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THE SURFACE PLASMON RESONANCE IN NANOPARTICLES OF ARBITRARY SHAPE

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In this paper, an optical properties of metal nanoparticles of arbitrary shapes were investigated. The effect of size and shape of the silver nanoparticles are studied by computational discrete-dipole approximation methods. The obtained results show that nanoparticle interaction results in the distinct collective modes. The spectral positions of the modes are analyzed as a function of the face numbers of the shape. It was found that the number of spectral bands decreases with the growth of the number of faces of nanoparticle, which can be described within the plasmon hybridization model. We have used the Blender suite to create and voxelize nanoparticles with different shapes and sizes.

Keywords: surface plasmon resonance, discrete dipole approximation, voxelization, polyhedron.

Metal nanoparticles and their composites have been attracting a great attention due to their size and shape dependent optical properties. The optical properties such as bright intense colors, are the result of interaction of free carriers in metals with the incident electric field. In the presence of the oscillating electromagnetic field of the light, the free electrons of the metal nanoparticle undergo a collective coherent oscillation with respect to the positive metallic lattice[1] and the resonance occures at a particular frequency of the light. This process is called the localized surface plasmon resonance (LSPR) oscillation.

The frequency, strength, and quality of the LSPR depends on the size, geometry, the metal composition of metal nanoparticles, and the refractive index of the local environment. Furthermore, the LSPR of a metal nanoparticle is sensitive to the presence of other nearby metal nanoparticles, their sizes, interparticle distance and material.

The optical response of metal nanoparticles can be tuned by controlling their size, shape, and environment, providing a starting point for emerging research fields like surface plasmon-based photonics or plasmonics[2]. On the other hand, new synthesis methods developed to fabricate nanoparticles with a specific size and shape enable us to tailor surface plasmon properties for clearly defined applications.

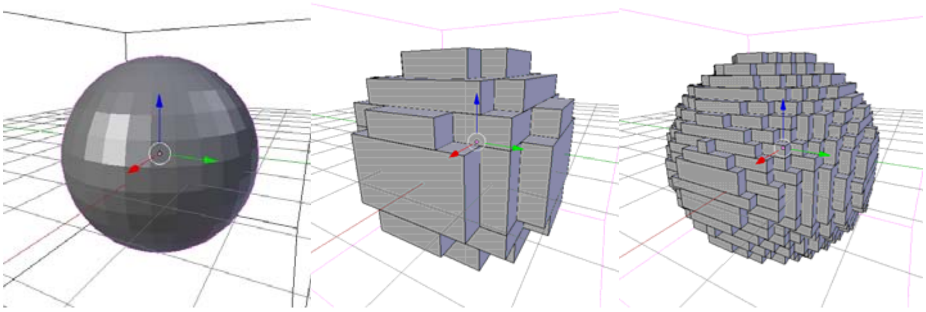
In recent years, the influence of the geometry on the optical properties of metal nanoparticles has been an active research field. In the real experiments we deal with nanocomposites with the nanoparticles of the irregular shape, different from sphere. A few analytical solutions are known for very simple geometrical shapes as spheres, cylinders or ellipsoids [3]. As long as the interest typically lies in nanoparticles with complex, arbitrary shapes, or interacting particles, a numerical approach is usually needed [4].

The discrete dipole approximation DDA provides an easy way to analyze the effects of the size and geometry on the SPR absorption, scattering and total extinction. Once the target is converted to a collection of dipoles, the scattering problem can be solved exactly for each dipole. Several studies have shown that the main optical features depend on geometry and size, and the optical response of spherical, spheroidal, cubic, and other geometrical shapes, like rods and triangular prisms, are now well identified. El-Sayed and co-workers adopted DDA and studied the optical properties of gold nanorods in different hydrodynamic size [5].

This paper studies the influence of the nanoparticles shape morphology on the surface plasmon resonances, that shows up in the extinction spectra. The spectra of the 3-dimentional silver nanoparticles that consist of the set of uniform dipoles were analyzed. The optical response was investigated for regular polyhedrons, such as tetrahedron, cube, octahedron, dodecahedron and the sphere. The changes of spectra are investigated to depend on the number of faces of the polyhedron nanoparticle.

Mesh generation. Mesh generation is an important pre-processing step for computational electromagnetics methods, such as the discrete dipole approximation method. Due to the difficulty of solving differential equations for complex geometries analytically, meshes are used to create discrete representations of complex physical objects and environments.

Mesh generation[6] refers to the process of discretizing a space into a set of smaller elements. The space is usually defined as the surface boundary that can be filled with solid units, in the simplest case pixels for two-dimensional space or voxels when the space is three-dimensional. Voxel is the smallest box-shaped unit of volume supplied with numerical values, such as a type of material, optical constants, void space, etc. A connected set of voxels of the same type represents a physical object.



(a) (b) (c)

Fig. 1. The voxel mesh generated for 6 nm radius sphere (a) with resolution (b) 0.7 nm per voxel side and (c) 0.3 nm per voxel side.

We have used the Blender suite [7] to create and voxelize nanoparticles with different shapes and sizes. The Blender suite is the software package that consists of several tools that is integrated together to perform mesh generation. The main tool is Blender - a free open-source tool and provides the GUI extensibility through add-ons written in Python programming language. The Remesh modifier and BlenderFDS plugin are used to generate voxel-based meshes and set material properties to the voxels.

The Blender suite meet the requirements for complex geometries simulation: to have a rich graphical user interface (GUI) to compose 3D complex objects; to generate mesh based on surface description of objects; to set material properties to the voxels; to change mesh resolution (size of voxels); to visualize and verify the generated mesh; to export generated mesh into a file.

The discrete dipole approximation. We use the discrete dipole approximation (DDA) method to calculate the optical response for the silver nanoparticles of irregular shape. Extinction cross sections are calculated from the resulting polarizations of DDA method, using the solving package "EMSimulation"[8]. The dielectric function of silver nanoparticles is taken as a bulk silver from the Johnson and Christy table[9].

The DDA was proposed in 1973 by Purcell and Pennypacker [10], who used it to study interstellar dust grains. The method consists of approximating the target by an array of dipoles, at each dipole location the polarizabilities are assigned based on the physical properties of the target (e.g., the silver). The extinction spectra can be found based on the polarizabilities of each dipole and an incident radiation field.

Consider a particle of volume V , represented by an array of N discrete dipoles located on a cubic lattice. For the discrete dipole model to provide a good approximation it is necessary for N to be large enough that the boundary of the cubic array satisfactorily approximate the desired shape.

The dipole polarizabilities a_i can be given by the Clausius-Mosotti polarizability [11]:

$$a_i = \frac{3d^3}{4\pi} \frac{\varepsilon_i^2 + 1}{\varepsilon_i^2 + 2}, \tag{1}$$

where d is the size of the cubic lattice of the dipole and the ε_i is complex dielectric function of the dipole medium .

The DDA method allows to get an oscillating dipole moments P_j for every monochromatic incident wave; from these P_j the absorption and scattering cross sections are computed[12,13]:

$$C_{ext} = \frac{4\pi k}{\left|E_0\right|^2} \sum_{j=1}^{N} \mathrm{Im}(E_{inc,j}^* \cdot P_j), \tag{2}$$

$$C_{abs} = \frac{4\pi k}{\left|E_0\right|^2} \sum_{j=1}^{N} \left\{ \mathrm{Im}(P_j \cdot (\alpha_j^{-1})^* P_j^*) - \frac{2}{3} k^3 \left|P_j\right|^2 \right\}. \tag{3}$$

To compare cross sections of dipoles with different radiuses, we use effective cross sections, which are calculated as

$$Q_{ext} = C_{ext} / A \tag{4}$$

$$Q_{abs} = C_{abs} / A \tag{5}$$

where A is the area of overlap between the incident beam and the target object.

We use the fast-fourier transform (FFT) techniques together with the conjugate gradient method to obtain solutions for targets.

Results and Discussion. We calculated the effective cross section extinction of the bulk sphere object, that contains only one dipole of 6 nm radius, and compared with the spectra of the voxelized sphere that consist of the several dipoles of radius 0.5 nm, that stands in the mesh node (fig. 2).

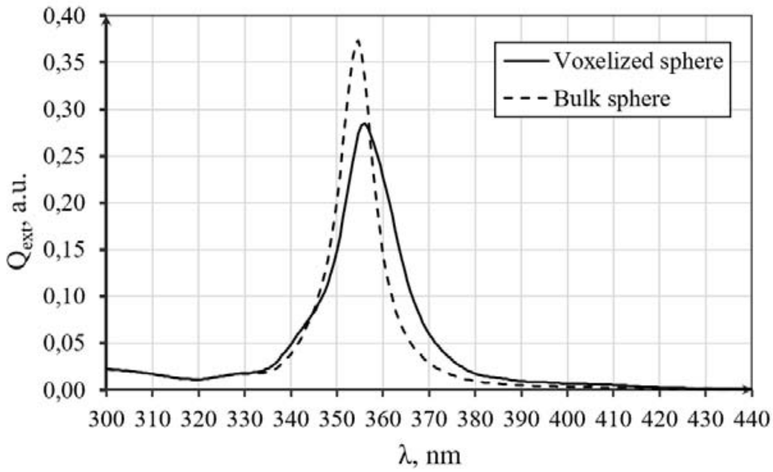
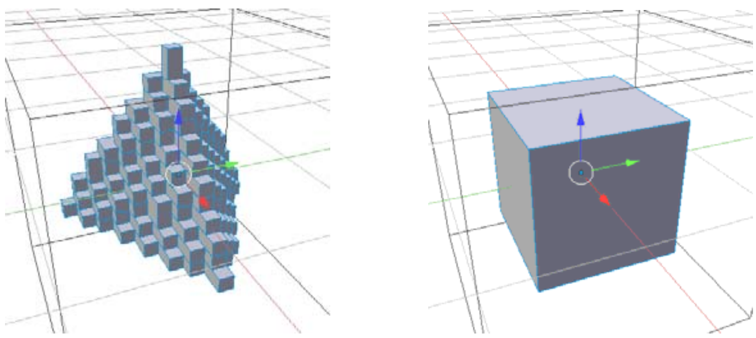


Fig. 2. Comparison of the effective cross section extinction spectra of the voxelized and bulk sphere.

The spectra show the long-wave shift of the voxelized sphere, but the bulk sphere extinction intensity is bigger. This behaviour can be explained by the phenomenon of molecular hybridization that appears in the electromagnetic coupling of the plasmon resonance between multiple dipoles inside the nanoparticle. Also voxelized sphere spectrum has the additional peaks, that can correspond to the high order modes resonances.

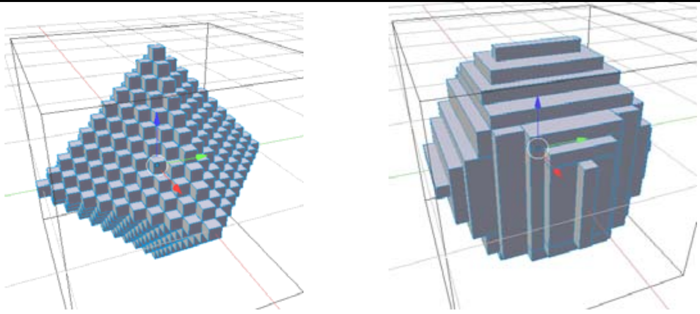
We have discretized and calculated the effective cross section extinction for the regular polyhedron objects: the tetrahedron, the cube, the octahedron and the dodecahedron, and compared the spectra with the sphere.



(a) (b)

Fig. 3. The voxelized representation of regular polyhedrons: (a) tetrahedron, (b) cube.

All polyhedrons have the same volume, which corresponds to the volume of the sphere with the radius of 6 nm.



(a) (b)

Fig. 4. The voxelized representation of regular polyhedrons: (a) octahedron, (b) dodecahedron.

The fig. 5 shows the effective extinction spectra of the figures with comparison to the sphere. We can observe the additional peaks at the tetrahedron and the cube that shows the plasmon modes resonances. Also the peak splits into several mode bands and those bands shift into the long-wave and short-wave regions around the sphere maximum respectively as the object has less faces.

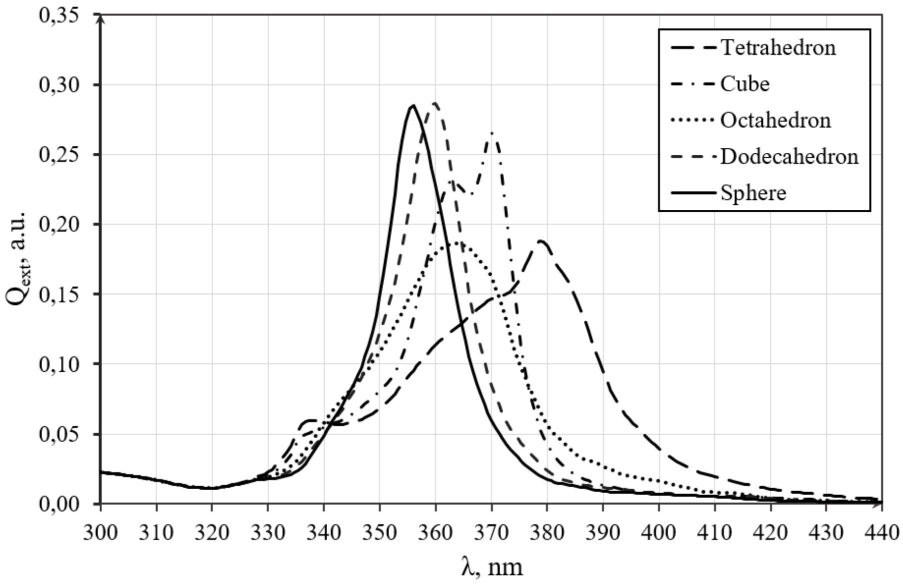


Fig. 5. The effective cross section extinction of the regular polyhedrons
and the sphere of the same volume.

As the number of faces increases, objects become more sphere-like. Despite the approximation error and the stair-case effect that shows up after the voxelization, we can observe the short-wave shift of the peaks when we increase the number of faces in the polyhedron. This effect is seen when compare the dodecahedron and the sphere objects, where the band split is missing, extinction intensity is the same, but the band shift is still observed.

Conclusions: In summary, the optical properties of plasmon resonant metal nanocomposites were investigated. Plasmon resonances are numerically evaluated in the silver nanoparticles with different sizes and shapes embedded in a vacuum. We have shown that the shape of the nanoparticle can lead to hybridization, splitting, and shifting of the plasmon energies, as well as the quadrupolar resonances formed by the interaction between the plasmons.

For polyhedral nanoparticles, the surface plasmon resonances have been studied as a function of the number of faces. The polyhedral nanoparticles composed with less faces show more spectral bands, and as the nanoparticle becomes more sphere-like, the main surface plasmon resonance is blue-shifted.

The Blender suite and the discrete dipole approximation method were used to calculate optical spectra of silver nanoparticles of different shapes. The obtained results can be used for analyzing the real nanocomposites and creating the nanomaterials with special properties.

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ПОВЕРХНЕВИЙ ПЛАЗМОННИЙ РЕЗОНАНС У НАНОЧАСТИНКАХ ДОВІЛЬНОЇ ФОРМИ

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В даній роботі було досліджено оптичні властивості металевих наночастинок довільної форми. Вплив розміру та форми наночастинок срібла вивчено з допомогою обчислень методом дискретних диполів. Отримані результати показують, що взаємодія наночастинок приводить до появи мод. Проаналізовано залежність спектральних позицій мод від кількості граней наночастинки. Було встановлено, що число спектральних смуг зменшується з ростом числа граней наночастинки, це може бути описано в рамках моделі плазмонної гібридизації. Ми використовували пакет Blender для створення і вокселізації наночастинок різних рормірів та форми.

Ключові слова: поверхневий плазмонний резонанс, метод дискретних диполів, вокселізація, многогранник.