

# Nonlinear optical response from single spheres coated by a nonlinear monolayer

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We detected the second-order nonlinear response from single isolated spheres comprised from a centrosymmetric material but covered by a layer of a material with strong second-order nonlinear properties and isolated from an ensemble by the optical trapping technique. We show that when large size parameter spheres are used, the measured second-harmonic efficiency deviates strongly from the prediction of the nonlinear Rayleigh scattering theory. Our results are in very good agreement with the predictions from the exact nonlinear Mie scattering theory. © 2008 Optical Society of America  
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The generation of optical nonlinear signals from single nano-objects opens new perspectives for the studies of optical phenomena at the nanometric scale. Free from ensemble averaging, simpler pictures of physical mechanisms of nonlinear optical processes permit more adequate comparisons with theoretical models. In such studies, particularly interesting are objects with a well-defined geometry, such as centrosymmetric spheres. Centrosymmetric spheres covered by a layer of nonlinear material have been used to generate second-harmonic (SH) light in ordered [1,2] and disordered [3] configurations. Theoretical models based on the Rayleigh–Gans approximation were developed to determine the efficiency of the SH process [1,3,4]. More recently, an exact nonlinear Mie scattering theory for spherical particles was presented in [5]. An experimental observation of such single-scatterer features requires the study of single spheres in an isolated configuration free from multiple scattering events. On the other hand, the nonlinear optical generation in single nanoparticles may have interesting applications as tunable sources of coherent laser radiation with subwavelength size [6,7].

Several experimental schemes were proposed to measure nonlinear optical effects in single micrometer-size particles: spheres stuck to a flat surface or single nanoparticles in a polymer solution excited by a strongly focused beam [8,9], single liquid droplets [10], and low-concentration solutions [11,12].

The SH generation from microscopic particles optically trapped by a strongly focused beam has also been studied extensively [13–18]. The condition of strong focusing, necessary for the optical trapping, is favorable for the effective excitation of nonlinear processes as well. An important advantage of the trap-

ping technique, over the method of detection from low-concentration solutions, is that the former permits one to unambiguously study a single particle of a desired size. However, the interpretation of the results is more difficult, because the use of an index-matching liquid maintaining intact the distribution of the incident optical beam is not possible. Nevertheless, the optical trapping technique combined with an independent pumping system opens new perspectives for the study of nonlinear optical effects in microstructures where the spatial distribution of the structures plays a crucial role. For example, by decreasing the distance between two gold nanoparticles, the four-wave mixing yield increases by 4 orders of magnitude [19]. A multiple-beam optical trap [20] can generate a pattern of nanoparticles with a desirable spatial symmetry and, combined with their nonlinear response, is a subject of much current interest.

The addressed problem concerns the detection of the second-order nonlinear response of spheres comprised from a centrosymmetric medium but covered by a monolayer of a material with strong second-order nonlinear properties. We detected the response of a single sphere, isolated from an ensemble by the optical trapping technique. To achieve this aim we used two optical beams of different wavelengths and confocal parameters. A strongly focused beam acts as the optical trap, and a second beam with a wide waist excites the nonlinear response.

We studied a mixture of two types of particles: carboxylate surface-modified polystyrene 0.4  $\mu\text{m}$  in diameter spheres (refractive index  $n=1.56$ ) from Ikerlat Polymers S. L. and carboxylate-modified Melamine resin 4  $\mu\text{m}$  in diameter spheres ( $n=1.68$ ) from Sigma-Aldrich. In the former case the parking area (i.e., the smallest area needed to place a mol-

ecule on the surface) is  $31.1 \text{ \AA}^2$  per carboxylate group, while in the latter one the parking area is estimated to be roughly  $1.5 \text{ \AA}^2$ . The carboxylate groups were covalently linked to modified crystal violet (CV) molecules, which are chromophores with high value of second-order hyperpolarizability. In both cases the parking area is significantly smaller than the dimensions of the CV molecule, which were determined to be  $100 \text{ \AA}^2$  [21]. In that event, if one follows the procedure described in [21], to chemically bind the CV molecules to the carboxylic groups, one ends up covering the entire sphere with one monolayer of CV molecules. In both cases there would be many carboxylic groups that cannot be reached by other CV molecules because they are blocked, either mechanically or electrostatically, by the already reacted groups. In summary, the surface coverage is similar in both cases, and the nonlinearity of the layer covering the sphere of both sizes may be assumed to be roughly the same.

The chemical composition of the monolayer on the particles' surfaces was verified using Raman spectroscopy combined with the optical trapping technique. The technique and experimental setup for this measurement were described previously [22]. A particle is trapped by a 785 nm, 5 mW cw focused light beam. The backscattered light collected by the same objective is passed through a holographic notch filter and a confocal system, before finally being focused onto the spectrometer slit. Figure 1 shows the Raman spectra obtained from single trapped spheres of 4  $\mu\text{m}$  and 0.4  $\mu\text{m}$  in diameter. The spectra contain the Raman characteristic lines of CV for the spheres of both sizes and those of melamine and polystyrene for the 4  $\mu\text{m}$  and 0.4  $\mu\text{m}$  spheres, respectively. The Raman signatures of these materials agree with previous measurements [23,24].

Upon verification of the presence of the CV layer the nonlinear response was measured for three types of particles: 0.4  $\mu\text{m}$  (sample 1) and 4  $\mu\text{m}$  (sample 2) spheres covered with CV, and 4  $\mu\text{m}$  spheres (sample 3) without the nonlinear layer.

Figure 2 illustrates the experimental setup for the nonlinear measurements. An expanded beam of a

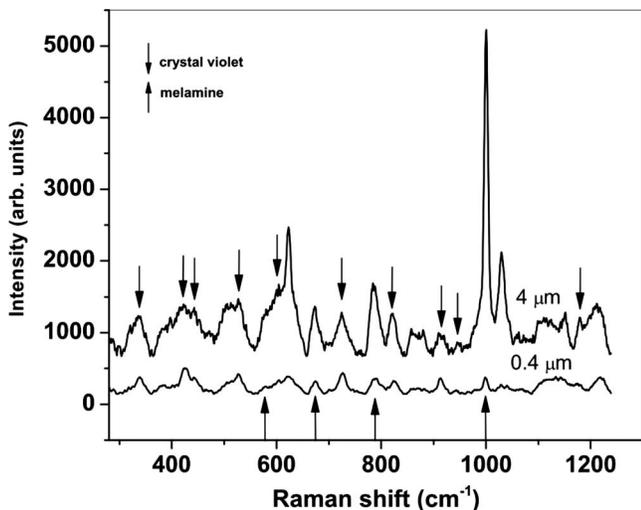


Fig. 1. Raman spectra of single optically trapped spheres with arrows showing characteristic lines of CV.

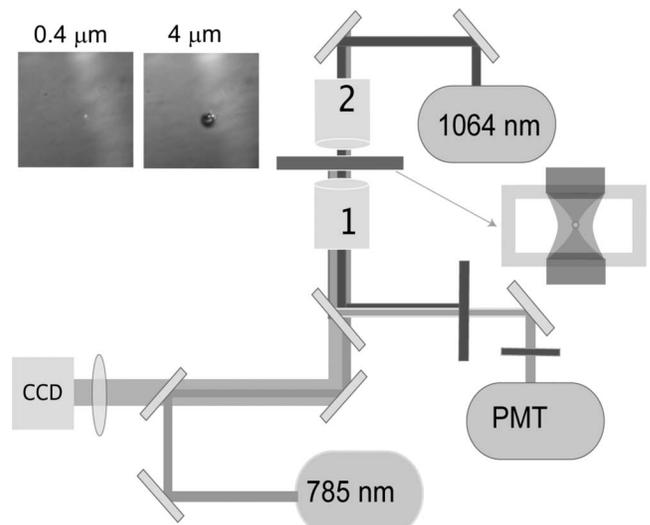


Fig. 2. Experimental setup. CCD, charged-coupled device; PMT, photomultiplier tube.

785 nm laser is focused by a NA=1.3 objective (1) inside a chamber made of two 80  $\mu\text{m}$  coverslips separated by a 60  $\mu\text{m}$  spacer. With a trapping power of approximately 10 mW at the focal plane of the objective, particles in the size range between 300 to 5  $\mu\text{m}$  can be trapped with stability. The beam of a Nd:YAG pulsed laser (1064 nm, 10 Hz repetition rate, 5 ns pulse duration, and 0.7 mJ before focusing lens) propagating in the direction opposite to the trapping beam is focused weakly by a lens (2). At the focal plane of the trapping beam the pump beam had an approximate diameter of 70  $\mu\text{m}$ , which gave a peak intensity of  $3 \text{ GW/cm}^2$ . Images of the 0.4 and 4  $\mu\text{m}$  optically trapped spheres are given in the inset. A slight periodical movement of the trapped sphere with the laser repetition rate was observed owing to the scattering force of the pump beam. For larger pump beam intensities, spheres could not be trapped for long periods of time.

The forward-scattered light of the 1064 nm pump beam and its SH were collected by the objective (1), and the SH intensity at 532 nm, after interference and absorption filters, was measured by a photomultiplier tube.

The values of the SH intensity (arbitrary units) were found as  $0.42 \pm 0.05$  (sample 1),  $4.6 \pm 0.3$  (sample 2), and  $0.58 \pm 0.03$  (sample 3). Comparing the SH intensity from the coated 4  $\mu\text{m}$  spheres with respect to the uncoated ones, an increase of approximately 1 order of magnitude was observed. This increase confirms the effectiveness of the chemical binding of the molecular layer to enhance the interface SH generation. The SH intensity measured from the coated 0.4  $\mu\text{m}$  size particles was 1 order of magnitude less than the one from the coated 4  $\mu\text{m}$  size ones. When the total SH generated power is considered, the integrated intensity deviates significantly from the  $(ka)^6$  power law of the Rayleigh approximation [5]. Nonlinear Rayleigh theory predicts an SH intensity that should be  $10^6$  larger for the 4  $\mu\text{m}$  size spheres with respect to the 0.4  $\mu\text{m}$  spheres. On the contrary, using

data presented in Fig. 3 of [5] for water droplets in air, we expect that in our case the nonlinear Mie theory would predict that such an increase in the size parameter would only amount to an increase in the SH efficiency between 1 and 2 orders of magnitude. As indicated above, in our experiments we measured an increase in SH efficiency of 1 order of magnitude. This limited increase agrees remarkably well with the deviation from the Rayleigh theory. Deviations from calculations [5] should be expected, since the index contrast between the spheres and the surrounding material is slightly different from the one in our experiments. In addition, angular integration in the theory is performed for  $360^\circ$ , while in our experimental setup the objective (1) performs an integration in a solid angle of  $170^\circ$  around the forward-scattering direction.

As for any nonlinear process, including those in microspheres, the total fundamental beam intensity distribution (which includes the incident, scattered, and internal waves) plays an important role. To provide a simple intuitive explanation of experimental findings we calculated the fundamental beam intensity distribution using the standard linear Mie scattering theory [25] for uncoated spheres. The results are shown in Fig. 3. For the  $0.4\ \mu\text{m}$  sphere the total field is inhomogeneous with a slight concentration of the field near the output surface of the sphere, while for the  $4\ \mu\text{m}$  sphere a strong concentration of the field was found in the surrounding medium outside of the sphere's surface. Hence this difference in the fundamental field distribution may be one of the reasons for the limited increase of the SH intensity for the  $4\ \mu\text{m}$  sphere. Determining the dependence of the nonlinear response on the pump intensity would have been ideal; however, a sufficiently accurate measurement could not be made owing to the small range of pump intensities available for this configuration. For low-pump intensities the signal-to-noise ratio was very low, and for high intensities the sphere

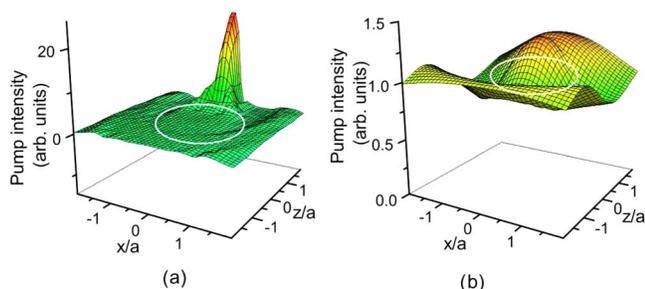


Fig. 3. (Color online) Distribution of the pump intensity near (a)  $4\ \mu\text{m}$  and (b)  $0.4\ \mu\text{m}$  spheres. An incident plane wave propagates in the  $+z$  direction. In the calculations the intensity of the incident wave is equal to 1. A white ring shows an interface between the sphere and air.

was ejected from the trap by the radiation force of the pump beam.

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