How to measure $\chi^{(3)}$ of a nanoparticle

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Most of the known methods to measure the nonlinear optical properties of materials deal with the bulk properties, but there are many demanding applications that require those measurements to be done on a single particle or a single molecule. We report a novel application of nonlinear optics to measure the third-order nonlinear optical susceptibility of nanoparticles in solutions. By measuring the power of the third harmonic generated in a diluted solution of nanoparticles, both the size and $\chi^{(3)}$ can be extracted from a simple set of measurements. © 2006 Optical Society of America

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The nonlinear optical properties of nanoparticles were the subject of extended experimental and theoretical investigations during the past decade.[1,2] Nano-objects play an important role in biology, chemistry, and materials science. For example, viruses can be considered nanometer-scale particles consisting of proteins; their sizes determine their ability to resist disinfectant chemical agents.[3] Cellular macromolecular complexes, which govern most cellular functions, are typically in the range of several tens of nanometers. Thus precise characterization of these nano-objects will improve our understanding of their functioning and behavior. Semiconductor nanocrystals is another area where nonlinear optical and size characterization is important, since nanocrystals exhibit optical and electronic properties that are dependent on their sizes.[4] Thus a noninvasive and real-time technique allowing simultaneous determination of nonlinear susceptibilities and sizes of nanostructures is necessary.

Most of the work for nonlinear optical characterization of quantum dots and metal nanoparticles has been performed by using third-harmonic generation (THG),[2,5] Z-scan,[6] and hyper-Rayleigh scattering (HRS)[7] techniques. The Z-scan technique is a simple method and can offer information on both the sign and the magnitude of nonlinearity; however, it is rather difficult to use it in the case of highly scattering media. In addition, it is not background free and is very sensitive to the beam quality.[8] Third-order HRS is quite complicated because it is a third-order noncoherent process, so it requires very precise alignment of the setup and very sensitive detection equipment. Besides, experiments on third-order HRS give the second hyperpolarizability, but not directly the third-order nonlinear susceptibility ($\chi^{(3)}$).

In this Letter we propose and experimentally demonstrate a simple novel method to determine not only $\chi^{(3)}$ but also the size of spherically shaped nanoscopic objects by employing a set of simple measurements. It is known that bulk THG cancels for a focused beam in materials because of the Gouy phase shift on both sides of the focus, but it still takes place in the vicinity of interfaces.[9] By making three independent measurements of the third-harmonic (TH) signal generated on air–glass and glass–liquid interfaces and inside a liquid containing nanoscopic objects (see Fig. 1), we can, assuming the known refractive indices and the known nonlinear optical susceptibility of the liquid and glass, derive two quantities by using a recently developed theoretical framework.[10–12] To experimentally verify this method, we apply it to determine $\chi^{(3)}$ and the sizes of single fused-silica nanospheres. The choice is driven by the known properties of this material.

First, we briefly state the assumptions made to get the equations used in this paper. We neglect the contribution from air because of the low value of its nonlinear susceptibility compared with that of a typical liquid ($\chi^{(3)}_{\text{air}} = 1.2 \times 10^{-17}$ esu, $\chi^{(3)}_{\text{water}} = 2.78 \times 10^{-14}$ esu, Ref. 13) and also because of tight focusing conditions in the experiment. The reflection from the first interface, $R(\omega_1)$, which results in $[1-R(\omega_1)]^3$ times smaller TH signal at the second identical interface, is
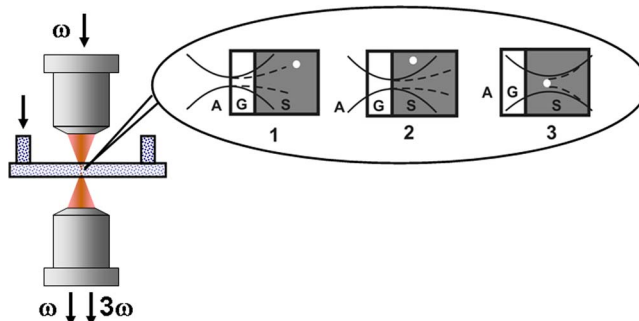

Fig. 1. (Color online) Schematic of the experimental setup. A, air; G, glass; S, solution.

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taken into account by introducing a corrective coefficient, since the reflected wave is not considered. When the beam waist is located on the second interface, we calculate that the waist at the first interface is 40 times larger, and therefore we can neglect the contribution to the TH signal from the first interface. We also neglect aberrations, assuming that they are not significant under moderate focusing conditions[14] (numerical aperture of lenses used in our experiments does not exceed 0.55). Finally, we assume that

a spherical nano-sized object has a radius smaller than a beam waist radius, confocal parameter, and coherence length. The fourth-power dependence of TH on the size of the nanoparticle is obtained assuming the slowly varying envelope approximation (SVEA) and index-matching environment.[11]

Then the interface-generated TH power can be described in terms of the refractive indices of two media for both the fundamental and the TH waves and $\chi^{(3)}$ of both media:

$$\frac{P_3^{(2)}}{P_3^{(1)}} = 1 + \frac{(t_1^3/t_3)[(t_1^3/t_3)n_{3\omega}^2(n_\omega/N_\omega)|\chi_m^{(3)}|^2|J_m|^2 + n_{3\omega}N_{3\omega}\sqrt{n_\omega/N_\omega}\chi_{gl}^{(3)}\chi_m^{(3)}(J_{gl}J_m^* + J_{gl}^*J_m)]}{|\chi_{gl}^{(3)}|^2|J_{gl}|^2N_{3\omega}^2}, \tag{1}$$

where $P_3^{(1)}$ and $P_3^{(2)}$ denote the total TH power generated at the air–glass and glass–solution interfaces, respectively; t_1 and t_3 are the transmissions for the fundamental and the TH waves, respectively, through the cell's walls; J_{gl} and J_m represent the integrals $(\int_{z_1}^{z_2}[\exp(-i\Delta kz)/(1+i2z/b)^2]dz)$ in the glass and in the medium (solution), respectively, with the parameters for the corresponding medium; n and N are the refractive indices of glass and the solution; $\chi_{gl}^{(3)}$ and $\chi_m^{(3)}$ are the third-order nonlinear susceptibilities of the cell's glass and the investigated substance (in our case, the solution). Each of these integrals can be numerically calculated for a given geometry. J_{gl}^* and J_m^* represent complex conjugate values of the corresponding integrals. By simultaneous measurements of the TH signals generated on two interfaces (Fig. 1), we can exclude the incident intensity from the equation, which sets the relationship between the optical constants among three media. Assuming the knowledge of optical constants for two media (air and glass), and the refractive index of the solution under study, then $\chi^{(3)}$ of the solution can be easily obtained by solving a simple algebraic equation.

On the other hand, TH power generated from the Rayleigh particle can be presented in the form[12]

$$P_3 = 1024\frac{n_3}{c^2n_1^3w_0^6}(\gamma_s - \gamma_m)^2R^4P_1^3, \tag{2}$$

where $\gamma_{s,m} = 3\pi^2\chi^{(3)}_{s,m}(x,y,z)/(\lambda_1 n_3)$ are nonlinear optical parameters of the sphere and the medium, respectively; P_1 is the power of the incident fundamental beam; w_0 is the radius of the beam waist, and R the radius of the sphere. There are several ways of estimating the application limit of Eq. (2). One way is to use the restrictions imposed by the applicability of the SVEA,[15] i.e., to calculate the size of a particle for which the backscattered signal becomes comparable with the one generated in the forward direction. This approach leads to the low limit of 20 nm for the particle's diameter. However, the other, stricter limit

comes from our experimental arrangement, in which the forward-generated TH signal has to be collected by a high-numerical-aperture lens. We estimate that this setup leads to a minimum particle size of about 100 nm.

Now, we want to determine $\chi^{(3)}$ of the particles. Let us first assume that we know the sizes of the spheres. Then we get the value for the nonlinear susceptibility of the solution without the nanospheres ($\chi_m^{(3)}$) and with them ($\chi_{eff}^{(3)}$) by using Eq. (1). Finally, the susceptibility of the nanosphere itself, $\chi_s^{(3)}$, can be obtained from the relation[16]

$$\chi_{eff}^{(3)} = (1 - p)\chi_m^{(3)} + p\chi_s^{(3)}, \tag{3}$$

where p is the volume fraction of the spheres in the solution. We will refer to these measurements as surface measurements. On the other hand, we can find the nonlinear susceptibility of the nanospheres by measurement of TH power generated from the spheres in the bulk of the solution. In this case, knowing $\chi_m^{(3)}$ from surface measurements and the sizes of the spheres specified by the manufacturer, we can get the sphere's nonlinear susceptibility by making a nonlinear fit to Eq. (2). If the values obtained from surface and bulk measurements are close, then the method works properly. Suppose now that we do not know either the sizes of the spheres or their nonlinear susceptibility; in this case $\chi^{(3)}$ of the spheres' material and their sizes can be obtained from the surface and volume TH measurements, respectively.

To test the proposed method we use fused-silica nanospheres of various diameters and measure the power dependence of the TH power generated by a single sphere as a function of its diameter. The spheres are provided by Banglabs Lab in a dry form. The available sizes are 0.20, 0.30, 0.55, 0.75, and 1.0 μm and have a typical 10% standard deviation distribution in size, as specified by the manufacturer.

The schematic of the experimental setup for measurements of $\chi^{(3)}$ for silica nanospheres is shown in Fig. 1. A femtosecond Cr:forsterite oscillator with a 26.5 MHz repetition rate ($\lambda = 1.25$ μm, $\tau = 40$ fs,
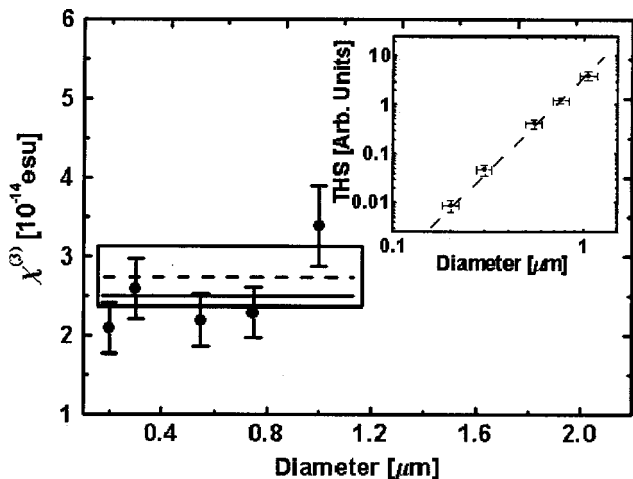
Fig. 2.   Third-order nonlinear susceptibility as a function of a diameter of the spheres. Solid line, value of $\chi^{(3)}$ for fused silica from the literature; dashed line, $\chi^{(3)}$ from volume measurements; solid rectangle, error of $\chi^{(3)}$ from volume measurements. Inset, TH intensity generated by a single particle in the index-matching liquid as a function of particle diameter; dashed line, forth-power dependence.

$P_{av}=300$ mW) is used as an excitation source.[17] The laser beam is focused with a high-numerical-aperture ($f=4.5$ mm, N.A.$=0.55$) aspheric lens into a flow-through fused-silica cell, and the TH signal is collected by another aspheric lens ($f=4.5$ mm, N.A. $=0.55$) and reimaged into the spectrometer with an attached CCD camera. The configuration with the flow cell prevents particle trapping and makes the measurements more precise, since the error of the measurements scales inversely with the number of particles passing through the focal volume. Estimations show that, at the concentrations we use (typically around 10^8 particles/cm^3), one or less than one particle is located in a focal volume ($\sim 10^{-10}$ cm^3) in one instance. The linear dependence of the TH signal on concentration proves that the probability of finding more than one particle in the focal volume in one instance is indeed low.

Measurements of $\chi_m^{(3)}$ of the index-matching liquid without microspheres from the surface (first air–glass and second glass–solution interface) THG give a value of $(3.19 \pm 0.3) \times 10^{-14}$ esu. Then the same measurements are done for the solution with nanospheres for each size of the sphere. Finally, from Eq. (3), the value of $\chi^{(3)}$ for fused silica is obtained for each sphere's size. The results are presented in Fig. 2. Performing experiments on THG from Rayleigh particles in the solution and fitting the theoretical curve [Eq. (2)] to the experimental points (Fig. 2, inset), we get the average value of $(2.75 \pm 0.27) \times 10^{-14}$ esu for $\chi_s^{(3)}$ of fused silica. We clearly see that our surface and bulk measurements are self-consistent and agree well with the previously reported data for fused silica. Then we check how the method works to determine the sizes of particles. Making a measurement of generated TH signal from

the particle of each size inside the solution and on the surfaces, we can get the diameters of the particles. The correspondence of the measured values and the values specified by the manufacturer was within 10%. Thus, when we do not know either the sizes of the particles or their $\chi^{(3)}$, we can obtain both values on the basis of three simple measurements.

In summary, we have demonstrated that by measurement of TH at the glass–solution interface and in the bulk of the solution containing nanospheres one can determine both particle $\chi^{(3)}$ and sizes. By normalizing the intensity of one signal over another, we avoid the ambiguity of the intensity determination in the focal spot of the laser beam. The method is simple, fast, and does not require a high beam quality of the laser source. We proved the validity of our methodology on a solution with fused-silica nanoparticles. Since the nonlinear susceptibility depends on the structure of the nanosized object, we believe this method can find applications in monitoring structural transformations of macromolecules.[18]

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