Optical properties of gold nanorods

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Outlook

1) General consideration

2) Second harmonic generation

3) Photoluminescence

4) Guiding and Fabry Perrot effects
   Nanoletters 8, 935 (2008)
1) General consideration

\[ \alpha(\omega)_i = \varepsilon_0 V \frac{\varepsilon_m(\omega) - \varepsilon_d}{\varepsilon_d + (\varepsilon_m(\omega) - \varepsilon_d) L_i} \]

Milieu extérieur : \( \varepsilon_d \)  Particule métallique : \( \varepsilon_m \)

M. A. El-Sayed Accounts of Chemical Research 34, 257 (2001)

Bohren et Huffman, « Absorption and Scattering of Light by small particles » John Wiley & Sons, 1983
Li : géometrical factor of i axis  \( \sum L_i = 1 \)

prolate : 

\[
L_a = \frac{1 - e^2}{e^2} \left( -1 + \frac{1}{2e} \ln \frac{1+e}{1-e} \right), \quad e^2 = 1 - \frac{b^2}{a^2}
\]

L decreases as particle size increases

sphere \( L_x=L_y=L_z=1/3 \)

\[ \rightarrow \text{Clausius-Mossoti} \quad \alpha = 3\varepsilon_o V \frac{\varepsilon_m - \varepsilon_d}{\varepsilon_m + 2\varepsilon_d} \]

Plasmons modes extensively studied in far/near field, example:

AFM image of near-field photo-induced mass transport \( \rightarrow \) Visualization of lateral excitation of charge density at the SPP resonance of the short axis

Nanoletters 5, 615 (2005)

FDTD (-I)
Lightning rod effect

Off resonant effect
Sensitive to the incident polarization

Bachelot et al. JAP 94, 2060 (2003)
E. J. Sanchez et al. PRL 82, 4015 (1999)
2) Second Harmonic Generation – Context

*Non linear optics*

\[ D = \varepsilon_0 E + P \]

\[ P = \varepsilon_0 \left( \chi E + \chi^{(2)} : EE + \chi^{(3)} : EEE + \ldots \right) \]

- Linear term
- Non linear terms

\[ P(2\omega) = P_{D}^{nl}(2\omega) + P_{Q}^{nl}(2\omega) + P_{M}^{nl}(2\omega) + \ldots \]

Inversion symmetry \( \rightarrow \) \[ P_{D}^{nl}(2\omega) \] vanishes
Case of Metals

- Inversion symmetry (bcc or fcc) → a priori \( P_D^{nl}(2\omega) = 0 \)

Gold :

\[
P_D^{nl}(2\omega) = P_{Dsurf}^{nl}(2\omega) + P_{Dbulk}^{nl}(2\omega)
\]

\[
(\chi^{(2)} : \chi^{(2)}_{surf} + \chi^{(2)}_{bulk})
\]

Surface and interfaces: symmetry can be locally broken! E.g. Observed in 1968 on smooth metal surfaces (Bloembergen et al. (PR 174,813) and in 1981 on rough surfaces (C. K. Chen et al. PRL 46, 145)


In plane symmetry broken with special configuration. B. Lamprecht et al. Appl. Phys. B 68,
Our study: spectroscopic evidence of the role of localized surface plasmons in SHG from gold nanorods

Made by e-beam lithography (lift off technique)

Length $L = 150-190 \text{ nm}$
Width $W = 50 \text{ nm}$
Height $H = 60 \text{ nm}$
Spacing $S = 200 \text{ nm} \rightarrow$ very little near-field coupling, no far-field grating effects (A. Bouhelier et al. *J. Phys. Chem. B* 2005, 109, 3195 (2005))
Experimental configuration

- **S : sample**
- **Obj : Objective lens**

**X20-1.3 µm spot**

- **100 fs, 80 MHz, Ti:Sa**
- **λ = [740-860] nm**

Control of power and polarization direction (linear polarization)

- Linearly polarized infrared pulse.
- Fundamental is rejected
Polarized Extinction spectroscopy

- Two in-plane dipolar modes.
  Major axis: $\lambda = 800$ nm (is red-shifted as the length increases).
  Minor axis: $\lambda = 550$ nm

\[
\alpha_j = \frac{4 \pi abc}{3} \frac{\varepsilon_m - 1}{1 + A_j (\varepsilon_m - 1)}
\]

\[
\varepsilon_m (\omega_{res}) = 1 - \frac{1}{A_j} \quad \varepsilon_m (\omega) = 1 - \frac{\omega_p^2}{\omega^2}
\]

\[
\omega_{res} = \frac{\omega_p}{\sqrt{\frac{1}{A_j}}}
\]

150 nm long rods
170 nm long rods
SHG

- \( \lambda_{\text{exc}} = 800 \text{ nm}, \lambda_{\text{SHG}} = 400 \text{ nm}, \)
  \( L = 170 \text{ nm} \)

→ Quadratic dependence of the excitation intensity (second harmonic process)

Broad band photoluminescence
SHG : Influence of the incident polarization

- $\lambda_{\text{exc}} = 800$ nm, $\lambda_{\text{SHG}} = 400$ nm, $L = 170$ nm

$$I(2\omega) \propto f^4(\omega)f^2(2\omega)I^2(\omega)$$

- $f(\omega)$ : Local field enhancement at $\omega$
- $f(2\omega)$ : Local field enhancement at $2\omega$
- $I(\omega)$ : Incident intensity

$\theta = 90^\circ$ → no resonance, no electromagnetic singularity at both $\omega$ and $2\omega$

$\theta = 0^\circ$ → High $f(2\omega)$ : off-resonance lighting rod effect

- High $f(\omega)$ : off-resonance lightning rod effect (electromagnetic singularity) + surface plasmon resonance (which term dominates ?).
SHG : Influence of the incident wavelength

Excitation spectroscopy

(incident $\lambda$ scanned from 740nm to 860nm)

Small variation in the $f(\omega)$ →
strong variation in $I(2\omega)$ →
extinction spectra broader than SHG spectra

Effect of surface plasmon resonance dominates in $I(2\omega) \propto f_4(\omega)f_2(2\omega)I^2(\omega)$
Origin of the SHG?

Rod: High in plane symmetry $\rightarrow$ Far field $I(2\omega)=0$ ?? (destructive interference)

Surface effect:

$$A_{2\omega}e^{j2\omega t+\phi}$$

Left and right: symmetry breaking effects are inverse to each others $\rightarrow$ theoretical total dipolar influence $= 0$

Imperfection in nanorod symmetry, defects in the crystalline structure, quadripolar contribution?

Near-field $X \rightarrow Z$ depolarization

e.g. Optics Express 13, 1319 (2005)
Conclusion of this part

- Gold nanorods generate SHG
- SHG results from dipolar plasmon resonance of the long rod axis
- SHG is very sensitive to polarization and incident wavelength
3) Photoluminescence of gold nanorods

Photoluminescence from metals


On gold and copper films
Photoluminescence of gold

d→sp Interband transition around the X and L points
Wavelength of emission corresponds to the gap involved in interband recombination

Three-step process: photoexcitation, nonradiative relaxation, radiative recombination (hv=Egap)

First Brillouin zone of gold
And symmetry points
Photoluminescence of gold nanostructures

- Over the past 20 years: Is the subject of interesting discussion (relatively few papers on the subject)


Context of SERS. Influence of the enhanced field on rough surfaces in two photon PL.
Role of localized plasmon resonance: associated enhanced local fields → acceleration of radiative processes.

First steps towards determination of the role of localized surface plasmons in PL from nanostructures...
PL from gold nanostructures
Three examples of studies


Possible photo stable biological labeling
No bleaching
No blinking
Biologically compatible
Quantum efficiency ? 10^{-10} for films, up to 10^{-4} for nanostructures

• PL spectrum from nanometer-sized gold structure differs from spectra from bulks
• Electronic transition in gold nanostructures are not sufficient to interpret PL spectrum. Localized surface plasmon must be included in the interpretation
Demonstration of relationship between PL and Surface plasmon spectra

- 150 fs pulsed laser centered at 785 nm (Ti:sapphire laser)
- Inverted optical microscope equipped with 1.4 NA lens
- Single-photon counting module
- Cooled CCD/Spectrograph
- Tapping-mode AFM head

• E-beam lithographed gold nanostructures
PL spectrum and Confocal PL image of a single elliptical particle

$P_{\text{exc}}$ average = 60 $\mu$W

Normalized spectrum

Wavelength [nm]

Clear unelastic process
PL from single nanorods
influence of the incident polarization

30 nm wide, 100 nm long nanorod

$P_{\text{exc}} = 60 \ \mu\text{W}$

$\lambda_{\text{PL}} = 400-700 \ \text{nm}$

$1.2 \times 10^6 \ \text{counts/s}$

$4 \times 10^3 \ \text{counts/s}$

Need of electromagnetic singularities
In agreement with recent results on PL, as observed by NSOM

A. Bouhelier et al.

→ PL very sensitive to the polarization; non linear effect: sensitive to local field strength
Influence of the incident power on the PL intensity

Two photon absorption (E_exc=1.58 eV, E_gap>3eV around symmetry points)
Influence of the nanorod aspect ratio ratio

The 100 nm nanorod has the highest count rate by far: optimum field enhancement?

→ Blue shift of the PL spectrum for decreasing rod’s length!

Similar shift is expected from surface plasmon resonance…
Influence of the rod aspect ratio

Comparaison with scattering spectra

Width: 30 nm, lengths: 50, 70, 100, 150, 300 nm

→ Blue shift of the PL spectrum for decreasing aspect ratio!

Similar shift is expected from surface plasmon resonance...

P_{exc} average = 60 µW

λ_{exc}: 785 nm (150 fs)
Shape-induced spectra in Nanorods - 100 nm (Thermal melting of nanorods)

- The PL spectrum changes irreversibly as a function of excitation power:

  \textit{Controlled reshaping of a 100 nm nanorod (initial }r=3.3\textit{)}

![Graph showing reversible and irreversible processes in PL intensity and wavelength.](image)

\textbf{AFM images}

- Original nanorod
- \( <P> = 350 \, \mu \text{W} \)
- \( <P> = 500 \, \mu \text{W} \)
- \( <P> = 0.8 \, \text{mW} \)
- \( <P> = 1.6 \, \text{mW} \)
Shape-induced spectra in Nanorods -100 nm (Thermal melting of nanorods)

PL Spectrum gets centered at the visible as the particle gets circular!
Origin of the photoluminescence points of view N°1: intraband coupling

1. Photo absorption $d \rightarrow \text{sp bands}$
   $> 3 \text{ eV (very sensitive to strong fields)}$

2. Intraband transition. Conservation of both energy and momentum:
   $\Delta E = \Delta k = k_{\text{plasmon}}$
   (coupling with plasmon eigenmode characteristic to the gold nanostructure)

3. Radiative decay of the plasmon ($\sim 70 \text{ fs}$)

3'. Radiative electrons-holes recombinaison ($\sim 50 \text{ fs, around 1.8 eV, as observed by Mooradian}$)

Novotny, Dulkeith,..
Origin of the photoluminescence point of view N°2: accelerating radiative processes

\[ I_L(\omega_2) = I^2(\omega_1) \cdot Y_{2\text{abs}} \cdot Y_R \cdot Y_{\text{em}} \]

- Intensity of luminescence
- Incident intensity
- Two-photon absorption rate
- Probability of relaxation
- Probability of radiative recombination at \( \omega_2 \)

\( \rightarrow \) Broad band photoluminescence at many \( \omega_2 \) around X and L convoluted by the plasmon spectrum

(Boyd, Okamato,..)
Conclusions of this part

- photoluminescence from Au nanorods is linked to localized surface plasmons
  - Triggered by two-photon absorption
  - Polarization anisotropy of the PL: emission only if EM singularities are excited
  - Blue-shift of the PL for decreasing particle size (plasmon-type behavior)
  - PL spectra similar to SP scattering spectra
  - PL spectral changes with controlled modification of the particle’s shape
  - Gold Band structure has to be considered
4) Guide and fabry perrot effects

Tool: Photoemission electron microscopy – Projet ANR peemplasmon

Based on the photoelectric effect (Einstein, 1905)

\[ h \nu \geq W \]

Far field Imaging of the ejected-accelerated electrons

Contrast: near-field intensity \( \alpha \)

number of ejected electrons/s

\[ \lambda_{elec} \ll \lambda_{photon} \rightarrow \text{description of photon-induced effects with a 20 nm resolution} \]

\( W = \) work function minimum energy to move an electron from the fermi level into vacuum
Photoemission electron microscopy – setup

Ejected electrons are accelerated (20 000 V) and far field detected.

Work function of amorphous gold 4.6 - 5.1 eV. Incident light $\sim$ 1.5 eV $\rightarrow$ three photon process

PEEM contrast = flux of ejected electrons (near-field optical intensity)$^3$

First proposition of PEEM for plasmonics: M. Cinchetti et al. PRL 95, 047601 (2005)
Samples

Gold Nanorods produced by e-beam lithography

L = 50-4000 nm
H = 35 nm
W = 2R = 30 nm

Glass
ITO
Au

2x2 μm² SEM image

First observation: case of a long rod

$\lambda_0 = 792 \text{ nm}$

SEM

PEEM

75°

$1 \mu m$

4 $\mu m$ gold rod

Two beating periods

$\lambda_0 = 792 \text{ nm}$

$75°$

Two beating periods

PEEM yield

Longitudinal position (nm)

period $\lambda_m = 466 \text{ nm}$

period $\lambda_p = 256 \text{ nm}$
A longitudinal charge oscillation propagates along the rod

Wave equation:
\[
\frac{\partial^2 F}{\partial t^2} = V_\varphi^2 \frac{\partial^2 F}{\partial x^2} + \tau^{-1} \frac{\partial F}{\partial t} + \frac{qE_0}{m_q} e^{i(\omega t - k_{\parallel} x)}
\]

Solution:

\[
F(x, t) = A_p e^{+iKx} + A_m e^{-iKx} - \frac{qE_0/m_q}{V_\varphi^2(K^2 - k_{\parallel}^2)} e^{-i(k_{\parallel} x)} e^{i\omega t}
\]

\(K = K_1 + iK_2\) propagation + damping

\(K = ((\omega^2 - i\omega/\tau)/V_\varphi^2)^{1/2}\)
Interpretation

Three involved waves

Three possible interferences:

- Forward surface wave + backward surface wave (damping)
  \[ k// \]

- Forward surface wave + incident field → beating period
  \[ \lambda_m = \frac{2\pi}{K_1 - k//} = 466\text{nm} \]

- Backward surface wave + incident field → beating period
  \[ \lambda_p = \frac{2\pi}{K_1 + k//} = 256\text{nm} \]

From measurements

\[ \lambda_{spp} = \frac{2\pi}{K_1} \approx 335\text{ nm} \]
Discussion about the obtained value for $\lambda_{spp}$

$\lambda_{spp} = \frac{2\pi}{K_1} \sim 335$ nm $< \lambda_o$

Also $< «$ classical $» \lambda_{spp} » = \lambda_o \sqrt{\frac{\text{Re}(\varepsilon_{or}) + \varepsilon_{air}}{\text{Re}(\varepsilon_{or}) \times \varepsilon_{air}}} = 0.97\lambda_o$

Comparaison with what was calculated in PRL 98, 266802 (2007) (L. Novotny):

$$\lambda_{SR-SPP} = 2\pi R \left( a_1 + a_2 \frac{\lambda_0}{\lambda_{0p}} \right) \sim 331 \text{ nm}$$

R radius cylindrical infinite guide, $a_1, a_2$ are functions of dielectric constant of surrounded medium ($\varepsilon_s$) and gold ($\varepsilon_{or}$)

Based on the wave guide theory, TM0 transverse mode in a cylindrical waveguide
Case of short rods (< 1 µm)–resonant wavelength

Fabry-Perrot-like resonance with $K_1 \times \text{rod length} = m\pi \quad m \in \mathbb{IN}$

\[
\lambda_{SR-SPP} = 2\pi R \left( a_1 + a_2 \frac{\lambda_0}{\lambda_0^p} \right)
\]

\[
\lambda_{0 \text{Res}}(m) = \frac{\lambda_0^p}{a_2 \left( \frac{1}{m\pi} \frac{L+2R}{R} - a_1 \right)}
\]

Takes into account both lateral and longitudinal rod confinement

(calculated with effective rod length = $L + 2R$ to take into account phase shift at the extremities, cf. L. Novotny, PRL 98, 266802, 2007).
Case of 75° incidence

Both odd and even modes can be excited at grazing incidence.
Sub-30 nm resolution PEEM imaging ($\alpha=75^\circ$)

L=100 nm, only dipolar mode can be excited (m=1)
Sub-30 nm resolution PEEM imaging ($\alpha=75^\circ$)

L = 250 or 300 nm, only quadripolar mode can be excited ($m=2$)
Conclusions of this part

Gold nanorods act as plasmons guides and resonators –

PEEM enables analysis of the charge distribution along the rod with a sub-30 nm resolution

Observation are in agreement with simple analytical model based on antenna/wave guide/fabry-perrot theory

Determination of propagation constant and effective wavelength

Determination of modal properties (observation of dipolar and quadripolar charge distribution)
General conclusion – examples of opened questions

Gold nanorods are fascinating light nano emitters. They also allow for light confinement and guiding.

Resonant surface plasmons strongly drives optical properties of gold nanorods.

How naive is the Fabry-Perrot picture for SPP? In particular, what about the phase shift experienced by the surface wave at the rod extremities? What about the influence of the metal crystal structure? ….

Merci pour votre attention!