

Single metal nanoparticle absorption spectroscopy and optical characterization

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Optical absorption spectra of small single metal nanoparticles are measured using a far-field technique combining a spatial modulation microscope with a broadband light source. Quantitative determination of the spectral and polarization dependencies of the absorption cross section of individual gold nanoparticles permits precise determination of their geometrical properties in excellent agreement with transmission electron microscopy measurements. © 2006 American Institute of Physics. [DOI: 10.1063/1.2172143]

Reduction of the size of an object down to a few nanometers is accompanied by large modifications of its physical and chemical properties. This is in particular the case for the optical response of nanoparticles that exhibits resonances, associated with carrier confinement in semiconductors and dielectric confinement in metals (local field effect). The characteristics of these resonances are very sensitive to the nanoparticle geometry and local environment.¹ These parameters fluctuate from particle to particle severely limiting the information that can be extracted from ensemble optical measurements. This limitation is overcome in single nanoparticle measurements that are now routine experiments for luminescent nano-objects such as quantum dots. For non-luminescent objects, such as metal nanoparticles, the recent development of far-field optical techniques now permits detection of single nanoparticle scattering or absorption and can yield access to their individual optical signature.²

Scattering-based methods are now well established but limited to large particles, of typically few tens of nanometers.^{3–6} For smaller particles, absorption strongly dominates the response and is thus the parameter to observe. It has been recently shown that the absorption cross section of a single metal nanoparticle can be quantitatively determined using a spatial modulation technique.² In this letter, we report on combination of this method with a broadband supercontinuum source to directly measure the spectral and polarization dependencies of the absorption of single gold nanoparticles. The measurements being quantitative, a full optical identification of the nanoparticle (size, shape and orientation) can be performed, i.e., an “optical image” of a nanoobject is obtained with a far-field technique.

The spatial modulation technique is based on modulation of the particle position.² A laser beam is focused by a 100× microscope objective on an isolated nanoparticle deposited on a substrate whose position is modulated over a few hundred nanometers at about 1 kHz. The transmitted light is collected by a second microscope objective and detected with a photodiode. A lock-in amplifier measures the ampli-

tude of the light modulation due to the particle displacement. This directly translates into the absolute value of the particle extinction cross section, σ_{ext} , at the laser wavelength, with a sensitivity of a few nm^2 .² For the small particles investigated here, scattering is negligible and the absorption cross section σ_{abs} can be identified with σ_{ext} .

To measure the absorption spectrum of a single gold nanoparticle we have coupled this technique demonstrated at a fixed laser wavelength with a tunable light source. As only few μW average power is required, a broadband spectrum has been created by injecting part of the output of a homemade Ti:sapphire oscillator into a nonlinear photonic crystal fiber. A supercontinuum covering the visible part of the spectrum from 450 nm to the near-infrared is thus generated.⁷ The white light is dispersed using a grating pair system and a small part is selected by a slit (bandwidth of $\Delta\lambda \approx 3$ nm). Injecting this beam into the previously described setup, the focal spot has been precisely calibrated for each wavelength and is in the 300–400 nm range. The limited spatial resolution of the far-field techniques requires the use of very dilute samples to address single particles (separated by typically more than 1 μm). They were prepared by spin coating a gold colloidal solution with mean size 16.2 nm on a glass substrate, with or without addition of a polymer (polyvinyl-alcohol). The glass and polymer refractive indices being close to 1.5, an almost homogeneous optical environment is obtained.

The σ_{abs} spectrum of a single gold nanoparticle measured with nonpolarized light is shown in Fig. 1(a) (open dots). The strong σ_{abs} enhancement around 540 nm is the well-known surface plasmon resonance (SPR), and the weaker small wavelength absorption due to interband transitions. Measurements performed with linearly polarized light show a wavelength shift of the resonance and a correlated modification of σ_{abs} with the polarization direction. The two extrema in SPR amplitude and wavelength position correspond to two orthogonal polarizations (Fig. 1(a)). This optical anisotropy is a signature of a nonspherical particle shape. It can be used to estimate the aspect ratio of the observed nanoparticle, assuming an ellipsoidal deformation.

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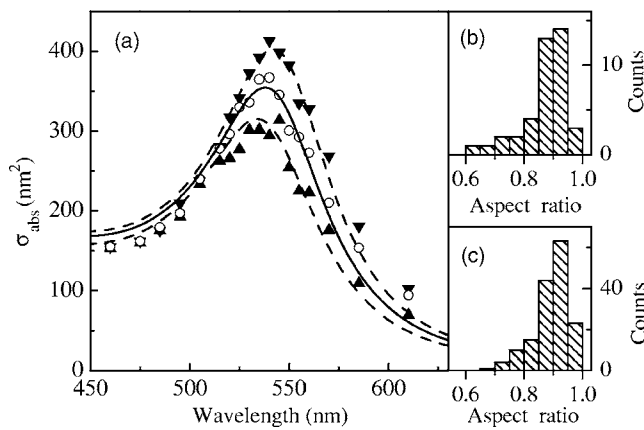


FIG. 1. (a) Absorption spectrum of a single Au nanoparticle measured with unpolarized light (open circles), and with two orthogonal linear polarizations corresponding to the extremal SPR wavelengths (up and down triangles). The solid line is the computed absorption spectrum of a nanosphere with diameter $D=17.6$ nm, for $n_m=1.5$ and $g=1$. The upper and lower dashed lines are computed for a light beam polarized along the long and short axes, respectively, of a nanoellipsoid with aspect ratio $\eta=0.92$ and major axis $2a=18.5$ nm; the same n_m and g values were used. (b) and (c) Histograms of the aspect ratio $\eta=c/a$ obtained from optical and TEM measurements, respectively.

The optical absorption of a nanoellipsoid much smaller than the wavelength λ embedded in a homogeneous matrix of refractive index n_m can be calculated in the quasi-static approximation.¹ For a light beam polarized along the i direction parallel to one of the main axes a, b, c of the elliptical particle, the absorption cross section σ_{abs}^i , is given by

$$\sigma_{\text{abs}}^i = \frac{2\pi V n_m^3}{\lambda L_i^2} \left| \frac{\epsilon_2}{\epsilon + \frac{1-L_i}{L_i} n_m^2} \right|^2, \quad (1)$$

where $\epsilon = \epsilon_1 + i\epsilon_2$ is the dielectric function of the metal nanoparticle and V its volume. L_i is a geometrical factor determined by the ellipsoid shape. For a prolate ($a \geq b=c$) or oblate ($a=b \geq c$) shape, L_i only depends on the aspect ratio $\eta=c/a$.¹ For a spherical particle $L_i=1/3$ and Eq. (1) reduces to the classical expression describing the absorption of a small nanosphere. For particles larger than a few nanometers, the weak size effect on ϵ can be introduced by adding an electron surface scattering term to its Drude part. The imaginary part of ϵ thus reads

$$\epsilon_2 = \epsilon_2^{\text{bulk}} + 2g v_F / D, \quad (2)$$

where v_F is the Fermi velocity and g a factor of the order of unity.¹ This additional term leads, in particular, to SPR broadening with size reduction. For ϵ^{bulk} we used the values of Ref. 8 that yield the best reproductions of ensemble measurements. The SPR wavelength λ_R^i is given by minimizing the denominator of Eq. (1), and is thus determined by the particle properties, through ϵ , its local environment, through n_m , and the light polarization.

The measured polarization dependent spectra can be well reproduced using this model, the two orthogonal polarizations corresponding to the nanoparticle main axes in the substrate plane [Fig. 1(a)]. For computing the spectrum, we have assumed a prolate shape but similar results are obtained for oblate shapes. The best fits of the spectra are obtained for $n_m=1.5$, a major axis length $2a=18.5$ nm, and an aspect ratio $\eta=0.92$, which fully characterizes the observed particle [Fig. 1(a), note that to slightly better reproduce the SPR width, the

surface contribution to ϵ has been added with $g=1$, but actually only weakly contributes for the investigated sizes]. Furthermore, the polarization directions for the extreme spectral position of the SPR determine the particle orientation on the surface.

The different parameters used for fitting the data are actually associated with different properties of the σ_{abs} spectra. They are to a large extent decoupled and can thus be precisely determined. The spectral position of the SPR is determined by the local refractive index n_m that also influences the σ_{abs} absolute value close to the SPR [Eq. (1)]. However, for a fixed λ_R^i (i.e., n_m), the σ_{abs} amplitude is set by the particle volume V [or a , Eq. (1)]. Finally, the SPR frequency shift and amplitude variation with polarization is only determined by the aspect ratio η . Its value being close to unity, only a small spectral shift is observed with, however, a large variation of σ_{abs} . This is a consequence of the overlap of the SPR with the interband transition threshold in gold: its blue-shift is accompanied by its broadening due to its increasing overlap with the interband transitions.

Polarization dependent measurements were performed on different nanoparticles to measure the fluctuations of η [Fig. 1(b)].⁹ Comparable results were obtained in the presence or in absence of polymer, showing that environmental anisotropy does not influence the data and that intrinsic nanoparticle properties are determined. This information can also be obtained in transmission electron microscopy (TEM) measurements, that also only yield access to the in-plane projection of the particle shape. The TEM data show that many particles are slightly nonspheric and exhibit elongated shapes characterized by a standard aspect ratio $\bar{\eta}=0.9$ identical to the optically measured one.¹⁰ The η histograms measured by the two techniques are also in excellent agreement [Figs. 1(b) and 1(c)], confirming the validity of our approach.

As expected, the nonpolarized experimental spectrum is well reproduced by averaging the polarized ones [Fig. 1(a)], but can also be phenomenologically reproduced assuming a spherical shape. Actually a good agreement is obtained using the same n_m value, $n_m=1.5$, and an effective diameter $D=17.6$ nm. This D value is consistent with the measured ellipsoid volume, yielding an effective diameter $2\eta^{2/3}a \approx 17.5$ nm. For a weak ellipticity, analysis of the nonpolarized spectrum in the spherical particle approximation thus yields consistent information on both the particle size and local environment as the full polarization dependent analysis. As most of the particles studied here fulfill this condition [Fig. 1(b)], we have extracted these parameters by analyzing the nonpolarized spectra in terms of the spherical model.

To illustrate the sensitivity of the measurements on the particle size, the nonpolarized absorption spectra of two single nanoparticles with almost identical SPR spectral position are shown in Fig. 2. They exhibit different amplitudes showing that they have different sizes. Fitting of the data with the spherical model yields $D=19.5$ nm and $D=18$ nm (using $n_m=1.43$). Though their sizes differ by less than 10%, they can be clearly identified [Fig. 2(a), note that the only parameters here are n_m and D]. The nanoparticle size histogram measured with this approach is in excellent agreement with the TEM measurement results [Figs. 2(a)–2(c)], yielding an average size of 16.6 and 16.2 nm, respectively.

In conclusion, combining the spatial-modulation far-field optical technique with a broadband supercontinuum source,

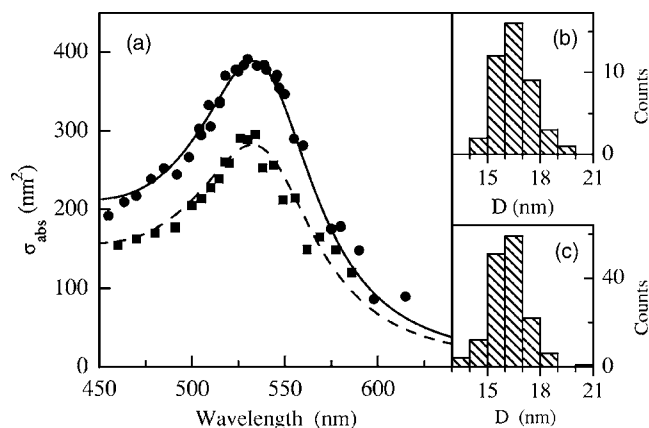


FIG. 2. (a) Absorption spectra of two single Au nanoparticles measured with unpolarized light (circles and squares). The solid and dashed lines are the spectra computed for spherical particles with diameters $D=19.5$ nm and $D=18$ nm, respectively, and the same environment refractive index, $n_m=1.43$. (b) and (c) Histograms of the diameter obtained from optical and TEM measurements, respectively.

the absorption spectra of single gold nanoparticles have been measured. Quantitative determination of the absorption cross section of the investigated particle and of its wavelength and polarization dependencies permits full optical determination of its properties: size, shape and orientation. The statistics of the results are in very good agreement with the TEM data. This demonstration of an optical characterization of a

nanoscale object with a far-field optical technique opens up many perspectives for identification and quantitative study of a metallic, or more generally, absorbing single nano-object via its optical signature.

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⁹Few particles with complex light polarization dependent spectrum were detected but not included in the statistics.

¹⁰Few particles with triangular-type shapes were observed in TEM but not included in the statistics.