Single nanoparticle Plasmonics: Shape matters

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Abstract

Metal nanoparticles exhibit a rich optical phenomenology due to the excitation of localized surface plasmons (LSPs). These resonances stem from the oscillations of free electrons, inducing a dipole with a resonance frequency typically in the visible [1]. In recent years, advances in nanofabrication techniques have made feasible a great variety of nanoparticle configurations, which have in turn fuelled interest in LSP resonances in metal nanostructures, giving rise to the concept of optical nanoantennas (cf. Ref. [1,2] and references therein). Concentrating light into small volumes leads to fascinating phenomena. LSPs supported by pairs of nanoparticles with a small gap between them [1-4] are able to greatly amplify local EM fields and the photonic local density of states, making these structures ideal for use in SERS and surface-enhanced fluorescence [2-5]. A special type of LSP resonances are highly promising for potential applications due to the extremely narrow (asymmetric) line shapes and fine sensitivity to environment changes: Fano LSP resonances [6]. Nanoantennas are also extremely suitable for biological applications because they enable the tracking of emission from markers in cells with sub-diffraction limit resolution, as well as the destruction of cancer cells using the resistive heating of resonant nanoparticles [7].

In general, most of the appealing optical properties of metal nanoparticles typically manifest themselves in optically coupled nanoparticles with stronger LSPs [2]. Namely, extremely large near-field and LDOS enhancements arise at resonance in gap nanoantenas and nanoparticle dimers (or aggregates), responsible for SERS and fluorescence. Fano LSP resonances also require complex multi-particle configurations involving wide, dipolar modes with narrow, dark modes. In this regard, we have investigated theoretically and numerically the optical properties of isolated nanoparticles with the aim of exploring how complex shapes might yield similar or improved phenomenology.

First, in connection with SERS, we have studied so called nanostars or nanoflowers [8,9], as described by, respectively, a 3D supershape formula [10] without axial symmetry and low-order Chebyshev 2D nanoparticles. Large field intensity enhancements are obtained both at the intersticies between nanoflower petals and at the nanostar tips, which make these Ag nanostars/nanoflowers specially suitable to host molecules for SERS spectroscopy and sensing applications, without the commonly needed aggregation. Not surprisingly, we have shown, by exploiting genetic optimization algorithms, that such shapes lead, among a variety of them, to maximized LSP cross sections [11]. Moreover, based on a simple model for temperature increase obtained from the calculated absorption cross section, Au nanostars have been shown to perform more than an order of magnitude better that Au nanospheres of equivalent size, due to their LSP in the near-IR [12]. Actually, these features hold promise for applications in photothermal cancer therapy.

On the other hand, we have evidenced that (single) elongated Ag nanoparticles such as nanospheroids, nanorods, and rectangular nanowires, suffice to exhibit asymmetric (Fano) resonances as a consequence of the interference between the broad, (dipole-like) half-wavelength mode, with dark, higher-order modes [13]; unlike the commonly belief (based on Mie theory) that coupled nanoparticles are necessary [6].

Finally, metal-dielectric (core-shell) nanoparticles have been investigated with the aim of obtaining electric (LSP) and magnetic resonances overlapping in the optical spectral regime [14,15]. Their use as building blocks for negative-index metamaterials in the visible range of the spectrum has been pointed out; again, single (core-shell) nanoparticles exhibit both resonances, making unnecessary multiple-nanoparticle configurations.

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Figures

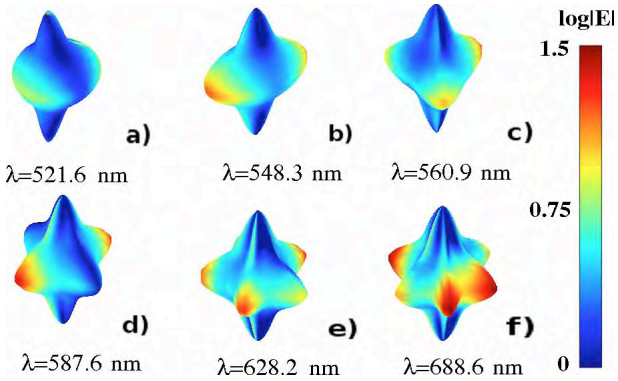

Figure 1: Distribution of electric field amplitudes in logarithmic scale on the surface of the Au nanostars at their corresponding LSP resonance wavelengths for an incident electric field polarized within the equatorial plane [12].

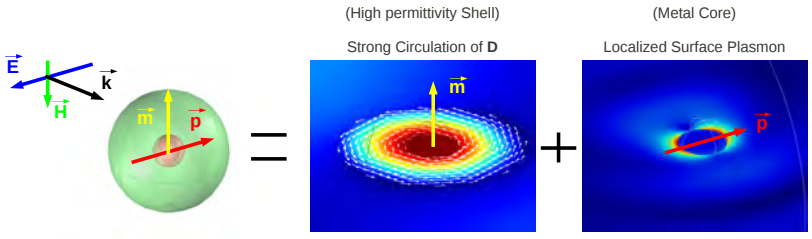

Figure 2: Schematic representation of the physics behind the core-shell nanoparticle configuration. The strong diamagnetic response is due to the lowest, dipolar magnetic resonance in the high-permittivity shell, where the electric field is forced to rotate as a consequence of the abrupt continuity conditions for the normal component between the shell and the surrounding medium. The electric resonance is a LSP resonance in the metal core [14].