Second Harmonic Generation of Individual Gold Metallic Nanoparticles

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Abstract

In this work, we report the Second Harmonic Generation (SHG) from individual gold metallic nanoparticles with an average diameter of 150 nm dispersed in a homogeneous and transparent solid matrix. This is achieved using a direction of collection for the harmonic photons at right angle from the 804 nm fundamental exciting beam direction with a scan of the cell in a plane perpendicular to the fundamental beam direction. A light polarization analysis of the SHG intensity is also performed, allowing us to provide a clear separation between single particles and aggregates.

1. Introduction

Over the last years, the observation of single objects with dimensions much smaller than the wavelength of light has received a particular attention. This interest mainly stems from the great sensitivity of the optical properties of the nano-objects to their morphology and environment. This is true for example for gold and silver nanoparticles where the collective excitation of the conduction band electrons, namely the surface Plasmon resonance (SPR), is highly sensitive to the physical properties of the particles like their size or their shape. It is in this case highly desirable to provide studies at the single particle level to avoid an averaging procedure over a large ensemble of particles and therefore over a large distribution of size and shapes. Linear optical studies of single metallic nanoparticles have been performed already [1]. It hence is possible to determine the absolute value of the extinction cross-section of a single particle and relate it to the exact morphology of the nanoparticle using a combined study with Transmission Electron Microscopy (TEM) [2]. In the nonlinear optical regime, this has also been performed for metallic nanoparticles deposited on substrates for Second and Third Harmonic Generation (SHG and THG respectively) [2-5]. However, rather weak signals are collected in the nonlinear regime and advantages from the experimental configuration must be sought. Hence, in the particular case of SHG, the process whereby two photons are converted into one photon at the harmonic frequency, a breaking of the centrosymmetry of the system is introduced with the substrate. This is critical since SHG is forbidden within the electric dipole approximation in centrosymmetric media. Nevertheless, an intrinsic breaking of the centrosymmetry can be introduced through the shape itself of the nanoparticles. This has been demonstrated for quasi-spherical metallic nanoparticles dispersed in a homogeneous medium, their shape being non perfectly spherical [6].

We report here in this work the first observation by SHG of individual gold metallic nanoparticles dispersed in a homogeneous and transparent matrix. Under this experimental configuration, the substrate breaking the centrosymmetry is absent and thus the true nonlinear optical properties of the particles are studied. However, because of the weak signals collected, the average diameter of the particles investigated was still 150 nm.

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2. Experimental Setup

The experimental set-up was designed after a conventional hyper Rayleigh scattering set-up following the details given in Ref.[7]. Briefly, the fundamental linear polarized light beam at a wavelength of 804 nm and a repetition rate of 76 MHz with a pulse duration of 180 fs from a femtosecond Ti-sapphire laser was focused on a fused quartz cell with a (X16, NA 0.32) microscope objective. The average power at the laser exit was about 300 mW. After careful separation from any scattered fundamental light with filters and a monochromator, the harmonic light was collected at right angle from the fundamental beam propagation direction in a photon counting regime.

Aqueous solutions of the gold nanoparticles, the average diameter of which was about 150 nm, were purchased and used as received. The gold nanoparticles were dispersed in a PolyAcryl Amide (PAA) polymer matrix.

The quartz cell was mounted on a three-axes translation stage in order to build SHG images. The scans of the cell were carried out perpendicularly to the incident fundamental beam direction. The random spatial distribution of the SH intensity peaks revealed areas with and without gold nanoparticles, see Figure 1 below.

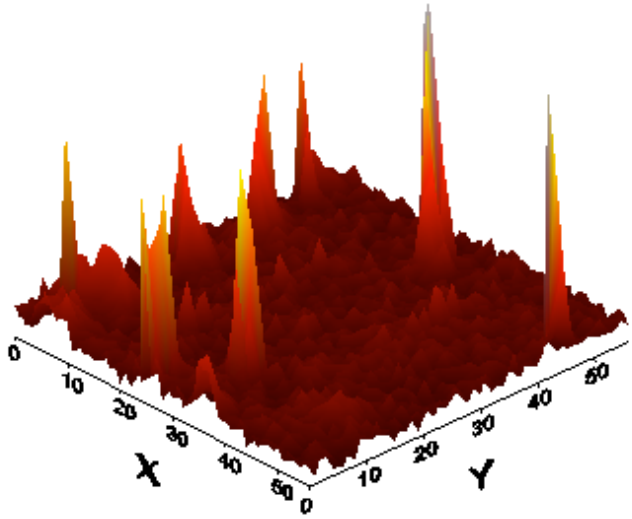

Fig. 1: 2D SHG intensity image of a gold nanoparticles containing PAA matrix. The fundamental beam propagation is along the Z axis and the SHG intensity collection is along the Y axis. The particle diameter is about 150 nm and the fundamental wavelength 804 nm.

3. Results and Discussion

With the scan of the quartz cell perpendicularly to the 804 nm fundamental beam, 2D SHG images were built of the 150 nm diameter gold nanoparticles containing PAA matrix. The intensities collected were in good agreement with the single particle sensitivity obtained with this same experimental set-up, as reported in an earlier work [8].

To obtain the nonlinear efficiency of a single metallic nanoparticle, first the subtraction of the SH intensity from the PAA matrix was performed. Similarly, the background photons arising from multiphoton excitations had to be removed. Then, the PAA polymer matrix was used as an internal reference to determine the quadratic hyperpolarizability of the 150 nm diameter gold nanoparticles. Using the quadratic hyperpolarizability of water as an external reference for the PAA matrix in absence of metallic nanoparticles, the quadratic hyperpolarizability for a single 150 nm diameter gold nanoparticle was found to be equal to $(1.19 +/- 0.15)x10^{-23}$ esu [9]. This value is in excellent agreement with ensemble measurements in solution or single particle measurements in a different matrix [7]. This result confirmed that the measurements could be indeed associated with single particles. It also shows

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that the quadratic hyperpolarizability of the 150 nm gold particles is, within experimental error, not affected by the nature of the surrounding medium.

A light polarization analysis of the SH intensity from a single 150 nm diameter gold nanoparticle was then undertaken. The leading emission term in the SHG response from a spherical 150 nm diameter nanoparticle is a quadrupole term, as demonstrated by theoretical analyses [10, 11]. Our observation was in perfect agreement with those results. However, the SH intensity was not exactly equal to zero for a vertically and horizontally polarized input beam and the four recorded lobes were not exactly equal owing to the imperfect spherical shape of the nanoparticle under study. Interestingly, in the case of an aggregate of particles, the SH intensity was drastically different. This behavior is attributed to the irregular shape of the aggregate, dramatically modifying its nonlinear optical properties. The polarization analysis of the SH intensity therefore allowed the complete discrimination between single nanoparticles and aggregates of nanoparticles.

4. Conclusion

In summary, we have studied single 150 nm diameter gold metallic nanoparticles embedded in a homogeneous and transparent PAA matrix. The results provide evidence that single gold nanoparticles have been observed despite the weak signals expected.

Finally, it is shown that the SH intensity from a single gold nanoparticle and from an aggregate of nanoparticle can be clearly discriminated by polarization resolved SHG measurements.

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