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Simulation and characterization of the bulk refractive index sensitivity of coupled plasmonic nanostructures with the enhancement factor

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ABSTRACT

The bulk refractive index (RI) sensitivity of coupled plasmonic nanostructures, namely gold and silver nanospheres and nanocubes in two-particle (dimer) arrangements, were simulated with the MNPBEM Matlab toolbox. The size of the nanoparticles (10–90 nm) and their separation distance were the running parameters. The enhancement factor (which characterizes the increased RI sensitivity of multi-particle arrangements compared to single particles) was introduced and used to evaluate the effect of particle coupling on the bulk RI sensitivity of the dimer arrangements. The enhancement factor is an exponential function of (D/D_0), where D is the separation between the particles and D_0 is the diameter of the spheres or the edge length of the cubes, and it was found that significant plasmonic coupling effects (e.g. EF > 1.5) starts below 0.5-0.3 D/D_0 for the investigated dimers, depending on their size. It was also found for the four investigated dimer arrangements (gold/silver nanospheres/nanocubes) that the absolute peak shift and the enhancement factor values are inversely proportional: the dimers which have a larger absolute extinction peak shift (at the same particle separation) have smaller relative enhancement compared to single particles.

1. Introduction

Surface plasmon polaritons (SPPs) are the collective oscillation of delocalized electrons at a metallic surface in response to an external electric field (light). In a classical SPR refractive index sensing measurement setup usually a thin film of metal is used. To incite plasmons in metallic thin films special illumination conditions have to be met, so usually a reflective optical setup with a prism and other additional optics is utilized (often referred to as Kretschmann or Otto configuration) [1]. Since their first application for sensing purposes in the early 80s [2], surface plasmon resonance (SPR) based instruments became one of the most widely used tools of our time for the label-free characterization of biomolecular interactions [3].

It the case of the so called localized surface plasmon resonance (LSPR), the conduction electrons of small metallic nanoparticles are excited with the incoming light, which incited plasmons are localized on the nanoparticle. The biggest difference between LSPR and classic SPR is that localized surface plasmon resonance on nanoparticles is more easily excitable, the problem of coupling the light into a thin film with suitable optics (e.g. prism) can be eliminated, and much simpler and more convenient measurement configurations can be used [4].

The refractive index sensitivity of localized surface plasmon resonance based sensors is depending on several parameters, including the material type, size and shape of the particle and also the spatial arrangement of multi-particle systems. In a review Tu et al. [5] collected the reported LSPR bulk refractive index sensitivity values for various realized nanostructures. Although the reported bulk refractive index sensitivity values have high variation (from 71 nm/RIU for gold nanospheres to 1933 nm/RIU for gold nanocages) and also, they are currently below the equivalent bulk refractive index sensitivity of classical thin film based SPR setups (can be above 3300 nm/RIU), it was already proven that with the proper nanostructures in the proper arrangement the so called molecular sensitivity of LSPR (considering molecular or biosensing applications) can reach the sensitivity of classic Kretschmann-configuration based SPR devices on the market [4,6,7].

Considering possible applications, the optimization of these critical parameters (nanoparticle size, shape and arrangement) is required and a suitable fabrication technology should be selected to produce the nanoparticle arrangements as sensor elements. One of the most important parameters of the listed is the separation distance between the particles. It was shown, both theoretically and experimentally, that reducing the distance between nanoparticles leads to increased refractive index sensitivity due to the coupled plasmon resonance between the particles [8–10,20–27]. The group of El-Sayed demonstrated

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in a series of works [20–23] that this interparticle coupling follows a universal exponential rule (depending on the interparticle distance) which was used as a plasmon ruler with biomolecules [20]. The effects of particle distance and orientation were further studied for metallic nanoshells [21] nanocubes [22,23] and others structures (e.g. ellipsoids, cylinders, bars [24], or core-shell structures [27]) as well. A common point in previous works is that for the characterization of these phenomena their either use the measured/simulated bulk refractive index sensitivity (S, [nm/RIU]), of nanoparticle arrangements [10,21,22,24,26–28], or the measured/simulated relative red shift of the absorbance spectrum (usually marked as $\Delta\lambda/\lambda_0$, where λ_0 is the absorbance peak of a single particle) to characterize the effect of interparticle separation [8,16,20,23,26,29]. Since these effects (refractive index sensitivity and particle arrangement, including separation) and are not independent, a parameter which incorporates both would be more beneficial to support the convenient design of nanoparticle arrangements for plasmonic sensors.

In our work we aim to investigate the plasmonic coupling effect between simple two-particle dimer structures – created from gold and silver nanospheres and nanocubes – by using boundary element simulation method, and focusing on the enhanced refractive index sensing capability of particle arrangements, considering sensor applications. For this purpose a new parameter called enhancement factor is calculated, which characterize both the refractive index sensitivity and the dependence of particle separation in the same time. The definition of this parameter and the benefit of using it compared to the conventional characterization methods is discussed in detail in Section 3.1. The results and conclusions of the simulations are good means for the design and optimization of the parameters of nanoparticle fabrication technologies, to increase the sensitivity and performance of LSPR based sensors.

2. Modeling and simulation parameters

For the modeling and simulation of the nanoparticle arrangements the MNPBEM Matlab Toolbox was used, which utilizes the boundary element method (BEM) approach, and provides a convenient way for the simulation of coupled plasmonic nanostructures [11]. Besides the advantageous short running times compared to other finite element methods, it also enables the relatively simple inclusion of substrates in the model [12].

The investigated nanosphere and nanocube arrangements were created with the 'trisphere' and 'tricube' functions, respectively, and are illustrated in Fig. 1. The running parameters were the particle diameter (for nanospheres) or the length of the nanocubes' edge (both marked with D_0 for the sake of further generalization) and the distance between the particles (D).

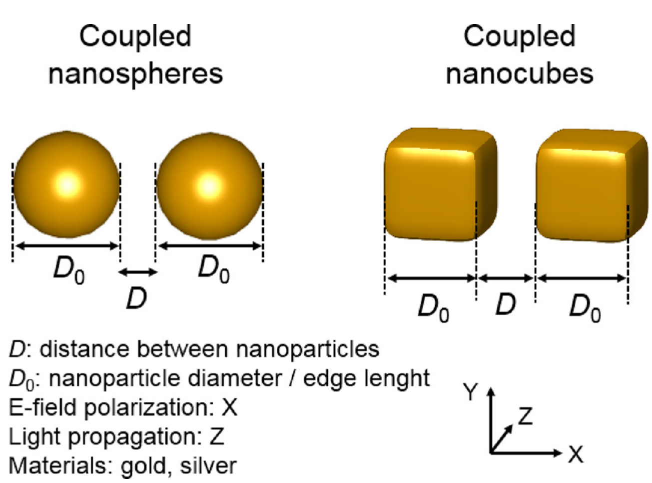

Fig. 1. Illustration of the investigated nanoparticle arrangements. The rendered particles were exported from the MNPBEM Toolbox.

To optimize the running speed of the simulations 256 vertices were used for nanosphere generation, while the grid density of the nanocubes was 9 division per edge (which corresponds to 486 surface vertices). Increasing the resolution of the model (number of vertices) did not cause any significant changes in the simulation results (based on the performed comparisons with 900 vertices for spheres and 864 vertices for cubes). A plane wave excitation was used with light propagation in the Z and light polarization in the X directions (see Fig. 1).

The absolute plasmonic peak shifts, bulk refractive index sensitivities and enhancement factors (which are defined in Section 3.1 in detail) were calculated from the normalized extinction spectra of the simulations. For varying refractive index simulations the medium surrounding the nanoparticles was changed between air (n = 1) and water (n = 1.33).

It has to be noted, that depending on the size, shape, particle separation, dielectric medium and material properties of the nanoparticles their extinction cross-section spectra could consist of multiple peaks, which correspond to higher mode plasmon peaks, also called multipole peaks (diploe, quadrupole, octupole, etc.). In our work we only focus on the dipole (first mode) plasmon peak and its sensitivity from the dielectric properties of the medium. The appearance, and interactions of higher order peaks is not in our scope, thus only smaller particle diameters ($D_0 < 90$ nm) are investigated, where their effect is not dominant.

Dielectric functions with tabulated values are available in the toolbox for the plasmonic simulation of both gold and silver particles, based on the optical constants of Johnson and Palik, respectively. Considering gold nanoparticles, although the peak shift (between air and water) obtained with the two different sets of constants are nearly the same, the Palik dielectric function yielded systematically shorter peak wavelengths (compared to the Johnson function and also compared to experimental data measured on colloidal gold nanoparticles). Taking these observations into consideration, the Johnson dielectric function was used for further calculations for both the gold and silver particles.

The solver of the MNPBEM Matlab Toolbox offers two simulation approaches for the investigation of the nanoparticle arrangements. For our investigations we used the 'retarded simulation', which solves the full Maxwell equations on the arrangement and thus could be considered more precise compared to the 'quasistatic' approach. Although the MNPBEM Toolbox enables the use of substrates under the nanoparticles, in this current work we did not utilized this possibility.

3. Results and discussion

3.1. The enhancement factor of nanoparticle arrangements

For the evaluation of the plasmonic behavior of the particle – in function of both the interparticle gap and the refractive index – two methods are generally used in the literature. The extinction cross sections are either used to calculate the bulk refractive index sensitivity (S, [nm/RIU]), which characterize the dependence on the refractive index, or a dimensionless number ($\Delta\lambda/\lambda_0$) to characterize the effect of interparticle distance. This latter is defined as the relative shift of the absorption wavelength ($\Delta\lambda$) of a dimer at an interparticle gap of D, compared to the absorption wavelength of a single particle (λ_0) (with the same size and in fixed medium), as in Eq. (1). $\Delta\lambda/\lambda_0$ is usually plotted in function of the particle gap (D) or even more commonly in function of the dimensionless D/D_0, as in [16,20,23,26,28].

$$\frac{\Delta\lambda}{\lambda_0} = \frac{\lambda_D - \lambda_0}{\lambda_0} \tag{1}$$

The bulk refractive index sensitivity (S) of a single particle is defined as the shift of the extinction peak per unit change in the refractive