Mueller matrix polarimetry of plasmon resonant silver nano-rods: biomedical prospects

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Internet Lecture
Outline

- Introduction to surface plasmon resonances
- Theoretical aspects
  - Quasi Static Approximation (QSA)
  - Beyond QSA: Mie-theory and T-matrix method
  - Scattering matrices and polarization aspects
  - Quantitative polarimetry
  - Mueller matrices: Polar Decomposition
- Geometric configuration of the system and methodology
- Results
  - Resonance bands (Q_{scat})
  - Polarization properties of SPR
  - Effect of ambient medium on polarization properties of SPR
- Potential applications to biosensing
- Conclusion
Surface plasmons are collective oscillations of free electrons at the metal-dielectric interface in resonance with the incident electromagnetic (EM) field. They can propagate along metal-dielectric interfaces or be localized in metal nano-particles (LSPR). They show strongly enhanced and highly localized electromagnetic fields and have numerous practical applications like ultra-high sensitive chemical and biomedical sensing, contrast enhancement in optical imaging, and development of new generation optical devices like plasmonic wave-guiding nano-devices for optical information processing and data storage.

In the context of biomedical applications, bio-conjugated nano-particles/structures: changes in optical absorption/scattering properties of nano-particles due to changes in local dielectric environment obtained in the scattering/absorption spectra can be used as contrast enhancement agent in biomedical imaging with nano-particles: high scattering cross section and control on size and shape of nano-particles. In the context of biomedical applications, Quantitative plasmon polarimetry can be used for contrast mechanism in nano-particle based imaging as they show highly enhanced polarization response as compared to the dielectric biological tissues. Polarization properties like retardance, diattenuation and depolarization can be used to eliminate background Rayleigh/Mie scattering from dielectric tissue scattering structures.
Available approximations and methods for characterization of LSPR in metal nano-particles: Mie theory, discrete dipole approximation (DDA), T-matrix, finite difference time domain (FDTD), finite element (FEM) and the multipole-multipole (MM) methods to name a few.

**Spheres** Quasi static approximation (QSA): $r << \lambda$: acts like a sphere placed in a static electric field. Dipolar plasmon resonance:

$$\alpha = 4\pi a^3 \frac{\varepsilon_1 - \varepsilon_m}{\varepsilon_1 + 2\varepsilon_m}$$

$$C_{sca} = \pi a^2 \frac{8}{3} \frac{x^4}{\varepsilon_1 - \varepsilon_m} \left| \frac{\varepsilon_1 - \varepsilon_m}{\varepsilon_1 + 2\varepsilon_m} \right|^2$$

$$C_{abs} = k \text{Im}\{\alpha}\}$$

Condition for dipolar resonance: $\varepsilon_1 = -2\varepsilon_m$ Contribution of higher multi-poles for larger particles in the extictions. Quadrupolar polarizability: $\alpha = \frac{\varepsilon_1 - \varepsilon_m}{\varepsilon_1 - (3/2)\varepsilon_m}$ and the quadrupolar resonance condition: $\varepsilon_1 = -(3/2)\varepsilon_m$.

**Non spheres**

Polarizability $\alpha_j = 4\pi abc \frac{\varepsilon_1 - \varepsilon_m}{3\varepsilon_m + 3L_j(\varepsilon_1 - \varepsilon_m)}$

For spheres: $a = b = c = \frac{1}{3}$

For spheroids: $a = b \neq c$

For ellipsoids: $a \neq b \neq c$
Theory

Beyond QSA: Mie theory & T-matrix method

- Mie scattering
  - For EM modes of a sphere of arbitrary size
  - Boundary conditions: the tangential components of the $\mathbf{E}$ and $\mathbf{H}$ are continuous at the interface of the sphere and the dielectric environment.
  - Solutions take the form of a set of spherical Bessel and Hankel functions.
  - Multi-pole expansion (EM modes) possible: electric dipole, magnetic dipole, electric quadrupole and so on.
  - If $d < \lambda/20$, only the electric dipolar term is physical and the Mie theory reduces to the Rayleigh theory.
  - Strong dependence on the $\varepsilon_m$.
  - For resonance, $\mathcal{R}\{\varepsilon\}$ should be negative.

- T-matrix method:
  - The incident and scattered $\mathbf{E}$ fields are expanded in terms of vector spherical wave functions.
  - Relation between the input and output Stoke’s vectors established by means of a transition (T)-matrix: $S_o = S(\theta)S_i$

$$
\begin{pmatrix}
  I_o \\
  Q_o \\
  U_o \\
  V_o
\end{pmatrix} = 
\begin{pmatrix}
  S_{11} & S_{12} & S_{13} & S_{14} \\
  S_{21} & S_{22} & S_{23} & S_{24} \\
  S_{31} & S_{32} & S_{33} & S_{34} \\
  S_{41} & S_{42} & S_{43} & S_{44}
\end{pmatrix}
\begin{pmatrix}
  I_i \\
  Q_i \\
  U_i \\
  V_i
\end{pmatrix}
$$

- For spheres, the T-matrix has a block diagonal form (the elements inside the red box are zero)
- For non-spheres, the T-matrix is fully populated.

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Theory
Scattering matrices and polarization aspects

- Amplitude scattering matrix - **Jones matrix**: defined in the scattering plane

\[
\begin{pmatrix}
E_{\parallel s} \\
E_{\perp s}
\end{pmatrix} = \frac{e^{ik(r-z)}}{-ikr}
\begin{pmatrix}
S_2 & S_3 \\
S_4 & S_1
\end{pmatrix}
\begin{pmatrix}
E_{\parallel i} \\
E_{\perp i}
\end{pmatrix}
\]

For sphere, \(S_3, S_4 = 0\), non-zero otherwise.

- For non-spherical axi-symmetric particles (e.g. spheroids & cylinders)

\[
s' = R^{-1}(\alpha)s(\theta)R(\alpha), R(\alpha) = \begin{pmatrix}
\cos(\alpha) & \sin(\alpha) \\
-\sin(\alpha) & \cos(\alpha)
\end{pmatrix}
\]

\(\alpha, \beta\) are Euler rotation angles.

- Preferential orientation: Laboratory frame’s Z-axis coincides with the symmetry axis of the particle:

\[
\begin{pmatrix}
E_{\parallel s} \\
E_{\perp s}
\end{pmatrix} = \frac{e^{ik(r-z)}}{-ikr}
\begin{pmatrix}
S_2 & 0 \\
0 & S_1
\end{pmatrix}
\begin{pmatrix}
E_{\parallel i} \\
E_{\perp i}
\end{pmatrix}
\]
Theory

Scattering matrices and polarization aspects

- **Scattering Mueller matrix**
  \[ S(\theta) = A \cdot (s \otimes s^*) \cdot A^{-1} \]
  
  where,
  \[
  A = \begin{pmatrix}
  1 & 0 & 0 & 1 \\
  1 & 0 & 0 & -1 \\
  0 & 1 & 1 & 0 \\
  0 & i & -i & 0 \\
  \end{pmatrix}
  \]

- **Spherical and preferentially oriented particles: Block diagonal structure**
  \[
  A = \begin{pmatrix}
  S_{11} & S_{12} & 0 & 0 \\
  S_{12} & S_{11} & 0 & 0 \\
  0 & 0 & S_{33} & S_{34} \\
  0 & 0 & -S_{34} & S_{44} \\
  \end{pmatrix}
  \]

- **Relation with the Jones matrix:**
  \[ S_{11} = \frac{1}{2} \left( |S_2|^2 + |S_1|^2 \right), \]
  \[ S_{12} = \frac{1}{2} \left( |S_2|^2 - |S_1|^2 \right), \]
  \[ S_{33} = \text{Re}(S_2^*S_1) \text{ and } S_{34} = \text{Im}(S_2^*S_1) \]

- **Example, Rayleigh scattering:**
  \[
  S(\theta) = \begin{pmatrix}
  \frac{\cos^2 \theta + 1}{2} & \frac{\cos^2 \theta - 1}{2} & 0 & 0 \\
  \frac{\cos^2 \theta - 1}{2} & \frac{\cos^2 \theta + 1}{2} & 0 & 0 \\
  0 & 0 & \cos \theta & 0 \\
  0 & 0 & 0 & \cos \theta \\
  \end{pmatrix}
  \]
Theory
Quantitative polarimetry

Need for Quantitative Polarimetry

The Stokes vector:

- Measurement and unique interpretation of all the polarization parameters is difficult.
- Incomplete information contained in the Stokes vector $S$.
- The individual polarimetry characteristics are ‘lumped’.
- Depends on the incident Stokes vector (non-unique)

- Mueller matrix carries information about the medium and describes the medium’s polarization properties completely.
- Mueller matrix can be decomposed to give the complete polarization characteristics of the medium

Medium polarimetry characteristics

Retardance: Phase shift between two orthogonal polarizations of light: Linear retardance: $\delta$ between $H/V$ and $P/M$. Circular retardance: $\delta_c = 2\psi$ between $L/R$. Optical rotation: $\psi$

Diattenuation: Differential attenuation of orthogonal polarizations for both linear and circular polarization states.

Depolarization: Reduction of the degree of polarization (DOP) of a 100% polarized (DOP=1) while passing through a medium.

$$
S = \begin{bmatrix}
I \\
Q \\
U \\
V
\end{bmatrix} = \begin{bmatrix}
E_x E_x^* + E_y E_y^* \\
E_x E_x^* - E_y E_y^* \\
E_x E_y^* - E_y E_x^* \\
\nu(E_x E_y^* - E_y E_x^*)
\end{bmatrix}
$$

$\nu = I_H + I_V$

$$
= \begin{bmatrix}
I_H + I_V \\
I_H + I_V \\
I_P - I_M \\
I_R - I_L
\end{bmatrix}
$$
**Algorithm**

- Measured Mueller matrix $M$
- Polar Decomposition
  - $M_\Delta$: Depolarization matrix
  - $M_R$: Retardance matrix
  - $M_D$: Diattenuation matrix
- $\Delta_L$, $\Delta_C$, $\Delta$: Linear Circular Net
- $\delta$, $\psi$: Linear Circular
- $d_L$, $d_C$: Linear Circular

Lu an Chipman’s polar decomposition scheme for Mueller matrices

- $M = M_\Delta \cdot M_R \cdot M_D$ is one of the six ways of performing polar decomposition of the Mueller matrices.
- $M_\Delta$: Depolarizing matrix (scattering)
- $M_R$: Retardance matrix (optical activity and birefringence)
- $M_D$: Diattenuation matrix (dichroic absorption)
Theory
Polar decomposition of Mueller Matrix

- Measured Mueller matrix contains all polarization effects.
- Decomposition: $M = M_\Delta \cdot M_R \cdot M_D$
- Extracted polarization parameters:
  - Diattenuation $d = \frac{1}{M_{11}} \sqrt{M_{12}^2 + M_{13}^2 + M_{14}^2}$
  - Net depolarization index: $\Delta = 1 - \frac{|\text{tr}(M_\Delta^{-1})|}{3}$
  - Linear retardance: $\delta = \cos^{-1} \left[ \sqrt{\{M_{(R,22)} + M_{(R,33)}\}^2 + \{M_{(R,32)} + M_{(R,23)}\}^2} - 1 \right]$
    where, $M_{(R,ij)}$ is the $ij^{th}$ element of $M_R$.
  - Optical rotation: $\psi = \tan^{-1} \left[ \frac{M_{R,32} - M_{R,23}}{M_{R,22} + M_{R,33}} \right]$
  - Total retardance: $R = \cos^{-1} \left[ \frac{\text{tr}(M_R)}{2} - 1 \right] = \cos^{-1} \left[ 2 \cos^2(\psi) \cos^2 \left( \frac{\delta}{2} \right) - 1 \right]$

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Methodology

Geometric configuration for nano-rods

- Equal volume sphere radius: \( r \)
  Aspect ratio (\( \varepsilon \)): \( d/l \); Oblate: \( \varepsilon > 1 \) and
  Prolate: \( \varepsilon < 1 \)

- Preferential orientation: Can be observed in single particle imaging: Dark field, confocal, NSOM, PS OCT

- Orthogonal dipolar polarizabilities aligned along the direction of the polarization vectors of scattered light polarized perpendicular and parallel to the scattering plane

- Varying:
  - Aspect ratio (\( \varepsilon \))
  - Orientation angle (\( \beta \))
  - Scattering angle (\( \theta \))
  - Ambient medium refractive index (\( n \))

- Random orientation \( \Rightarrow \) Orientation averaging \( \Rightarrow \) Bulk studies on colloidal suspension.

- Scattering matrix decomposition (preferential and random)
  - Intrinsic polarization properties
  - Diattenuation \( d \)
  - Linear retardance \( \delta \)
  - Depolarization \( \Delta \)

\[ \beta = 0^\circ \quad \beta = 90^\circ \]

Incident beam along \( Z \) direction
Results
Optical properties of silver nano-rods

**Dipolar and Quadrupolar Resonance in Silver Nano-rods**

- **Longitudinal dipolar** at longer wavelengths.
- **Transverse dipolar** → ~400nm-450nm.
- **Transverse quadrupolar** → ~350nm-400nm

**Diattenuation Effects for Preferential Orientation**

- Strong diattenuation effects \(d \sim 0.9\) with distinct spectral characteristics
- \(d \sim 0.33\) for similar dielectric particle
- Magnitude of diattenuation peaks at the dipolar & quadrupolar resonance bands.
- Sharp concavity at the overlap regions of the plasmon bands.
- Gradual increase in \(d\) with increasing \(\varepsilon\).
- No depolarization \(\Delta \sim 0\).

Varying \(\varepsilon\) for equal volume sphere radius of 20nm

Varying \(\varepsilon\) for \(\beta = 90^\circ, \theta = 45^\circ\)

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**Reasons for diattenuation**

- Preferential orientation:
  For the longitudinal and transverse dipolar modes
  \[ |S_2(\theta)|^2 \propto |\alpha_x|^2 \cos^2(\theta) \]
  \[ |S_1(\theta)|^2 \propto |\alpha_y|^2 \]

- Large enhancement at the two resonance bands corresponding to resonances of $|\alpha_x|$ & $|\alpha_y|$ at different wavelengths ⇒ **Strong diattenuation**

- Quadrupolar resonance (350-400nm) ⇒ Transversal ⇒ Confirmation $S_{12}(\lambda)$ ⇒ Differential excitation by orthogonal polarization ⇒ Significant diattenuation at the QP band.

Equal volume sphere radius 20nm, $\varepsilon = 0.65$ for different orientations $\beta$. 

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Retardance $\delta$ effects for preferential orientation

- Very strong linear retardance $\delta(\lambda)$ even in forward scattering angles ($\theta < 90^\circ$)
- Magnitude of $\delta(\lambda)$ peaks around the overlap spectral region of the two dipolar and quadrupolar bands
- $S_{34}, S_{43} = \pm (S_2^* S_1 - S_1^* S_2) \neq 0$
- Non-zero complex value for both $S_2$ & $S_1$ ($S_2 \neq S_1$)

Complex polarizabilities

Longitudinal and the transverse plasmon polarizabilities with inherent phase differences
Results
Orientation effects

- **Diattenuation**: Decreasing $\beta \Rightarrow$
  - Decreasing magnitude of $d$.
  - Relative change in magnitudes at dipolar and quadrupolar resonance bands
    Differential excitation of plasmon modes

- **Retardance**: Decreasing $\beta \Rightarrow$ Decreasing magnitude of $\delta$.

Enhanced depolarization for random orientation

- Magnitude of depolarization $\Delta$ peaks around the overlap spectral region of the two dipolar plasmon bands $\Rightarrow \Delta(\lambda)$

- Incoherent addition of diattenuation retarder Mueller matrices (from preferentially oriented nanoparticles) having random orientation of retardation axes leads to the Mueller matrix corresponding to a pure depolarizer.

$r=20\text{nm}, \theta = 45^\circ$, varying $\varepsilon$
Results
Implications of quantitative Mueller matrix polarimetry

Quantitative differences in intrinsic polarization parameters of non-spherical metal nanoparticles & background tissue (cell) dielectric structures
Polarization as additional contrast mechanism to discriminate against background Rayleigh/Mie scattering with optimal choice of wavelength

Distinct spectral variation of polarization parameters may be exploited for sensing

$r = 20 \text{nm}, \varepsilon = 0.65, \theta = 45^\circ$
High diattenuation figure of merit ($\gamma$) may be exploited for bio-sensing!!!
Potential applications to biosensing

OBSTACLES IN BIO-IMAGING USING LSPR

- Scattered light from tissue microscopic dielectric structures swamps nano-particle signature, limiting the detectability of nano-particles in such media.
- Develop novel schemes to eliminate background Rayleigh/Mie scattering from tissue dielectric structure.

Biomedical applications of LSPR

Quantitative plasmon polarimetry for contrast enhancement in nano-particle based imaging.

LSPR IN BIO-SENSING

- In-vitro & in-vivo diagnosis
- Contrast enhancement in biomedical Imaging
- Ultra sensitive bio-sensing
- Photo-thermal therapy
- Drug delivery

ROLE OF PLASMONIC POLARIMETRY:

- Can be used as a highly sensitive contrast enhancement tool.
- Can used in both imaging and spectroscopy for extraction of functional information from the background Rayleigh like scattering.
- Can be used in both elastic and inelastic spectroscopy of biological samples tagged with nano-particles.

OTHER APPLICATIONS

The geometric dependence of the plasmonic polarimetric characteristics could present such nano-rods as candidates to study spin orbit coupling.

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Conclusions

- Enhanced polarization characteristics of nano-rods like depolarization, retardance and diattenuation as compared to similar sized dielectric particles.
- Sharp and highly media sensitive concavity of diattenuation which can be used as a contrast enhancer in bio-sensing.
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