Identification of Multipolar Surface Plasmon Resonances in Triangular Silver Nanoprism with Very High Aspect Ratios Using the DDA Method†

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The extinction spectra of 5-nm thick, triangular silver nanoprism are calculated using the discrete dipole approximation (DDA) method. The calculations are proved to accurately converge by satisfying the usual criteria related to the applicability of the DDA. The ultrathin thickness of the nanoprism considered here has the advantage of making it possible to largely tune their aspect ratio (AR) from 5 to 40, and simultaneously limit all their dimensions below the wavelength of the incident light. For nanoprism with AR ≥ 15, several intense bands are observed. These bands correspond to the well-known, in-plane, dipolar surface plasmon resonance (SPR) and several multipolar modes emerging at higher energies. Because of the high AR of the nanoprism considered in this work, the multipolar SPR are particularly well observed, thus making it possible to examine them in detail. The calculated extinction spectrum shows a clear dependence on the edge length, the thickness, the aspect ratio and the volume of the nanoprism. The evolution of the extinction spectrum when simulating the presence of a substrate is also investigated as well as that induced by changing the size of the truncation in snipped nanoprism. The qualitative agreement of the presented simulations with previous experimental observations made by other groups confirms the ability of the DDA method to predict the optical properties of such ultrathin triangular nanoprism.

1. Introduction

The special optical behavior of metal nanocrystals results from the interaction of their free conduction electrons with the incident light.1 The surface plasmon resonance (SPR), which is shown by the emergence of an intense band in the extinction spectrum, arises when the oscillating electric field of the incident light resonantly couples with the conduction electrons making them collectively oscillate at the same frequency. The SPR spectra of noble metal nanocrystals have been demonstrated to markedly depend on the structural characteristics of the nanocrystals such as their size and shape,2 as well as their external dielectric environment.3 Detailed information on how all of these parameters can influence the optical properties of nanocrystals is crucial in order to use the surface plasmon resonance (SPR) of these nanocrystals for various applications such as those developed in optics,4–6 surface enhanced Raman spectroscopy (SERS),7,8 biosensor,9 and medical diagnostics.10–14

Several groups have developed new syntheses to produce triangular nanoparticles, also called nanodisks or nanoprism, with various truncations and aspect ratios.8,9,15–22 They showed that the SPR spectra of these nanoprism are highly sensitive to all the aforementioned parameters.8,15–17 Most of these experimental data were supported by simulations based on the discrete dipole approximation (DDA) method in order to assign the various bands observed in the SPR spectrum, as it has been already reported for silver and gold nanoprism.15,23–26 Among all of these bands, the most intense corresponds to the in-plane dipole resonance. The extreme refractive index sensitivity of its energy was recently pointed out as the highest yet measured for nanoprism.15 The other bands, which are assigned to higher multipolar resonances, exhibit much weaker intensity and suffered of quite poor investigation until recent past. From all the previously reported experiments, it can be stressed that the proper observation and identification of the multipolar SPRs of triangular nanoprism often remain difficult or uncertain because of the low intensity and partial superimposition of the corresponding bands. Some way to go beyond such a limitation consists therefore in looking for nanoprism with very high aspect ratios. In a previous work,23 the Schatz’s group reported theoretical studies on the optical properties of gold triangular prism with various edge lengths and widths and a maximum aspect ratio of 40. Multipolar excitations were assigned to different in-plane plasmon modes up to the third order of a multipole expansion through the corresponding vector polarization plots. In another theoretical work,24 Y. He and G. Shi have graphically assigned the SPRs of thin silver nanoprism. In spite of the previous studies, it is worth to note the current lack of results dealing both with the synthesis of ultrathin triangular prism of few nanometers in height and the study of their optical properties to provide a complete description and better knowledge of the multipole plasmon modes.

As mentioned above, the synthesis of triangular particles with aspect ratios as high as 40 or more is a difficult task to achieve but this has been very recently carried out in our laboratory.27,28 These silver nanoprism are obtained by using multiply twinned silver nanocrystals with 5 nm in size as former constituents. Briefly, the nanocrystals are first deposited on highly oriented pyrolitic graphite (HOPG) where they spontaneously self-organize in such a way to form assemblies consisting of well ordered mono- and multilayers. After mild annealing of the sample under atmospheric pressure at 50 °C and the subsequent nanocrystals coalescence, very thin triangular silver nanoprism are formed in coexistence on the substrate with thicker crystalline coalesced nanocrystals of various shapes. Figure 1 is a
transmission electron microscopy (TEM) image showing a mixture of both kinds of the obtained particles together with some not coalesced primitive 5 nm particles that are randomly distributed on the substrate. As deduced from TEM analysis, both triangular prisms and large faceted particles exhibit quite large size and shape dispersions. Most of the nanoprisms appears with homogeneous contrast and slight darkness (inset of Figure 1), which indicates they are very flat and thin single domain crystals. Obviously, the selective formation of prisms with precisely defined structural parameters, i.e. with controlled size, AR or truncation, is not yet achieved by using this route and still remains a challenging issue. The coexistence of so many different particle sizes and shapes in the same sample prevents from properly studying the optical response of these particles by extinction spectrophotometry. Apart from the inconvenient mentioned above, the synthesis protocol has nevertheless some interesting advantage. Indeed, using dynamic force microscopy (DFM), the nanoprisms height was estimated to not exceed only 5 nm.29 To our knowledge, such formed nanoprisms exhibit probably the thinnest height that has never been reported in the literature until now. Because of the absence of experimental results, all information about the optical properties of nanoprisms with geometry comparable to that of the produced ones, is therefore not only a guide for our work but also motivate future efforts toward monodisperse syntheses or size-selective separation of these thin nanoprisms. Using the DDA method to predict the optical features of very flat and thin nanoprisms and to identify their various SPRs is therefore important in order to enable their future comparison with experimental measurements when the control of their geometry will be achieved.

Here, we assign the multipolar excitation peaks of ultrathin triangular silver nanoprisms with high aspect ratios (5 ≤ AR ≤ 40) via the DDA method. We combine a very low thickness (5 nm) with edge lengths ranging from 25 to 200 nm. This makes it possible to correctly distinguish the bands corresponding to the in-plane quadrupolar (l = 2) and higher multipolar (l = 3) modes, in addition to the dominant dipole resonance. Also, we report on the dependence of the multipolar excitations on the nanoprism geometry.

2. Computational Approach for the Simulations: Discrete-Dipole Approximation

Several numerical techniques are now available to calculate the optical properties of nanocrystals with different shapes by solving the electromagnetic scattering problem, such as the boundary element method (BEM),30,31 the discrete-dipole approximation (DDA), the finite-difference time-domain method (FDTD)32 and the finite element method (FEM).33 Note that the three former methods have been compared for modeling the optical properties of gold nanoparticles.34 Among all these techniques, the DDA, which is also known as the coupled dipole approximation, is a widely used, flexible and powerful method for computing scattering and absorption by targets of arbitrary geometry.35–37 In this paper, the versatility of the DDA method is exploited to largely tune the aspect ratio of silver triangular nanoprisms by choosing both their size and geometrical parameters in order to facilitate the study of their multipolar plasmon resonances.

2.1. Target Geometry. The DDA method was first introduced by Purcell and Pennypacker38 and then, developed by Draine and Flatau.36 The approximation involved in this method consists in representing the simulated object, which is the so-called target, by a finite array of polarizable points. Each of these points acquires a dipole moment in response to both the incident electric field and the fields created by all the other dipoles in the target. The target built to mimic a large triangular crystalline nanoprism is shown in Figure 2. This is a nanoprism whose triangular faces are oriented perpendicularly to the wave vector of the incident electromagnetic radiation. The latter is considered here to propagate along the x-axis direction and to be linearly polarized with its electric field being oriented along the y- or z-axis direction. It was checked by testing that the rotation of the target in the (yz) plane just changes the plasmon band intensity while the plasmon frequency remains unchanged in the extinction spectrum. In order to avoid long computing times we keep the same geometric incidence configuration for all our calculations. The dielectric function of the silver nanoprisms was taken to be the bulk experimental value, as published in Palik’s handbook39 since the nanoprisms under investigation in this work are large enough (with edge lengths of several tens of nanometers) to neglect the size dependence of their dielectric function. In addition, the silver triangular nanoprisms are simulated in vacuum with the refractive index of the surrounding medium fixed at unity. The typical dimensions of the nanoprisms range from 50 to 200 nm in edge length and from 5 to 7 nm in thickness. The aspect ratio, AR, which

![Figure 1](https://example.com/figure1.png) TEM image showing silver triangular nanocrystals and other well-crystallized particles with different sizes and shapes. All of them are formed by mild annealing of 5 nm silver nanocrystals self-organized on HOPG. Inset: TEM image of one triangular silver nanocrystal with very high aspect ratio. The scale bar stands also for the inset.

![Figure 2](https://example.com/figure2.png) Schematic representation of a nanoprism with triangular faces oriented perpendicularly to the x-axis direction. The edge length and the thickness of the nanoprism are denoted L and e, respectively.
is defined as the ratio of the edge length \( (L) \) to the thickness \( (e) \) of the nanoparticle, and it typically ranges from 5 to 40.

2.2. Applicability of the DDA to the Simulation of Ultrathin Nanoprisms. In the literature, there are various examples\(^\text{26,24,25}\) for which interdipole distance spacings such as 1 or 2 nm were found to accurately represent the optical properties of gold and silver nanoprisms with dimensions similar to those presented in this work. Here, several values of interdipole spacings ranging from 0.25 to 4 nm were employed to test the convergence of the DDA calculations when considering such ultrathin triangular nanoprisms. Figure 3A shows representations of the DDA target designed to simulate triangular silver nanoprisms with the same AR = 5 (25:5) and different interdipole distances, \( d \), and number of dipoles, \( N \), are used, i.e., \( d = 1 \) nm \((N = 1360)\), 0.75 nm \((N = 3507)\), 0.5 nm \((N = 10830)\), and 0.25 nm \((N = 86580)\).

Figure 3. (A) Representation of the DDA targets designed to simulate four silver triangular nanoprisms with the same AR = 5 (25:5) for which different interdipole distances, \( d \), and number of dipoles, \( N \), are used, i.e., \( d = 1 \) nm \((N = 1360)\), 0.75 nm \((N = 3507)\), 0.5 nm \((N = 10830)\), and 0.25 nm \((N = 86580)\). (B) Comparison of the extinction spectra calculated for a (25:5) silver nanoprisms as modeled by using the different targets previously described. (C) Evolution of the extinction spectrum calculated for silver nanoprisms with different sizes but all with the same aspect ratio \( (AR = 5) \). Here, the nanoparticle size is varied either by changing the \( d \) parameter and keeping \( N \) constant (solid curves) or, inversely, by keeping \( d \) constant and assigning \( N \) (dashed curves) to 85 580, 292 260, and 692 760 dipoles for the (100:20), (150:30), and (200:40) nanoprisms.

At Figure 3A, one can also expect that using an interdipole spacing larger than 0.5 nm to mesh the dipole grid can induce significant variations in the design of the target compared to the perfect triangular nanoprismatic shape. Indeed, when the interdipole spacing is set at \( d = 1 \) nm, it is worth noting that only five layers of dipoles are stacked along the thickness of the (25:5) nanoprisms. Furthermore, such a crude meshing of the dipole grid favors the formation of sharp tips, as seen in Figure 3A for the target generated by using \( d = 1 \) nm. As a result of both the imperfect design of the nanoprisms and the sharpness of its tip, spurious effects are likely to affect the calculations and artifacts can therefore emerge in the simulated extinction spectrum.

A pertinent pathway to go further in this analysis logically consists now in discerning the respective influence of the two parameters involved in the meshing of the dipole grid on the convergence of the calculations, i.e., the total number of dipoles, \( N \), and the interdipole distance, \( d \). For this, the evolution of the extinction spectrum calculated for silver nanoprisms with different sizes is presented in Figure 3C. All the nanoprisms considered here, were modeled by keeping, whatever the size, the aspect ratio at 5. In order to correctly estimate how the variation of the \( d \) and \( N \) parameters can independently affect the result of the DDA simulations, the nanoprisms size was varied through two different procedures. On the one hand, the interdipole spacing was changed \((0.5 \text{ nm} \leq d \leq 4 \text{ nm})\) while keeping the total number of dipoles constant \((N = 10830)\) and on the other hand, \( d \) was fixed at 1 nm while setting \( N \) to different values between 10830 and 692760 dipoles. From the comparison of the spectra plotted in Figure 3C, it appears that both of the two proposed protocols enable us to observe the same general effect on the extinction spectrum, that is the significant red shift of the dipolar plasmon band on increasing...
the nanoprism size. Nevertheless, when comparing, for the largest sizes, the profile and amplitude of the spectra, one concludes that the results obtained by carrying out the calculations following the second procedure are converged. At variance, the spectra calculated by considering the nanoprisms as modeled according to the first procedure exhibit profiles with small ripples comparable to those which are observed in Figure 3B in the spectrum calculated for $d = 0.75$ nm. All of the observations described above make it possible to expect our calculations to accurately converge, with the requirement of using a meshing that is fine enough to well design the target shape. For most of the nanoprisms under investigation in this work, fixing the interdipole spacing at $d = 0.5$ nm is likely to satisfy this condition since this value actually does not exceed a tenth of the thickness of the thinnest nanoprisms. Another criterion that still needs to be satisfied, before ensuring the applicability of the DDA method, is that the interdipole spacing must be small compared to the wavelength in vacuo, $\lambda$. This second criterion is usually expressed as $|m|kd < 0.5$, where $m$ is the complex refractive index of silver, and $k = 2\pi/\lambda$, the magnitude of the wave vector. The maximum value of $|m|kd$ remains less than 0.05 for all of our calculations, thus providing the guarantee for their validity. Finally, note also that the DDA simulations reported in this work require a large computational effort. For instance, the calculations carried out by using an IBM BladeCenter JS21 server for simulating the (200:5) nanoprism with $d = 0.5$ nm ($N = 692820$ dipoles) necessitate around 70 days of computing time. Thus, it appears rather unfruitful to adjust the meshing to values smaller than 0.5 nm when doing the balance between the extent of the additional effort to be invested and the limited gain to be expected in the accuracy of our results.

3. Results and Discussion

3.1. Polarization Dependence of the Extinction Spectrum.

The extinction spectra plotted in Figure 4 were calculated for a silver nanoprism with AR = 20 (100:5), with the incoming light being successively polarized in the three Cartesian directions. The two spectra calculated for the electric field of the incident wave oriented, respectively, along the y and z directions, i.e., for in-plane polarization of light, appear very similar in profile. Both of these spectra exhibit three bands centered at 1.5, 2.3, and 2.6 eV, respectively. From the examination of the polarization vectors for each resonance, one can then identify the corresponding excitation modes. Figure 5A shows the polarization vectors determined at 1.5-eV energy, i.e., at the maximum of the most intense extinction band (Figure 4). As clearly revealed by the schematic representation in Figure 5B, the SPR mode emerging at this energy corresponds to the dipolar resonance ($l = 1$ mode) associated with in-plane polarization. When looking now at the main directions of the polarization vectors obtained at 2.3 eV (Figure 5C,D), the corresponding...
energies when the AR is increased. For a nanoprism with AR = 7, with all of the SPR bands being shifted toward lower energy. We note a significant evolution of the spectra plotted in Figure 6. For a nanoprism with AR = 15.6 (125:13), we observe two bands. In parallel, for a nanoprism with AR = 9.6 (125:13), three bands are observed. The bands at high energy, corresponding to multipolar SPR, are well resolved. Also, from data obtained previously, the lower energy band is due to the in-plane quadrupolar SPR (l = 2 mode) whereas that at higher energy corresponds to the higher multipolar SPR (l = 3 mode). The condition for observing the in-plane quadrupolar band in the spectrum seems therefore to be more sensitive to the nanoprism AR than its volume. Actually, this band is observed only for large values of AR. The increase in the band amplitude with AR at constant volume can obviously be explained by the fact that the triangular face area also increases. Note that, as expected, the in-plane dipolar resonance is shifted toward lower energies by increasing the aspect ratio.34

The spectra of triangular nanoprism simulated for different edge lengths ranging from L = 25 to 200 nm by steps of 25 nm are shown in Figure 7B with a constant thickness (e = 5 nm). As expected, the in-plane dipolar SPR band (l = 1 mode) moves toward lower energies on increasing the edge length. Note that for AR ≥ 30, the dipolar SPR band moves out of the energy range under consideration in the present calculations. For the multipolar modes, the in-plane quadrupolar (l = 2 mode) and in-plane higher multipolar (l = 3 mode) SPR bands are also observed to shift toward lower energies when the edge length increases. For AR < 10, only the l = 3 mode is observed. Then, on increasing the nanoprism AR, the band associated with the in-plane quadrupolar SPR (l = 2 mode) is observed for AR ≥ 15. Furthermore, for higher values of the AR, the in-plane quadrupolar SPR band strengthens and “competes” in amplitude with the in-plane higher multipolar SPR band. Finally, for ARs as large as 40, the amplitude of the in-plane quadrupolar SPR band dominates the higher multipolar one (l = 3 mode). Also it is evident that the energy difference between the various SPR bands does not vary by changing the AR (Figure 7B inset).
3.3. Effect of Truncation. From data obtained for rather thick silver\textsuperscript{42,15,43} and copper nanodisks,\textsuperscript{44} we know that the SPR spectrum is drastically affected by snipping. For very thin and rather large silver nanoprisms, this statement still remains an open question. The degree of truncation, TR, is defined as \( \alpha/L \), where \( \alpha \) is the length of the snip (inset of Figure 8). In order to avoid a large variation in AR resulting from the truncation of a nanoprism, the extinction spectra were calculated with the TR not exceeding 0.2. The Figure 8 inset shows a front view of a snipped nanoprism. Before truncation (\( \alpha = 0 \)), a nanoprism with AR = 20 (100:5) is considered. From this nanoprism used as the original shape, different truncated nanoprisms were then investigated for various TR values up to 0.2, incremented by steps of 0.05, which correspond to the snips: \( \alpha = 5, 10, 15, \) and 20 nm, respectively. Note that the snipping slightly changes the AR. Figure 8 shows that the SPR bands shift toward higher energies when the TR increases. As previously described, in addition to the intense dipole resonance, two low intensity SPR bands are observed in the extinction spectrum for TR \( \leq 0.15 \): the quadrupolar in-plane resonance (\( l = 2 \) mode) and the higher order in-plane resonance (\( l = 3 \) mode). From the evolution of the spectra shown in Figure 8, one can expect the strength of the quadrupolar in-plane resonance to be nearly insensitive to the change in truncation whereas that of the \( l = 3 \) mode progressively decreases until it disappears at TR = 0.2.

In order to confirm this assignation, the polarization vectors of a (100:5) nanoprism are determined for TR = 0.1 at SPR energies of 2.5 and 2.7 eV. The polarization vectors are plotted in Figure 9, panels A and B, from which one can observe four and six distinct poles, respectively. This makes it possible to accurately assign the SPR bands centered at 2.5 and 2.7 eV to the quadrupolar in-plane resonance (\( l = 2 \) mode) and the multipoles \( l = 3 \) mode, respectively. Equivalently, when considering the same nanoprism as before with the largest truncation (TR = 0.2) and the corresponding polarization vectors as plotted in Figure 9C, it appears that the unique low-intensity SPR band centered at 2.5 eV can be attributed to the in-plane quadrupolar resonance (\( l = 2 \) mode).

3.4. Influence of a Dielectric Substrate. The dielectric environment may influence the optical properties of silver nanoprisms.\textsuperscript{3} For this reason, it seems pertinent to take into account the presence of a substrate in order to simulate the optical response of a system not only consisting of free nanoprisms but also, more realistically, of nanoprisms deposited on a solid base. As described in reference,\textsuperscript{3} the substrate is represented in the DDA target by a thin cylindrical slabs with a diameter twice the nanoprisms edge length and with a thickness equal to that of the triangular nanoprisms. Such a dimensioning of the substrate has been shown to be the best compromise between the minimum size of the target to be designed to ensure the convergence of the calculations and the limitation inherent to the large computational endeavor that is required for larger sizes.\textsuperscript{3}
4. Conclusion

The surface plasmon resonance spectrum of silver triangular nanoparticles with high aspect ratios is studied by using the DDA method. The applicability of this numerical method is established. The calculated spectrum exhibits several bands corresponding to extinction of light due to the $l = 1-3$ excitation modes. A significant dependence of the extinction spectrum is clearly revealed on the polarization of the incident electric field, the volume and the aspect ratio of the nanoparticles as well as their truncation. By changing the light polarization, bands originating from in-plane and out-of-plane plasmon modes can be identified in the spectrum. All the observed plasmon resonances dramatically shift toward lower energies on increasing the volume and/or the aspect ratio. Also, the aspect ratio and truncation are demonstrated to play a key role in determining the strength of the multipolar SPR.

The theoretical study typically illustrates how DDA can guide design of nanostructures with unique optical properties when the experiment itself is fraught with practical difficulties. From the DDA simulations presented in this work, one can expect that such a high sensitivity of the optical properties of triangular nanoparticles with high aspect ratios to their shape and size characteristics should open interesting opportunities in using similarly shaped silver nanocrystals for practical applications.

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References and Notes

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