Plasmonic Properties of Bimetal Nanoshell Cylinders and Spheres

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Abstract: Plasmonics is a new branch of the fascinating field of photonics and develops concepts to quench light beyond the diffraction limit and enhance electromagnetic fields. These enhancements occur in metals as localized surface plasmon polaritons (LSP) a coupling of the the surface density oscillations of the electron gas to the incident light. With three-dimensional nanostructures of coinage metals that are brought in intimate contact with analytes of interest such as molecules one can utilize the locally enhanced electromagnetic field to excite characteristic vibrational modes. This enhanced Raman effect (surface enhanced Raman scattering - SERS) gives the possibility to create spectroscopic vehicles which can act as highly sensitive molecular detector using Raman signals as a fingerprint of the analyte. The effectivity of the metal nanostructures for local field enhancement strongly depends on the geometry of the nano-particle and its orientation with respect to the incident exciting laser light.

Keywords: localized surface plasmon, Mie theory, core shell particles, SERS, dimer

1 Introduction

For optimizing our experimentally designed LSP-active surfaces and tips we study finite element (FE) model systems of bimetallic cylinder dimers and nanoshell dimers. This approach allows for reduction of our complex and strongly silicon-influenced nano systems down to the elementary plasmonic acting components (figure 1).
The dimer structures ensure the existence of a so-called hot spot, where the local electric field enhancement reaches its maximum. The hot spot is located in-between the dimer junction and is caused by the coupling of the two particle's plasmon modes. Due to this interaction significantly higher field values compared to single plasmonic particles are reached which are most likely responsible for the exceedingly strong Raman enhancements observed in experiments on collodial silver [3] . Since the main contribution of the observed Raman signal enhancement seems to be electromagnetic, the field enhancement factor reachable in dimer's hot spot provides a well-founded basis for the estimation of expected Raman intensity enhancements. As a rule of thumb the fourth power of the local electric field enhancement $\alpha = E_{peak}/E_{inc}$ yields an estimation of the Raman intensity enhancement factor.

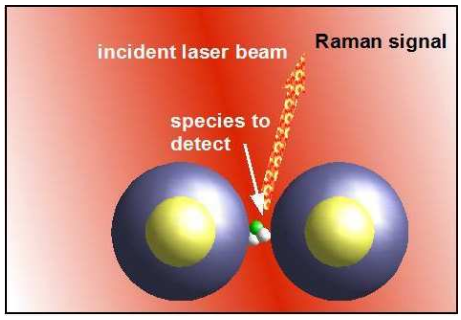

Fig. 1: Principle of molecule detection using the surface enhanced Raman scattering enabled in the hot spot of a plasmonic acting dimer nanostructure.

2 Theory

Scattering processes of electromagnetic waves involving particles are ruled by the macroscopic Maxwell's equations from which a wave equation for the fields can be derived. Under the assumption that all fields can be composed of time harmonic field components this wave equation turns to the well-known Helmhotlz-equation in the frequency space. For the case of linear, homogeneous,

isotropic but dispersive media it reduces to:

$$\Delta\ \vec{E}(\vec{r},\omega) + \frac{\omega^2}{c^2}\varepsilon(\omega)\ \vec{E}(\vec{r},\omega) = 0 \qquad (1)$$

for the frequency dependent Fourier coefficient of the electric field. The effect of the electric field on the media is reflected in

$$\vec{D}(\vec{r},\omega) = \varepsilon_0\varepsilon(\omega)\vec{E}(\vec{r},\omega)\ . \qquad (2)$$

The electric displacement $\vec{D}(\vec{r},\omega)$ contains the polarization field and is ruled by a phenomenological complex dielectric function ε which describes the material's response.
To ensure that our models remain in the well-established framework of classical electrodynamics we restrict ourselves to models with minimum particle diameters of 20 nm, minimum shell thicknesses of 2 nm and dimer junctions of 2 nm.

3 Proof of Concept

Prior to describing our dimer model systems we will compare FE models to plasmonic standards like single spheres or single cylinders for which an analytical solution of the Helmholtz equation has been proposed by Mie [4]. For that comparison we used modified Mie scattering Fortran codes from Bohren and Huffman [1] which provide for the exact solution for the scattering problem and therefore serve as a benchmark. Like the standard Mie codes these are restricted to the far-field evaluation of spherical symmetric problems optionally with coatings. An extension to multiple scatterers is highly elaborate. (To the best of our knowledge the only 'multi-scatterers' Mie code which provides for full near-field information is the relatively new GMM_FIELD from Ringler[1] based on the extended Mie code GMM from Xu[2].)

3.1 Infinitely Long Cylinder

The most common pseudo 3D scattering problem is the infinitely long cylinder under oblique incidence.
In figure 2 the comparison of FE-modeled and Mie solved scattering at a 30 nm radius silver cylinder under incorporation of the same material response [2] is shown. The

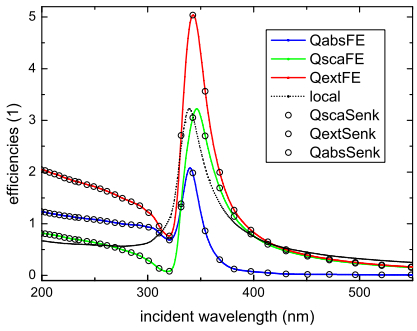

Fig. 2: Comparison of Mie's analytical solution with our FE simulations for an 30 nm radius silver cylinder under oblique incidence.

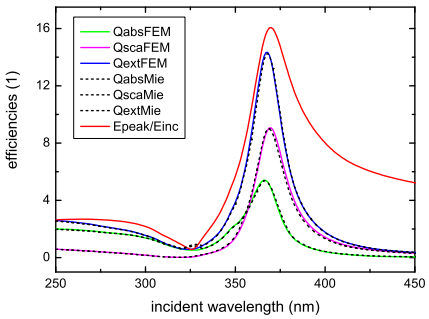

Fig. 3: Comparison of Mie's analytical solution with our FE simulations for an 30 nm radius silver sphere.

efficiencies of absorption, scattering and extinction are plotted in colored lines while the circles give the comparison with the Mie data. The FE model shows perfect agreement with the analytical solution but yields in addition the full near-field information that is given by the dashed line that represents the local electric field enhancement factor E_{peak}/E_{inc} at the cylinder's surface.

3.2 Pure Metal Sphere

An identical comparison was carried out using the scattering paradigm of a silver sphere with a radius of 30 nm. In the respective Mie code the material's response was interpolated and thus the Mie solution shows up as curves as well. Figure 3 shows the FE modeled efficiencies for absorption, scattering and extinction in colored lines which match almost perfectly the analytical solution plotted in dashed lines. Only a small feature in the analytical solution at 330 nm is not reproduced with the FE model. An explanation is presented elsewhere. Again

[1] http://moritz-ringler.name/dissertation/GMM_FIELD.tar.bz2
[2] http://diogenes.iwt.uni-bremen.de/vt/laser/codes/shu.zip

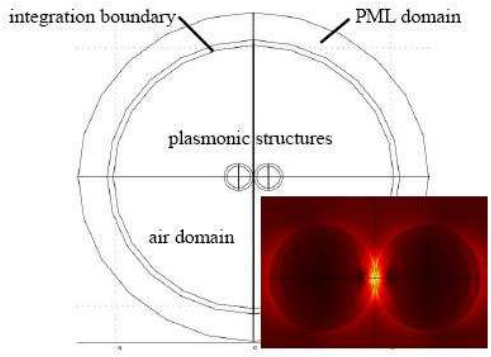

Fig. 4: Scematic view on the circular active domain which is surrounded by PML's and with a bimetal nanoshell dimer inside. The inset shows the plasmonic lightening of this dimer structure.

FE provides for the complete near-field information as illustrated by the extraction of the local electric field enhancement factor E_{peak}/E_{inc} at the sphere's surface.

4 Modeling and Results

We realize our finite element models as shown in figure 4 using the scattering mode of the RF-modul to solve the Helmholtz equation. Especially for 3D modeling a compromise between calculation domain size and solving time needs to be determined. Small domain sizes seem to cause an overestimation of the field peak values. By normalizing the incident electric field we can observe the local field enhancement factor directly in form of the time averaged normalized electric field normE_rfw and normE_rfweh respectively. For far-field evaluation we use our definitions of the radial component of the total and scattering Poynting-vector in the global expressions. Using these specifications one obtains the values for scattering, absorption and extinction efficiencies with the boundary integration coupling variables by considering of the appropriate normalization. Our calculations are carried out using a script file for running the wavelength as parameter. Moreover, we can visualize the corresponding surface charges by appropriately projecting of the electric displacement onto the surface normals of our nanostructures and defining the corresponding terms in the boundary expressions separately for each of the active interfaces.
Our standard geometry is composed of two nanoshell cylinders with diameters of 100 nm surrounded by air and separated by a junction of 2 nm. The circular active domains contain 2 μm^2 and 1.7 μm^3 respectively and are delimited by perfectly matched layers (PML) in order to reach perfect absorption at the outer boundaries (figure 4).
The incident field is assumed to be an electromagnetic plane wave with in-plane polarization (TM mode). Former studies on nanoshell dimer strucures [5] showed that maximum electric peak values are reached for polarization along the dimer axis therefore we restrict ourselves to the following case - incident wave from above and electric field vector in plane along the dimer axis. As the variable parameter we choose the incident wavelength in general varying from 200 nm to 1000 nm in one-nanometer steps. Our nanoshells are designated as follows: Au@Ag-(40,50) refers to a gold shell of 10 nm thickness on a 40 nm silver core. Therefore, the brackets denote inner and outer radii.

4.1 Bimetal Nanocylinder Dimers

A common way to estimate the expected SERS enhancement is to use far-field spectra like the extinction. In this section, we will show that the relative heigth of plasmon resonances found in the far-field does not necessarily correspond to strong field enhancements in a dimer's hot-spot.

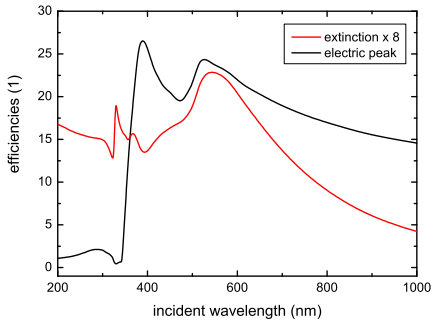

Fig. 5: Extinction efficiency and local field enhancement for an Ag@Au (42,50) nanocylinder dimer with 2 nm separation.

In figure 5 the comparison between near- and far-field for an Ag@Au (42,50) dimer is shown. In this example the silver shell is designed in such a way that one observes two coexisting resonant plasmon modes in the hot-spot arising from the gold core at 526 nm and from the silver shell at 395

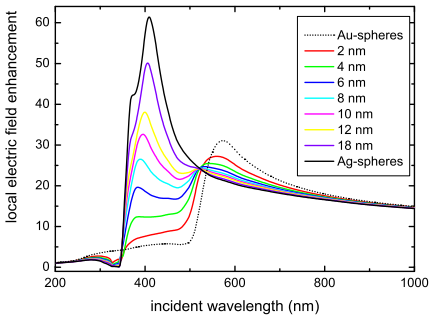

Fig. 6: Local electric field enhancement factors in the hot-spots of Ag@Au dimers with varying shell thicknesses.

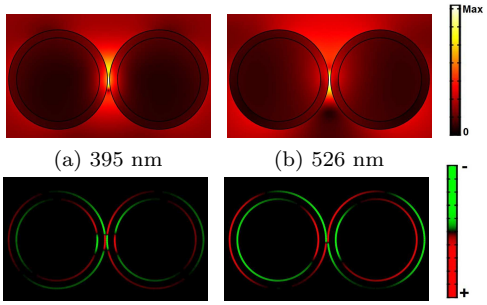

Fig. 7: Visualization of the plasmon resonances in the Ag@Au (42,50)-cylindershell. The surface plots of (a) and (b) show the electric field enhancement factor E_{peak}/E_{inc} while the corresponding polarization charges are shown thereunder.

nm. The local field enhancement of around $25 * E_{peak}/E_{inc}$ correlates with a moderate Raman peak intensity enhancement of around $4 * 10^5$. In the red extinction curve one recognizes a clear underestimation of the silver plasmon mode while an aditional resonance at 330 nm appears. Therefore, in our optimization of plasmon active SERS substrates we prefer the investigation of the local field enhancement factor. In figure 6 the plasmon modes are shown for varying shell thicknesses from 2 nm up to 18 nm while the overall radius remains constant at 50 nm. For comparison the spectra of pure silver and gold sphere dimers, respectively, are added and therefore influence of varying shell thickness on the two coexisting plasmon modes can be derived. All dimers have a separation distance of 2 nm.

4.1.1 Visualization of Surface Charges

To unveil the nature of the localized surface plasmons it is very useful to define terms which represent the surface charges. Especially in the case of dielectric-filled nanoshells, where couplings of different orders arise, this method enables us to clearly visualize the polar character and the kind of coupling in plasmon resonant modes.
In figure 7 two surface plots of the electric field enhancement factor at wavelength corresponding to the core and the shell resonances are shown. In both cases the hot spot is clearly visible. Thereunder the distribution of the surface charges is visualized. For the silver core resonance one can discern a strong junction-concentrated quadrupolar plasmon mode at the gold-silver interface. This mode has no significant coupling to the outer surface. For the gold shell resonance shifted dipolar plasmons at the two interfaces are found. While the coupling phenomena for dielectric-filled structures are well understood they are not yet fully explained for bimetal shells. Most likely the plasmons in bimetallic structure exhibit no specific coupling.

4.2 Bimetallic Nanoshell Dimers

To compare the simulations with our experimental designed structures three-dimensional models are preferable. However such simulations involve a series of problems like long solving durations and problems with the convergence behavior. Nevertheless, the crucial enhancement factors for a set of spheres where all field components can interact, are larger than for a set of respective cylinders.

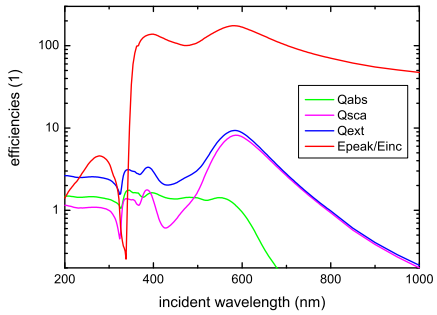

Fig. 8: Efficiencies of absorption, scattering and extinction compared to the local ehancement factor of an Ag@Au (40,50) bimetal shell dimer with 2nm separation.

Figure 8 shows the spectrum of an Ag@Au (40,50) dimer with spherical nanoshells sep-

arated by 2 nm. Again the peak value exhibits the two well-known plasmon resonant modes from the gold core and the silver shell and again the relative heigth of the extinction does not match to the strength of local field enhancement. Remarkably, one can observe enhancement factors greater than 100 in a wide range beginning at 370 nm up to 700 nm. This means that Raman intensity enhancement of 10^8 can be reached.

5 Conclusions

We show the proper applicability of FE calculations to scattering problems in plasmonics by comparison with analytical solutions after Mie. Even though there are options to extend Mie theory to core shell structures and a couple of scattering spheres, there is no code yet which combines both. FE calculations have no restrictions in geometry of structures and they provide for complete near-field information and for the option to extend the system to non-spherical scatterers. Other simulation methods like e.g. finite-difference-time-domain (FDTD) can be applied but use an analytical fit of the dielectric particles response, which is usually restricted to a sum of Lorentzian terms. Furthermore in FDTD there is no smooth behaviour on interfaces which impedes surface charge visualizations. Therefore FE simulations are our first choice for investigations of scattering phenomena in complex plasmonic structures of scientific and technological interest.

Acknowledgements

This work was founded by the joint FhI MPI project 'nanoSTRESS'.

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