Are Volume Plasmons Excitable by Classical Light?

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Volume plasmons are collective eigenmodes of the free-electron gas inside a metal. Because of their longitudinal character and the transversal nature of light, the photoexcitation of volume plasmons is forbidden in classical electrodynamics. Nevertheless, we show their existence for metallic nanoshells using analytical solutions of the classical scattering problem. Solely for the case of a vanishing real part of the shell permittivity, a local maximum at the natural plasma frequency appears in the extinction spectra. For explaining our observations, we suggest a simple physical picture which is supported by examples on silver and gold shells.

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Currently, plasmonic properties of metallic nanostructures are an intensely studied topic. The free-electron gas inside a metal exhibits collective oscillation eigenmodes, which can be interpreted in terms of material excitations as quasiparticles, called plasmons. Using an excitation by means of light, one expects modes of a transversal nature and with a strong confinement to the surface. Volume plasmon modes with longitudinal oscillations accompanied by compressions of the electron gas are not excitable by the transversal light in classical theory. For the special geometry of a nanoshell, consisting of a dielectric core surrounded by a metallic shell, several resonant modes show up in the spectrum. In this Letter, we identify the nanoshell high-energy mode to be a photoexcited volume plasmon which is contrary to the current view. We present a simple physical picture explaining the nature of all arising modes.

Let us begin with the calculation scheme used in this work. The scattering problem for particles with diameters down to several nanometers can be described in the framework of classical electrodynamics. The behavior of the continuous electron gas is completely specified via the frequency dependent complex permittivity $\varepsilon(\omega)$. The permittivity contains information on the material response like the degree of polarization and the relative phase of response. Furthermore, all additional loss effects like interband transitions can be included. It is widely accepted that the optical constants for noble metals determined in thin-film experiments [1] give the correct response for nanoparticle diameters down to 10 nm. For demonstration purposes, we also utilize a standard Drude description which approximates the experimental data via

$$\varepsilon(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 - i\gamma\omega}, \tag{1}$$

with the plasma frequency ω_p, the damping constant γ, and the permittivity ε_∞ [2]. For spherical geometries, the Helmholtz equation, describing the wave propagation for harmonic time dependence, can be solved exactly. This is known as the Mie scattering problem [3]. We consider the sum of scattering and absorption effects and therefore calculate the Mie extinction efficiencies after [4]:

$$Q_{\text{ext}} = -\frac{\int_A \vec{S}_{\text{ext}} \cdot \vec{e}_r dA}{I_i \cdot G}, \tag{2}$$

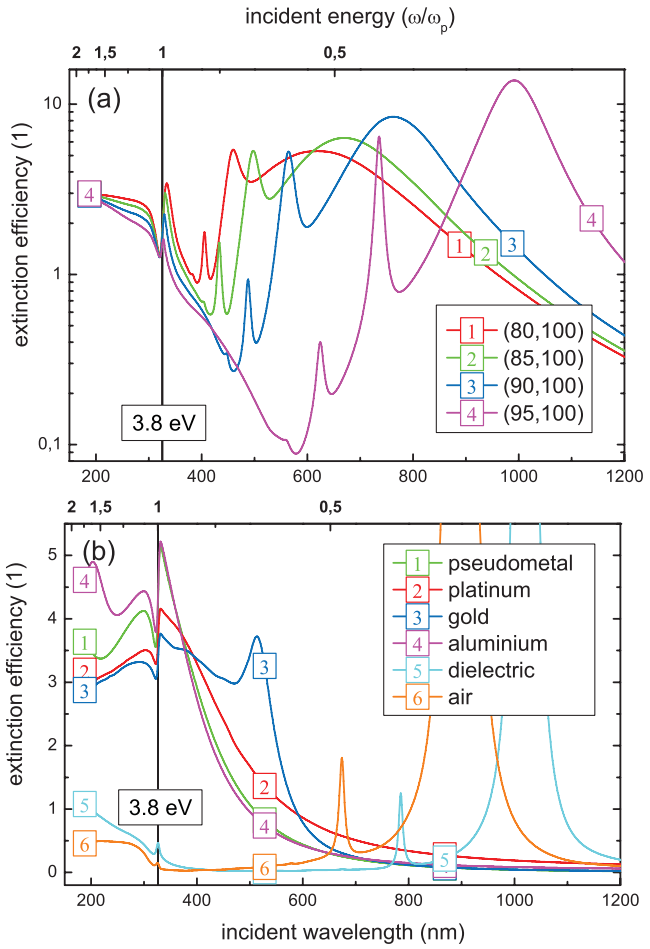

FIG. 1 (color). Calculated Mie extinction efficiencies for silver shells: (a) different aspect ratios with dielectric cores, (b) (48,50) shells with different cores. The vertical line shows the energy position of the vanishing real part of the permittivity.

normalized with the incident irradiance I_i and the geometrical shadow G [5] and using the Poynting vector of extinction

$$\vec{S}_{\text{ext}} = \frac{1}{2}\text{Re}\{\vec{E}_i \times \vec{H}_s^* + \vec{E}_s \times \vec{H}_i^*\} \quad (3)$$

with the incident and scattered fields $\vec{E}_i$, $\vec{H}_i$, $\vec{E}_s$, and $\vec{H}_s$. In the textbook of Bohren and Huffman [4], FORTRAN codes for the calculation of Mie coefficients after Mie [3] and Aden [6] are given which are well established. With these coefficients, the respective optical spectra, e.g., the Mie extinction efficiencies of spherical nanoshells, are completely defined. Our shell structures are designed as follows: (r_1, r_2) denotes the aspect ratio with inner and outer radii r_1 and r_2.

In Fig. 1, calculated Mie extinction efficiencies for silvershell nanostructures are shown. In both graphs, the vertical line designs the position of the vanishing real part of the silver permittivity [1]. The upper graphs show Mie extinction efficiencies of silver shells with dielectric cores ($\varepsilon = 2.08$) and constant overall radii of 100 nm but varying aspect ratios $x = r_1/r_2$. One can distinguish different resonances above 400 nm which are typically explained in terms of symmetric coupling of the inner and outer surface resonant modes [7]. The respective lowest energy peak has a dipolar character followed by the quadrupolar and octupolar mode with increasing energy [8]. As expected, these modes show a distinct redshift and enhancement with decreasing shell thickness. In Fig. 1(b), a study is shown for thin silver shells of (48,50)-type with several core materials such as platinum [9], gold [1], aluminum [10], and some constant loss-free permittivities like $\varepsilon = -16$ (pseudometal), 2.08 (dielectric), and 1 (air). For all of the different cores, we observe a fixed resonance at around 330 nm, which is strongest for the pseudometal and relatively weak for a dielectric core. In the case of gold (line 3), as an example, we can additionally distinguish the two coexisting plasmon resonant modes from the gold core around 550 nm and the silver shell around 400 nm.

Remarkably, in both graphs of Fig. 1, we find a distinct mode around 330 nm which does not exhibit obvious shifts provided the shell is not too thick. Hence, the position of this resonance is independent of both the aspect ratio of the nanoshell and as well of the special core material. Because of the fact that the position of this mode is determined by the position of the vanishing real part of permittivity, we term it volume plasmon. Furthermore, the amplitude of this resonance does not correspond to the amplitudes of the surface modes which are stronger for thinner shells explained by an increased coupling behavior in the hybridization model [11].

Although Mie calculations provide for the exact determination of expected optical spectra, they give no insights into underlying physical mechanisms. Because of the high complexity of the Mie scattering coefficients, it is impossible to give any prognoses about the spectral behavior in general like, e.g., resonance positions or the kind of excitation. To get deeper insight into the ruling physical mechanisms, a hydrodynamical model was used to explain arising plasmon modes of order l [12] in metallic nanoshells of aspect ratio $x = r_1/r_2$ via

$$\omega_{l\pm}^2 = \frac{\omega_p^2}{2}\left[1 \pm \frac{1}{2l+1}\sqrt{1 + 4l(l+1)x^{2l+1}}\right]. \quad (4)$$

This formula, derived in the context of density functional calculus, was interpreted as a kind of plasmon hybridization in an incompressible electron fluid [11] where the inner and outer shell surface modes can couple symmetrically and antisymmetrically [13]. This model seems to exclude any volume oscillations. For this reason, we will suggest a simple physical picture which explains all arising resonances, the symmetrically coupling modes in terms of enhanced localized surface plasmons and, in particular, the antisymmetric modes in terms of enabled volume plasmons. This explanation of the high-energy resonance in terms of a volume plasmon is in agreement with observations and their interpretation on C_{60} ions [15]. Furthermore, recent experimental findings on natrium nanoclusters support the possibility of the photoexcitation of volumelike modes [16].

Figure 2 shows a schematics of the two different kinds of photoexcitations in metallic nanoshell geometries. In the transversal case 2(a), the electric field can act as a driving force for the electron movement due to the small particle

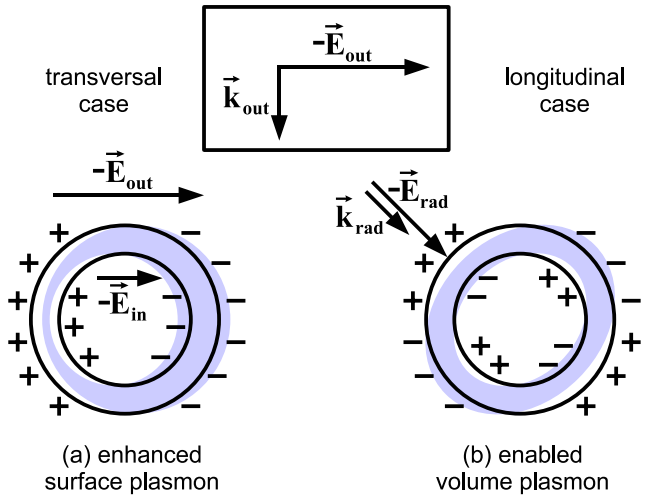

FIG. 2 (color online). Excitation of localized plasmons corresponding to standing waves of electron gas oscillations on a shell geometry. In (a), the dipolar surface plasmon excitation is shown where the electrons move in phase with the driving electric field in a tangential direction. At the inner shell surface, the residual electric field causes an enhancement of the surface mode. In contrast, the enabled volume plasmon in (b) shows a radial electron movement caused by sufficiently large radial field and momentum components.

size, and it causes a tangential displacement of the electron cloud. As long as the electrons, described as a continuous medium, can immediately follow the field a dipolar mode is excited. With increasing energy, the response velocity of the electron gas becomes too small, and retardation effects occur. In this regime, higher polar modes can be excited. For the special case of a shell geometry, the electric field penetrating the shell causes an additional driving force inside the cavity, and therefore the surface modes will be enhanced depending on the shell thickness. The enhancement, which is depending on the losses inside the shell, will show up in form of two effects: With decreasing shell thickness, the strength of the surface mode increases. Therefore, also higher polar modes will be visible in the spectrum. On the other hand, the additional internal field facilitates the photoexcitation of surface modes which causes their redshift. Taking into account the tangential nature of the electron movement caused by the skin effect, this explains why the so-called symmetric coupling is occurring at lower energies. Of course, these effects arise only if an electric field exists inside the shell, thus, for dielectric core materials. Furthermore, with increasing permittivity, the polarization of dielectrics gets stronger. Hence, the free charges in the shell experience additional forces due to the oriented dipoles inside the core which as well facilitates the excitation resulting in a redshift for increasing permittivity. Consequently, in Fig. 2(a), we used the denotation "enhanced surface plasmon" as a natural alternative to the symmetric coupling description in [7]. In contrast to the aforementioned surface modes, the high-energy excitation has a different physical nature.

In general, electron gas oscillations of radial character as shown in Fig. 2(b) are enabled by a vanishing permittivity. For the case of vanishing permittivity, standing longitudinal waves can exist inside the bound medium corresponding to a localized volume plasmon. However, there is the open question how to excite these modes with transversal electromagnetic waves. From experiments, it is known that hard photons can excite measurable volume plasmons while for the visible region in general the classical excitation probability is too small [17]. Nevertheless, for the case of thin films radiated with polarized light under oblique incidence, volume plasmons of different orders could be observed [18]. Figure 2(b) shows the impinging radial components of electric field and momentum which can couple to the evanescent extensions of the longitudinal electron gas eigenmodes in the outer space. In conjunction with the small radial electron gas volume to be moved in the shell geometry, volume plasmons can be enabled. In this context, the nonvanishing photoexcitation probability of volume modes represents a near-field effect occurring for nanoscale structures smaller than the wavelength. In contrast to the surface modes, the existence and the resonance positions of the volume modes are independent of the shell thickness and the core material. Because of the special geometry and retardation effects in this energy regime, preferentially localized volume plasmons of quadrupolar character should be excited (see supplementary material [8]). An important consequence of our picture is that, in principle, photoexcitation of volume plasmons is possible in any nanoparticle with vanishing permittivity, and its mode will appear in the spectrum if a sufficiently high excitation probability exists. In this context, all kinds of shell-like nanostructures [15] as well as structures with no center of inversion symmetry [19] should provide measurable volume excitations in their optical spectra if they are thin enough.

If our assumptions on volume plasmons are correct, then a gold shell with dielectric core should exhibit no localized volume mode due to the fact that the permittivity of gold [1] has a nonvanishing real part down to 210 nm. Furthermore, the enhancement effect for the surface modes should be considerably weaker because of the interband transitions of gold in the visible, causing a distinctly higher absorption. In Fig. 3, we show extinction efficiencies for a (48,50) gold shell with dielectric core ($\varepsilon = 2.08$) based on different material responses. The dashed line (red) refers to calculation based on experimental data [1] while the straight one (blue) refers to the corresponding Drude fit [20]. Our Dude fit represents a reasonable approximation in the range from 450 up to 1000 nm but has a vanishing real part of permittivity around 420 nm. Accordingly, the surface modes in Fig. 3 show a good agreement for both material responses. However, for the Drude gold, a distinct mode at 420 nm arises corresponding to the position of vanishing real part of permittivity at 2.95 eV sketched with a vertical line. Again, we interpret this mode in terms of a enabled volume plasmon solely excitable in the artificial Drude gold [21].

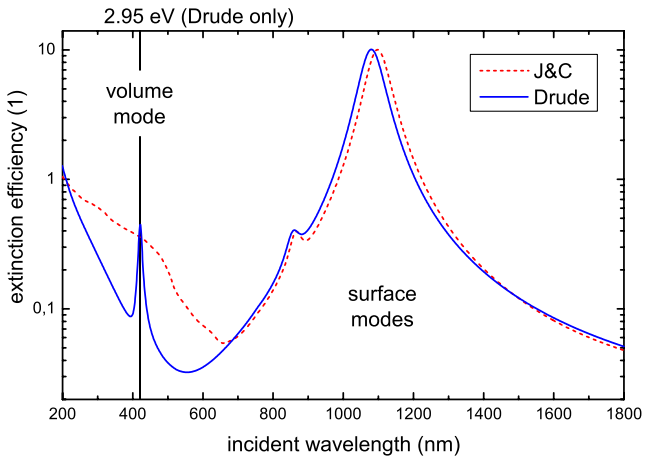

FIG. 3 (color online). Mie extinction efficiencies for a (48,50) gold shell with dielectric core for two different material responses. The dashed (red) line shows Mie extinction with experimental data; the straight (blue) line is based on the Drude fit.

In this work, we have shown that for core-shell nanostructures, a special plasmon resonance arises which is independent of the core material. The existence and position of such a resonance is dependent on a vanishing shell permittivity as shown for the case of silver and gold shells. Therefore, we term it a photoexcited volume plasmon. As expected, the silver volume plasmon is fixed at around 330 nm which corresponds to the experimentally determined value of the silver plasma frequency at 3.8 eV [22,23] also in agreement with optical constants measured by Johnson and Christie [1]. We have suggested a simple model for the understanding of the physical nature of the different modes which implies the photoexcitation of volume plasmons for a potpourri of particles. Not only spherical shells [15] but also various types of thin nanosized structures are expected to exhibit measurable volume excitation effects in their spectra.

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