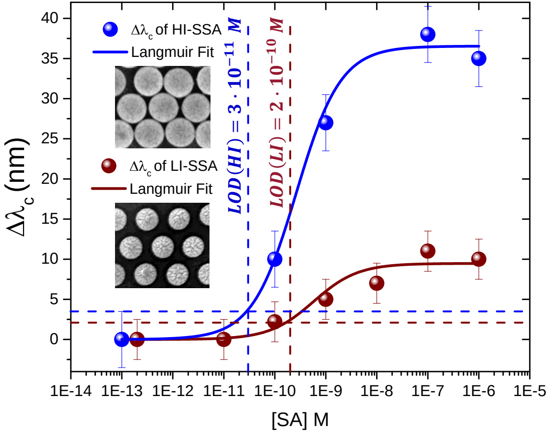


Russo, V. *et al.* Gold–silver alloy semi-nanoshell arrays for label-free plasmonic biosensors. *Nanoscale* **9**, 10117–10125 (2017).

Semi-NanoShell Array (SNSA)

$$\Delta\lambda_c = \frac{\Delta\lambda_{c_{sat}} \cdot K_a \cdot [SA]}{1 + K_a \cdot [SA]}$$

Langmuir Isotherm



Low Interaction

- Saturation value
- $\Delta\lambda_{c,sat}$ = 10 ± 1 nm
- LOD = 2 $\cdot 10^{-10}$ M

High Interaction

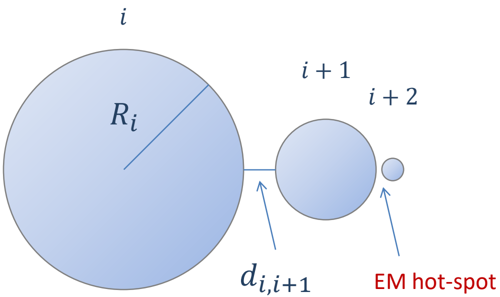
- Saturation value
- $\Delta\lambda_{c,sat}$ = 36 ± 1 nm
- LOD = 3 $\cdot 10^{-11}$ M

Russo, V. *et al.* Gold–silver alloy semi-nanoshell arrays for label-free plasmonic biosensors. *Nanoscale* **9**, 10117–10125 (2017).

3. Interacting NP

3.3 Self-similar nanolens

Asymmetric nanolens



$$d_{i+1,i+2} = s\, d_{i,i+1} \qquad \boldsymbol{s = 1/3}$$

$$R_{i+1} = s\, R_i$$

A rough estimate…

- $s \ll 1$
- dipolar approx.

$$E_1 = fE_0 \sim \frac{3\varepsilon_m}{\varepsilon_2} E_0 \sim 10 E_0$$

$$E_2 = fE_1 = f^2 E_0$$

…

$$E_n = f^n E_0 \gg E_0$$

$$s = \frac{1}{3}, n = 3$$

$$R_1 = 45\ nm$$

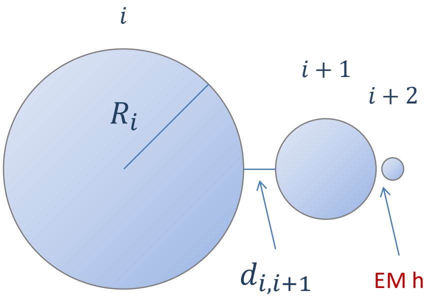
$$R_2 = 15 nm$$

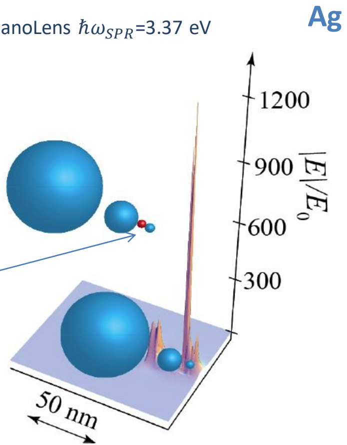
$$R_3 = 5\ nm$$

$$d_{i,i+1} = 0.6\, R_{i+1}$$

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).

Asymmetric nanolens





$$d_{i+1,i+2} = s\, d_{i,i+1} \qquad \boldsymbol{s = 1/3}$$

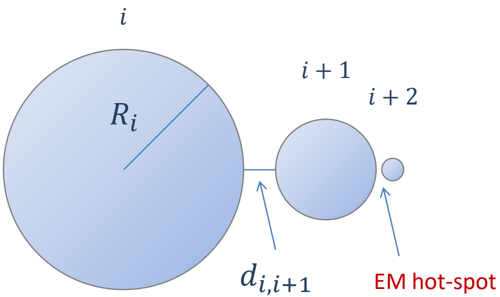
$$R_{i+1} = s\, R_i$$

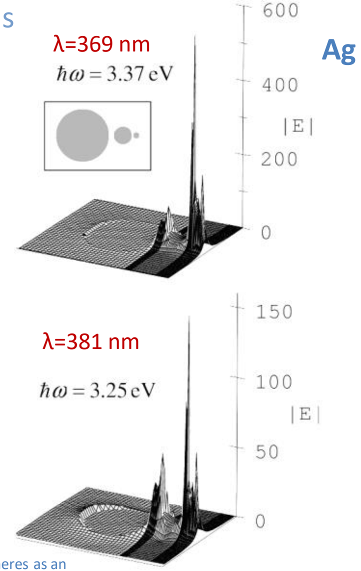
K. Li, M. I. Stockman, and D. J. Bergman, "Self-Similar Chain of Metal Nanospheres as an Efficient Nanolens," Phys. Rev. Lett. 91, 227402 (2003).

Isolated NP $\hbar\omega_{SPR}$=3.5 eV

Self-similarity

Asymmetric nanolens





$$d_{i+1,i+2} = s\, d_{i,i+1} \qquad s = 1/3$$

$$R_{i+1} = s\, R_i$$

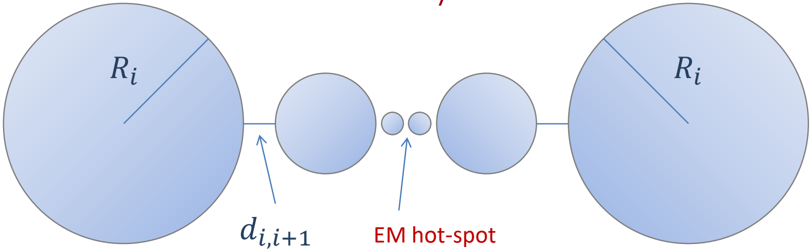
K. Li, M. I. Stockman, and D. J. Bergman, "Self-Similar Chain of Metal Nanospheres as an Efficient Nanolens," Phys. Rev. Lett. 91, 227402 (2003).

Isolated NP $\hbar\omega_{SPR}$=3.5 eV

Self-similarity

Symmetric nanolens

$s = 1/3$



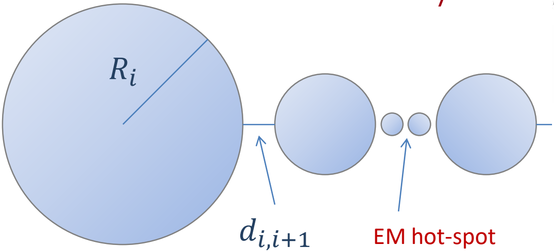
$$d_{i+1,i+2} = s\, d_{i,i+1}$$

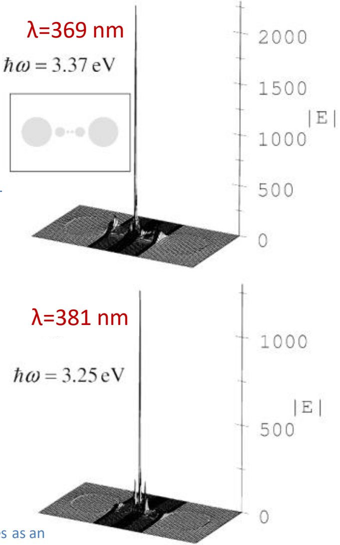
$$R_{i+1} = s\, R_i$$

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).

Symmetric nanolens

$s = 1/3$





$$d_{i+1,i+2} = s\, d_{i,i+1}$$

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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).

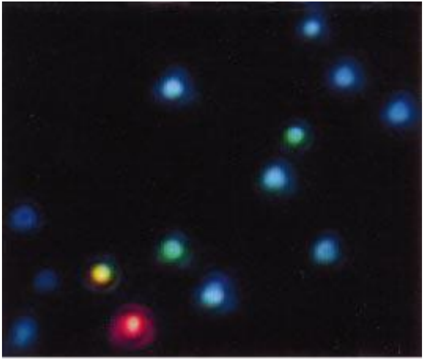
4. LSPR Imaging

4.1 Dark-field Microscopy

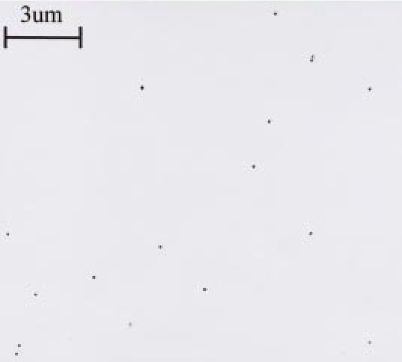
LSPR in Ag NP: DFM

Ag NPs colloidal solutions

Dark-field optical microscopy



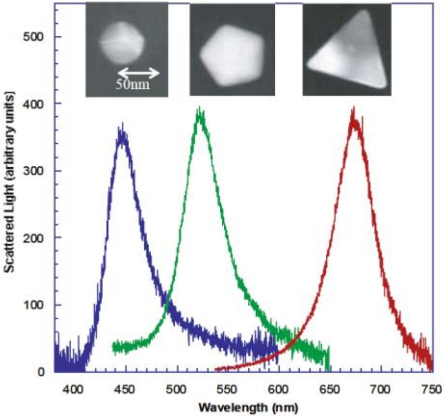
TEM

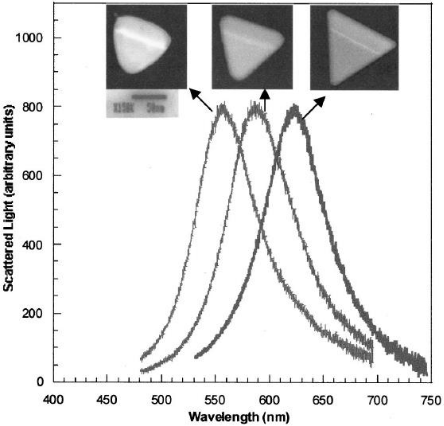


J. J. Mock et al., "Shape effects in plasmon resonance of individual colloidal silver nanoparticles," The Journal of Chemical Physics **116**, 6755–6759 (2002).

LSPR in Ag NP: DFM

Dark-field optical microscopy





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