Eur. Phys. J. D **43**, 271–274 (2007)
DOI: 10.1140/epjd/e2007-00112-y

THE EUROPEAN
PHYSICAL JOURNAL D

Optical extinction spectroscopy of single silver nanoparticles

P. Billaud[1], J.-R. Huntzinger[1], E. Cottancin[1], J. Lermé[1], M. Pellarin[1], L. Arnaud[1], M. Broyer[1],
N. Del Fatti[1,2], and F. Vallée[1,2,a]

[1] LASIM, CNRS, Université Lyon 1, 43 boulevard du 11 novembre 1918, 69622 Villeurbanne, France
[2] CPMOH, CNRS, Université Bordeaux 1, 351 cours de la Liberation, 33405 Talence, France

Received 4 August 2006 / Received in final form 30 October 2006

Abstract. The extinction spectrum of single silver nanoparticles with size ranging from 20 to 80 nm is investigated with the spatial modulation spectroscopy technique using either a tunable laser or a white lamp as the broadband source. Results are in good agreement with the prediction of the Mie theory, permitting to extract the nanoparticle size from the measured absolute value of the optical extinction cross-section. In contrast, the deduced refractive index of the nanoparticle environment and the reduction of the electron mean free path show a large dependence on the precise value of the bulk silver dielectric function.

PACS. 78.67.-n Optical properties of low-dimensional, mesoscopic, and nanoscale materials and structures – 78.67.Bf Nanocrystals and nanoparticles – 78.40.-q Absorption and reflection spectra: visible and ultraviolet – 78.40.Kc Metals, semimetals, and alloys

1 Introduction

The specific optical properties of metal nanoparticles are mostly associated to electron driven local enhancement of the electromagnetic field. The spectral signature of this effect, known as the Surface Plasmon Resonance (SPR), is directly connected to the nanoparticle geometry (size, shape, structure) and local environment (adsorbed molecules, matrix). These parameters fluctuate from particle to particle severely limiting the information that can be extracted from ensemble optical studies. These limitations can be overcome by performing single nanoparticle measurements that are now routine experiments for luminescent nanoparticles such as quantum-dots [1]. For non or very-weakly luminescent nanoparticles, such as metallic ones, this requires the development of very high sensitivity methods to detect their optical absorption or scattering.

Several far- or near-field methods have been recently developed in this context [2–8], only the far-field spatial modulation technique yielding quantitative information on the detected nanoobject [7,9]. It permits optical detection and direct measurement of the absolute extinction cross section of a single metal nanoparticle [7]. Single gold particles with diameter down to 5 nm were thus investigated with a sensitivity of a few nm^2. This new method offers the fascinating issue to deduce the shape and size of a nanoparticle only from optical measurements [9]. Combining it with a broadband supercontinuum source, we have shown that the quantitative spectral and polarization dependencies of the absorption of a single gold nanoparticle can be used as a signature of its morphology. A full optical identification of the studied nanoparticle (size, shape and orientation) can thus be performed, i.e., an "optical image" is obtained [9]. In this paper, we discuss extension of the Spatial Modulation Spectroscopy (SMS) method to single silver nanoparticle study, using either a laser based source or a white lamp.

2 Spatial modulation spectroscopy set-up

The SMS technique is based on modulating the position of a single nanoparticle in the focal spot of a tightly focused optical beam and lock-in detection of the resulting modulation of the transmitted light. Figure 1 shows the principle of the experiment with a white lamp as a light source: a quartz-tungsten-halogen lamp illuminates a micrometric pinhole, which is the point source of the experiment. The beam is then collimated using mirrors, coated to reflect light from near UltraViolet (NUV) to near InfraRed (NIR), typically 300 to 900 nm. It is focused close to the diffraction limit (typically 1 μm) on the sample surface by a reflecting microscope objective. The sample is formed by isolated nanoparticles separated by a distance larger than the focal spot size. Its position is modulated along a direction perpendicular to the beam direction at the frequency f using a piezoelectric translator. When a nanoparticle is under the focal spot, this

---

[a] e-mail: vallee@lasim.univ-lyon1.fr

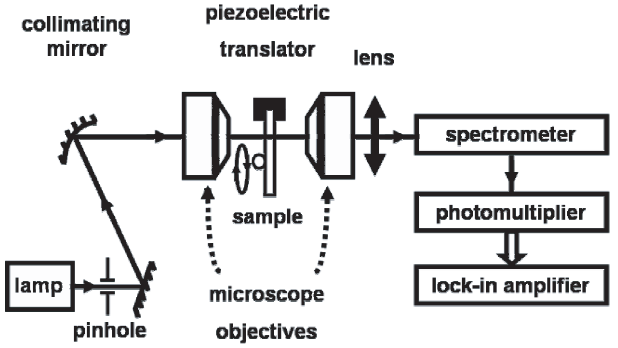

Fig. 1. Experimental setup for Spatial Modulation Spectroscopy measurements in the near UV — visible — near IR range using a white lamp.

position modulation translates into a modulation of the transmitted power [7]. A second identical microscope objective collects the transmitted light, which is sent into a spectrometer and detected by a photomultiplier. The modulated part of the light is then detected by a lock-in amplifier either at the f or $2f$ frequency. Provided that the focal spot is precisely known, the detected signal directly yields the absolute value of the nanoparticle extinction cross-section σ_{ext} [9]. An image of the sample is then taken by scanning its position in the plane perpendicular to the beam direction using a XY piezoelectric-stage.

Similar measurements were performed using a home-made Ti:sapphire oscillator frequency doubled in a BBO crystal. This provides a light source tunable in the 400−450 nm range, close to the silver nanoparticle SPR [10]. Refractive microscope objectives were thus used and the transmitted light was detected with a photodiode without any spectral selection.

3 Results and discussion

3.1 Small nanoparticles: tunable laser measurements

The extinction spectra of two single silver nanoparticles measured using the tunable laser source are shown in Figure 2. The samples were prepared by spin-coating a colloidal solution on a glass substrate after addition of a polymer (polyvinyl-alcohol). It acts as an embedding layer for the particles providing a more homogeneous environment. Conversely to the gold case [9], the SPR lies below the interband transition threshold of silver and shows up as a well defined quasi-Lorentzian line in a spectral region where absorption is dominated by intra-conduction band electron transitions (quasi free electron absorption) [11]. Compared to the ensemble spectrum of the colloidal solution, the individual spectra are red-shifted and show a narrowed surface plasmon resonance. The observed wavelength displacement is consistent with the change of the particle environment, i.e., the increase of its refractive index n_m from the solution to deposited samples in a polymer environment. The larger width observed in ensemble measurements is ascribed to inhomogeneous broadening due to nanoparticle size and shape distributions.

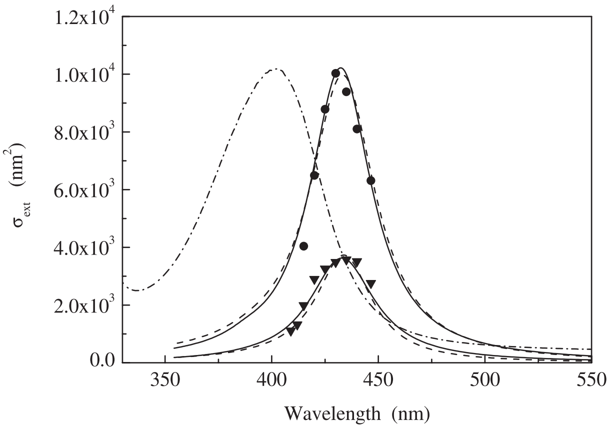

Fig. 2. Extinction cross-section of two single Ag nanoparticles (circles and triangles) deposited on a glass substrate in the presence of a polymer (polyvinyl-alcohol). The solid lines are the spectra of spherical particles of diameter $D = 21$ nm and 30 nm, computed using Mie theory with the dielectric constant measured by Johnson and Christy. The dashed lines correspond to Mie theory with the dielectric constant reported by Palik, for spherical particles of diameter 21 nm and 31 nm. The dash-dotted line is the normalized ensemble extinction spectrum of the Ag colloidal solution with average size $\langle D \rangle = 20$ nm.

As the absolute value of the extinction cross section is measured, comparison of the computed and measured spectra permits characterization of the studied single nanoparticle and, in particular, determination of its volume. Assuming that the nanoparticles only weakly deviate from sphericity this can be done using the equivalent sphere approach [9]. For a non-absorbing and isotropic embedding medium of refractive index n_m, the measured spectra can be reproduced using the Mie theory [12,13]. An important input in this fitting is the dielectric constant of silver, ε. We used here two sets of bulk ε values reported by Palik [14], and by Johnson and Christy [15], respectively. They were corrected for electron mean free path reduction in a nanoparticle by introducing an electron-surface scattering term in the Drude part of the dielectric function (i.e., using an electron scattering rate: $\gamma = \gamma^{bulk} + 2gv_F/D$) [13]. Three parameters were thus used in the fitting procedure but differently impact the measured extinction spectrum. The g value essentially influences the width of the resonance, n_m its spectral position and D the absolute value of the extinction cross-section. For the two studied particles, a good reproduction of the experimental data is obtained for a diameter $D = 21$ nm and 30 nm, respectively, using the Johnson and Christy set of ε values (Fig. 2), with very similar values, $D = 21$ nm and 31 nm, using Palik's data.

Note that, conversely to gold nanoparticles of similar size, scattering already plays a significant role in the measured silver nanoparticle extinction (sum of the absorption and scattering). For instance, the absorption over scattering cross-section ratio is about 8 for the 21 nm particle (it scales as about the inverse of the particle volume V). In both cases, the optical response is dominated by the dipolar contribution, i.e., the lowest order term in the Mie's theory [16].

Using the Palik dielectric constants, the position of the measured surface plasmon resonance is well reproduced with a refractive index of the environment $n_m = 1.52$ and 1.58 for the 31 and 21 nm particle, respectively. These values are consistent with a polymer-glass environment. The slight n_m variation is ascribed to spatial fluctuation of the environment for different silver particles, as observed in the case of gold [9]. In this fitting, no SPR broadening due to surface corrections has been introduced ($g = 0$), indicating that the imaginary part of the dielectric constant is overestimated in this ε set (in silver, the width of the SPR can be correctly defined and is directly proportional to the imaginary part of ε [11]). In the SPR spectral range, Johnson and Christy measured a smaller value of the imaginary part of the bulk silver dielectric constant. Using their data, a good reproduction of the measurement is obtained using a more realistic surface broadening constant $g = 2$. It has to be noted that, as measurements are performed with unpolarized light, the SPR width also includes a contribution from a possible elongation of the particle (an effect lumped in the actual broadening, i.e., in g). This effect is much larger in silver than in gold where the SPR position is blocked by its overlap with the interband transitions [16]. However, this fitting yields too large n_m values, 1.62 and 1.68 for the 30 nm and 21 nm nanoparticles, respectively. As the SPR spectral position is roughly given by the condition $\varepsilon_1 + 2\varepsilon_m = 0$ [16], this suggests overestimation of the real part ε_1 of the silver dielectric function in the SPR spectral range. This is consistent with its larger value in the Johnson and Christy data as compared to the Palik ones. The difference in the available bulk ε values is most probably related to the different crystallinity of the studied thin film samples [17] and to the difficulty in precisely measuring the weak value of the imaginary part of ε in this spectral range. Note that in the case of gold, the two sets of ε values yield very similar results, probably because of the larger contribution of the interband transitions to ε (the interband transitions both block the spectral position of the SPR and determine its width) [16].

3.2 Large nanoparticles: white lamp measurements

Due to its much lower brightness, a white lamp is less efficient than a laser for SMS experiments, the measurement sensitivity being limited by the number of available photons, i.e. the shot noise. However, the experimental system is much simpler and spectra can be easily recorded over a very large spectral range. This approach is thus very well adapted to large particles, extinction cross-section scaling as V for its absorption part and the square of V for its scattering part. In the present experiments, we investigated silver nanoparticles deposited on a porous alumina substrate of refractive index $n_{porous} = 1.66$. The samples were prepared by spin coating colloidal solutions with nanoparticle mean diameter of $\langle D \rangle = 40$ and 80 nm and standard deviation 3.2 and 6.4 nm, respectively.

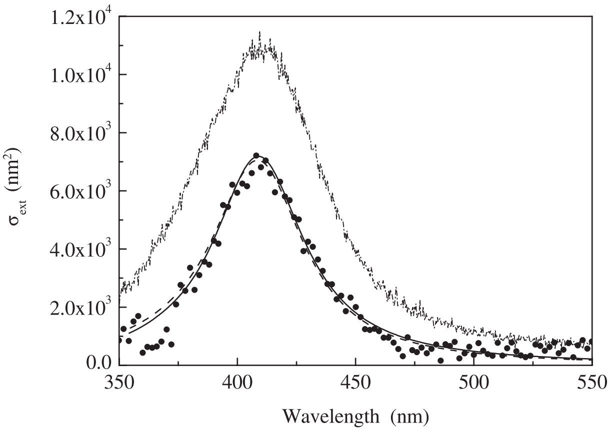

Fig. 3. Normalized spectrum of the $\langle D \rangle = 40$ nm colloidal solution and measured extinction cross-section of a single silver nanoparticle. The dashed line is a fit using the Mie theory with Palik's dielectric constant, for a $D = 32$ nm nanoparticle in a mean media of refractive index $n_m = 1.37$. The solid line corresponds to a fit using Johnson and Christy data set, yielding $D = 31$ nm and $n_m = 1.47$.

The spectrum of the $\langle D \rangle = 40$ nm colloidal solution is shown in Figure 3 together with the measured extinction spectra of a single deposited nanoparticle. As discussed before, the width of the SPR band is slightly broader than the theoretical one as a consequence of the size and shape dispersion in the colloidal solution. As for smaller particles, the single nanoparticle data can be very well reproduced using the Mie theory up to the fifth order for $D = 32$ nm. This size is consistent with the size dispersion of the colloidal solution. Though the nanoparticle environment is strongly inhomogeneous (particle deposited on a substrate without polymer) a good fitting is obtained assuming a homogeneous environment with an effective refractive index $n_m = 1.37$ using the Palik's data. This is close to the mean value of the air and porous alumina refractive index, $n_{av} = 1.33$, in agreement with the mean medium approach frequently used to describe the optical response of particles deposited on a substrate [13].

Conversely to the small nanoparticle case, a non-zero surface scattering coefficient $g = 1.6$ has to be used to broaden the computed SPR to reproduce the experimental data. This discrepancy is due either to a slight elongation of the particle shape and/or to the anisotropy of the environment experienced by the nanoparticles deposited at the air-substrate interface. Fitting the experimental results using the dielectric function values of Johnson and Christy yields larger values of $n_m = 1.47$ and $g = 6$, deviations that are consistent with those obtained for the small nanoparticles.

The impact of retardation effects are clearly seen in larger particles, i.e., for the sample prepared with the $\langle D \rangle = 80$ nm colloidal solution. The extinction spectrum of a single nanoparticle shows a red shift of the dipolar main peak, accompanied by a large blue wing due to multipolar contributions (Fig. 4). Assuming again a spherical particle in a homogeneous environment (Mie theory), the

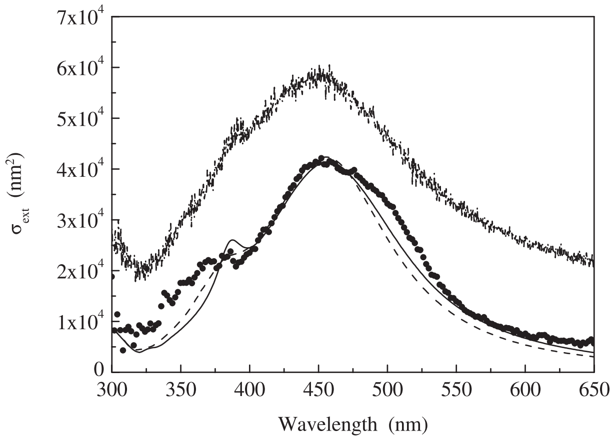

Fig. 4. Normalized extinction spectra of $\langle D\rangle = 80$ nm silver colloidal solution (up-shifted for clarity) and extinction cross-section of a single nanoparticle. The dashed (solid) line is a fit using the Mie theory for a $D = 78$ nm particle in a mean media of refractive index $n_m = 1.32$ (1.4), using the silver dielectric constant reported by Palik (Johnson and Christy).

main peak position and the absolute value of the extinction cross-section are well reproduced using $D = 78$ nm, $n_m = 1.32$ and $g = 2$ in agreement with the results for the 32 nm particle. The red wing deviation between the experimental and calculated shapes is probably due to deviation of the particle shape from sphericity. A better agreement is obtained with the Johnson and Christy ε data, but again using a larger n_m value ($n_m = 1.4$). The origin of this discrepancy could be further analyzed performing polarization dependent measurements to get further information on the particle shape [9].

The additional structure around 375 nm is ascribed to the quadrupolar term. Its calculated amplitude strongly depends on the set of ε value, and can also be influenced by a possible shape distortion of the nanoparticle. More detailed comparison of the experimental and theoretical data requires complete numerical calculations of the optical response of a nanoparticle on a surface, including shape distortion effects [18] and further experimental analysis of the polarization dependence of the measured spectrum.

4 Conclusion

Spatial Modulation Spectroscopy is a very efficient and unique tool for *quantitative* investigation of the optical response of a single nanoparticle. Depending on the amplitude of the extinction cross-section of the investigated nanoparticle, measurements can be performed over a broad spectral range using either laser-based high-brightness sources or a white lamp.

The first results obtained on silver nanoparticles with sizes ranging from 20 to 80 nm show a good agreement with the prediction of the Mie theory permitting to extract the nanoparticle size from the measured absolute value of the extinction cross-section. However, the deduced electron-surface scattering effect and surrounding refractive index are sensitive to the choice of the bulk silver dielectric function. Actually, this sensitivity offers the unique possibility of testing the different reported sets of bulk silver dielectric constant and of determining its modification in confined silver, provided that single nanoparticles in well-controlled homogeneous environment are investigated.

The authors thank E. Benichou and I. Russier-Antoine for providing the colloidal solutions. P.B., E.C., J.L., M.P., J.R.H., L.A. and M.B. acknowledge support from the Lyon NanOpTec Center, Institut Universitaire de France and Commissariat à l'Énergie Atomique. N.D.F. and F.V. acknowledge financial support by Conseil Régional d'Aquitaine.

References

1. S.A. Empedocles, D.J. Norris, M.G. Bawendi, Phys. Rev. Lett. **77**, 3873 (1996)
2. T. Klar, M. Perner, S. Grosse, G. von Plessen, W. Spirkl, J. Feldmann, Phys. Rev. Lett. **80**, 4249 (1998)
3. W.E. Moerner, M. Orrit, Science **283**, 1670 (1999)
4. C. Sonnichsen, S. Geier, N.E. Hecker, G. von Plessen, J. Feldmann, Appl. Phys. Lett. **77**, 2949 (2000)
5. D. Boyer, P. Tamarat, A. Maali, B. Lounis, M. Orrit, Science **297**, 1160 (2002)
6. K. Lindfors, T. Kalkbrenner, P. Stoller, V. Sandogdhar, Phys. Rev. Lett. **93**, 037401 (2004)
7. A. Arbouet, D. Christofilos, N. Del Fatti, F. Vallée, J.-R. Huntzinger, L. Arnaud, P. Billaud, M. Broyer, Phys. Rev. Lett. **93**, 127401 (2004)
8. I.I. Smolyaminov, J. Elliott, A.V. Zayats, C.C. Davis, Phys. Rev. Lett. **94**, 057401 (2005)
9. O.L. Muskens, N. Del Fatti, F. Vallée, J.-R. Huntzinger, P. Billaud, M. Broyer, Appl. Phys. Lett. **88**, 063109 (2006)
10. O.L. Muskens, N. Del Fatti, F. Vallée, Nano Lett. **6**, 552 (2006)
11. C. Voisin, N. Del Fatti, D. Christofilos, F. Vallée, J. Phys. Chem. B **105**, 2264 (2001)
12. C.F. Bohren, D.R. Huffman, *Absorption and Scattering of Light by Small Particles* (Wiley, New York, 1983)
13. U. Kreibig, M. Vollmer, *Optical Properties of Metal Custers* (Springer, Berlin, 1995)
14. E.D. Palik, *Handbook of Optical Constants of Solids* (Academic Press, New York, 1985)
15. P.B. Johnson, R.W. Christy, Phys. Rev. B **6**, 4370 (1972)
16. M.-M. Dujardin, M.L. Theye, J. Phys. Chem. Solids **32**, 2033 (1971)
17. O. Muskens, D. Christofilos, N. Del Fatti, F. Vallée, J. Opt. A **8**, 264 (2006)
18. P. Moreno, F. Gonzalez, J.M. Saiz, Opt. Lett. **31**, 1902 (2006)