Nonlinear Optical Response of Colloidal Gold Nanoparticles Studied by Hyper-Rayleigh Scattering Technique

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Hyper-Rayleigh scattering (HRS) technique is used to study the nonlinear optical response of nanocrystalline gold particle suspensions. The signal intensity measured at 400 nm has a cubic dependence on the pump laser energy at 1064 nm, indicating that the measured signal is due to a third-order nonlinear optical process, namely three-photon excited fluorescence (3PF). To the best of our knowledge, this is the first experimental observation of 3PF for colloidal gold nanoparticle suspensions.

Hyper-Rayleigh scattering (HRS) is a nonlinear incoherent light scattering process that has recently been employed to measure the first hyperpolarizability β of molecules in solutions.[1] Briefly, HRS method relies upon the random fluctuations of the density or orientation of chromophores, which instantaneously break the centrosymmetry of the isotropic media and create conditions of net frequency doubling. Compared to the more traditional technique of electric-field-induced second harmonic generation (EFISH), HRS method offers the advantage that it can be performed in a liquid phase without the need of application of an aligning electric field. HRS therefore allows the determination of molecular first hyperpolarizability β for charged chromophores and non-dipolar chromophores dissolved in isotropic media, which was previously impossible using EFISH technique. Consequently, HRS has been successfully applied to study nonlinear optical properties of molecules,[2] protein[3] and colloidal nanoparticles.[4] Recently, enormous HRS signal from gold nanoparticle suspensions has also been reported.[5]

In HRS experiments, the sample in solution was pumped with laser pulse of fundamental frequency (1064 nm), and HRS signal was measured at harmonic frequency (532 nm). Here by performing the measurement at a shorter wavelength of 400 nm, we obtained the first experimental evidence of three-photon excited fluorescence (3PF) for colloidal gold nanoparticle suspensions.

Aqueous gold colloid used in the experiments was prepared by following the method of Turkevich et al.[6] To prepare the colloids, 4 mL of 1% sodium citrate solution was added to 100 mL of 0.01% boiling tetrachloroauric acid solution. The mixture was stirred till deep wine red color was obtained indicating formation of colloidal gold suspension. The optical absorption spectrum showed a maximum at a wavelength of 525 nm, which is in agreement with previous reports.[5] Transmission Electron Microscope (TEM) study reveals that the prepared gold particle has a narrow distribution of particle sizes with a mean diameter of about 15 nm. Before HRS measurement, the colloidal gold suspension was diluted with distilled water to a desired concentration (number density) of 5×10^{15} cm^{-3}.

The HRS experimental setup used here is similar to that of Clays et al.[7] The light source was a Q-switched Nd:YAG laser (Continuum, Surelite II) with a pulse duration of 8 ns full width half maximum (FWHM), operating at a repetition rate of 5 Hz at a wavelength of 1064 nm. The pump laser beam was focused into a glass sample cell by a spherical and cylindrical lens system. The light was collected at 90° to the incident beam and was measured with a photomultiplier tube (Hamamatsu, R105UH). The signal was integrated with a boxcar averager (EG&G 4420) or measured with a digital oscilloscope (Tektronix TDS 3032). Wavelength discrimination was accomplished by means of a 13 nm bandwidth interference filter centered at 400 nm. No second-order nonlinear optical process such as HRS and 2PF will be involved at 400 nm since this wavelength is shorter than the second harmonics (532 nm) of the pump laser (1064 nm).

The experimental conditions were first assessed on *p*-nitroaniline (*p*NA) in methanol with a number density of 2×10^{19} cm^{-3}. The HRS signals of pNA were measured at various pump laser energies. The pump energy $I(\omega)$ was controlled by rotating a half-wave plate (HWP) between two polarizer and can be expressed as: $I(\omega) = I_0 \cos^2(2\phi)$, here I_0 and ϕ are the energy intensity and HWP rotation angle, respectively. Curve (a) of Figure 1 shows the intensity dependence of the measured energy on the HWP rotation angle, which is in very good agreement with the theoretical results calculated with above equation. The HRS signal of *p*NA measured at 532 nm is shown in Curve (b) of Figure 1. The HRS intensity is proportional to the square of laser energy, which is in consistent with the theoretical prediction and previous results.[7,8]

When pumped with high intensity laser pulse with a wavelength of 1064 nm, the colloidal gold nanoparticle suspensions display measurable signal at 400 nm. Moreover, the signal intensity measured at 400 nm has a cubic dependence on the

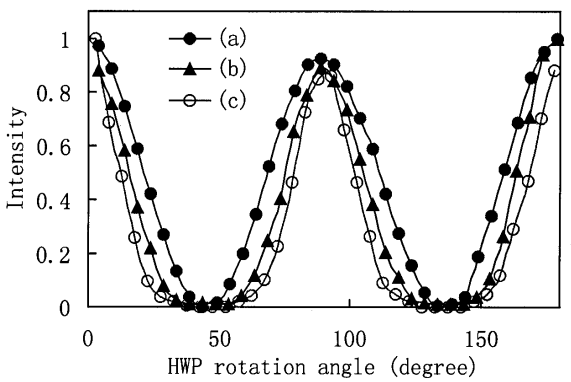

Figure 1. The signal intensity change with the HWP rotation angle, (a) signal from an energy monitor, (b) HRS signal measured at 532 nm for pNA, (c) 3PF signal measured at 400 nm for colloidal gold suspension.

pump laser energy at 1064 nm, as shown in Figure 1 curve (c). Figure 2 shows the logarithm of the measured signal increases linearly as the logarithm of the pump laser intensity. The slope of the best-fit line is 1.03, 2.05 and 3.11 for signal from an energy monitor (line (a)), HRS signal of *p*NA (line (b)), and signal of colloidal gold suspensions measured at 400 nm (line (c)), respectively. It is obvious that the HRS signal of *p*NA is proportional to the square of the pump energy while the signal of colloidal gold suspension is proportional to the cube of the pump energy. This indicates that the measured signal of gold colloid at 400 nm is indeed due to a third-order nonlinear optical process, namely three-photon excited fluorescence. So far as we aware, this work represents the first experimental observation of 3PF for colloidal gold nanoparticle suspensions.

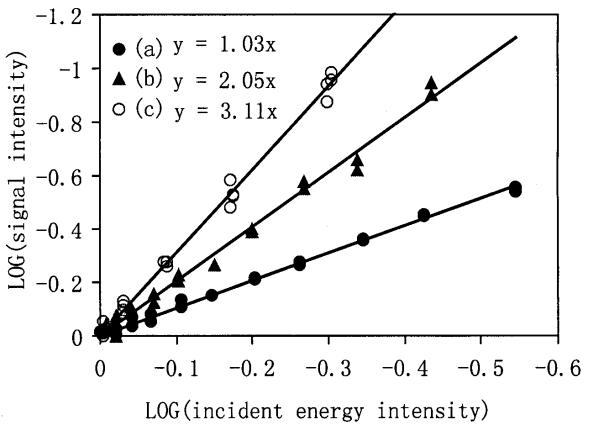

Figure 2. The logarithm of the measured signal increase linearly with the logarithm of the pump laser intensity. The slope of the best-fit line is 1.03, 2.05 and 3.11, indicating a linear, quadratic, and cubic dependence on the laser energy for signal from an energy monitor (a), HRS signal of pNA (b) and signal of colloidal gold suspension measured at 400 nm (c), respectively.

Semiconductor nanocrystals have been reported to be highly fluorescent and used as biological labels.[9] In contrast, the colloidal gold nanoparticle suspensions show no measurable fluorescence signal, as studied by a fluorescence spectro-photometer (Shimadzu RF5000). Both HRS signal reported by Hupp et al.[5] and 3PF signal measured here are due to nonlinear optical properties of colloidal gold nanoparticles. The enormous HRS signal reported previously is a second-order nonlinear optical process and thus has a quadratic intensity dependence on the pump laser energy.[5] The 3PF signals measured here are due to a third-order nonlinear process and therefore have a cubic dependence on the pump laser energy.

It was pointed out that the measurement of first hyperpolarizability β of molecule in solution using HRS could be severely affected by the possible contribution from the multiphoton excited fluorescence.[8] The experimental results reported here suggest that the monochromaticity test should also be performed when HRS technique is used to determine β of colloidal gold suspensions, especially at low concentrations as studied here. In addition, the experimental findings reported here have important biological implications. For example, colloidal gold has been widely used as a biological probe in electron microscopy (TEM and SEM)[10]. The 3PF nature of colloidal gold reported here may lead to further applications such as a biological indicator in multiphoton laser scanning fluorescence microscopy.[11] The spectral features of 3PF and the effect of gold colloidal aggregation on 3PF are currently being investigated and will be reported later.

In summary, we reported here the first experimental observation of 3PF for colloidal gold nanoparticle suspensions. We believe that the experimental results presented should have high potential for further scientific and technological applications.

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