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2328-23

Preparatory School to the Winter College on Optics and the Winter College on Optics: Advances in Nano-Optics and Plasmonics

30 January - 17 February, 2012

Experimental performance of plasmonically enhanced luminescence and Raman scattering

S.V. Gaponenko
Stepanov Institute of Physics
Minsk
Belarus

Experimental performance of plasmonically enhanced luminescence and Raman scattering

S. V. Gaponenko

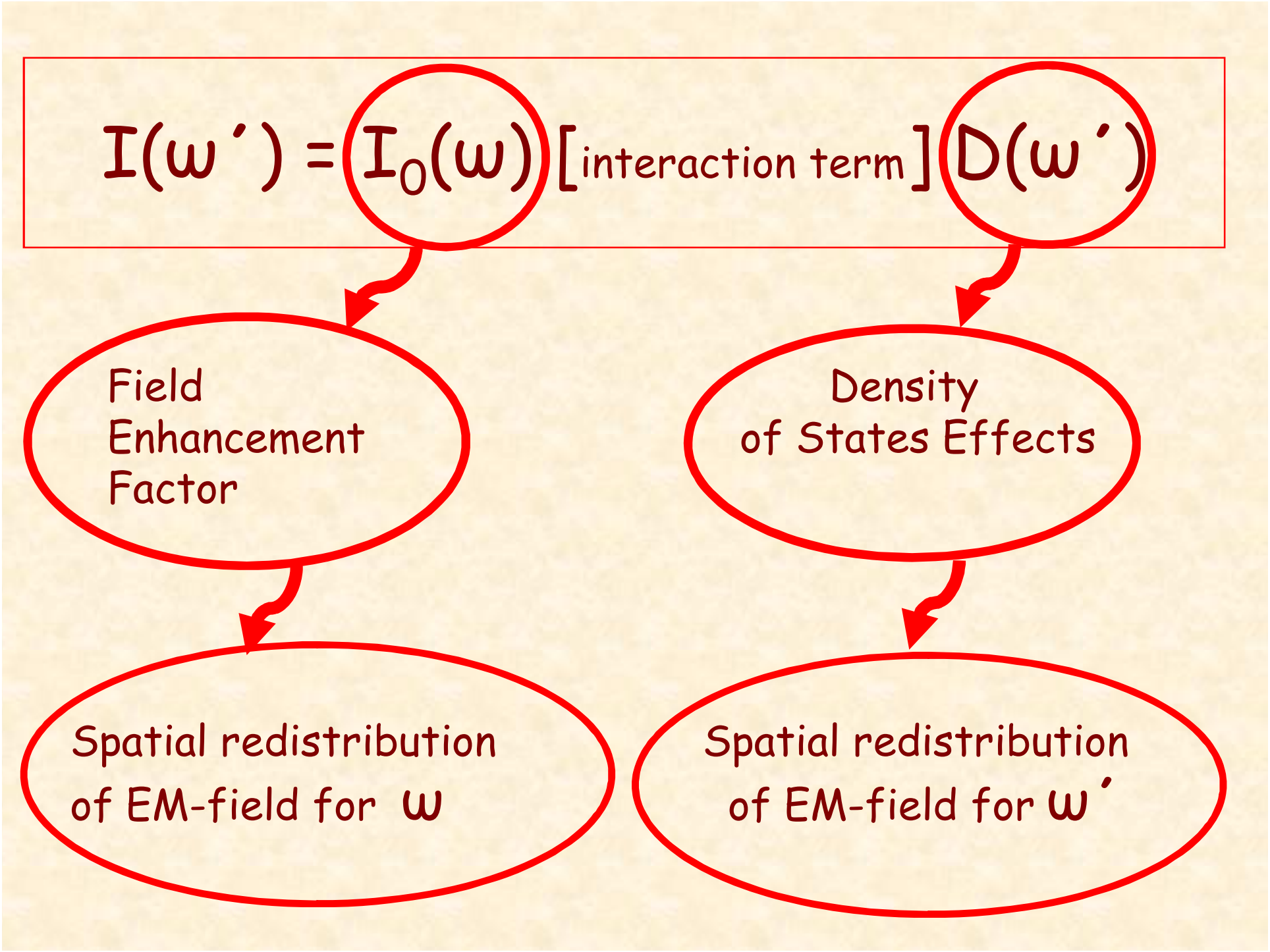
B. I. Stepanov Institute of Physics,
National Academy of Sciences of Belarus

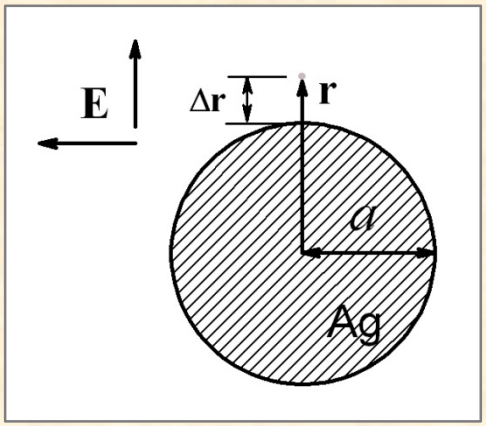
Outline

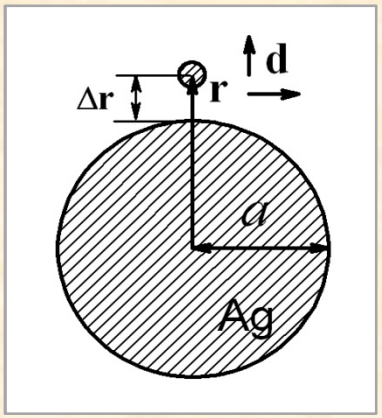
- Photoluminescence enhancement
- Raman scattering enhancement
- Rayleigh scattering enhancement

Photoluminescence enhancement

- Molecules
- Quantum dots
- Rare-earth ions


I(ω′) = I0(ω) [interaction term] D(ω′)
Field Enhancement Factor
Density of States Effects
Spatial redistribution of EM-field for ω
Spatial redistribution of EM-field for ω′





Field +metal body

Metal body +molecule

$$F(\omega,\omega',\mathbf{r}) = G(\omega,\mathbf{r})\,Q(\omega',\mathbf{r}) = \frac{|\mathbf{E}(\omega,\mathbf{r})|^2}{|\mathbf{E}_0(\omega)|^2} \cdot \frac{\gamma_{rad}(\omega',\mathbf{r})}{\gamma_{rad}(\omega',\mathbf{r}) + \gamma_{nonrad}(\omega',\mathbf{r})}$$

Intensity enhancement

Quantum yield

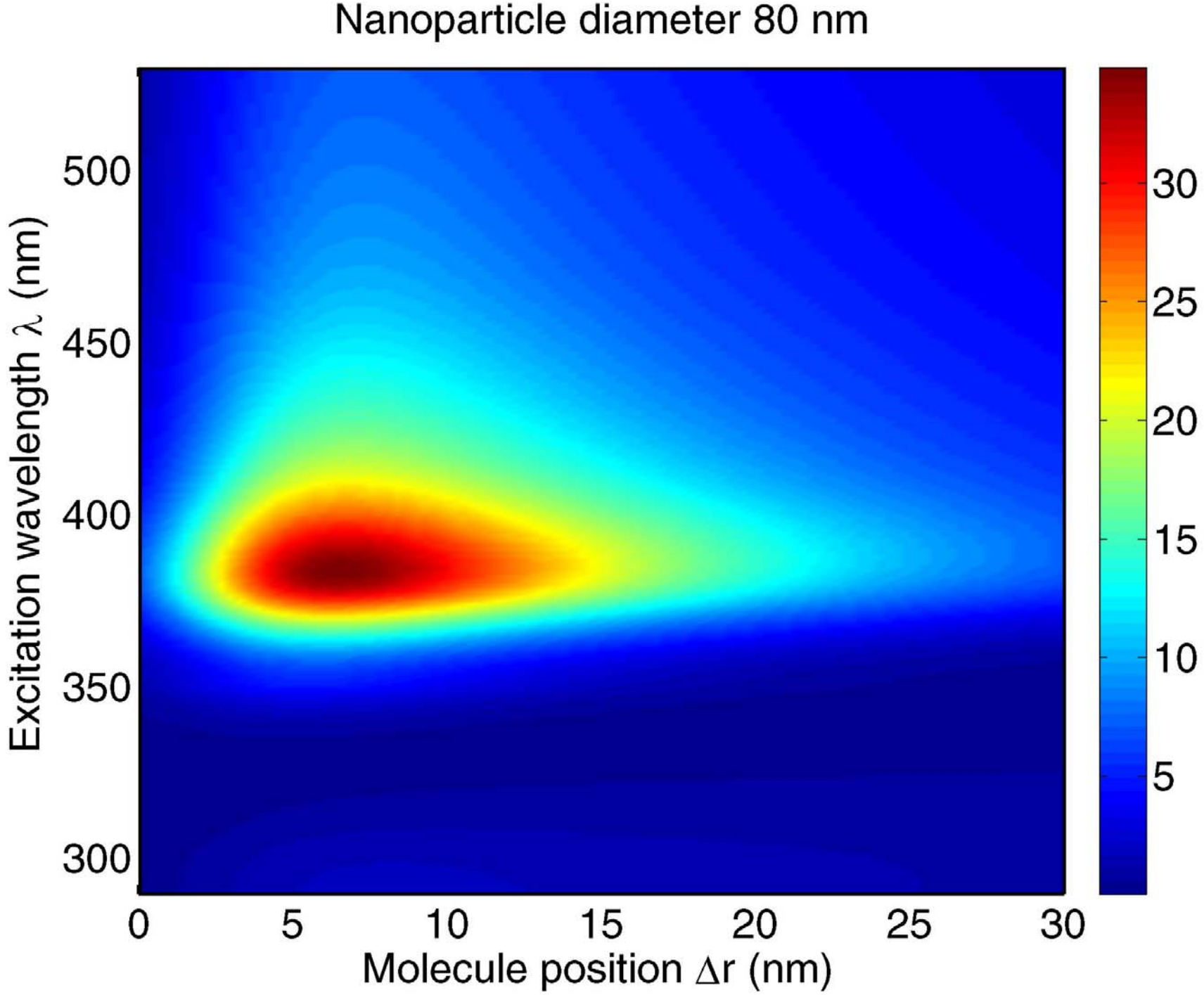
High quantum yield F = 1…50

Low quantum yield F > 1000! - biomicroscopy!

General recipe

Put a liminescent object (atom, molecule, quantum dot) in a position where:

- excitation radiation is enhanced
- photon DOS for emission spectrum is enhanced
- non-radiative rate enhancement does not overtake the 2 above enhancement factors

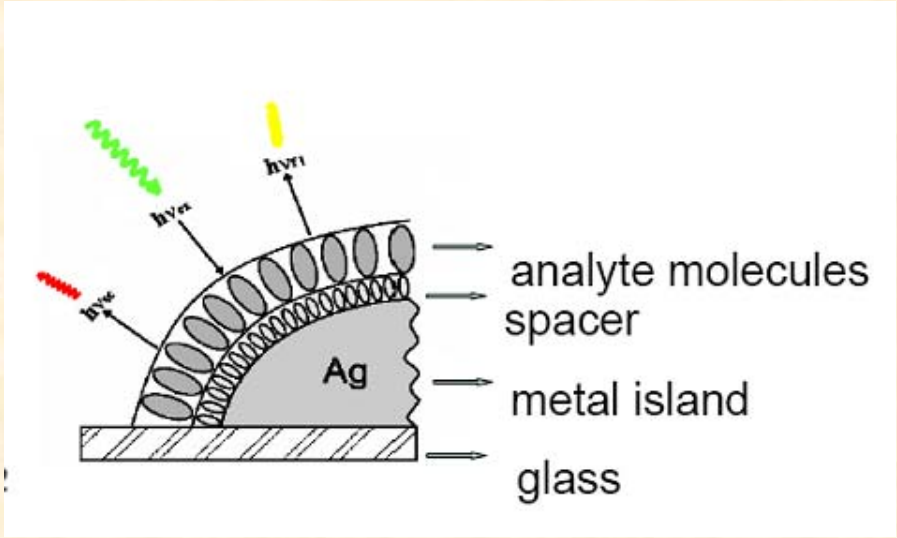

Nanoparticle diameter 80 nm
Excitation wavelength λ (nm)
500
450
400
350
300
0
5
10
15
20
25
30
Molecule position Δr (nm)
30
25
20
15
10
5

Surface enhanced luminescence

- Optimal metal surface structure:
  - chemical colloidal technigues
  - physical deposition techniques + annealing
  - nanolithography + deposition

- Optimal metal—luminophore spacing:
  - Langmuir—Blodgett films
  - polyelectrolyte films
  - Vacuum deposition of dielectric film

O.Kulakovich, N.Strekal, M.Artemyev, A.Stupak, S.Maskevich, S.Gaponenko.
Nanotechnology **17**,5201 (2006)



Fluorophore deposition atop a polyelectrolyte spacer

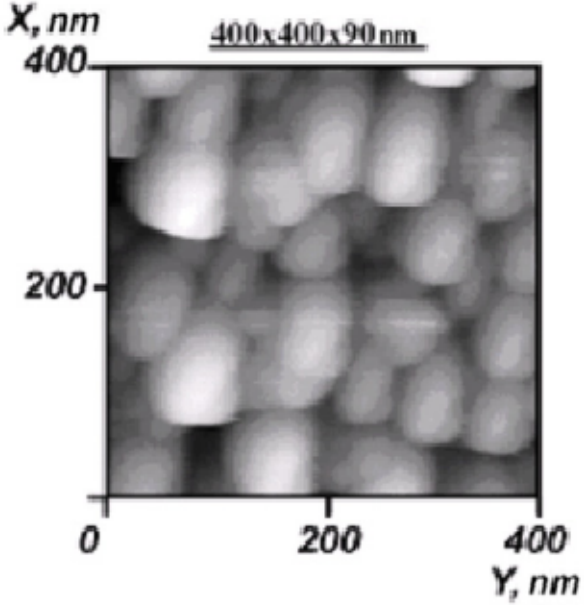
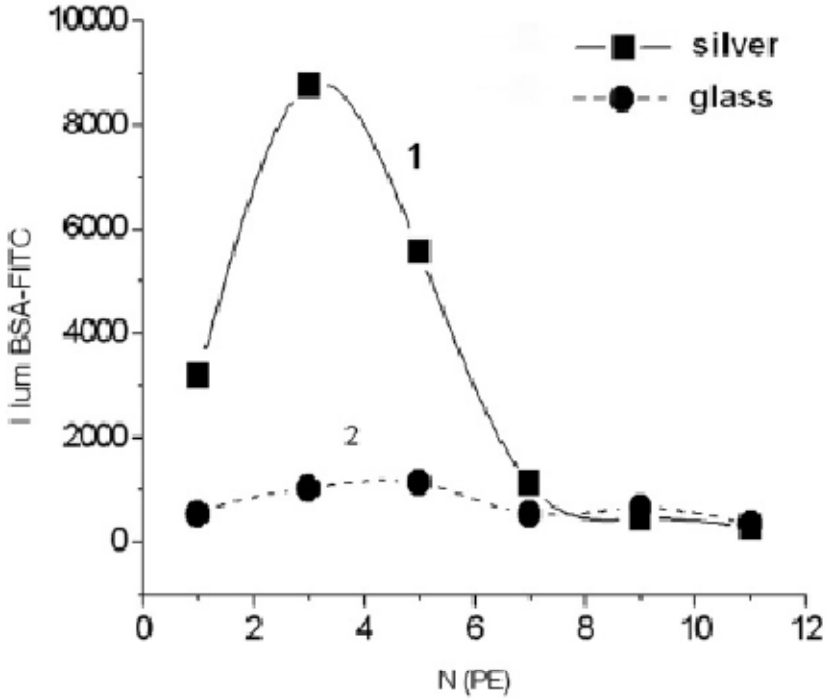
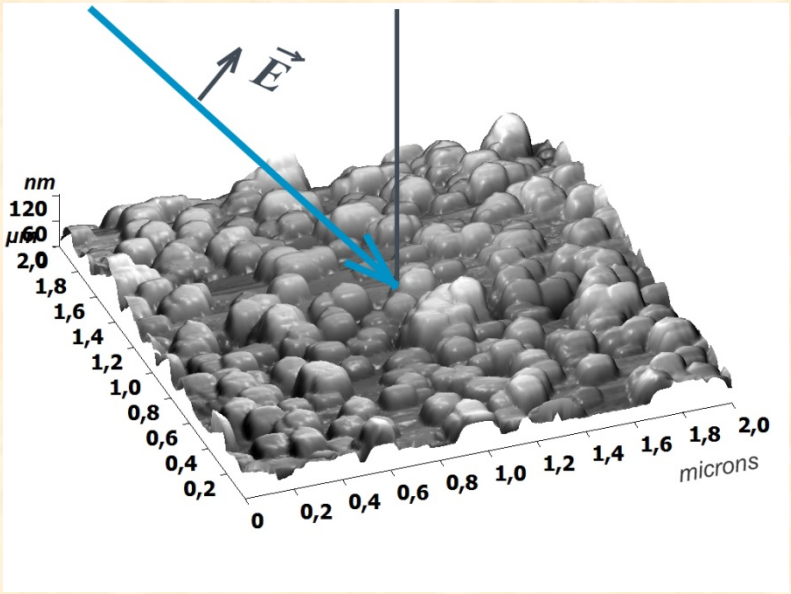
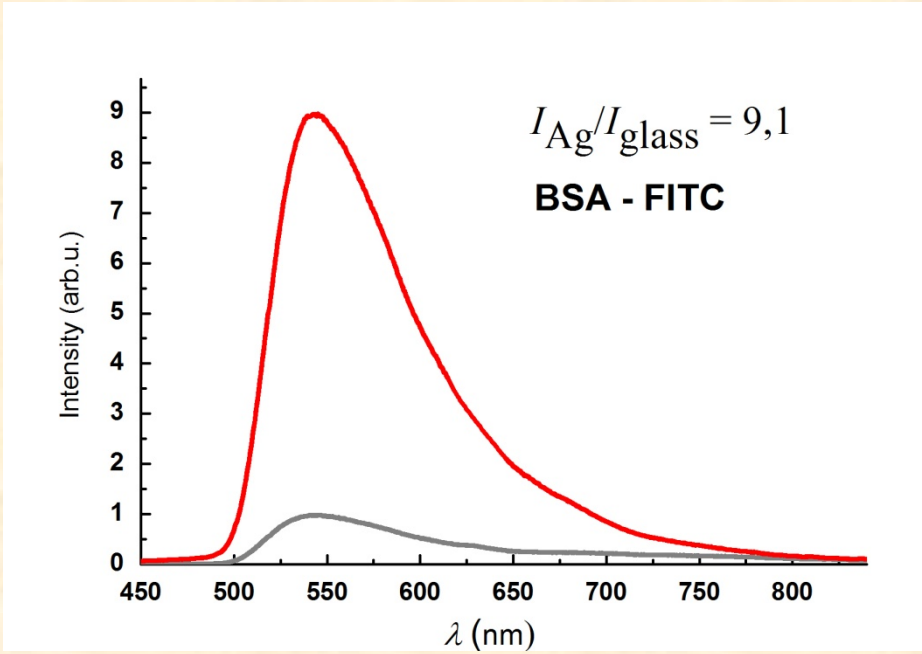
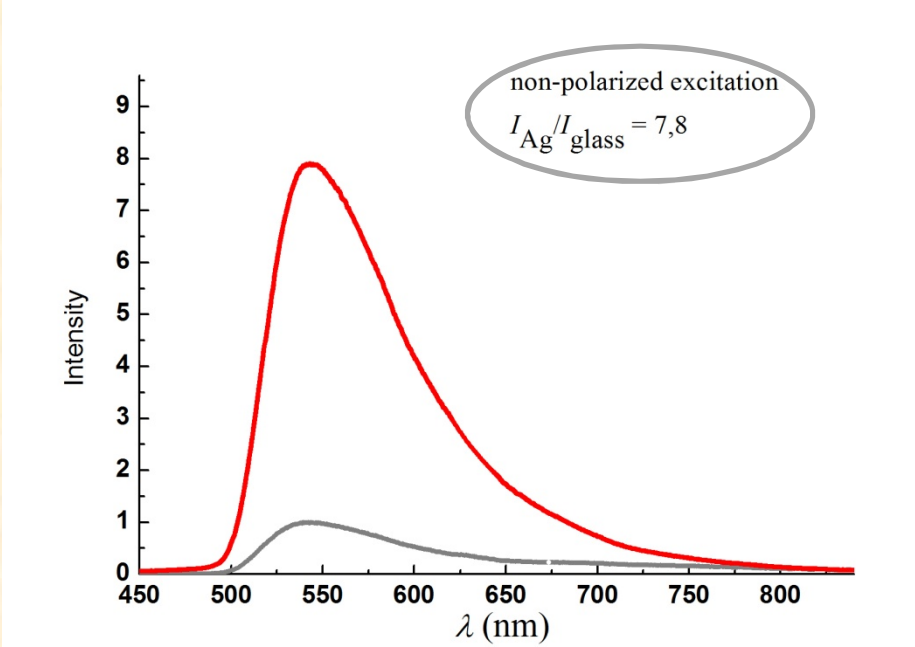


Figure 3. AFM image of nanostructured silver films annealed at 340 °C.

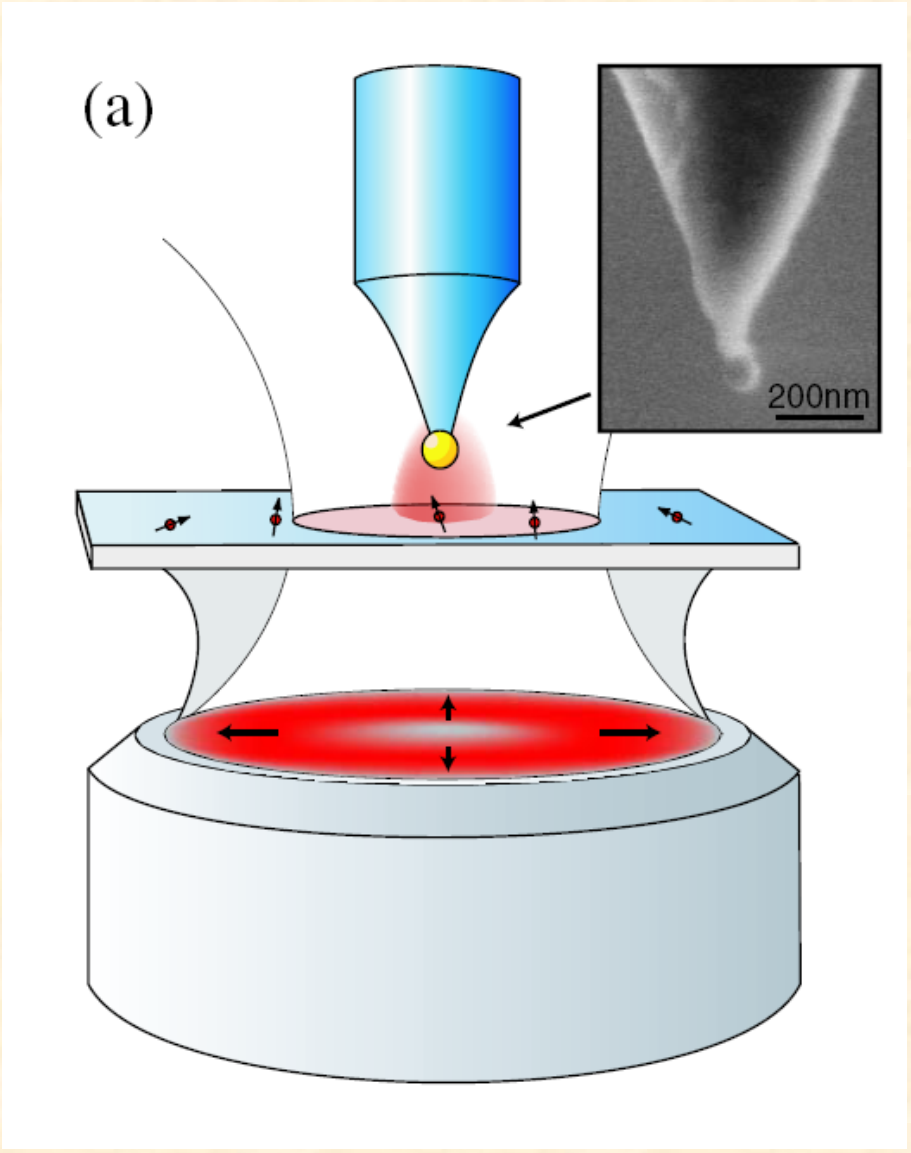


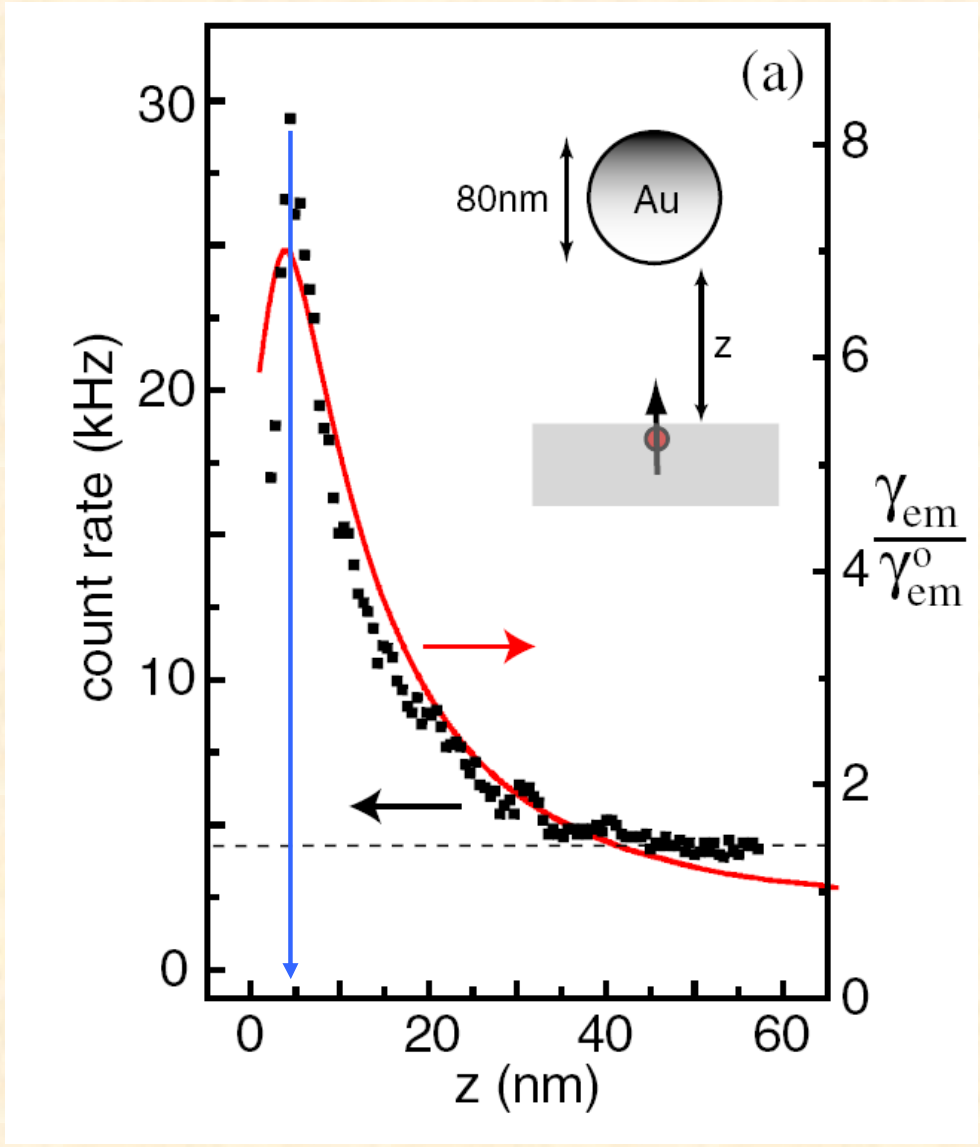

E
nm
120
μm
2,0
1,8
1,6
1,4
1,2
1,0
0,8
0,6
0,4
0,2
0
0,2
0,4
0,6
0,8
1,0
1,2
1,4
1,6
1,8
2,0
microns


I_{Ag}/I_{glass} = 9,1
BSA - FITC
Intensity (arb.u.)
λ (nm)

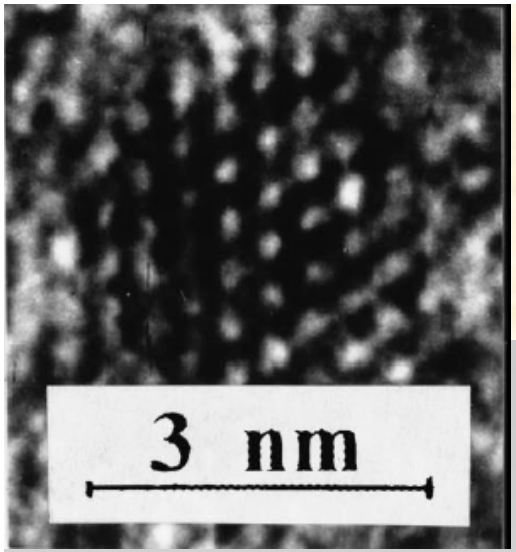

non-polarized excitation
I_{Ag}/I_{glass} = 7,8
Intensity
λ (nm)

Tip-enhanced spectroscopy





Anger, Bharadwaj, Novotny PRL 2006 **96** 113002



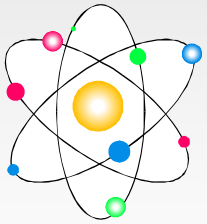
Semiconductor nanocrystals

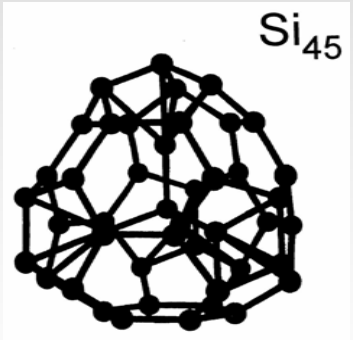
Atoms

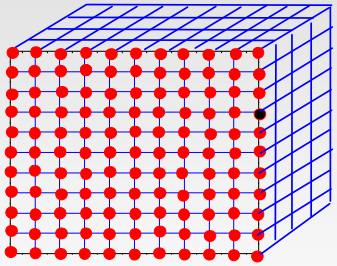
Clusters

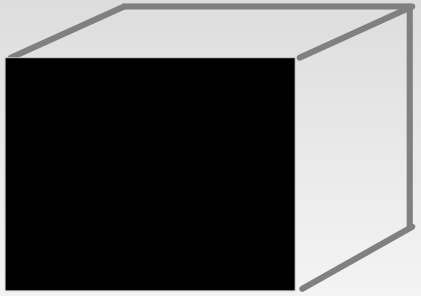
Nanocrystals

Solids









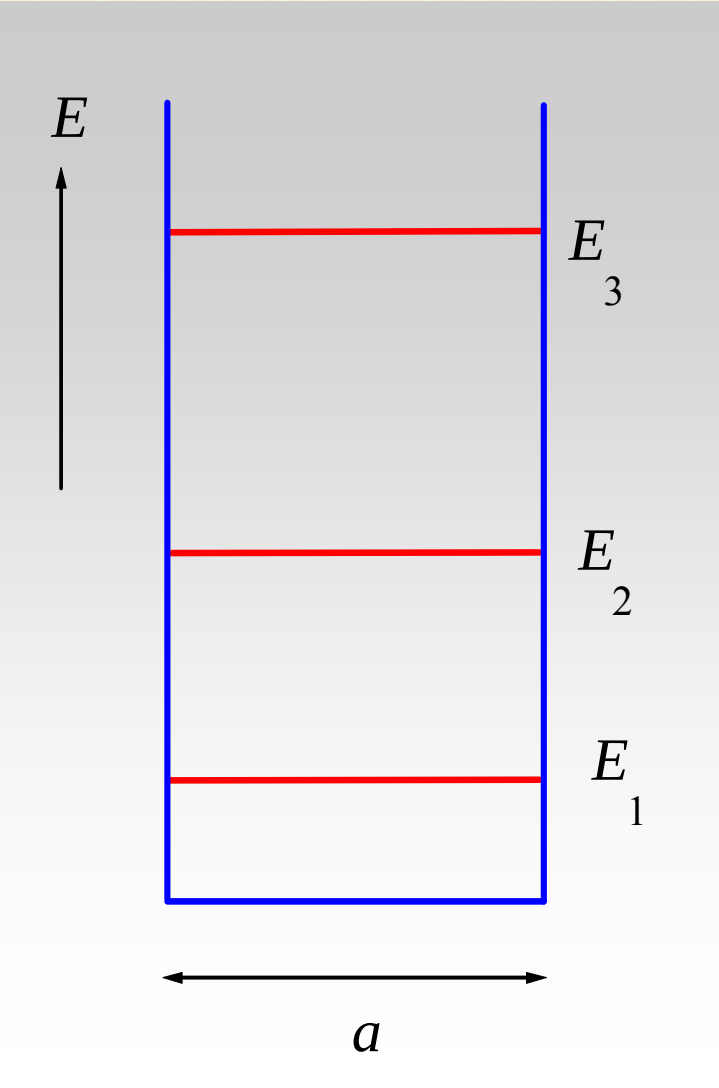
Number of atoms

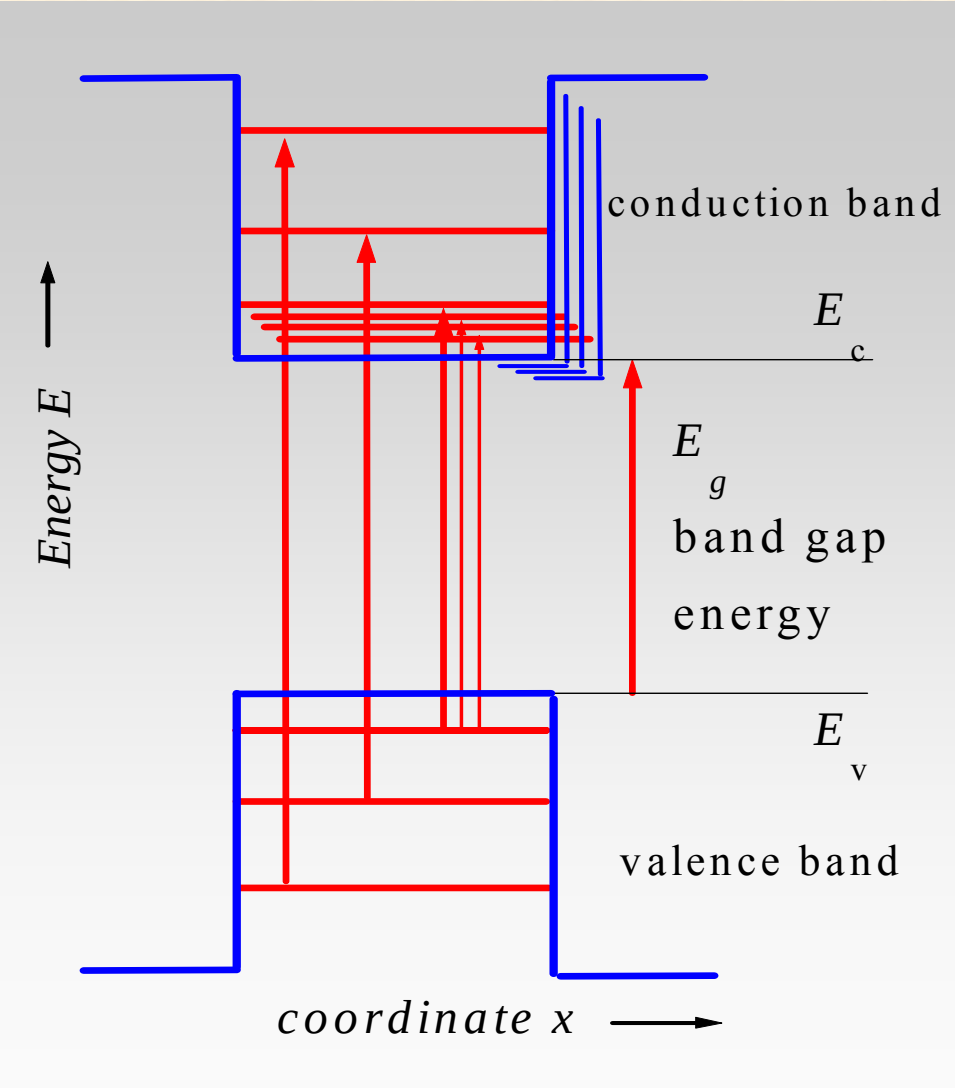
3-10^2

10^2 –10^6

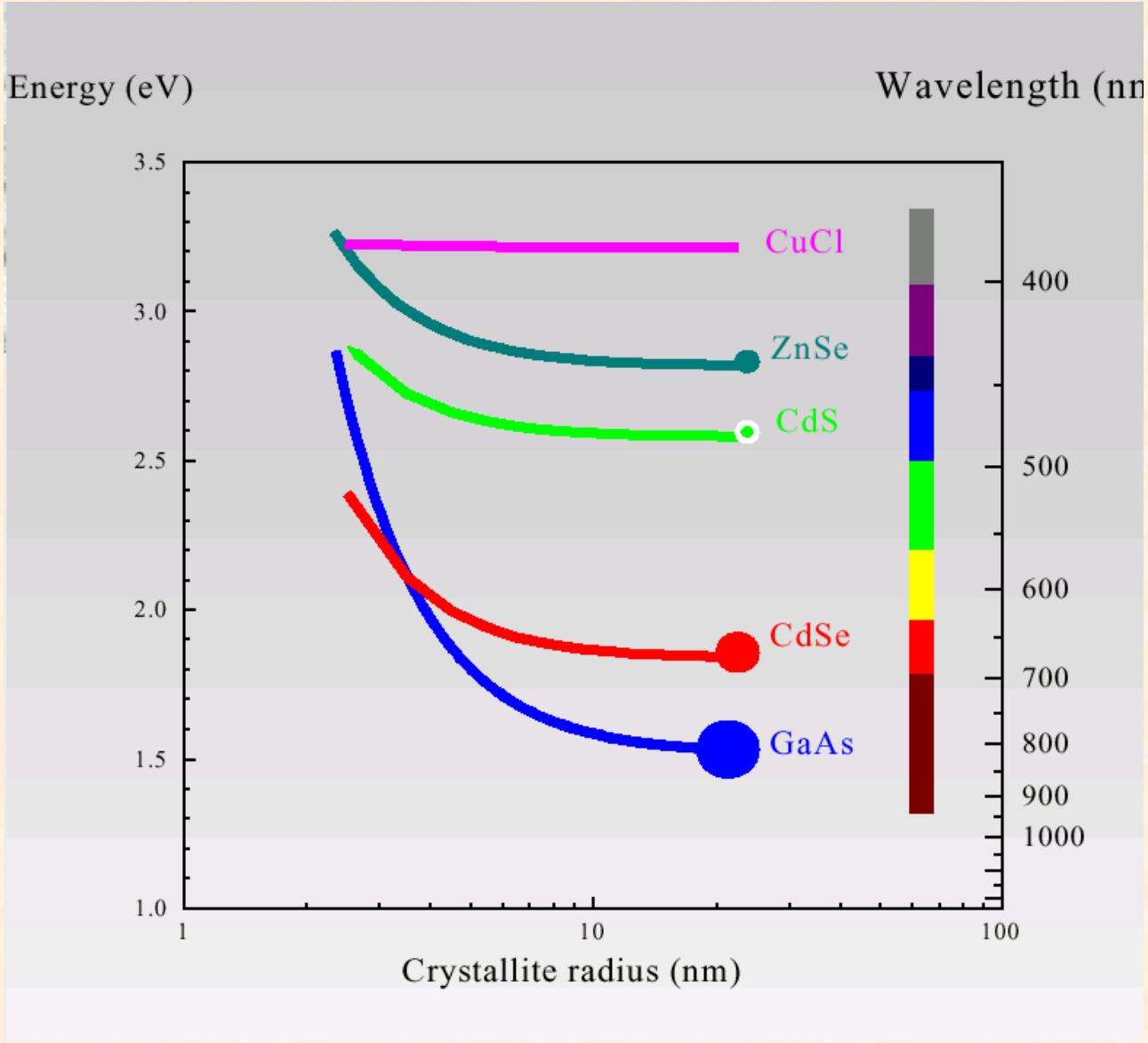
>10^6

Quantum confinement effects





Size-dependent absorption and emission spectra



Cambridge Studies in Modern Optics

Optical Properties of Semiconductor Nanocrystals

S.V. Gaponenko

中国加拿大高等教育项目资助

材料科学翻译丛书

[英] S.V.Gaponenko 著

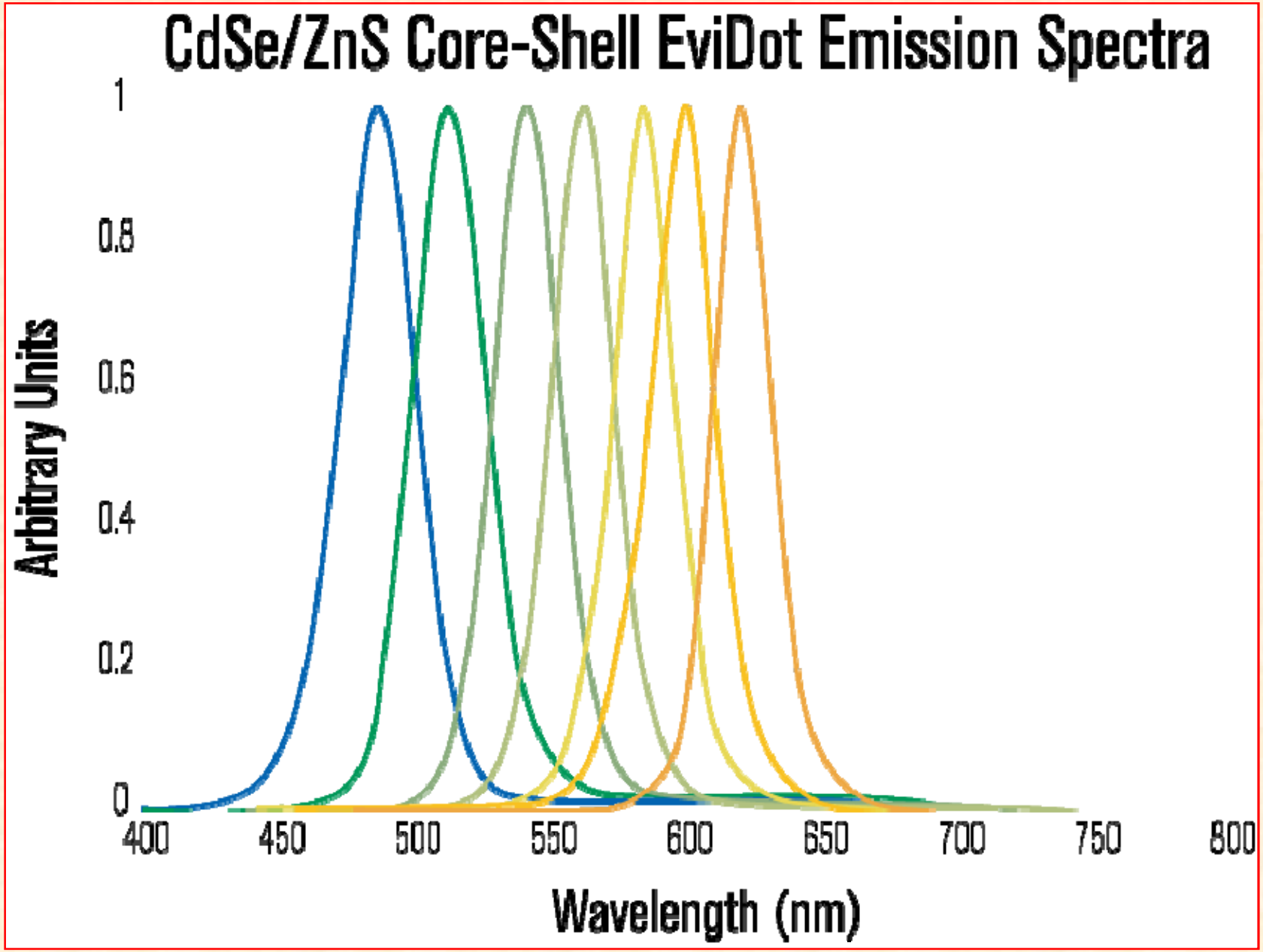
马锡英 译

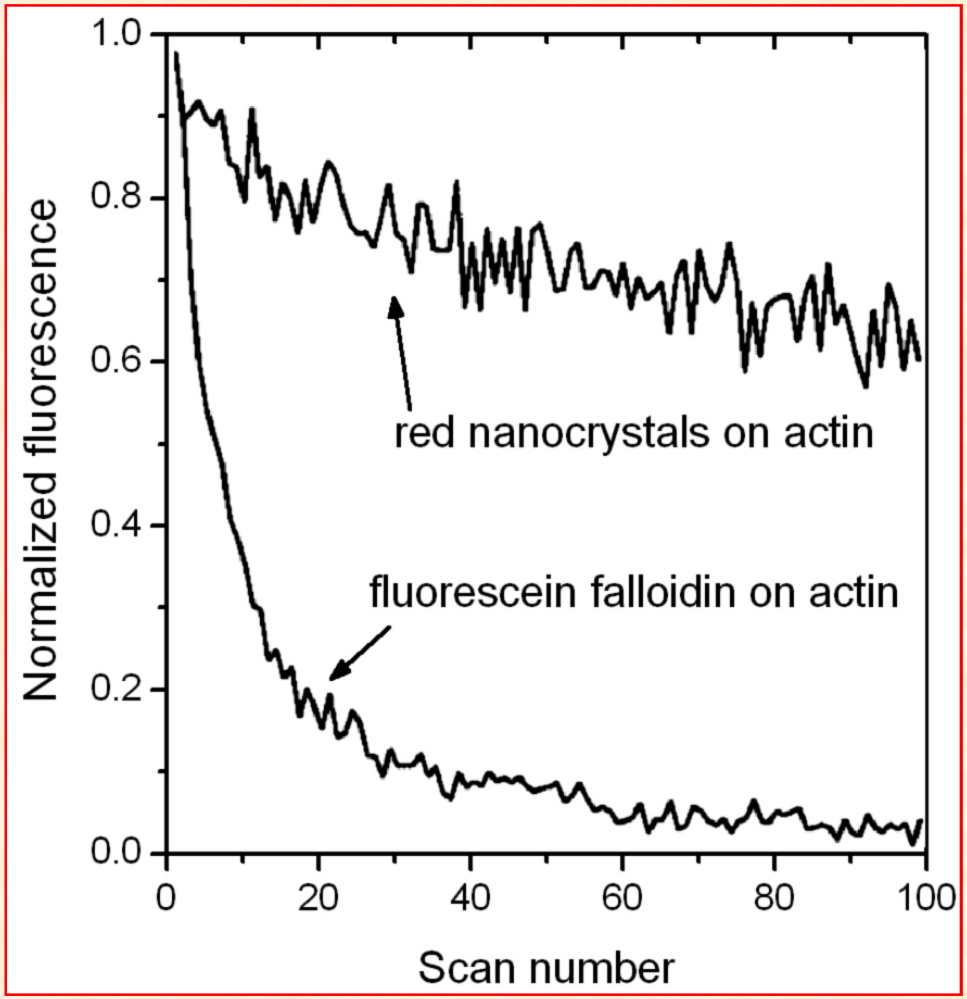
BANDAOTINAMIJINGTIDE

半导体纳米晶体的光学性质

GUANGXUEXINGZHI

兰州大学出版社


CdSe/ZnS Core-Shell EviDot Emission Spectra
Arbitrary Units
1
0.8
0.6
0.4
0.2
0
400
450
500
550
600
650
700
750
800
Wavelength (nm)



Bruchez, M. Moronne, M., Gin, P., Weiss, S., Alivisatos, A.P. Semiconductor nanocrystals as fluorescent biological labels. Science **281**, p.2013-2016 (1998).

In 2002 two groups reported first results on QD PL enhancement :

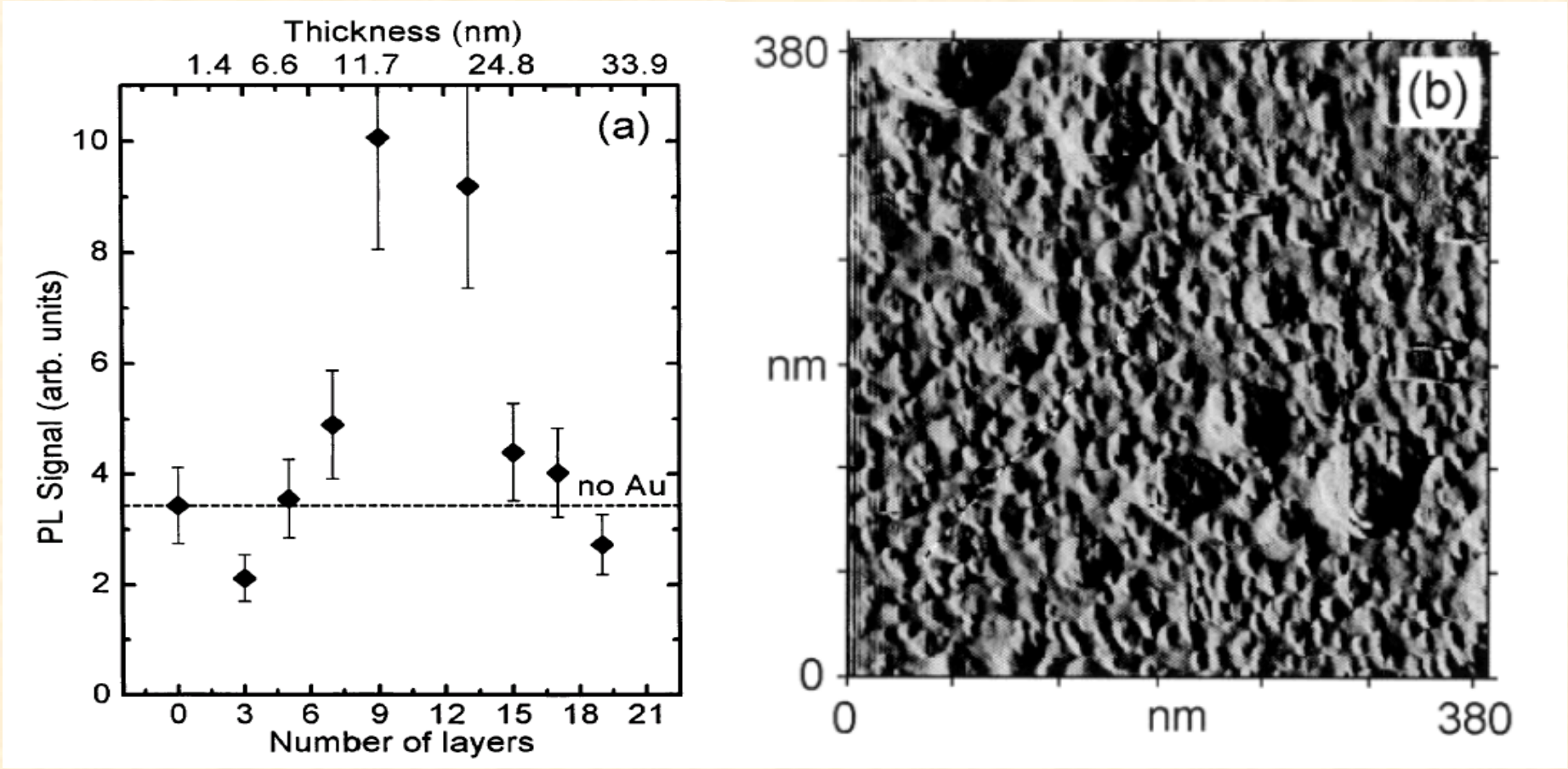
Shimizu,K.T., Woo,W.K., Fisher,B.R., Eisler,H.J. & Bawendi, M.G. Surface-enhanced emission from single semiconductor nanocrystals.
Phys. Rev. Lett. **89**,117401(2002).

NANO LETTERS

2002
Vol. 2, No. 12
1449−1452

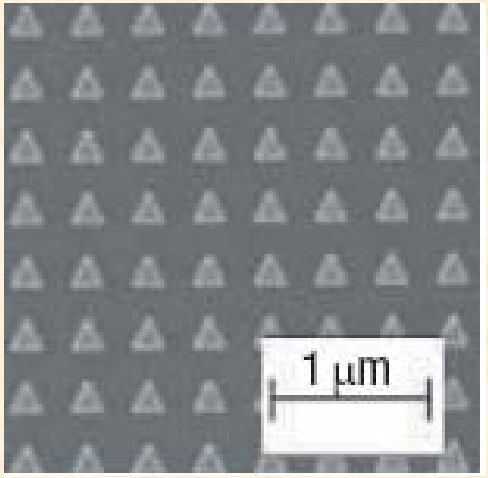
Enhanced Luminescence of CdSe Quantum Dots on Gold Colloids

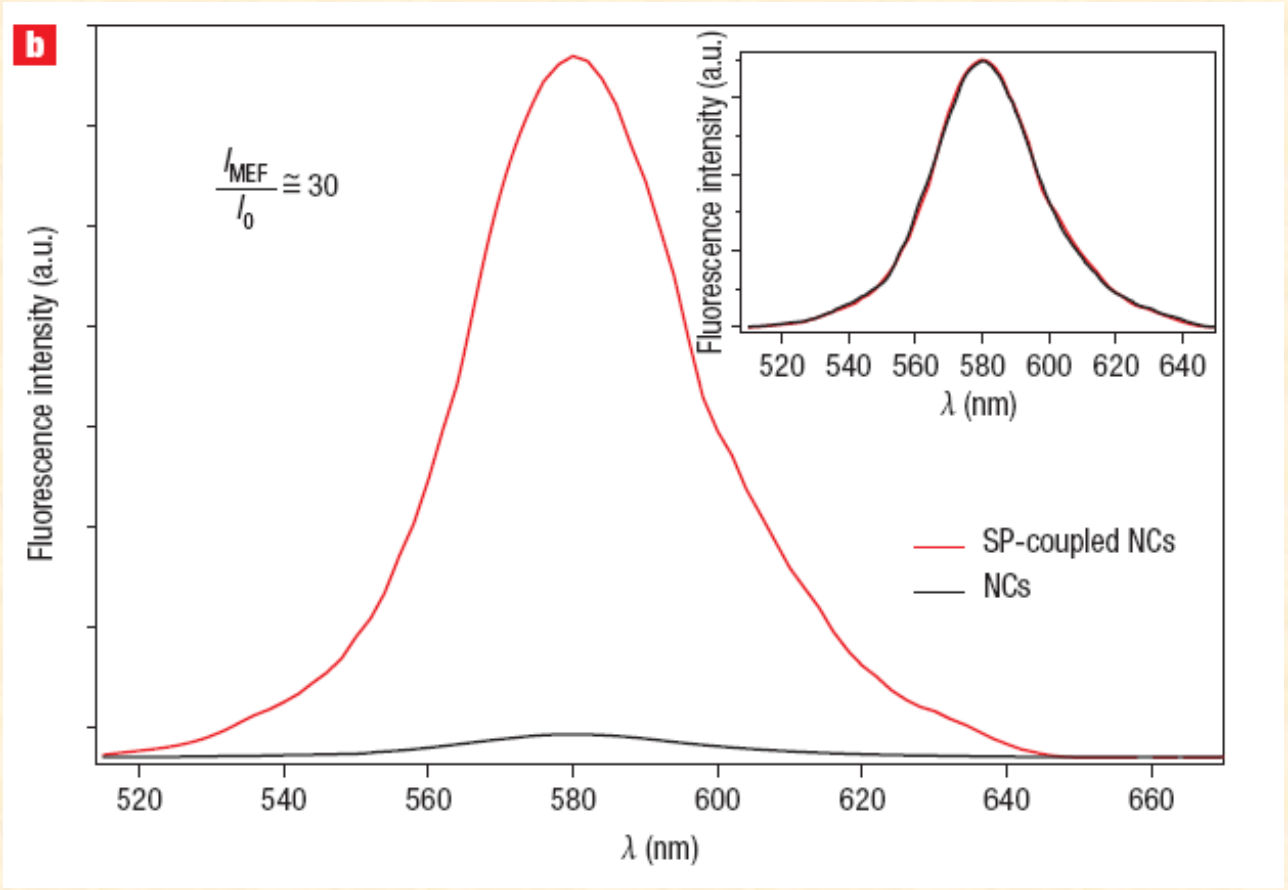
Olga Kulakovich,[†] Natalya Strekal,[‡] Alexandr Yaroshevich,[‡] Sergey Maskevich,[‡] Sergey Gaponenko,[†] Igor Nabiev,[§] Ulrike Woggon,[∥] and Mikhail Artemyev*[,⊥]


Thickness (nm)
1.4 6.6 11.7 24.8 33.9
(a)
PL Signal (arb. units)
0 2 4 6 8 10
no Au
0 3 6 9 12 15 18 21
Number of layers
380
nm
0
(b)
0
nm
380

30-fold QD PL enhancement reported

Pompa et al, Nature Nanotechnology 2006 **1** 126

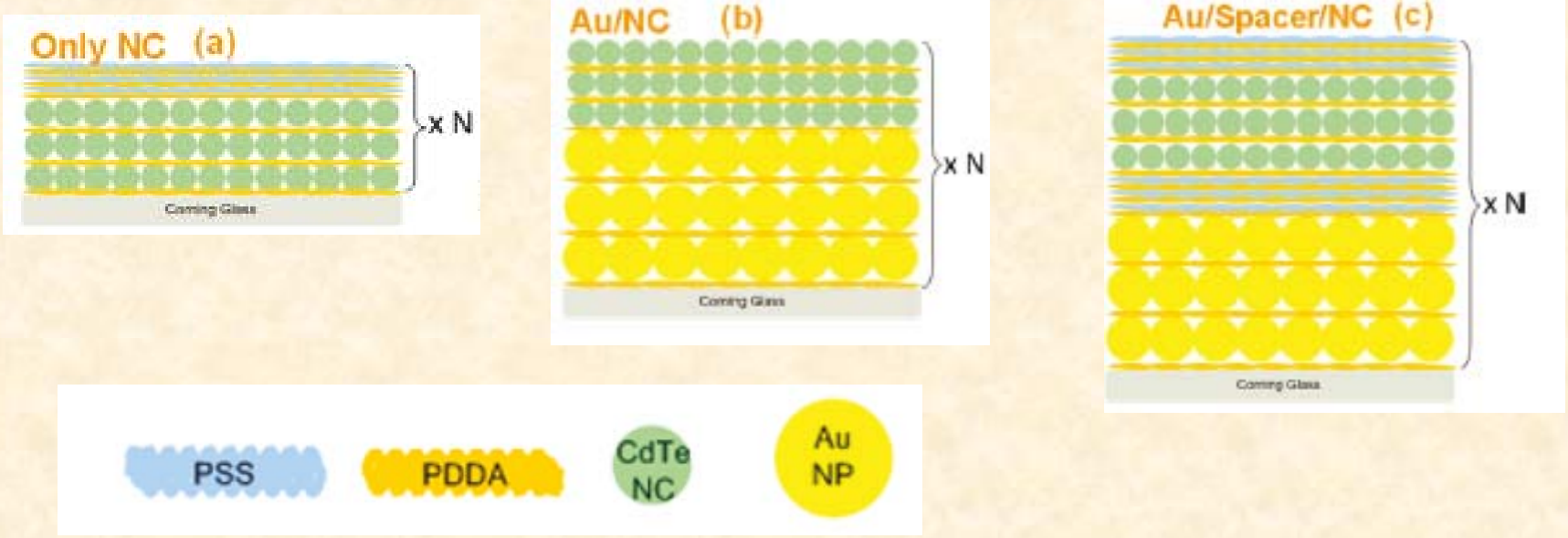


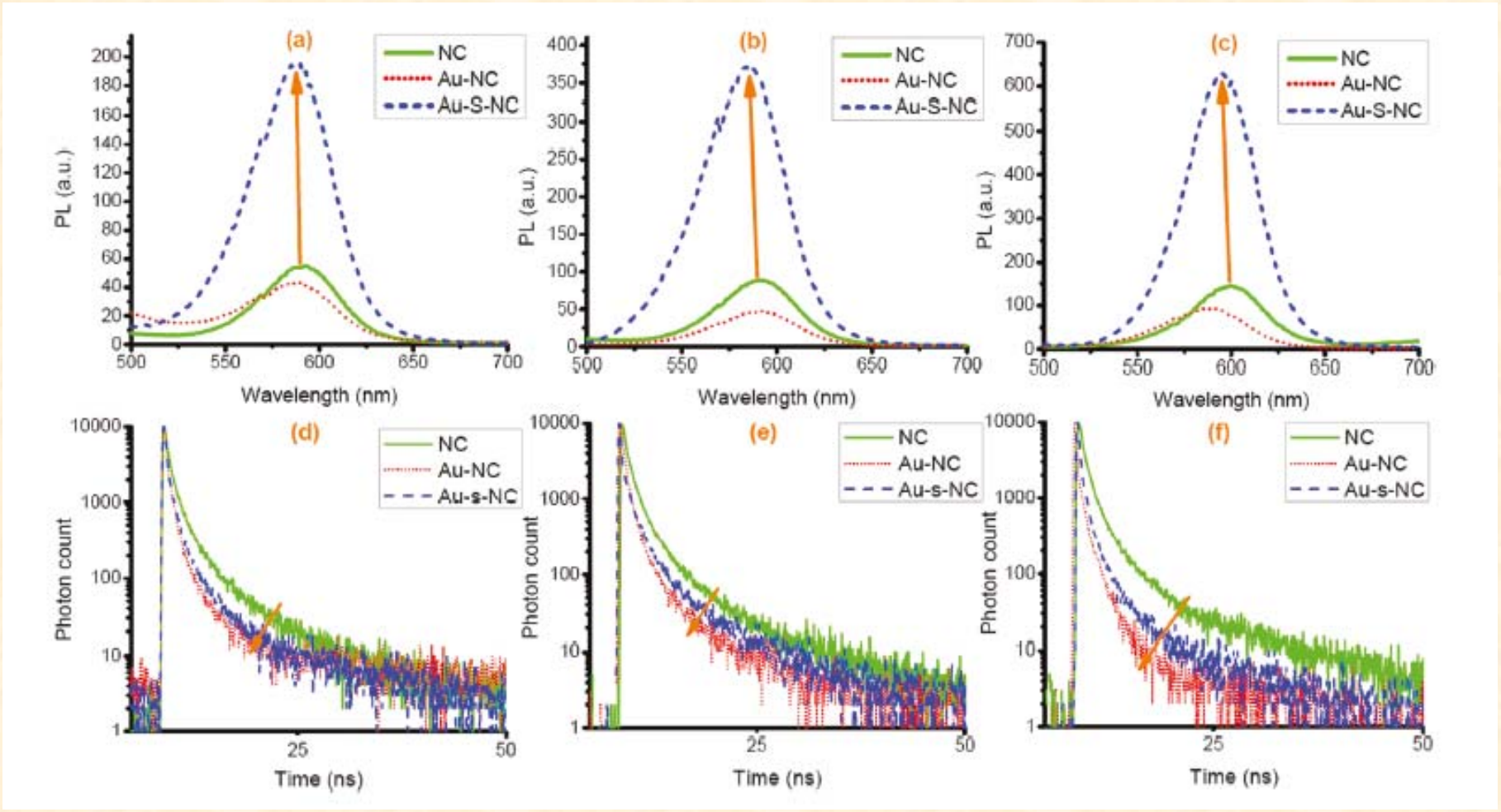


Anisotropic Emission from Multilayered Plasmon Resonator Nanocomposites of Isotropic Semiconductor Quantum Dots

ACS NANO **2011**
v. 5, p.1328–1334.

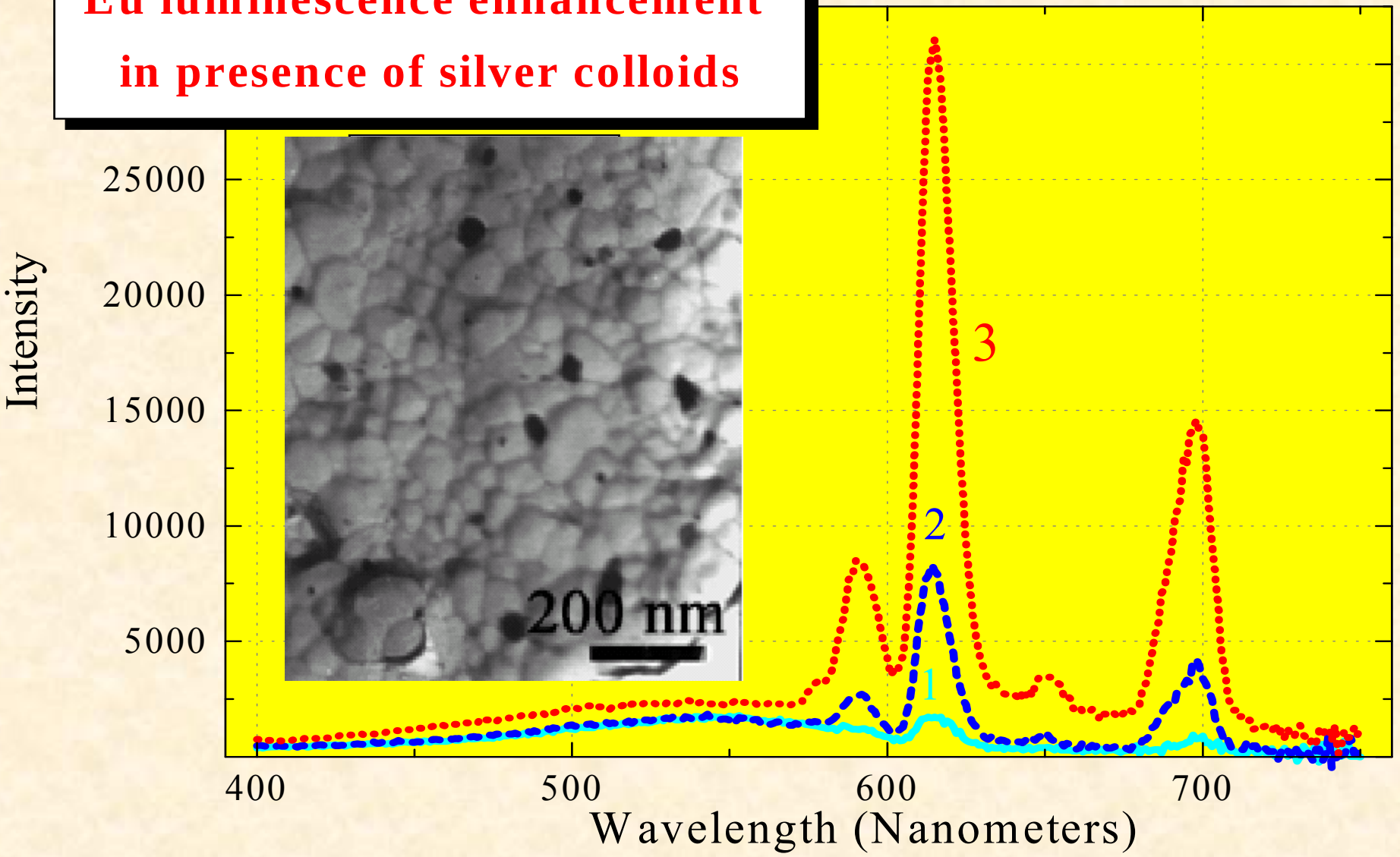
Tuncay Ozel,[†] Sedat Nizamoglu,[†] Mustafa A. Sefunc,[†] Olga Samarskaya,[†] Ilkem O. Ozel,[†] Evren Mutlugun,[†] Vladimir Lesnyak,[‡] Nikolai Gaponik,[‡] Alexander Eychmuller,[‡] Sergey V. Gaponenko,[§,*] and Hilmi Volkan Demir[†,⊥,*]





N unit cells N = 2, 3, and 5

Eu luminescence enhancement in presence of silver colloids



Svetlana Serezhkina, Minsk, PhD Thesis, 2006

Raman scattering enhancement

Katrin Kneipp Martin Moskovits
Harald Kneipp (Eds.)

Surface-Enhanced Raman Scattering

Physics and Applications

With 221 Figures, 3 in color

Springer 2006

Chem. Rev. **1999,** *99,* 2957–2975

Ultrasensitive Chemical Analysis by Raman Spectroscopy

Katrin Kneipp,* Harald Kneipp, Irving Itzkan, Ramachandra R. Dasari, and Michael S. Feld

VOLUME 78, NUMBER 9 PHYSICAL REVIEW LETTERS 3 MARCH 1997

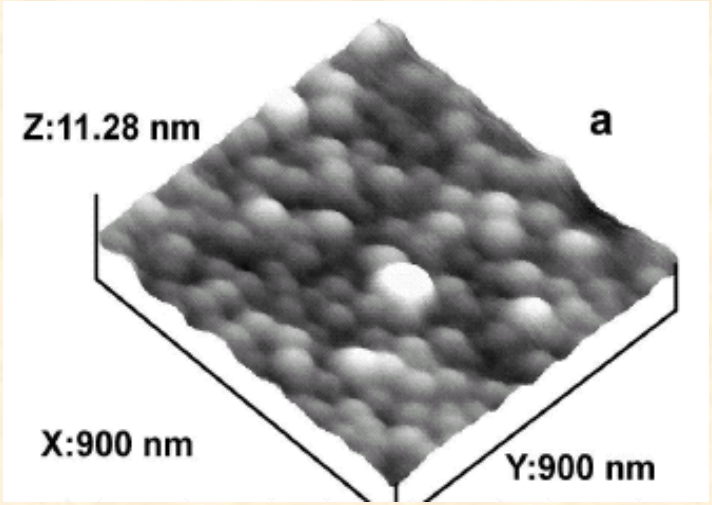
Single Molecule Detection Using Surface-Enhanced Raman Scattering (SERS)

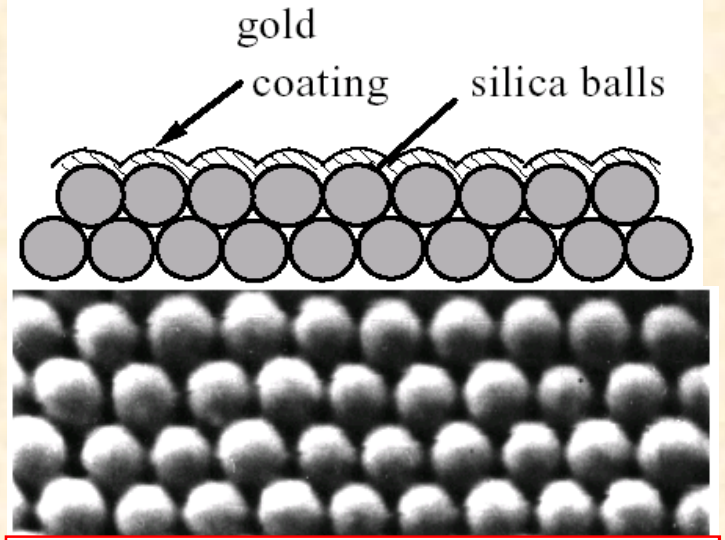
Katrin Kneipp, Yang Wang,* Harald Kneipp, Lev T. Perelman, Irving Itzkan, Ramachandra R. Dasari, and Michael S. Feld

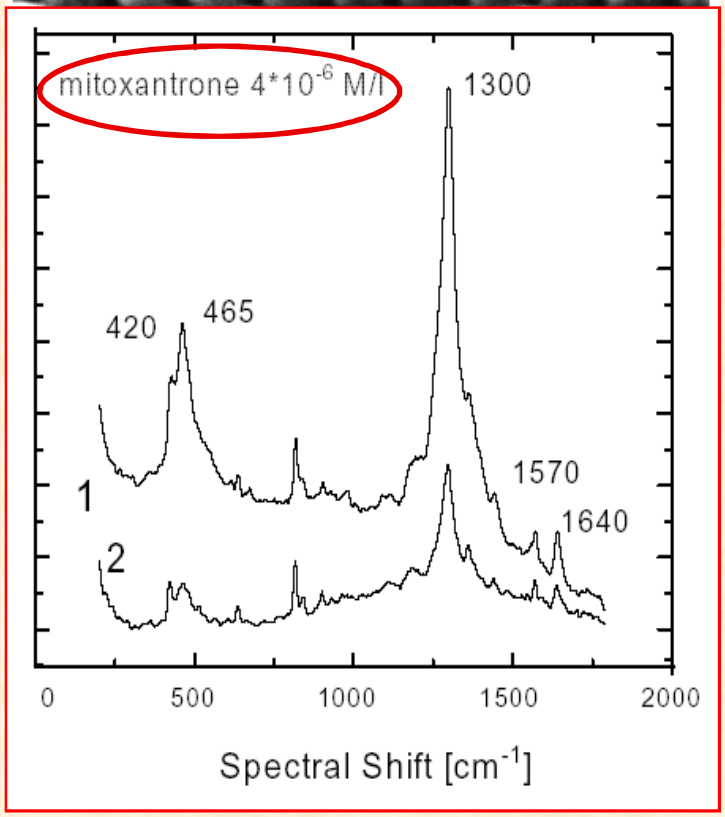
Probing Single Molecules and Single Nanoparticles by Surface-Enhanced Raman Scattering

Shuming Nie* and Steven R. Emory

SCIENCE • VOL. 275 • 21 FEBRUARY 1997 1102



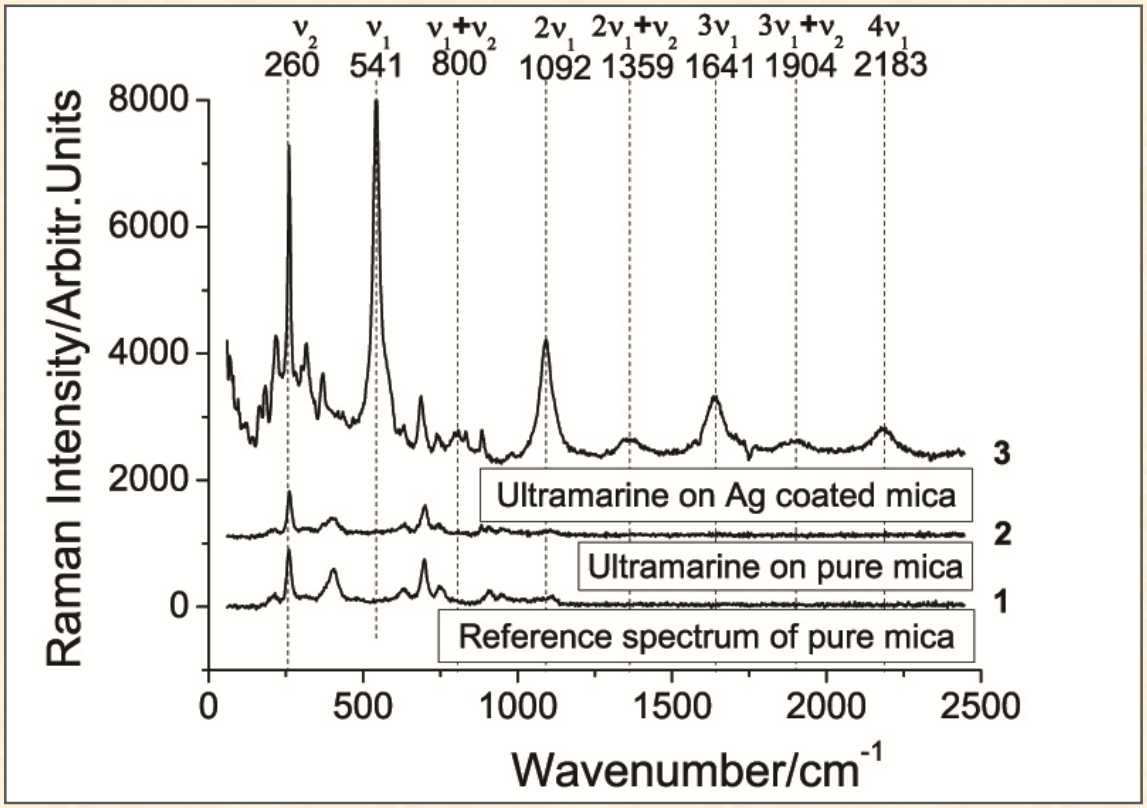


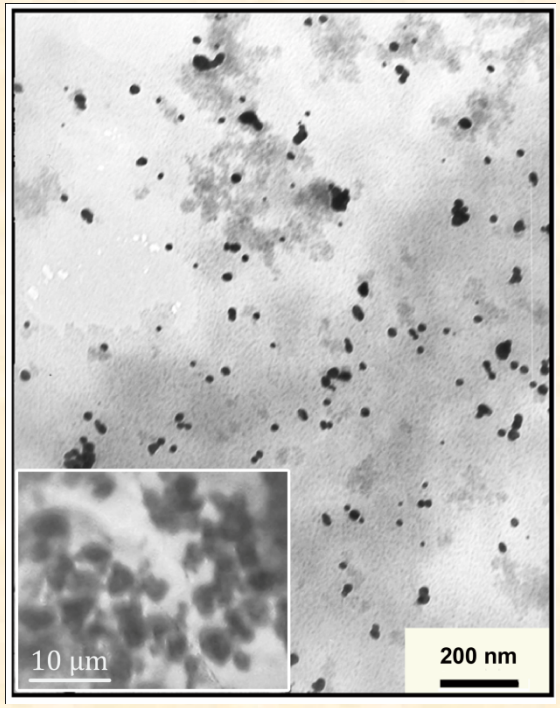


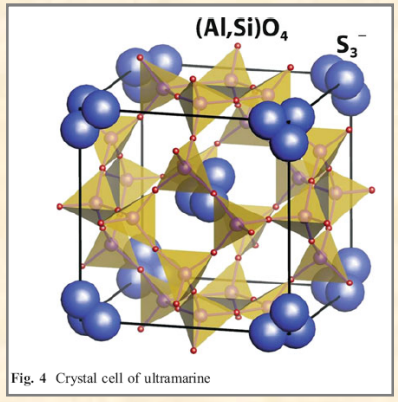
Raman Scattering Enhancement using Crystallographic Surface of a Colloidal Crystal[1]

S. V. Gaponenko[1]*, A. A. Gaiduk[1], O. S. Kulakovich[1], S. A. Maskevich[2], N. D. Strekal[2], O. A. Prokhorov[3], and V. M. Shelekhina[3]

JETP Letters, Vol. 74, No. 6, 2001, pp. 309–311







Klyachkovskaya et al. Plasmonics, 2011, **6**, 413; J. Raman. Spectr. 2012

Summary

- Photoluminescence can be enhanced by 1-2 orders of the magnitude (ensemble averaged) and can be used in fluorescence labelling and novel luminophores

- Raman scattering can be enhanced for individual molecules up to 10^{14} times and about 10^{6} averaged