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Hyper-Rayleigh scattering from gold nanoparticles: Effect of size and shape

K. Das [a,*], A. Uppal [a], R.K. Saini [a], G.K. Varshney [a], P. Mondal [b], P.K. Gupta [a]

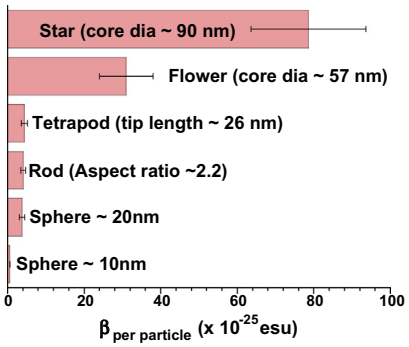
[a] Laser Bio-Medical Applications & Instrumentation Division, Raja Ramanna Center for Advanced Technology, Indore 452013, MP, India
[b] Indus Synchrotrons Utilization Division, Raja Ramanna Center for Advanced Technology, Indore 452013, MP, India

HIGHLIGHTS

- Hyper-Rayleigh scattering from five different gold nanoparticles are compared.
- Star and flower shaped particles were observed to have highest hyperpolarizability.
- The hyper-Rayleigh scattering from the nanoparticles showed a dipolar response.

GRAPHICAL ABSTRACT

First hyperpolarizability (β) values of gold nanoparticles: Effect of size and shape



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ABSTRACT

We report hyper-Rayleigh scattering (HRS) properties of gold nanoparticles (GNPs) of five different shapes, quasi-spherical (~10 and ~20 nm diameter), rod (aspect ratio ~2), and branched shapes, tetrapod, flower and star with 800 nm, 150 fs laser excitation. Using ~10 nm spherical GNPs as reference, the first hyperpolarizability (β) values were calculated for all other shapes. Star and flower shaped GNPs have the highest hyperpolarizability (~130 and ~52 times higher, respectively), while rod and tetrapod shaped GNPs only have modest enhancement (~7 times), which is similar to ~20 nm size quasi-spherical particles. These enhancements are attributed to reduced symmetry as well as the presence of sharp tips on GNP surface. When the β values are normalized with respect to the number of atoms per particle, the flower and star shaped GNPs still have the highest hyperpolarizability values. The polar plots of vertically polarized HRS signal as a function of the angle of polarization of the incoming incident light shows two lobes, indicating that excitation is predominantly dipolar in nature although the size of some GNPs are big enough to show a quadrupolar response. It is believed that the presence of sharp tips at the surface of these large sized GNPs is responsible for the observed dipolar response. This study shows that GNPs having sharp tips might be a better candidate when their nonlinear properties are used for sensing applications.

* Corresponding author. Tel./fax: +91 0731 2488436.
E-mail addresses: kaustuv@rrcat.gov.in, kaustuv1965@gmail.com (K. Das).

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Introduction

Nanomaterials made from gold and silver generally absorb in the visible region of the spectrum due to the collective excitation of the conduction band electrons. This phenomenon is known as the surface plasmon resonance (SPR). Their non linear optical (NLO) properties are superior to organic chromophores due to their strong extinction at SPR wavelength [1–16]. The NLO properties of metallic nanoparticless are often judged by their hyperpolarizability (β) values. Recent reports have shown that NLO properties of these nanomaterials can be used for biological and chemical sensing [1,13,17–21]. For sensing applications it is desirable to have nanomaterials with high hyperpolarizability (β) values. Because gold is chemically inert, non-toxic nanomaterials made from gold are preferred. Due to the lack of a good dipole moment, hyper-Rayleigh scattering (HRS) is the method of choice for the measurement of the first hyperpolarizabilities of nanoparticles dispersed in a liquid solution [2–16]. HRS from a NP solution originates from the lack of centrosymmetry of the particle as demonstrated earlier for *nearly* spherical gold and silver nanoparticles [2–9]. In this paper we compare the suitability of five different shaped gold nanoparticles (GNPs) for sensing applications utilizing their NLO properties. The suitability was judged by comparing their first hyperpolarizability values determined by the HRS method using 800 nm, 150 fs laser excitation. It may be noted that the HRS signal is also accompanied by a strong multi-photon luminescence background. However, the narrow spectral bandwidth of the HRS signal makes it more convenient for user selected detection range and quantification which makes it a desirable property to be utilized for sensing applications.

Materials and methods

The various GNPs were prepared according to methods available in literature and the preparation details are given in supporting information. The shapes and sizes of these GNPs were analyzed from their transmission electron microscope (TEM) images. The TEM was a Philips CM200 with W-filament as cathode and was used at an accelerating anode voltage of 200KV. Extinction spectra of the various GNPs were recorded using a Cintra absorption spectrophotometer having a resolution of 2 nm. HRS experiments was performed by exciting the GNP samples with ~150 fs pulses centered at 800 nm obtained from a tunable Ti-Sapphire laser (Coherent Mira). The laser beam was focused by a 20 cm lens into a 1 cm path length quartz cuvette containing the nanoparticle solution. The solution was constantly stirred during the experiment to reduce any unwanted photothermal effects. The HRS from the GNPs was detected at right angle to the laser beam and a bandpass filter (transmission range 380–700 nm) was used to cut off the excitation light. The polarization state of the excitation light was selected with a rotating half-wave plate. A thin film polarizer was kept on the emission side to select the polarization state (horizontal or vertical) of the emitted HRS light. The light scattered from the nanoparticles was detected and analyzed with the LifeSpec Red TCSPC system from Edinburgh instruments. The spectral bandwidth was kept at 1 nm for all measurements. For the detection of *both* HRS and multi-photon induced luminescence from the GNPs, a spectral scan (380–650 nm) was taken with 1 nm step size and one second integration time per point. For β value measurements, the polarization state of the excitation light as well as HRS signal was kept horizontal [11,21,22]. For polarization resolved HRS experiments, the polarization state of the detected HRS signal was kept vertical while the polarization of the excitation light was varied from 0 to 360° where 0° corresponds to vertical polarization.

Results

Fig. 1 shows the TEM images of the six GNP's used in this study. The two sets of quasi-spherical GNP's have an average size of 10 ± 2 and 20 ± 3 nm. While the smaller particles are more spherical in shape the bigger particles are significantly irregular in shape. The star and flower shaped GNPs were observed to have pointed tips. While the flower shaped particles have average core diameter of 60 ± 15 nm, the star shaped particles have an average core diameter of 90 ± 20 nm. Tetrapods show four tips (average tip length of 26 ± 5 nm) and depending upon their relative orientation on the carbon coated copper grid, their TEM images shows two distinct shapes. Nanorods have an average aspect ratio of ~2 (length: 38 ± 4 nm; breadth: 17 ± 3 nm). Table 1 summarizes the average sizes of these GNPs. The extinction spectra of these GNPs are presented in Fig. 2. The two sets of quasi-spherical GNP's have nearly identical spectra. However for all the other shapes, significant red shifts in the spectra were observed. In addition, the spectral shape becomes asymmetric and broad, particularly for the flower shaped NPs. The spectral response of these NPs against 800 nm femtosecond laser excitation is shown in Fig. 3. The sharp peak at 400 nm corresponds to HRS which is associated with a broad background. This broad background is attributed to luminescence due to multi-photon absorption [23–33]. It is clear that HRS and luminescence intensity changes significantly with size and shape. The HRS intensity increases significantly for the tetrapod, flower and star shaped GNPs and the broad luminescence background were observed to be significant for star, tetrapod and rod shaped GNPs. The inset in Fig. 3 provides a comparison of the integrated HRS and luminescence intensities obtained from the different GNPs. For all GNPs, the luminescence background was observed to be significantly higher than the HRS signal.

The HRS intensity $I_{2\omega}$ is given by:

$$I_{2\omega} = G(N_1\langle\beta_1^2\rangle + N_2\langle\beta_2^2\rangle)I_\omega^2 e^{-N_2\alpha_2 l}$$

where I_ω is the incident light intensity; $I_{2\omega}$ is the intensity of generated HRS signal; G is an constant which depends upon the experimental conditions, β denotes the first order hyperpolarizability, N denotes the number density and the exponential term accounts for the re-absorption of HRS signal at the second harmonic wavelength by the GNP itself. The subscripts 1 and 2 refer to solute and solvent, respectively. As noted earlier, the HRS signal rides on a background signal whose intensity increases significantly for some shapes (Fig. 3). Therefore, in order to extract the actual HRS signal, a spectral scan around 400 ± 20 nm is taken which is then fitted by a Lorentzian function.

To calculate the first hyperpolarizability of the different GNPs, their number densities are required. The number densities of spheres and rods can be estimated from their sizes calculated by analysis of their TEM pictures. However the tertapod, star and flower shaped NPs are irregular in shape and therefore some approximation (regarding their shape) is necessary to get an estimate of their concentrations. For tetrapods, the tetrahedron shape was assumed and the center to tip distance was used to calculate their concentrations. For flower and star shaped particles the shape was assumed to be spherical and the core diameter is used to calculate their concentrations. It is pertinent to note that the number densities obtained in this way are not accurate, but provides a close enough estimate of their concentrations.

For the first hyperpolarizability estimation, the HRS intensities of GNPs were recorded against varying incident laser power at six different GNP number densities shown in Fig. 1, supporting information. From the polynomial fits (Table 1, supporting information) it can be seen that the observed changes in HRS intensity depends quadratically on the laser power and linearly on the GNP