

Surface Plasmon Resonances of Metal Polyhedral Nanoparticles

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ABSTRACT

The surface plasmon response of metal nanoparticles is studied in terms of their shape. We found that polyhedral nanoparticles composed with less faces show more surface plasmon resonances, where a main resonance with a dipolar character was identified as well as other secondary resonances. It is also found that as the nanoparticle becomes more symmetric, the main resonance is blue-shift.

Keywords: optical properties of metal nanoparticles, surface plasmon resonances

1 Introduction

New synthesis methods have been developed to fabricate nanoparticles (NPs) with specific size and shape that in turn have enabled us to control surface plasmon (SP) properties to reveal new aspects of their underlying science and to tailor them for clearly defined applications. For instance, SPs are now being investigated for their potential in optics, magneto-optic, photonics, as a nanoengineered substrate on which the Surface Enhanced Raman Scattering (SERS) response can be precisely controlled and optimized, and for chemical and biosensing applications, such as optical addressable diagnostic methods, devices, and therapies based on the plasmonic response of metallic NPs [1]. These advances that allow metals to be structured and characterized on the nanometer scale have renewed the interest in SPs by physicists, chemists and materials scientists to biologists.

The interesting observation that NPs support SP resonances that can be tuned by controlling their size and shape, offers a starting point for the emerging plasmonic research field [2]–[4]. The understanding of SP resonances provides a design rule that guides the development of more complex nanostructures with an optical response that we can both predict and experimentally realize. In this article, we give some insights of the SP response as a function of the geometry for NPs of different polyhedral shapes.

2 Formalism

When a particle is excited by an electromagnetic (EM) field, the electrons start to oscillate with the same frequency as the one of the incident EM. The excited charges can transform energy from the incident EM wave into, for example, thermal energy in a so-called absorption process. However, the charges can be also accelerated and they can radiate energy in any direction in a so-called scattering process. The sum of both effects is called the light extinction. For nanoparticles of less than 10 nm, radiation processes are negligible, so the particle only absorbs energy mainly, through the excitation of surface plasmon resonances. Surface plasmons are evanescent electromagnetic waves that propagate along the surface of conductors. By altering the surface, i.e., modifying size, shape, and/or environment of the conductor, the properties of SPs can be tailored. The SP resonances of small particles can be study in terms of the strength of the coupling to the applied field of the optically active electromagnetic surface modes of the system. The location of the resonant frequencies of the proper modes of the system and the calculation of their coupling strength to the applied field are not immediate, because it usually requires taking the non-dissipation limit, a procedure that might call for a vast amount of numerical effort. To study the SP resonance of metal particles with nanometric sizes, we employ the discrete dipole approximation or DDA.

2.1 Discrete dipole approximation

Purcell and Pennypacker developed the discrete dipole approximation (DDA) to model the interaction of light with dust particles in space [5]. The main idea behind DDA is to approach the particle with a finite number of polarizable entities to mimic its optical response to an applied electromagnetic field. DDA is also known as the Purcell-Pennypacker method and along these years has suffered several modifications and improvements to study solid targets with non-spherical shapes. These improvements have been done mainly by Draine and coworkers [6]–[8], who have made available the so-called DDSCAT computational code. In this work, we employed DDSCAT to study the optical response of nanoparticles.

DDSCAT builds up a solid object using an array of N polarizable entities located in a periodic lattice which resembles the shape and size of the particle under study. It assigns to each entity a dipole moment given by

$$\vec{p}_i(\omega) = \overleftarrow{\alpha}_i(\omega) \cdot \vec{E}_{i,\text{loc}}(\omega), \quad (1)$$

where ω is the frequency, $\overleftarrow{\alpha}_i(\omega)$ is the dipolar polarizability of the entity located at \vec{r}_i , and $\vec{E}_{i,\text{loc}}(\omega)$ is the total electric field acting on the i -th dipole, also called the local field. The local field due to an array of point dipoles under an applied electromagnetic field is given by

$$\vec{E}_{i,\text{loc}}(\omega) = \vec{E}_{i,\text{app}}(\omega) + \vec{E}_{i,\text{ind}}(\omega), \quad (2)$$

where $\vec{E}_{i,\text{app}}(\omega)$ is the applied field, and $\vec{E}_{i,\text{ind}}(\omega)$ is the induced field acting on the i -th entity due to the radiation of all the others $N - 1$ dipoles which compose the nanoparticle. Therefore, a system of $3N$ complex coupled equations is obtained, from where we can calculate the set of dipole moments that mimic the optical response of the particle [2], [4]. Once we know each $\vec{p}_i(\omega)$, then it is possible to obtain the light extinction and absorption cross sections using the following expressions [5]:

$$C_{\text{ext}} = \frac{4\pi k}{|\vec{E}_0|^2} \sum_{j=1}^N \text{Im}\{\vec{E}_{j,\text{inc}} \cdot \vec{p}_j^*\}, \quad (3)$$

$$C_{\text{abs}} = \frac{4\pi k}{|\vec{E}_0|^2} \sum_{j=1}^N \left\{ \text{Im}[\vec{p}_j \cdot (\alpha_j^{-1})^* \vec{p}_j^*] - \frac{2}{3} k^3 |\vec{p}_j|^2 \right\}, \quad (4)$$

where $(*)$ means complex conjugate, k is the magnitude of the wave vector of the incident light of frequency ω , and E_0 its amplitude. By definition, the scattering cross section C_{sca} is found as the difference between extinction and absorption cross sections,

$$C_{\text{sca}} = C_{\text{ext}} - C_{\text{abs}}. \quad (5)$$

The periodic lattice employed by DDSCAT is a cubic array of dipoles, each one with a polarizability given by the Lattice Dispersion Relation (LDR) [7]. We assume that the polarizability is isotropic and is the same for all the entities, i. e., $\overleftarrow{\alpha}_i(\omega) = \alpha^{\text{LDR}}(\omega)$, where

$$\alpha^{\text{LDR}}(\omega) = \frac{\alpha^{\text{CM}}(\omega)}{1 + \alpha^{\text{CM}}(\omega) [b_1 + b_2\epsilon + b_3 S\epsilon(\omega)] (k^2/d)}. \quad (6)$$

Here, $\epsilon(\omega)$ is the bulk dielectric function of the particle; S , b_1 , b_2 , and b_3 are coefficients of the expansion to a third order in k to incorporate radiation effects, and $\alpha^{\text{CM}}(\omega)$ is the polarizability given by the well known Clausius-Mossotti relation:

$$\epsilon(\omega) - 1 = \frac{4\pi n \alpha^{\text{CM}}(\omega)}{1 - 4\pi n \alpha^{\text{CM}}(\omega)/3}. \quad (7)$$

In general, the bulk dielectric function has contributions from *interband* (inter) and *intraband* (intra) electron transitions, such that,

$$\epsilon(\omega)_{\text{bulk}} = \epsilon_{\text{inter}}(\omega) + \epsilon_{\text{intra}}(\omega). \quad (8)$$

The *intraband* transitions can be described by the Drude model of electrons:

$$\epsilon_{\text{intra}}(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i/\tau)}, \quad (9)$$

where ω_p is the plasma frequency and $1/\tau$ is a dissipative term due to dispersion effects suffer by the electrons in the material. On the other hand, *interband* contribution comes from transitions among electronic bands of different index, such that, they usually are in the UV region and do not contribute to the SP resonances [2], [3].

Here, we are interested in nanoparticles whose sizes are smaller than 10 nm, such that, physical phenomena associate to radiation effects, like scattering and radiation damping, are negligible ($C_{\text{sca}} \approx 0$) [3]. However, we have to consider that conduction electrons suffer an additional damping effect due to surface dispersion or finite size effects. The surface dispersion effects depend on the particle's size and shape. Here, we consider the surface dispersion of a sphere of radius a , such that the dielectric function also depends with a as [9]:

$$\epsilon(\omega, a) = \epsilon_{\text{bulk}} - \epsilon_{\text{intra}} + \left\{ 1 - \frac{\omega_p^2}{\omega(\omega + i/\tau + i/\tau_a)} \right\}, \quad (10)$$

where $1/\tau_a$ is the surface damping term given by $1/\tau_a = v_f/4a$, with v_f the Fermi velocity of the electron cloud. In this work, we use the values of ω_p and v_f found by Kreibig for silver nanoparticles of less than 10 nm [9]. As smaller is the particle, the surface dispersion becomes more important. However, the surface dispersion does not change the location of the surface plasmons significantly, but as the particle becomes smaller, the resonance is less pronounced and broadening [3].

3 Optical properties

We calculate the extinction efficiency of silver different polyhedral NPs of 10 nm suspended in vacuum. The extinction efficiency per unit area, A , is defined as

$$Q_{\text{ext}} = \frac{C_{\text{ext}}}{A}. \quad (11)$$

To understand the shape influence on the SP resonances, we start by studying the extinction efficiency of cubic particles and comparing it with those obtained for different truncated cubes and the sphere. The truncated cubes are obtained by symmetrically cutting the eight corners of the cube by $l \times r$, where l is the length of

the cube's side and $0 < r \leq 1/2$. We label the different truncations with respect to the length l of the cube, with the number r . When $r = 1/2$ a cuboctahedron is obtained. All the truncated cubes, are composed by six octagons and eight triangles, while the cuboctahedron is composed by six planar squares and eight triangles. Finally, if we performed a symmetric truncation of the cube with an infinite number of planes, one arrives to the sphere, as shown in Fig. 1.

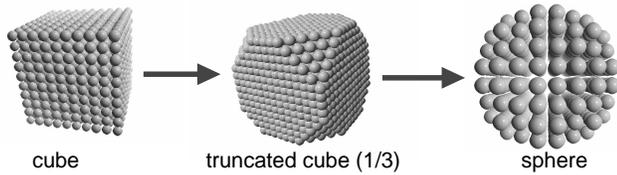


Figure 1: Cube, truncated cube and sphere.

In Fig. 2, we show the extinction efficiencies of a cube, different truncated cubes and a sphere. In all cases, the spectra were calculated within DDA using more than 10^5 dipoles to assure convergence. The structure below 335 nm is the same for all the particles, independently of their geometry. This is because the main absorption mechanism are the *interband* electron transitions which are independent of the shape of the particle, and only depend on the bulk electronic properties of silver.

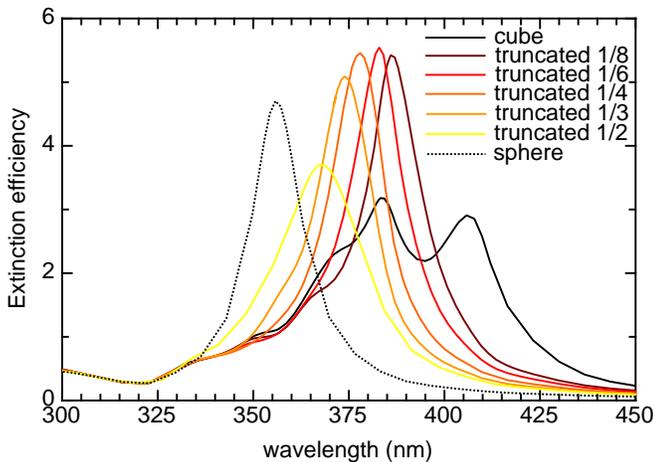


Figure 2: Extinction efficiency of different polyhedral nanoparticles.

Between 335 and 450 nm the spectra are sensitive to the NP's shape. In Fig. 2, the spectrum for the cubic NP shows a rich structure of peaks, contrary to the case of the sphere with a single resonance. These peaks are associated to the SP resonances inherent to the cubic geometry [10], because in this case, the charges can arrange in many different ways, while for the sphere

a single homogeneous arrangement given by a dipolar charge distribution is observed. For the cubic NP, at least five different modes are obtained, being the dipolar and quadrupolar charge distributions the ones that contribute more to the extinction, and are located at 406 nm and 383 nm, respectively. Also, there are more SP resonances at smaller wave lengths (< 370 nm) which make wide the energy range of the response spectrum. Now, with a small truncation of $r = 1/8$, the dipolar resonance becomes the more important one and moves to smaller wave lengths. The location of the dipolar and quadrupolar resonances are now very close and now, only one wider peak is observed around 386 nm, while the structure below 370 nm remains almost identically.

From Fig. 2, we observe that as the length-size of the truncation increases:

- (i) the main resonance is always blue shift,
- (ii) the peaks at smaller wave length are closer to the dominant resonance, such that, they are hidden, and
- (iii) the width of the main resonance increases.

For example, the full width at the half maximum (FWHM) of the $1/8$ truncated cube is about 20 nm, while the one for the cuboctahedron is 40 nm. This means that the secondary resonances do not disappear but they are hidden by the dominant resonance. For comparison, we have included the spectrum of a silver nanosphere of 10 nm of diameter. In this case, the sphere shows a single SP resonance located at 356 nm and shows a FWHM of 20 nm. Remember that the sphere has only one resonance. Therefore, as the number of faces increases the energy range of the spectrum becomes smaller.

3.1 Surface plasmon resonances

We have already mention that the location of the resonant frequencies of the proper modes of the system are not immediate, because it requires taking the non-dissipation limit. Here, to find the location of each one of the SP resonances of each particle, we have considered that the constants τ and τ_a in Eq. (10) tend to ∞ .

In table I, we show the positions of the main resonances of the cube, the different truncated cubes (t.c.) and the sphere. The cube shows five visible resonances from 338 to 406 nm. With a small truncation of the cube ($r = 1/8$), the main resonance is blue shift about 20 nm to be now at 386 nm. In this case, only four resonances are visible. When the size of the truncation increases the number of resonances reduces to two, and the main resonance is always blue shift, but it never reaches the position of the single resonance belonging to the sphere. We also find that as the number of faces

Table 1: Location of SP resonances of silver NPs. The main resonance is in bold face.

Shape	# faces	main SP (nm)	SP 2(nm)	SP 3(nm)	SP 4(nm)	SP 5(nm)
cube	6	406	383	373	353	338
t. c. (1/8)	14	386	365	350	336	
t. c. (1/6)	14	383	349	336		
t. c. (1/4)	14	378	336			
t. c. (1/3)	14	374	336			
t. c. (1/2)	14	369	335			
sphere	∞	356				

of the NP increases, the number of visible resonances decreases.

It is known that metal nanoparticles of few nanometers show different structural motifs depending on their size, composition and energetic conditions. [11], [12] Therefore, one might suppose that if one is able to control the size of nanoparticles, it would be also possible to manipulate their shape, and then their SP resonances. This has been demonstrated recently, where the NP's shape of a silver colloidal suspension with small dispersion of size distribution was elucidated evaluating its SP resonances [4].

4 Conclusions

The location of the surface plasmon resonances of silver nanoparticles of different cubic shapes was obtained. It is found that as the size truncation of the cubic nanoparticle becomes larger, the main resonance is blue shift, and hides the secondary resonances, increasing its full width at half maximum. It is also found that nanoparticles with less faces show resonances in a wider range of wave lengths. These results provide theoretical support for the behavior of the surface plasmon resonances as a function of their shape. It is expected that this information would be useful to motivate the development of more complex nanostructures with tunable surface plasmon resonances.

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