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NANOANTENNAS FOR SURFACE ENHANCED INFRARED SPECTROSCOPY: EFFECTS OF INTERACTION AND HIGHER ORDER RESONANT EXCITATIONS

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ABSTRACT. The sensitivity in surface enhanced infrared spectroscopy (SEIRS) strongly depends on where the resonant excitation is spectrally located compared to the molecular vibration that is to be enhanced. In this contribution, we study the effect of coupling in the electromagnetic properties of 2D gold nanorod arrays in the IR. We also study the SEIRS activity of higher order resonant excitations in long nanoantennas to identify polaritonic signals of a supporting SiO_2 layer with nanometer thickness (3 nm) on a silicon substrate.

1. Introduction

Since the resonant excitation of metallic nanostructures by light can yield considerable electromagnetic near field enhancement, the optical properties of metal nanoparticles, acting as nanoantennas, have been subject of many studies [1]. In particular, interaction between particles in multimers and arrays of nanoantennas modifies and influences the optical properties of the system. The interaction properties depend on the separation distances to adjacent neighboring antennas as well as on the distribution of the antennas within the array. These effects have been broadly analyzed experimentally and theoretically in the visible spectral range for many different arrangements of particles [2, 3] while only few studies have analyzed the IR range [4], where retardation is especially important.

These antenna-like nanostructures can confine electromagnetic radiation on the nanoscale when resonantly scattered and therefore enhance the electromagnetic fields in their vicinity, which can be exploited for field-enhanced spectroscopy techniques like surface enhanced infrared spectroscopy (SEIRS). As shown recently [5], the only precondition for SEIRS is a good match between the vibrational frequency of the adsorbate and the fundamental mode of the plasmonic excitation of the nanoantenna. But not only the near field of the fundamental mode ($l = 1$) can be used to enhance vibrational signals, but also higher order excitations ($l = 3, 5, 7$).

In this contribution, we first report on the effect of coupling in the electromagnetic properties of 2D gold nanorod arrays in the IR range ($1 - 12\mu$m). We numerically and experimentally investigate the influence of interaction between neighboring antennas along the

longitudinal and transversal direction in an ordered rectangular array of wire nanoantennas prepared on a silicon substrate.

We also demonstrate the SEIRS activity of higher order resonant excitations of isolated antennas to detect more efficiently the polaritonic signals of a SiO_2 layer with nanometer thickness (3 nm) supported by a silicon substrate.

2. Longitudinal and transversal interaction

Figure 1 shows the experimental and calculated resonance wavelength, λ_{res} vs the rod length L for gold nanoantenna arrays of three different longitudinal separation distances between the antennas, d_x. The nanoantennas are deposited on a silicon substrate, which has a $3nm$ thick SiO2 layer on its top. A red shift of the resonance wavelength is clearly observed for small values of d_x (40 nm) while for larger longitudinal separation distances (1μm) the results are almost identical to the non-interacting antennas ($d_x = 5\mu$m). This spectral red shift for small d_x can be understood in terms of coupled dipoles that include retardation [6]. It predicts that the decline of the far-field intensity and the broadening of the resonance are evidences of the interaction. The same studies show near-field increase for small d_x. Also, SEIRS measurements [7] indicate increased electromagnetic field enhancement for coupled nanorods when longitudinally aligned.

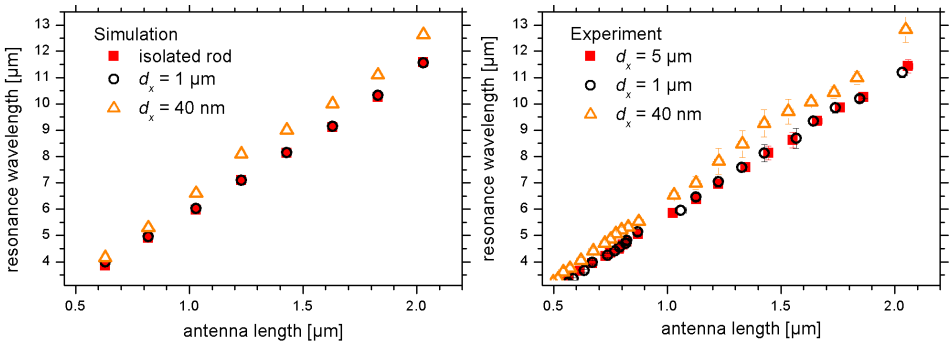

Figure 1. (left) Calculated and (right) experimental resonance wavelength vs. rod length for different longitudinal rod separation distances d_x.

The increase of the relative extinction cross section, $\sigma_{ext}(\lambda_{res})/\sigma_{geo}$ with the resonant wavelength λ_{res}, for large separation distances can be explained by the fact that the oscillating positive and negative charges are locally more separated in longer rods (featuring longer λ_{res}). Therefore, the induced dipole moment is larger, explaining the larger far-field intensity.

Regarding the transversal interaction (not shown here), significant blue shift of the extinction cross-sections and extraordinary broadening can be experimentally and theoretically observed for transversal separation distances, d_y smaller than λ_{res}. Interestingly, for large gaps, the extinction spectrum is narrower with higher maximum extinction than for

the non-interacting case. Since this happens for rather large gaps, one can exclude dominant near-field dipolar coupling and this effect is attributed to the interference of radiative dipolar coupling.

3. Higher order resonant excitations

In the following we demonstrate the SEIRS activity of higher order resonant excitations when interacting with polaritonic signals of a SiO_2 layer with nanometer thickness (3 nm) supported by a silicon substrate. On top of the natural SiO_2 layer, rectangular shaped gold nanoantennas with different length L (width and height of about 100 nm) arranged in arrays were deposited by EBL and lift-off techniques. The distances between nanoantennas in one array are large enough to avoid any kind of interaction. The relative infrared transmittance,

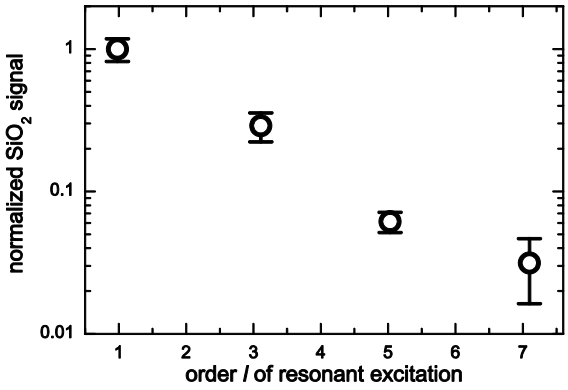

Figure 2. SiO_2 signal strength (normalized to the fundamental mode $l = 1$) for resonant excitations of different order l. The largest enhancement is found for the fundamental ($l = 1$) mode.

acquired with infrared spectroscopy of such arrays shows an enhanced polaritonic signal of the SiO_2 layer every time the polaritonic signal matches a resonant excitation of the nanoantenna. As observed in Fig 2, the SiO_2 signal enhancement is largest for the fundamental mode ($l = 1$) and decreases for higher order resonant excitations ($l = 3, 5, 7$). Modes with even l cannot be excited since they feature no net dipole moment and therefore do not contribute to the signal enhancement. As proven by the polarization dependence (maximum enhancement for polarization of light parallel to the long rod axis and no signal for perpendicular polarization) and the Fano-type line shape we obtain, the appearance of the SiO_2 signal is due to enhanced electromagnetic near fields. The SiO_2 signal appears in the range of the Fuchs-Kliewer surface-phonon polariton of the SiO_2 layer [8], which is confirmed by electromagnetic scattering simulations using finite difference time domain. Since the surface phonon-polariton cannot be excited directly by light, additional momentum is necessary. This additional momentum, is provided by the near field of resonantly excited nanoantennas [8].

4. Conclusions

The modification of optical properties by antenna arrays due to interaction effects can be exploited for sensing applications like surface enhanced infrared spectroscopy (SEIRS). The sensitivity in SEIRS strongly depends on where the resonant excitation is spectrally located compared to the molecular vibration that is to be enhanced. Therefore, the relation between spectral resonance positions and geometrical properties of the nanostructures, as presented here, is essential for the optimization of sensing devices.

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