LOCALIZED SURFACE PLASMON RESONANCE OF COPPER NANOPARTICLES USING FINITE ELEMENT METHOD

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**Recommended Citation**  
DOI: [https://doi.org/10.54729/YVTL7572](https://doi.org/10.54729/YVTL7572)
1. INTRODUCTION

Reducing the size of metallic particle on a scale of a few tens of nanometers leads to strong changes of the physical properties and particularly of its optical properties (Bohren et al. 2008, Sattler et al. 2010). Noble metal nanoparticles have fascinating and unique optical properties (Faraday et al. 1857, Maxwell-Garnett et al. 1904). They are dominated by the Localized Surface Plasmon Resonance (LSPR) in the visible range. LSPR of a nanoparticle is defined as the collective oscillation of electrons in the conduction band due to incident electromagnetic radiation (Kreibig and Vollmer, 2013). In the plasmon resonance condition, the noble metal nanoparticles exhibit a very large enhancement of electromagnetic field at their surface (Halas et al. 2011, Romero et al. 2006). A number of applications based on the LSPR of noble metal nanoparticles have been exploited from molecular fluorescence detection (Ringler et al. 2008, Acimovic et al. 2009), diagnostics (Elghanian et al. 1997, Jain et al. 2008), to Raman scattering measurements (Nie and Emory, 1997).

The extinction cross-section $\sigma_{\text{ext}}$ of Cu nanoparticles can be calculated by analytical expressions developed in the frame of Mie theory, which allows the study of single nanoparticles of spherical or elliptical shapes (Lermé et al. 2008). However, when the nanoparticle loses its symmetry shape, the exact solution of Maxwell’s equations is not possible. One of the frequently used numerical methods for the calculation of the optical response of metallic nanoparticles is the Finite Element Method (FEM) (Noguez et al. 2007, Gonzalez et al. 2005).

In this paper, we report a theoretical analysis on the LSPR of single Cu nanoparticles using FEM simulations. We study the influence of size, shape and dielectric environment on the LSPR spectral characteristics. Further, we design Cu nanostructures composed of nine nanoparticles of 25 nm in diameter and 1 nm interparticle distance having various distributions. The Cu nanoparticles are distributed along x axis or taken the form of sine or cosine functions with different amplitudes. We investigate the effect of disorder of nanoparticles on the extinction cross-section spectrum. The calculations are performed over a broad spectral range from 300 to 900 nm.

2. MIE THEORY AND FINITE ELEMENT METHOD SIMULATIONS

An electromagnetic plane wave is incident to a nanoparticle of dielectric permittivity $\varepsilon$ and magnetic permeability $\mu$ embedded in transparent medium $\varepsilon_{\infty}$. The electromagnetic wave interacts with the free electrons existing in the conduction band of the nanoparticle (Baida et al. 2009). This produces the LSPR phenomenon. To obtain the far-field optical response of nanoparticle, we should determine the solution of Helmholtz equations:

$$
\begin{align*}
\vec{\nabla}^2 \vec{E} + k^2 \vec{E} &= 0 \\
\vec{\nabla}^2 \vec{H} + k^2 \vec{H} &= 0,
\end{align*}
$$

where, the electromagnetic field $\{\vec{E}, \vec{H}\}$ is described by Maxwell’s (Kreibig and Vollmer, 2013) and $k^2 = \varepsilon \mu \omega^2$.

The extinction cross-section $\sigma_{\text{ext}}$ of spherical nanoparticles can be calculated by analytical expressions using Mie theory (Mie, 1908). The important final result is that the extinction, scattering and absorption cross-sections are simply experienced in the form of series:

$$
\begin{align*}
\sigma_{\text{ext}} &= \frac{2\pi}{k^2} \sum_{j=1}^{\infty} (2j + 1) \operatorname{Re} (a_j + b_j) \\
\sigma_{\text{sca}} &= \frac{2\pi}{k^2} \sum_{j=1}^{\infty} (2j + 1) \left| \left| a_j \right|^2 + \left| b_j \right|^2 \right| \\
\sigma_{\text{abs}} &= \sigma_{\text{ext}} - \sigma_{\text{sca}}.
\end{align*}
$$

where, $a_j$ and $b_j$ are the Mie coefficients.
In the case of non-spherical nanoparticles (cube, cylinder, pyramids, star…) (Amendola et al. 2010, Nehl et al. 2006) or assembled nanoparticles (dimer, trimmer… chains) (Marhaba et al. 2009, Billaud et al. 2008 and Sawitowski et al. 2001) or arrays of nanoparticles (Marhaba, 2015), the solution of Maxwell’s equations are determined numerically. Extinction cross section spectra of nanoparticles of arbitrary geometries can be calculated using different methods such as finite difference time domain (FDTD) (Vial et al., 2005), coupled dipole approximation (CDA) (Draine and Flatau, 1994), discrete dipole approximation (DDA) (Draine and Flatau, 2008) and finite element method (FEM). In this paper, FEM is applied to compute numerically the electric field and the optical response of Cu nanoparticles using COMSOL Software for Multiphysics Simulation (Liu et al. 2008) in Radio Frequency Module (Electromagnetic Wave, Frequency Domain). In this paper, the finite element method (FEM) is used to calculate numerically the electric field of the Cu nanostructures. This numerical method, implemented in the frame of Comsol Multiphysics (Fernandes and Kang, 2021), is suitable for computing both far and near-field response. The modelled arrangements are in the form of monomer (spherical or in prolate ellipsoid), and a chain of nanoparticles composing from nine equidistant spheres of different degrees of disorder as will be shown later.

All designed nanostructures are excited by a plane wave using symmetry boundary conditions to truncate computational domain. The incident light intensity of the plane wave is

\[ I_0 = 1 \text{mW/µm}^2 = 10^5 \text{W/cm}^2 \]

This plane wave is travelling in the positive z direction, with longitudinal (\( E_x = E_0 e^{-i k z} e_x \)) or transverse (\( E_y = E_0 e^{-i k z} e_y \)) polarizations. Fig.1.a shows a model of nine Cu spheres of 25 nm diameters and 1 nm interparticle distance distributed as sine function fig.1.a. The optical index of the surrounding environment is 1.33. We apply a perfect matched layer (PML) dedicated to absorb and prevent reflection of the incident fields as shown in fig.1.b. For a given range of wavelengths and polarization of light beam interacting with complex nanostructure, FEM numerical calculations solve Maxwell’s equations on three-dimensional polyhedral meshes (fig.1.c). The method is based on domain decomposition with boundary elements on the surfaces of the polyhedral volume elements (Gracia et al. 2008). The scattering and absorption cross-sections are computed by evaluating the surface and volume integrals according to the following equations:

\[ \sigma_{sc} = \frac{1}{I_0} \int \left( \vec{n} \cdot \vec{S}_{sc} \right) dS , \]

(2.3)

and

\[ \sigma_{abs} = \frac{1}{I_0} \iiint Q dV , \]

(2.4)

where \( I_0 \) is the incident light intensity, \( \vec{n} \) is the normal vector pointing outward from the considered surface element, \( \vec{S}_{sc} \) is the scattered intensity vector and \( Q \) is the power loss density inside the nanoparticle.
The extinction cross-section spectra are calculated as the sum of absorption and scattering cross-sections:
\[ \sigma_{\text{ext}} = \sigma_{\text{sc}} + \sigma_{\text{abs}}, \] (2.5)

For all the calculations presented in this paper, the experimental dielectric function \( \varepsilon = \varepsilon_1 + i\varepsilon_2 \) of Cu is shown in fig.2 taken from Johnson and Christy measurements (Johnson and Christy, 1972). Cu nanoparticles are distinguished from alkali nanoparticles (governed by Drude Model) by the presence of the valence d band energetically close to the conduction sp band, resulting from the hybridization of the s and p bands. The inter-band transitions are obtained from d band to sp band located around 2 eV as shown in the imaginary part of \( \varepsilon \) (fig.2). The transitions induced between two levels of the sp band, located in the visible – infrared regions, are called intra-band transitions, which correspond to LSPRs.

3. RESULTS AND DISCUSSION

The extinction, scattering and absorption cross section spectra of single Cu nanoparticle of diameter 90 nm are shown in fig.3a. The extinction cross section of metal nanoparticle is the sum of absorption and scattering cross-sections (Bohren et al. 2008 and Kreibig et al. 2013). It can be seen that the extinction is dominated by the absorption cross-section. The extinction spectrum shows a spectral peak which corresponds to the LSPR between 550 and 600 nm when the nanoparticle is placed in air (\( \varepsilon_m = 1 \)). The spectra have a plateau below 550 nm, which corresponds to the inter-band transitions. The optical response is practically zero from 750 nm.

![Fig.2: Real part a) and imaginary part b) of the dielectric function of copper. The experimental results of Johnson and Christy (*) are compared to the Drude model (solid lines).](image)

![Fig.3: a) Extinction, absorption and scattering cross section spectra of Cu nanoparticle of diameter 90 nm placed in air and calculated by FEM. b) Extinction cross sections of Cu nanoparticles of different diameters placed in silica and calculated by FEM.](image)
Fig. 3 b) shows the variation of the extinction cross section $\sigma_{\text{ext}}$ as a function of the wavelength $\lambda$ of spherical Cu nanoparticle for different diameters placed in silica SiO$_2$ ($\varepsilon_m = 2.15$). The spectral peaks are attributed to the dipolar mode of LSPR. The increase of the size induces a broadening and red shifting of the resonance due to the increasing influence of the multipolar terms. Regarding the width of LSPR, multiple phenomena will play on its evolution with the size of the particle. For a single Cu nanoparticle, the width of the resonance reflects the life time of the collective excitation. The width is inversely proportional to the life time (Baida et al. 2009). All processes of collisions of the electrons (electron-electron, electron-phonon ...) will limit the lifetime of the plasmon resonance contributing to the dissipation of energy, which decreases the spectral amplitude and broadens the spectral width of LSPR.

![Graph](image)

The extinction cross-section spectrum is very sensitive to the value of $\varepsilon_m$ as shown in fig.4. For a given metallic nanoparticle, the LSPR characteristics can be modified by its environment by means of its dielectric constant $\varepsilon_m$. The extinction cross section of Cu nanoparticle in different environments was calculated using FEM. The spectral position moves to red by increasing $\varepsilon_m$. The redshift of the resonances is correlated to the increase of the dielectric constant of the external environment. For Cu nanoparticle, the redshift is followed by enhancement and broadening of the plasmon resonance.

![Graph](image)

Fig. 4: Extinction cross sections spectra for Cu nanoparticle with a diameter of 90 nm calculated by FEM in different environments: Vacuum ($\varepsilon_m = 1$), silica ($\varepsilon_m = 2.15$) and alumina ($\varepsilon_m = 3.1$).

Fig. 5 illustrates the evolution of LSPR as a function of the shape of the ellipsoid in the case of Cu nanoparticle. The cross sections are calculated using FEM for a prolate ellipsoid whose volume is equivalent to that of a 100 nm nanoparticle embedded in silica. First, due to the anisotropy of the nanoparticle, there are two distinct modes for LSPR on either side of the LSPR position of a sphere of the same volume. The difference between the two cases is more marked by decreasing the aspect ratio $\eta$, as seen in Fig. 5 for $\eta = 0.9$ and 0.5. Indeed, the mode along the major
axis gives a larger cross section because it is equivalent to a larger volume of material probed with respect to a spherical nanoparticle. In the case of the aspect ratio $\eta = 0.5$, it is found that the mode along the minor axis is wider than that along the major axis because the coupling with the inter-band transition becomes stronger.

Fig. 6: Nine equidistant spheres of different degrees of disorder. S1: spheres distributed on x-axis, S2: spheres distributed on sine function of small amplitude, S3: spheres distributed on sine function of average amplitude, S4: spheres distributed on sine function of large amplitude, S5: spheres distributed on cosine function of small amplitude, S6: spheres distributed on cosine function of average amplitude, S7: spheres distributed on cosine function of large amplitude.

Fig. 7: Extinction cross sections spectra calculated using FEM of Cu spheres (S1, S2, S3, S4, S5, S6 and S7) for polarization parallel to y axis. The spheres are of diameter of 25 nm, separation distance $d = 1$nm and embedded in water ($\varepsilon_m = 1.76$).
Fig. 7 shows the extinction cross-section spectra of Cu nanostructures composed of nine nanoparticles of 25 nm in diameter and 1 nm interparticle distance having different distributions for polarization parallel to y axis. These distributions can be outlined by a chain along x-axis (S1), a distribution according to the sine function (S2, S3 and S4) and a distribution according to the cosine function (S5, S6 and S7) as shown in fig. 6. The nanostructures (S2, S3, S4, S5, S6 and S7) are distributed in the xy plane perpendicular to the direction of propagation of the incident plane wave. For nanostructure S1, the peak position of LSPR appears around 570 nm. It should be noted here that the peak position of LSPR is practically independent of the number of nanoparticles when the incident light is polarized perpendicular to the chain axis. It is very close to that of a single nanoparticle as shown in figure 3. In addition, the cross-section magnitude for S1 could be considered as almost (9×) that obtained for a single Cu nanoparticle of diameter 25 nm. As the nanoparticles start to adapt in a sine function, the LSPR spectral features exhibit modifications. First, it is characterized by a slight redshift occurring around 615 nm, 610 nm and 605 nm for S2, S3 and S4 respectively. The minor blue-shifted peak observed in increasing the amplitude of the nanoparticles versus x-axis is certainly due to the partial induction of the overall arrangement caused by this polarization. The analysis for the nanoparticles distribution along cosine function is analogous to sine function where the LSPR peak occurs around 630 nm, 620 nm, and 620 nm for S5, S6 and S7 respectively. It should be mentioned here that for both function distributions (sine and cosine), the LSPR peak is broadened for S2 and S5 compared to S3 and S6 as well as for S4 and S7. The broadening of the LSPR is due to the strong influence of the inter-band transitions and radiative damping. Furthermore, a clear enhancement of the extinction spectrum has been evidenced when increasing the amplitude of the nanoparticles versus x-axis. The enhancement of the electromagnetic field is due to the plasmonic coupling occurring along the nanostructures.

We also calculated the extinction spectra of these Cu nanostructures for polarization parallel to x axis as shown in fig. 8. The behavior of LSPR features in the visible region demonstrates spectacular variations. When the nine nanoparticles of the chain are all arranged along the x-axis (S1), we obtain a much more intense and redshifted resonance than the other nanostructures.
Hence, the LSPR shows enormous emergence for longitudinal electromagnetic wave excitation compared to transverse excitation. The spectrum appears a resonance around 680 nm dedicated to the dipolar resonance mode. This model arises in the infrared region of the spectrum and results from the oscillation of the electron acquiring high spatial confinement in the interparticle spacing. Hence, in the longitudinal excitation, all the produced dipoles oscillate in phase along the interparticle axis. Furthermore, a small second resonance in the extinction cross-section spectrum appears around 500 nm due to the excitation of quadrupolar mode. Accordingly, a chain of nanoparticles linearly distributed has emerged as a simple nanostructure that may be made to generate extremely strong electromagnetic fields. Various parameters can affect the LSPR features such as the diameter D of the nanoparticles, the chain length (number N of nanoparticles in the chain), and the distance d between the nanoparticles. However, by distributing the nanoparticles along a sine function (as shown in fig.6 for S2, S3 and S4), the extinction spectra shown in fig.8 exhibit LSPR intensity smaller than for S1. For various amplitudes in the sine function, small for S2, average for S3 and large for S4, the LSPR occurs around 655 nm, 645 nm, and 625 nm respectively. For S2 the chain stays nearly parallel to the incident light polarization. As the amplitude of the sine function increases (S3 and S4), the dipolar mode of the LSPR blueshifts with decreased intensity. This is due to the reduced surface charge induction between the nanoparticles as the amplitude of the sine function increases. Similar reasoning can be applied to the distribution of the nine Cu nanoparticles along a cosine function (as represented in fig.6 for S5, S6 and S7). For various amplitudes in the cosine function (small S5, average S6 and large amplitude S7), the LSPR occurs around 650 nm, 640 nm, and 625 nm respectively. For S5 the chain stays nearly parallel to the incident light polarization and shows the same optical response as S2. A blue shifting of LSPR occurs by increasing the amplitude of the cosine function (S6 and S7). The polarization induces only part of the overall arrangement (sine and cosine functions from S2 to S7). Further, by increasing the amplitude of the nanoparticles versus x-axis, the extinction spectra intensity gradually decreases due to its strong dependence on the polarization of the incident light towards the nanoparticles arrangements.

4. CONCLUSION
In this paper, we calculated the extinction cross sections of single Cu nanoparticles using FEM. The spectra of the extinction cross-section present a resonance attributed to the collective oscillation of electrons in the conduction band called LSPR. We showed that LSPR spectral profile is very sensitive to the size, shape and environment of the nanoparticles. It is concluded that as the size of the spherical Cu nanoparticle increases, the extinction magnitude enhances whereas the spectral peak position of LSPR is red shifted. Moreover, enhancement of spectral amplitude and red-shifting on the spectral peak position are observed for nanoparticles embedded in high refractive index medium. In the case of elongated Cu nanoparticle (ellipsoid), LSPR characteristics depend on the polarization direction of the incident electromagnetic wave. Further, we have proved that several Cu nanoparticles assembled together composing as chain or taking any other shape (sine and cosine functions) strongly affect the LSPR features. A blue shift and reduction of intensity of the LSPR are observed by changing the arrangements from chain to gradually disorder in sine or cosine structures. All these parameters affecting the LSPR of Cu nanoparticles will certainly induce a large enhancement of electromagnetic field at their surface leading to a wide range of nowadays applications.

REFERENCES


