Dependence of the localized surface plasmon resonance of noble metal quasispherical nanoparticles on their crystallinity-related morphologies

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The absorption spectra of 5 nm noble metal nanoparticles (Ag, Au, and Cu) with typical morphologies of multiply twinned particles (MTPs) and single crystals are calculated by using the discrete dipole approximation method. Among the considered morphologies, it is found that icosahedral, cuboctahedral and truncated octahedral particles behave like quasispherical particles whereas the optical response of the decahedral particles significantly differs from the others. This result, which originates from the shape anisotropy of the decahedron, points out the capacity to discriminate decahedral MTPs from a population of particles with mixed crystallinities and related quasispherical shapes. © 2011 American Institute of Physics [doi:10.1063/1.3523645]

I. INTRODUCTION

Noble metal nanocrystals represent the transitional regime between the bulk metal and metal-cluster compounds, where bulk properties of the material begin to change due to finite-size effects. The control of the structure (ordering of atoms in nanocrystals) of the nanoparticles (NPs), called nanocrystallinity, is one of the most fundamental challenges in condensed matter science. Face-centered cubic (fcc) noble metal nanocrystals exhibit different shapes directly related to their nanocrystallinity. The single-domain nanocrystals are commonly cuboctahedral or truncated octahedral while their multiply twinned counterparts, usually called multiply twinned particles (MTPs), are decahedra and icosahedra. The influence of nanocrystallinity on the chemical and physical properties of metal nanocrystals suffers from an extensive lack of knowledge and remains an open question. In this context, recent advances in the methods of synthesizing NPs of chosen crystallinity could be very helpful for a better understanding of how the crystallinity of the NPs can affect their properties through the influence of internal crystal defects and/or due to variation in morphology from one crystal structure to the others.

The optical properties of noble metal NPs related to the dipolar localized surface plasmon resonance (LSPR) band are attributed to the collective oscillation of the conduction electrons of the nanoparticle due to their resonant coupling with the electric field of the incident light. Experimentally and from various numerical models, the frequency and strength of these oscillations strongly depend on the size of the nanocrystals, and their local dielectric environment. Recently, the atomistic structure dependence of the LSPR in metal NPs of up to 4000 atoms with a diameter of around 4 nm has been studied by using a time-dependent self-consistent tight-binding method. Besides, the extinction spectra of noble metal NPs of various shapes have been also theoretically studied by using the discrete dipole approximation (DDA) method in order to analyse the evolution of their optical response when the NP’s shape becomes anisotropic. Comparing the extinction spectra of Au, Ag and Cu NPs with different geometries commonly observed for seeds to those of elongated NPs shows that the position of the parallel and perpendicular (to the axis of revolution) plasmon components depends both on the aspect ratio and the NP end shape. In another work, González et al. already studied the influence of the polyhedral shape of Ag NPs on their optical response through the comparison of experimental absorption spectra of colloidal solutions with theoretical results obtained using the DDA method. The authors concluded that colloidal suspensions of Ag NPs with a narrow size distribution show few structural shapes.

Here, we compare the calculated optical responses of noble metal NPs with different typical crystallinity-related morphologies that are chosen in reference to those frequently observed for quasispherical NPs with either a multiply twinned or single-domain crystal structure. It is clearly demonstrated that even for ultrafine NPs whose size does not exceed 5 nm, the optical response of decahedra is discriminable from that of other polyhedra, such as icosahedral, cuboctahedral and truncated octahedral. Indeed, this comparison reveals that the latter polyhedra behave like a sphere whereas the decahedral NPs exhibit specific behavior due to their shape anisotropy.

II. RESULTS AND DISCUSSION

A. Typical crystallinity-related morphologies of quasispherical metal nanoparticles

Silver, gold, and copper are three metals that crystallize in the fcc crystal structure. At the nanometer scale, the nanocrystals have morphologies that are representative of their crystal structure. The MTPs are favorable crystal structures for small nanocrystals due to the fact that the most stable (111) faces surround such particles. Figure 1 shows the two major geometrical shapes of particles belonging to...
the family of MTPs, which are the decahedron and the icosahedron formed by assembling, respectively, five and twenty single crystalline fcc tetrahedral subunits to a single apex. Although the aforementioned MTPs probably constitute some of the major crystal structures observed for the most commonly synthesized metal NPs, it is noteworthy that other morphologies also exist, in particular those related to single crystalline NPs. As typical examples of the most frequently observed morphologies of single crystals with an fcc structure, one finds polyhedrals with $O_h$ symmetry, like the cuboctahedron and the truncated octahedron. Schematic representations of their geometric shapes are also presented in Fig. 1. These two morphologies result from different growth rates between the [111] and [100] facets. Defining by $R$ the ratio of the growth rate along the $<100>$ to that of the $<111>$, the cuboctahedron is formed for $R = 0.87$, while the truncated octahedron appears when $R = 1.15$. Other morphologies such as twinned nanorods, irregular multipods or branched NPs will not be considered in this work more specifically dedicated in studying the optical response of NPs with a quasispherical shape. Thus, the simulations reported below deal with the various typical morphologies shown in Fig. 1.

B. Experimental study of Au nanocrystals by transmission electron microscopy and photoabsorption measurement

Au nanocrystals have been synthesized by using a one-step one-phase route. Here, the colloidal nanocrystals are coated by dodecanethiol molecules and dispersed in toluene. Looking at their transmission electron microscopy (TEM) image shown in Fig. 2(a), one notes that all these nanocrystals exhibit quasispherical shapes and a narrow size distribution with an average diameter of 5.3 nm, as indicated by the size histogram plotted in the inset of Fig. 2(a). Besides, comparing the measured visible absorption spectrum of the Au colloidal solution to that of one single Au nanosphere calculated by the DDA method allows pinpointing out the similitude between their profiles. Indeed, examining the two corresponding absorption spectra shown in Fig. 2(b), one notices that both are dominated by one single LSPR band growing at around 520 nm. More precisely, this band is centered at 519 nm in the experimental spectrum while it is observed to be slightly redshifted at 524 nm in the calculated one. This redshift can be explained by the small overestimation of the refractive index of the host medium, which probably does not strictly match that of the dodecanethiol molecules as it was assumed in our calculation. In spite of the narrow size distribution of the Au nanocrystals, it is worth noting that neither anomalous feature nor significant blueshifting (∼5 nm) of the LSPR is observed in the measured spectrum. Therefore, one concludes that the average optical response of the Au nanocrystals seems actually to be not affected by the spatial nonlocality of their dielectric function. For that reason, the calculations presented in this work do not account for such nonlocal effects as those predicted by McMahon et al. for spherical Au NPs of a few nanometers in size.

A careful examination of the TEM image presented in Fig. 2(c) allow observing faceted Au nanocrystals, revealing their shapes to differ from the perfectly spherical one. Let us mention that detailed morphological analysis by HRTEM has been already performed for various kinds of fcc structured metal nanocrystals. Depending on the presence or not of defects in the crystal structure of the nanocrystals, these latter can be classified as either polycrystalline or single-domain nanocrystals, respectively. These two types of nanocrystals can be more easily distinguished in a dark field TEM image where their polycrystalline composition is clearly revealed by inhomogeneous patterns, as seen in the image shown in Fig. 2(d). As mentioned above, among the variety of existing defects, twinning is one of the most frequently observed in fcc metal nanocrystals. Briefly, twinning originates from two subgrains sharing a common crystallographic plane, in such a way that the structures of these subgrains look like the mirror images of each other relative to the twin plane, which is usually a [111] plane in fcc nanocrystals. Decahedron and icosahedron are known to be the most typical morphologies of MTPs.

Interestingly, the correlation between the nanocrystals morphology and their crystallinity offers the capacity to discriminate their optical response through the shape dependence of the SPR characteristics. In this regard, the slightly oblate shape of decahedral MTPs is expected to favor their selective excitation by using an appropriate monochromatic light source in spectroscopic measurements based on a plasmon-mediated process. For instance, the discrimination of decahedral MTPs from nanocrystals with quasispherical morphologies is likely to explain the crystallinity dependence recently observed in plasmon resonant Raman scattering measurement of anisotropic Au nanocrystals. Indeed, the contribution of the MTPs to the Raman scattering signal was observed to increase with respect to that of single-domain nanocrystals when turning the excitation wavelength from the green to the red, which
FIG. 2. (a) TEM image of 5.3 nm Au nanocrystals and the corresponding size distribution histogram (inset) determined over a population of 2000 nanocrystals; (b) Measured visible absorption spectrum of the Au colloidal solution described in (a) plotted together with the absorption spectrum of one single 5 nm Au sphere calculated using the DDA method. For this calculation, the surrounding medium of the sphere is assumed to be that of the dodecanethiol ($n = 1.46$); (c) Bright field and (d) conical dark field scan TEM images of Au nanocrystals. The scale bar shown in (d) also stands for (c).

C. Numerical approach: Discrete dipole approximation

The numerical approach used in this work to simulate the absorption spectra of noble metal NPs of different morphologies consists of the so-called discrete dipole approximation method. In fact, this method has been extensively used during the last few years to simulate the optical response of various systems composed of either individual or multiple objects of any size and shape. The DDA method appears therefore as being particularly well suited to model and study the LSPR spectra of crystalline particles having similar shapes, like those frequently observed at the nanoscale by using scanning or transmission electron microscopy techniques. In our calculations, the effective radius of the NPs, which corresponds to the radius of the isovolumic sphere, is fixed at 5 nm. In order to account for the finite size effects on the dielectric properties of such ultrafine metal particles, the dielectric functions used were size-corrected by applying the same procedure as that described elsewhere. It should be also noted that the refractive index of the surrounding medium is set to a constant value of $n = 1.46$ to simulate the presence of dodecanethiol molecules on the NP surface, in regard to their common use as a coating agent in various routes for the synthesis of metal nanocrystals. Instead of using the DDA method for simulating the optical response of noble metal NPs, other numerical approaches, which are currently being used for studying the electromagnetics properties of metallic nanoobjects, would be likely to reproduce similar results as those reported in this work. In particular, the boundary element method (BEM) and the time-dependent self-consistent tight-binding method allow simulating the optical response of metal NPs with arbitrary morphologies. However, it should be also noted that the ability of the DDA method for simulating the absorption spectra of metal NPs has been already shown for a variety of morphologies, such as nanodisks, triangular nanoprism, nanocubes and nanocylinders. As the present...
study actually does not aim to compare the different computational approaches available for simulating the absorption spectra of well-defined polyhedral NPs, the results reported below are exclusively based on the DDA method.

**D. Calculated absorption spectra of Ag, Au, and Cu NPs with various morphologies**

As mentioned above, the DDA simulations under consideration are dedicated to decahedral, icosahedral MTPs as well as cuboctahedral and truncated octahedral single-domain NPs. The absorption spectra are plotted in Fig. 3, for Ag, Au, and Cu NPs. The spectra of the cuboctahedral NPs are calculated by taking the incident electric field oriented parallel to one square (100) facet of the cuboctahedron. This choice is somewhat arbitrary since no significant change in the optical response can be observed when the orientation of the target is varied. This arises from the fact that the quasispherical shape of the cuboctahedron makes its optical response roughly comparable to that of a sphere. Similarly, the spectra calculated for the icosahedral and truncated octahedral NPs exhibit no significant dependence on the target orientation knowing that, as for the former case, these latter spectra remain almost unchanged for all orientations. In contrast with the previous cases, the spectrum of the decahedron is orientationally averaged in order to account for its oblate-like shape. Note that the absorption spectrum calculated for a sphere with a diameter of 5 nm is plotted in each graph of Fig. 3 for comparison with the other crystallinity-related morphologies.

Looking at the calculated absorption spectra shown in Fig. 3, the LSPR band of quasispherical NPs, either with icosahedral, cuboctahedral or truncated octahedral shapes, appears to be slightly redshifted with respect to that of a nanosphere of equivalent size. At variance, a much larger redshift as well as a significant broadening of the LSPR band are observed for the decahedral NPs. These latter characteristics make the absorption band profile of the decahedral NPs very different from that observed for the other morphologies. This difference is particularly evident from the spectra plotted in Fig. 3(a) for Ag NPs. It should be noted that the absorption spectra of Au and Cu decahedra also exhibit a much broader and redshifted LSPR band than that observed for the other NP shapes but the change in the band profile is less pronounced in these two last cases, as seen in Figs. 3(b) and 3(c). The variable sensitivity of the LSPR characteristics to the NP shape, from one metal to the others, obviously arises from their intrinsic dielectric properties. A careful examination of the different metal dielectric functions, which is actually outside the scope of this work, would be required to precisely assign the origin of the variation in the LSPR sensitivity. Nevertheless, we will see below that this question can be reasonably addressed by studying, in more detail, the dependence of the LSPR characteristics on the respective orientations of the decahedron and the incident electric field.

**E. Optical response of decahedral MTPs**

To further analyze the optical response of the decahedral NPs, the absorption spectra of Ag, Au, and Cu decahedra have been calculated for the three target orientations schematically illustrated in Fig. 4(a). The different configurations considered in the following discussion correspond respectively to an incident electric field oriented either parallel (orientation 1) or perpendicular (orientation 2) to the pentagonal middle plane of the decahedron, or parallel to one of its facets (orientation 3). The absorption spectra of an Ag decahedron calculated for these three configurations are shown in Fig. 4(b). Depending on the target orientation, the profile of the spectrum

![FIG. 3. Calculated absorption spectra of (a) Ag, (b) Au, and (c) Cu NPs with cuboctahedral (blue curve with label 1), truncated octahedral (pink curve with label 2), decahedral (red curve with label 3), and icosahedral (green curve with label 4) morphologies. The spectrum calculated for one single sphere (black curve with label 5) is plotted in each graph for comparison with the other shapes. The targets of different morphologies are equally sized by taking an effective radius of 2.5 nm for all of them.](http://jcp.aip.org/jcp/copyright.jsp)
FIG. 4. (a) Schematics representing the three particular target orientations considered for calculating the absorption spectra of (b) Ag, (c) Au, and (d) Cu decahedra. The decahedral target is sized by setting its effective radius to 2.5 nm.

is drastically modified. For orientation 1, the spectrum exhibits a broad absorption band centered at 514 nm related to the collective oscillation of the conduction electrons parallel to the pentagonal middle plane of the decahedron. This band will be hereafter referred to as the parallel SPR absorption component. In contrast, when looking at the spectrum calculated for orientation 2, one observes a narrower and less intense band whose maximum is located at 355 nm. This latter band reveals the absorption of light corresponding to the perpendicular component of the SPR and related to the collective motions of the conduction electrons along the direction of the fivefold symmetry axis of the decahedron. Besides, on the basis of elementary geometrical considerations, it is easily deduced that the electric field projects on both the parallel and perpendicular directions to the pentagonal middle plane for orientation 3, therefore explaining the structured profile of the band observed in that configuration. Indeed, such a structured band arises from the weighted contributions of the parallel and perpendicular components of the SPR. This also explains the origin of the atypical profile of the LSPR band of the Ag decahedron observed in the orientationally averaged spectrum plotted in Fig. 3(a), as compared to that of the other quasispherical shapes.

Unlike the case of Ag, each of the absorption spectra calculated for Au and Cu decahedra with the orientation 3 exhibits a broad LSPR band with no apparent substructures, as shown in Fig. 4(c) and 4(d). However, similarly to the Ag decahedron, plotting the spectra calculated for orientations 1 and 2 enables observing, respectively, the bands related to the parallel and perpendicular components of the SPR for both Au and Cu decahedra, and also allows estimating the wavelength at the position of each band maximum. The parallel and perpendicular components of the SPR are peaked respectively at 586 and 514 nm for Au, and at 620 and 580 nm for Cu. Comparing these values to those measured above for Ag clearly shows that the amplitude of the splitting between the two SPR absorption components is significantly larger for Ag. In contrast, the amplitude of this splitting is observed to remain inferior to the halfwidth of the broader SPR band (i.e., the parallel component) in the spectra of Au and Cu decahedra. This explains why the perpendicular and parallel SPR absorption components, due to their superimposition, are not spectrally resolvable and appear as one single unstructured broadband in the two latter spectra.

III. CONCLUSIONS AND PERSPECTIVES

In summary, DDA simulations have been carried out to calculate the absorption spectra of 5 nm Ag, Au and Cu NPs with different typical morphologies. Namely, the icosahedron and decahedron are chosen in reference to the most common morphologies of MTPs while the cuboctahedron...
and truncated octahedrons are used to simulate single-domain nanocrystals. From the comparison of the absorption spectra of all these NPs with that of a sphere, we show that most of them behave like quasispherical NPs, except the decahedron whose LSPR band is found to be much broader and more redshifted than the others, whatever the metal is. Analyzing the dependence of the optical response on the orientation of the decahedron allows attributing this specific feature to shape anisotropy inherent to the decahedral geometry.

Single metal absorption measurements would be very helpful to more properly investigate the influence of the crystallinity-related morphology on the optical response of the nanocrystals and overcome the limitation of the information that can be extracted from ensemble optical measurements. Several techniques are now available to characterize the optical response of individual metal NPs with size down to a few nanometers, such as the photothermal heterodyne imaging method\(^32\) or the spatial modulation spectroscopy (SMS) technique.\(^{33}\) In parallel, it has also to be noted that the precise determination of the crystal structure and morphology of each particle under investigation requires using a powerful characterization technique like high-resolution TEM. Setting up and combining two sophisticated techniques, such as SMS and TEM, to precisely correlate the geometry of the nanocrystals to their optical response has been recently shown to yield successful results\(^34\) but remains however a challenging manipulation.

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