T.3: Effect of Shape on the Optical Properties of Metal Nanoparticles

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1. Introduction

When the dimensions of a material are reduced to nanometer scales almost all of its properties change. There are two main types of confinements which play a strong role in determining the optical properties of metal particles, namely dielectric and quantum confinements. When dimensions of the particle are smaller than the mean free path of the electrons the energy level structure for the particle changes. This change shows up in various optical, electrical and thermodynamical properties of nanoparticle. Such modifications are due to quantum nature of charge carriers confined inside the metal particles, and are called as quantum confinement effects. The metal particles are usually embedded inside a host which has different dielectric properties. The difference in the dielectric constants between the host and metal particles leads to change in the electromagnetic field distribution inside and around the particle. This leads to what is known as the dielectric confinement. Localized surface plasmon resonance (LSPR) is one of the manifestations of the dielectric confinement. The dielectric confinement and hence the LSPR of the sample depends on shape and size of the particle, orientation of the particle with respect to the field, refractive index of the host medium, the substrate which holds the particles, adsorbed molecules, distribution of particles within the sample etc..

By controlling the shape and dimensions of the particle it is possible to tune the properties of the material to suit a required application. The color of the colloid can be changed from red to blue covering the entire visible region just by changing the shape of the silver nanoparticle in water. This is a striking example of how much the optical property of metal nanoparticle depends on its shape. The change in color occurs due to the collective response of free-electrons inside the metal particle to the applied optical field. Many applications of metal nanoparticles are based on this collective response. Another special property of metal nanoparticles near LSPR is their ability to focus the light to a region much smaller than the diffraction limit. This ability to focus light, also called the local field enhancement, has applications in near field microscopy, surface-enhanced Raman scattering and in nanooptics.

The nonlinear optical properties of metal nanocolloids get enhanced due to the local field enhancement. Measurements have shown that metal nanoparticles possess larger third-order nonlinear refractive index compared to their bulk forms. The time response of the nonlinearities is of the order of subpicosecond. Thus, metal nanoparticles could be ideal

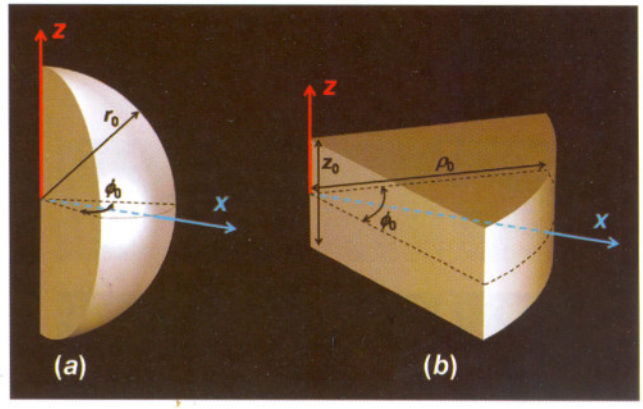

Fig. T.3.1 Shapes of metal nanoparticles for which optical properties has been calculated: (a) Sector-shaped nanoparticle with radius r_0 and azimuthal angle ϕ_0. (b) Wedge-shaped nanoparticle with radius ρ_0, azimuthal angle ϕ_0, and thickness z_0.

materials for developing ultrafast optical switches in optoelectronic circuits. Such large numbers of applications demand a deeper investigation of the optical properties of metal nanoparticles having different shapes. Unlike spherical nanoparticles, which have been studied extensively both theoretically and experimentally, there are only a few studies of particles having shapes other than sphere.

In this article, experimental and theoretical work carried out to understand the effect of the shape of a nanoparticle on its linear and nonlinear optical properties are reported. The quantum confinement effects on the linear and second-order

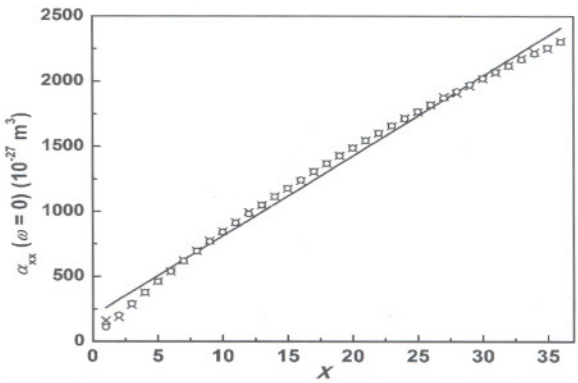

Fig. T.3.2 Variation of DC linear polarizability along the x direction as a function of X for wedge-shaped particles having 240 electrons. The crosses are the theoretically calculated values of DC polarizability α_{xx}. The solid line shows the expected scaling behavior of α_{xx} for wedges with the full length of the particle. The circles are the scaling behavior with the effective electron cloud length.

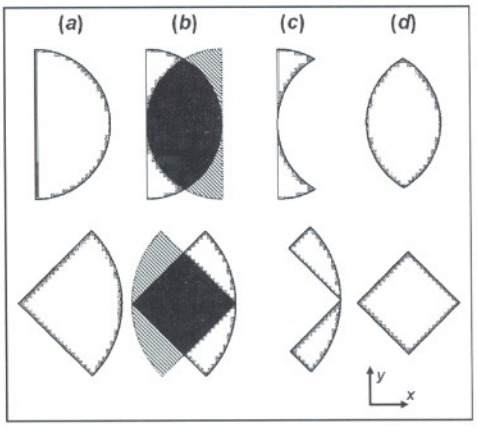

Fig. T.3.3 A geometric explanation for the method of calculating asymmetric volume of wedge or sector-shaped particle with azimuthal angles π (top row) and π/2 (bottom row). For clarity only the xy plane of the particle at z = 0 is shown. (a) Particle under consideration; (b) the nanoparticle and its reflected image (shaded region); (c) Nonoverlapping and (d) overlapping volumes of the nanoparticle, respectively.

polarizabilities for small metal particles with sharp tips were studied theoretically. Metal nanoplatelets of different cross-sections and spheres were prepared and their linear and nonlinear optical properties were studied experimentally.

2. Effect of Shape of Nanoparticle on the Linear and Second-order Polarizabilities

The linear and second-order polarizabilities of two new classes of shapes, namely sectors and wedges (Fig.T.3.1),

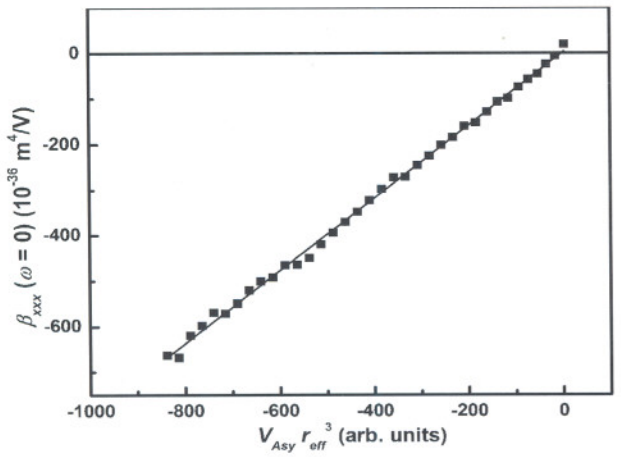

Fig. T.3.4 The plot between the static value of β_{xxx} and $V_{Asy}r_{eff}^{3}$ of wedges having 240 electrons. The solid line is the least squares fit to the data.

which are a segment of sphere and cylinder respectively, were studied theoretically. It is important to study the properties of hemispheres and triangular prisms since these shapes can be prepared experimentally. The hemispheres are a subset of sectors and wedges are a good approximation for triangular prisms.

The single-particle wavefunctions and the eigen energies of free-electrons confined inside hard walled sector and wedge-shaped particles are obtained by solving Schrodinger equation [1,2]. The resulting wavefunctions of electrons confined in sectors and wedges are a subset of wavefunctions of spheres and cylinders respectively. The ground state electron density at 0 K is very low near the edges and corners of the nanoparticles. Such low-density regions are found where ever the space available for the electrons is less than half of de'Broglie wavelength of Fermi-electron. The low-density regions play a role in the scaling behavior of linear and second-order polarizabilities.

Various components of the linear polarizabilities of the sector and wedge shaped nanoparticles have been calculated for different radii and azimuthal angles ($\phi_0 = \pi/X$). The results of the calculations show that the linear polarizability along the x direction scales as the square of length of the particle along the x direction, along with a correction for the low-density regime of electrons (Fig. T.3.2). This shows that in metal nanoparticles the free-electrons contribution to the linear polarizability scales as the square of free-electron cloud length. Wedges with very small azimuthal angle behave almost like a one dimensional electron cloud.

The sector and the wedge shapes lack an inversion center along one of its direction x (See Fig.T.3.1) and can have a finite second-order nonlinear response. For a fixed particle volume the magnitude of β_{xxx} at zero frequency increases with decreasing azimuthal angle for both wedges and sectors except for the case when azimuthal angle is π/2. A new quantity called "asymmetric volume" was introduced to quantify the asymmetry of a given particle shape and hence to explain the changes in the second-order polarizability with respect to the shape of the particle. As shown in Fig. T.3.3, the asymmetric volume (V_{asy}) of a particle is obtained by overlapping the original shape of the particle and a shape obtained by its reflection and removing the overlapping regimes. Further, β_{xxx} depends also on the electron cloud length along x direction. Calculation shows that β_{xxx} scales as the product of third power of electron cloud length and the asymmetric volume of the particle (Fig. T.3.4). The sign of β_{xxx} for particles with azimuthal angle π is negative while for all other angles it is positive. This difference in the sign of β_{xxx} is due to the difference in location of the tips along x direction for particles with different X. Moreover, particles having very small energy difference between the highest occupied and the

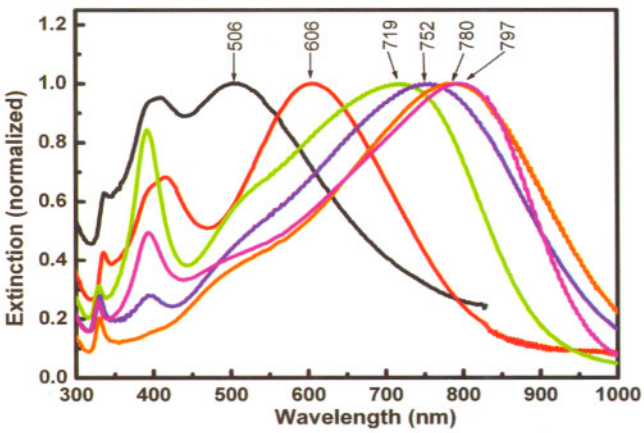

Fig. T.3.5 Extinction spectrum of colloids having nanoplatelets of different aspect ratios. The arrows indicate the in-plane dipole LSPR peak positions of the silver nanoplatelets. The in-plane dipole peak wavelengths increase with increase in aspect ratio of the nanoplatelets.

lowest unoccupied levels do not follow these scaling rules. Frequency dependence of the second-order polarizability shows that the maximum value of β_{xxx} itself behaves similar to the zero frequency case. The two-photon resonances of β_{xxx} which occur exactly at half the frequencies of resonances of linear polarizability along x direction are important since at those wavelengths β_{xxx} is high and simultaneously linear absorption is low.

3. Experimental studies on linear and nonlinear optical properties of metal nanoparticles

In order to study the effect of shape of the metal particles on its linear and nonlinear optical properties, metal nanoparticles of different shapes were prepared. Silver nanoplatelet colloids were prepared by two different methods. In the first method chemically prepared nanospheres were converted to nanoplatelets by exposing the sample to light. In the second method the nanoplatelets were prepared chemically using different capping agents. In the photoinduced conversion method the LSPR peak position can be exactly tuned to certain wavelength, depending on the wavelength of light used in conversion. However, in the pure chemical method the LSPR of the particles can be tuned to any required wavelength by changing the ratio of chemicals used. The linear optical properties of the nanocolloids were measured using spectrophotometer. Fig. T.3.5 shows the extinction spectrum of the silver nanoplatelets prepared by chemical method with different aspect ratios. Using the chemical method, the in-plane dipole peak of the colloid could be tuned to any wavelength from 506 nm to 797 nm.

The effect of aggregation on the optical properties was studied for nanoparticles of different shapes [3]. Aggregation brings about significant changes in the optical extinction spectrum of the sample. These changes in the extinction spectrum due to aggregation can be explained using a simple model of electromagnetic interaction between two nanoparticles in different orientations. Discrete dipole approximation (DDA) was used to calculate the extinction spectrum of the nanostructures. Comparison of numerical and experimental spectrum shows that a large number of particles present in the prepared aggregates could be touching each other at their base or close to it. The observed changes in the extinction spectrum of the nanospheres aggregates are in agreement with those predicted by the numerical calculations. Further, the nanoplatelet aggregates can be deaggregated using a nanosecond laser of suitable power.

It has been shown earlier that irradiation of a nanoplatelets by a high intensity femtosecond laser causes the platelets to

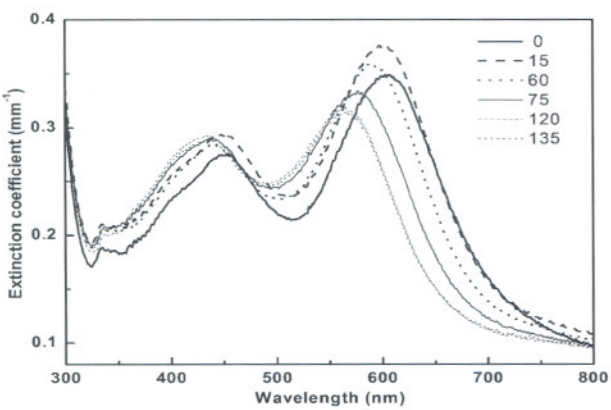

Fig. T.3.6 Extinction spectra of the nanoplatelets solution during exposure to femtosecond laser at fluence 20 mJ cm^{-2}.

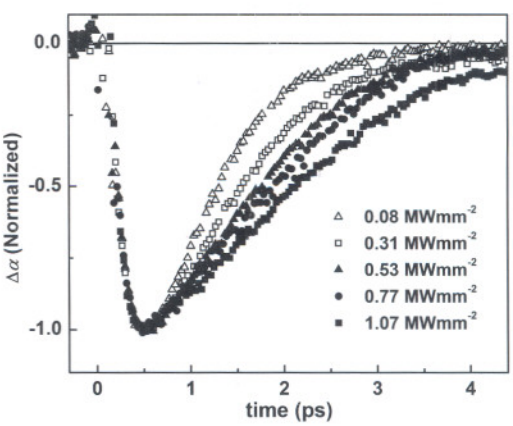

Fig. T.3.7 The change in the absorption of silver nanocolloids at different times and at different pump intensities.

fragment and it gets converted to nanospheres. In case of our samples, irradiation at fluence of the order of 20 J cm^{-2} fragments the nanoplatelets into small spheres. However, irradiation at fluence of the order of 20 mJ cm^{-2} shifts the LSPR peak wavelengths. The changes in the extinction spectrum show that the aspect ratio of the platelets reduces with increasing exposure time. Addition of capping agent PVP to the colloid arrests such peak shifts. DDA analysis of the changes in the extinction spectrum of the sample indicates that during exposure to laser the nanoplatelets reshapes mainly at the tips.

In order to understand the effect of shape of the metal particles on the third-order nonlinearity of the samples, $\chi^{(3)}$ of silver nanospheres and nanoplatelet colloids was measured using two beam self-diffraction technique [4]. The measurements were done at two wavelengths, 398 nm and 590 nm. These wavelengths correspond to the LSPR of nanosphere and nanodisk respectively. The nonlinearity was measured with 100 fs pulses using the transient grating geometry. Results show that for all shapes the optical nonlinearity of a metal nanoparticle gets strongly enhanced around the localized surface plasmon resonance peak. The ratio between the third order nonlinear susceptibility ($\chi^{(3)}$) and the linear absorption coefficient (α) of nanodisk at 590 nm is 3 times than that of $|\chi^{(3)}|/\alpha$ for spheres at 398 nm. Using a randomly oriented ellipsoidal model, it can be shown that the increase in $|\chi^{(3)}|/\alpha$ for nanodisk at 590 nm can be attributed to the change in the field enhancement factor and the imaginary part of dielectric constant due to size and shape associated quantum confinement effects. A sample containing both nanospheres and nanodisks shows strong enhancement of optical nonlinearity at 398 nm as well as at 590 nm. Thus, with a suitable mixture of shapes it should be possible to obtain a sample, which has high nonlinearity at several wavelengths.

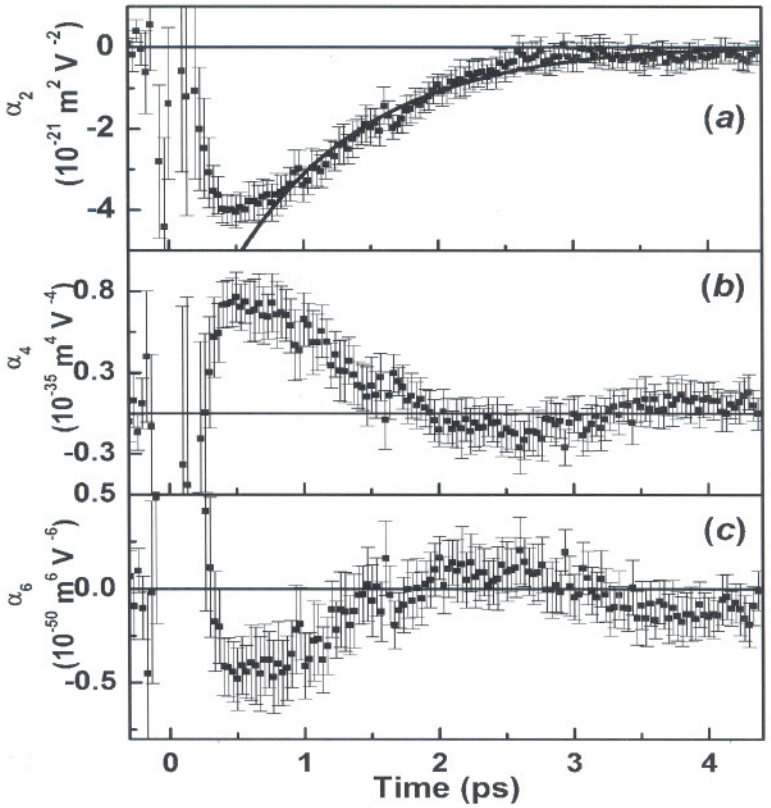

Fig. T.3.8 Variation of (a) α_2, (b) α_4 and (c) α_6 with delay between pump-probe pulses. The solid line in the case of α_2 is an exponential fit to the decay part of α_2.

To measure the higher-order nonlinearities and their decay times, transient absorption of metal nanoplatelets at different

pump intensities was measured using conventional pump-probe technique [5]. A 190 fs Ti-Sapphire laser operating at 778 nm, close to the in-plane dipole peak of the nanoplatelets was used for the measurements. The intensity of the pump was chosen such that it covered both weak and strong perturbation regime of metal particle excitation. Fig. T.3.7 shows the change in the absorption of the sample at different times for some of the pump peak intensities. By fitting a third-order polynomial to the peak change in absorption with respect to the pump intensity, the magnitude and sign of $Im[\chi^{(3)}]$, $Im[\chi^{(5)}]$ and $Im[\chi^{(7)}]$ of silver nanoplatelet colloid were obtained. The higher order nonlinearities in metal particles get enhanced much more than the lower order nonlinearities. Time dependence of the polynomial fitting coefficients was used to deduce the decay times of the third, fifth and seventh order nonlinearties to be 0.9 ± 0.04 ps, 0.41 ± 0.05 ps and 0.27 ± 0.06 ps respectively. The decay time of higher order nonlinearities is smaller than that for the lower-order nonlinearities. A two temperature model incorporating the temperature dependence of the electron specific heat explains the observed behavior of the transient absorption signal.

5. Conclusions

The linear polarizability of particles with dimensions of the order of few nanometers is very different from that of bulk and it depends strongly on the shape of the particle. Field calculations performed for particles with dimensions of few nanometers, should incorporate the size and shape dependent dielectric constants. The scaling behavior of second-order polarizability reported here should be helpful in designing new shapes with large second-order polarizability. It was expected that nonlinear response from metal nanoparticles with sharp tips will be much larger than particles with smooth surfaces. However, our results show that experimentally available particles are large and their tips are not sharp enough to show the expected very large field enhancements compared to spheres at their respective SPR peaks. In future, measurement of nonlinearities on small nanoparticles with different sharpness could give more insight on the effect of sharpness on field enhancements. On the other hand, nonspherical particles have the advantage of allowing a strong wavelength tunability of local field enhancements and can increase the nonlinearity of the metal colloid at the required wavelength. Our measurement also shows that this enhancement increases with order of nonlinearly. To take advantage of this tunability, different techniques for preparation of nanoplatelets, which can tune the SPR peak to a required wavelength were investigated. One method is by controlling the chemical constituents during preparation. Another way is to expose the nanoplatelet colloid to femtosecond irradiation of suitable fluence for tuning the SPR peak to a required wavelength. The results and methods presented here are general and are applicable for particles of other shapes also and hence will be useful for understanding properties of metal nanostructures.

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