Two-Dimensional Quasistatic Stationary Short Range Surface Plasmons in Flat Nanoprisms

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ABSTRACT We report on the nanometer scale spectral imaging of surface plasmons within individual silver triangular nanoprisms by electron energy loss spectroscopy and on related discrete dipole approximation simulations. A dependence of the energy and intensity of the three detected modes as function of the edge length is clearly identified both experimentally and with simulations. We show that for experimentally available prisms (edge lengths ca. 70 to 300 nm) the energies and intensities of the different modes show a monotonic dependence as function of the aspect ratio of the prisms. For shorter or longer prisms, deviations to this behavior are identified thanks to simulations. These modes have symmetric charge distribution and result from the strong coupling of the upper and lower triangular surfaces. They also form a standing wave in the in-plane direction and are identified as quasistatic short range surface plasmons of different orders as emphasized within a continuum dielectric model. This model explains in simple terms the measured and simulated energy and intensity changes as function of geometric parameters. By providing a unified vision of surface plasmons in platelets, such a model should be useful for engineering of the optical properties of metallic nanoplatelets.

KEYWORDS EELS, plasmon, metallic nanoparticle, spectral imaging

Metallic nanoparticles have recently been the center of much attention from both the scientific and industrial communities, particularly because of their unique optical properties. The origin of the rich absorption, extinction and scattering properties observed at the nanoscale are related to the excitation of surface plasmon (SP) resonances. SPs are the collective excitations of the conduction electrons of metallic nanoparticles. The main properties (energy, lifetime, intensity, and so forth) of these surface excitations can be precisely tailored over a wide spectral range by tuning the nanoparticle size, composition, and dielectric environment, among other parameters. Associated with surface plasmons resonances (SPRs) are huge enhancements of the local electromagnetic field, on which many phenomena and applications rely. For instance, Raman signals in surface enhanced raman scattering (SERS) are dramatically enhanced by the presence of a nanostructured metallic surface. As most of the potential applications for these phenomena involve optical wavelengths, there is a growing need for nanoparticles with SPRs in this wavelength range. Additionally, most applications are based on the subwavelength spatial variation of the SPRs electromagnetic field (plasmonics). Thus, understanding the precise link between the overall structure of the nanoparticles and the nature of the plasmonic modes (their energy value, relative intensities and spatial distribution over the nanoparticles) is of primary interest.

Platelet systems have been found to be ideal for such studies. Indeed, intensive theoretical and experimental investigations have pointed out how intricate is the relationship between the structure and the optical properties of these systems. One of the difficulty for their experimental investigation is the access to the variation of electromagnetic field properties at the nanometer scale. This bottleneck has been recently broken using different techniques,1–4 among which electron energy loss spectroscopy (EELS) in a scanning transmission electron microscope (STEM) is particularly attractive since it allows mapping the mode variations within individual silver flat triangular nanoprisms.1 The intimate link between EELS plasmon maps and a quantity closely related to the electromagnetic local density of states (EMLDOS) polarized perpendicularly to the platelet faces has been demonstrated.5

Triangular platelets have been extensively examined during the past few years, both because of the tight control that can be achieved on their size but also because they exhibit SPR modes with well-defined energies and excitation probabilities, which can be related to known field patterns.1,6–9 The most intense optical modes in nanoplates have been associated with dipolar and quadrupolar excitations, in analogy to spherical nanoparticles.6 Such modes correspond to field enhancements at the corners (dipolar mode) and at the edges (quadrupolar mode) as predicted by simulations.10 Corner and edge modes have also been evidenced by STEM-
EELS measurements.\textsuperscript{1} We will discuss the similarity in the induced field patterns due to an electronic or photonic excitation of these modes later in this paper. So far, the experimentally observed size dependence of the SPR energy of metallic nanotriangles has been associated with electromagnetic retardation effects.\textsuperscript{8} This explanation is puzzling because the sizes of the investigated particles were essentially much smaller than the equivalent wavelength of light in vacuum and because it is contradicted by the aspect ratio dependence noted for small particles.\textsuperscript{11}

Therefore, a systematic investigation on the effects of size and aspect ratio on global and local electromagnetic properties related to SP excitations in nanoplatelets is still necessary. We present in this paper a nanometer scale mapping of the SPR signal on a collection of 16 different silver nanoprisms using EELS in a STEM, as well as related discrete dipole approximation (DDA) simulations. We show experimentally that SPR mode energies and intensities do depend essentially on the aspect ratio, \( R = L/t \), with \( L \) the edge length and \( t \) the nanoprism thickness. In the two limits not investigated experimentally (\( L < 70 \text{ nm} \) and \( L > 300 \text{ nm} \)), DDA simulations show an additional length dependence. Using a simple continuum dielectric model, we show that the energy and intensity dependence on \( R \) can be explained as a result of the existence of stationary, quasi-static short range surface plasmons (SRSP). Those stationary SRSP have a symmetric charge distribution resulting from the strong coupling between the upper and lower triangular surfaces and thereby forming a standing wave in the in-plane direction. This model extends and links to arbitrary geometries and dielectric functions (real or not) earlier, apparently unrelated theories devoted to nanoantennas\textsuperscript{3,12} and plasmonic waveguides.\textsuperscript{13}

The silver triangular nanoprims analyzed here were synthesized as reported in ref 14. After synthesis, the nanoparticles were dispersed in water. For electron microscopy characterization, the particles were drop cast onto a freshly cleaved mica substrate (Agar Scientific, Ltd.) and then glued to a standard 3 mm, 300 mesh copper grid. To minimize electromagnetic coupling between nanoprims, the deposited volume of solution was optimized to achieve an average interparticle distance of the order of a hundred nanometers. Morphological characterization by high-angle annular dark field (HAADF) imaging and spectroscopic analysis by spatially resolved EELS were realized in a cold-FEG STEM VG HB501 operated at 100 kV. The EELS spectra were acquired with a homemade detection system described elsewhere.\textsuperscript{1} The loss spectra over the UV–vis-NIR domain were acquired in the spectrum-image mode\textsuperscript{15} in which a 0.7 nm focused electron beam was scanned with constant spatial increments over the nanoparticles. At each point of the scan, a number of complete spectra was then acquired over the energy range of interest. Each spectrum-image comprised 32 × 32 pixels with 50 individual spectra per pixel. Each spectrum was acquired in 2.5–3 ms, leading to a total acquisition time of the order of 15 min. The step increments ranged between 3 and 12 nm. To access to spectral features in the UV–vis-NIR domain, each set of spectra per pixel was realigned, summed and deconvoluted by means of the point spread function of the acquisition system.\textsuperscript{16} Subsequent analysis of the resulting spectrum-images enabled the generation of maps for either mode amplitude, energy shift or width, for any spectral features present over the energy range of interest, as described in ref 1. The measurement also provides information about the particle thickness through the inelastic mean free path of the fast electrons.\textsuperscript{17}

Figure 1 shows EEL spectra acquired at a corner, the middle point of an edge and the center of (a) a 97 nm edge-long (thickness 4 nm) (b) and a 176 nm edge-long (thickness 6 nm) nanoprisms, respectively. The corresponding insets show the HAADF images of each nanoprin and the exact positions at which the EEL data were measured. In each case, three main resonances were identified. The energies of these modes vary from one prism to another. Panels (c,e,g) present maps of the intensity distributions of the main resonances detected on the prism in (a). Similarly, panels (d,f,h) show the intensity maps of the two modes on the prism in (b). For each set of three maps, the common intensity scale is linear and expressed in arbitrary units. The general inset of this figure defines the two dimensions \( t \) and \( L \).

![Image](https://example.com/image.png)
red-shifted for the larger particle, and the relative intensities of the different modes are noticeably different.

We studied 16 structures with edge lengths ranging from 77 to 303 nm and thickness ranging between 4 and 6 nm, except for one triangle (8 nm). All of them exhibited three modes with similar spatial distributions but different energy positions and relative intensities (Figure 2). It is tempting to attribute the observed energy redshift with particle size to a simple linear length effect (Figure 2a), as expected for a surface polaritonic effect. However, another relevant parameter in the case of a flat nanoparticle is the particle aspect ratio \( R \). On Figure 2b, we observe a linear dependence of the SPR wavelength with \( R \). In the following, we will analyze this dependence based on numerical simulations and an analogy for thin film surface plasmon dispersion.

The numerical simulations were carried out within a discrete dipole approximation for both optical absorption (DDSCAT code) and EELS using tabulated dielectric data. As shown in Figure 3a, our simulations confirm that the main optical mode (for light polarization in the platelet plane, red stars) and the EELS corner mode (red solid circles) have the same excitation energy, as are the second less intense optical mode (often called quadrupolar mode, blue stars) and the EELS edge mode (blue solid circles). Later in the paper, we will show that the SP modes excited by EELS and by electromagnetic plane waves are identical based on a deeper analysis of the electromagnetic field induced by SP excitation in both cases. The agreement between the experimental (solid lines) and simulated (symbols) dependence of the SP wavelength for large \( R \) is very good regarding the experimental error bars and the possible rounded corner of the triangular particles. For small \( R \), in a range where no experimental data are available, the calculated SP energies deviate from the linear scaling.

Figure 3b illustrates the dependence of the SPR wavelength as a function of the length of the triangle edge at a fixed aspect ratio value \( R = 4 \) for the dipolar mode (resonance around 2 eV) and the quadrupolar mode (around 3 eV). As expected from the experimental data, we observed almost no edge length dependence at constant \( R \) for particle sizes much smaller than the excitation wavelength in vacuum, that is, for \( L < 300 \) nm for the main optical mode (inset). An
explicit \(L\) dependence arises for larger particle sizes as a consequence of retardation effects. The experimentally analyzed particles being characterized by \(L < 500\) nm, such retardation effects can be excluded when explaining the behavior observed in Figure 2. In the specific case of the particles experimentally investigated here, \(t\) does not vary much, while \(L\) does. We conclude that the apparent size dependence is thus essentially an aspect ratio dependence for particles with basically constant thickness (4 to 6 nm).

Considering the wavelike nature of the modes evidenced by the maps of Figure 1, together with the dispersion of energies with structural parameters, we interpret these excitations as stationary surface plasmon waves. Indeed, it seems natural to make the comparison with, for example, optical waves in a 1D cavity and to quantify the wavevector, \(q_n = nL\) where \(n\) is an integer indexing the mode. For an infinite half space, the quasistatic surface plasmon energy, \(\hbar\omega_{sc}\), is independent of the transfer momentum and all the modes \((q_n)\) should have the same energy. A dispersive regime is recovered for small \(q\) \((q < 3\ \mu m^{-1})\) in the relativistic approach (Figure 4a). The energy of the modes with wavevectors \(q_n = nL\) \((L < 300\) nm) should then have all the same energies. The \(L\) dependence of the SP modes then cannot be explained by this semi-infinite space approach.

Considering now a slab, the SP modes split into a symmetric (low-energy) and antisymmetric (high-energy) mode due to the coupling of the SP,24–26 (Figure 4a for a \(d = 5\) nm Ag film). The symmetry/antisymmetry of the mode is defined by the relative sign of the charge distribution of both triangular faces. In the quasistatic regime, the mode energies depend on the product of the surface wavevector \(q\) times the slab thickness \(t\)25,27,28 and only very weakly on the separate quantities in the relativistic case (Figure 4a, inset). Because of the dispersion of the SP interface modes, the quantification of \(q_n\) gives rise to an energy dependence as a function of \(R = L/t \quad (q_n t = n R)\) for the system of finite thickness. Such in-plane stationary waves constructed upon coupled surface modes will be called stationary short range surface plasmons, in analogy with the traveling short range surface plasmon polaritons.13 This model explains at the same time the stationary wave behavior of the plasmons and the aspect ratio dependence of the mode energy as experimentally observed. In the following, we use experimental and simulated results in order to validate this approach.

First, both experimental and simulation results indicate that for a given mode, the energy increases with increasing \(q_t\) (decreasing \(R\)). In the quasi-static regime (large \(q\)), only the symmetric (S) modes have such trend (Figure 4a). We can then attribute a S symmetry to the SRSP under investigation. DDA simulations (Figure 5b) confirm the symmetry of the mode. The fact that the antisymmetric (A) modes are not measured in EELS has already been observed for infinite slabs.25 On Figure 4b, we reproduce the EELS probability for a 100 keV electron traveling perpendicularly to an infinite silver slab of thickness \(t = 5\) nm, deposited on a mica substrate, as a function of both wavevector and energy loss, computed within the fully retarded theory by Chen and Bolton,28 as coded in ref 29. The antisymmetric mode has a vanishingly small EELS probability for large \(q\) and is thus not detectable. We are not aware of optical works reporting such a mode either. These antisymmetric modes are however likely to be very weak, as the effective dipole is proportional to the vanishingly small thickness of the slab (to be compared to the symmetric modes having dipoles roughly proportional to the length of the prism); see, for example, ref 26.

Second, the stationary wave character of the excitation (and the \(q_n = nL\) relation) can be verified as follows. For each prism under consideration, an equivalent wavevector can be determined thanks to the dispersion relation of a slab, based on the SP energy (see the scheme in Figure 4a). We plotted in Figure 4c the equivalent wavevector as a function of the inverse length (independently measured from the}

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**FIGURE 4.** Surface plasmon resonances of triangular nanoprisms as stationary short range surface plasmons. (a) Schematic representation of the dispersion relation of the surface modes for a 5 nm thick Ag slab (red solid lines) and semi-infinite Ag planar surface (dark solid line). Quantification of the associated wave vector in the arbitrary condition limit are also depicted in the case of a nanosystem of characteristic length \(L\). Inset: Universal dependence of the dispersion relation for SP with respect to \(q_t\) in the quasistatic case. Only the low-energy mode, charge symmetric, is shown. (b) EELS probability (log scale) of the surface modes supported by a 5 nm thick Ag slab deposited on a 30 nm thick mica surface, as a function of energy and transferred wavevector as deduced from simulations.29 We note that the probability of detecting the high energy, antisymmetric mode is very low as compared to the symmetric one. Panel (c) shows the in-plane wavevector \(q\) of the symmetric mode as a function of the inverse of the edge length, \(q\) is deduced from the knowledge of the mode energy, the thickness of the associated nanoprism and the computed dispersion relation of a Ag slab with the appropriate thickness (see text for further details). Red triangles, corner mode; blue triangles, edge mode; black triangles, center mode. Solid lines: linear fit to the experimental data. In (d), the intensity ratios of the first and second modes as deduced from the experiment (red triangles) and extracted from the dispersion relation (black dots) are compared.
HAADF image). The relation shows the expected linear behavior. The slopes of the linear interpolation are 0.27/0.9/1.98, roughly corresponding to a 1/3/6 ratio. This ratio does not correspond to harmonic ratios for a simple resonator (like nanoantenna). This is however not surprising for a less simple triangular shape. Also, the DDA simulations of the electric field clearly demonstrate that the stationary SRSPs have no simple oscillation pattern (Figure 5).

Third, for a given thickness, the EELS probability (Figure 4b) for an infinite slab varies with the wavevector value. For a finite slab, it means that the relative intensity of the modes vary with size (or aspect ratio). To check this prediction, we have plotted in Figure 4d the ratio between the intensity of the corner mode and the edge mode, for the experimental data as well as those deduced from the q dependence of the intensities for the slab. We see again that the agreement between experimental data and our model is very reasonable.

The closest examples of standing wave interpretation of SRSP in the literature are those proposed for slabs and nanoantennas. In the case of 1D slabs of rectangular sections, that is, plasmonic waveguides, excitations do not form standing but propagating waves. These excitations were mainly described as surface plasmon polaritons (i.e., retarded waves) of S symmetry. As it is the case for nanoprisms, the A modes are also inactive, but for a different reason (because of the absence of phase mismatch with respect to the light modes necessary to ensure abrupt boundary conditions). In the opposite limit, SP in 1D nanoantennas with radii smaller than the skin depth (ca. 20 nm for silver in the visible range) have been described as stationary SRSPs in a hydrodynamic model. This model is similar in essence to the one described here (but particular for cylindrical geometry) and developed in the frame of the Drude model for the electrons. It does not provide any predictions for the intensities of the A or S modes. The present model extends the approach of ref 12 for 2D systems and arbitrary dielectric functions. The framework presented here is a priori valid for any planar geometry with one dimension much smaller than the skin-depth and the other two larger than the skin-depth (even large enough to be in the retarded limit). The study of platelets presenting other symmetries (i.e., squares) might thus challenge our interpretation, when available.

If we now consider systems with an edge length on the order of the skin-depth, we should expect a deviation for the aspect ratio dependence due to the coupling between the rectangular surfaces of the prisms. This has been observed in the DDA simulations for small R (Figure 3a). In the opposite limit, for large (e.g., >500 nm) edge length, the energies do depend on the thickness and edge length separately (Figure 3b). This behavior is however included in our model, as the dispersion relations are calculated in the fully retarded frame. Finally, as R grows, and experimental resolution increases, modes of higher orders are expected to be observed.

We have mentioned throughout this paper the link between the EELS and optical spectroscopies and it is worth commenting further on that point. As discussed in some length in ref 5, EELS gives access to a quantity very close to the z-polarized part of the electromagnetic density of states (the quantitative relationship between the EELS and the EMLDOS in the particular case of small metallic nanoparticles is discussed in refs 5 and 31) where z is the direction parallel to the electron path (and perpendicular to the nanoprisms faces in the present experiments). The equivalence in energy has already been pointed above in the paper. In Figure 5a, we display the computed electron energy loss probability for the corner and edge modes along a line scan parallel to the triangle edge. For each mode, the maximum of the electron energy loss probability is related to the E symmetry (top), and an optical excitation with a given polarization is exemplified in Figure 5b. The z-polarized electric field (Ez) due to the SP excitations by electrons (bottom) and optical plane waves (top) at the energy of the dipolar-corner SP (left), and quadrupolar-edge SP (right), are plotted. The optical induced field maps in the triangular plane are similar to those published earlier. The triangular side views reveal the S symmetry and the stationary wave nature of the optically
active SP. Similarity between SP excited by electrons and plane waves are moreover striking. It is also clear that the EELS signal (Figure 5a) peaks where the eigenmodes have large $E_z$ values (Figure 5b).

The induced field distribution obviously depends on the electron trajectory for EELS and on the light polarization for optics where the energy of the modes will not. For example, the dipolar-corner mode can be viewed as three degenerate modes that are excited with different probabilities depending on the trajectory/polarization. We note here that all the modes in such structures can be understood as harmonics of SRSPs with essentially quasistatic nature. To this end, we have developed a simple model based on the dielectric continuum theory. We expect that this work will help to better understand the nature of the plasmon modes in systems with at least one dimension smaller than the skin-depth, and as a consequence will serve as a guide for tailoring surface plasmon properties.

In conclusion, we have shown that the optical properties of nanoplatelets are essentially driven by their aspect ratio. This includes the energy positions as well as the intensity ratios. We have also demonstrated that the modes in such structures can be understood as harmonics of SRSPs with essentially quasistatic nature. To this end, we have developed a simple model based on the dielectric continuum theory. We expect that this work will help to better understand the nature of the plasmon modes in systems with at least one dimension smaller than the skin-depth, and as a consequence will serve as a guide for tailoring surface plasmon properties.

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