Measuring plasmon-resonance enhanced third-harmonic $\chi^{(3)}$ of Ag nanoparticles

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By coinciding the plasmon frequency with the third-harmonic frequency of the excitation light, the authors determined the plasmon-resonance enhanced optical third-harmonic-generation (THG) susceptibility of a polyvinylpyrrolidone-coated Ag nanoparticle with a 5–7 nm diameter. With dispersed Ag nanoparticles on a quartz surface and through measuring the frequency dependent THG intensities, interface THG showed evident enhancement when the third harmonic of excitation matched the Ag-nanoparticle's plasmon-resonant frequency. According to the effective medium theory and by analyzing the interface THG under focused Gaussian beams, the ensemble-averaged $\chi^{(3)}(3\omega;\omega,\omega,\omega)$ of a Ag nanoparticle can be estimated to be on the order of 2×10^{-11} esu. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2240738]

In recent years, third-harmonic generation (THG) has been emerged as an important imaging modality in biological and material researches.[1–4] Its advantages include no energy release and intrinsic optical sectioning capability. Because THG takes place in the vicinity of interfaces due to the breakage of axial symmetry,[1] it can be used as a three-dimensional morphological imaging tool.[1,2,4] Compared with the popular two-photon fluorescence (2PF) or second-harmonic generation, the general efficiency of THG in a biological tissue is relatively weak.

With the help of nanometer-sized noble metals, the excitation field with photon energy matched to that of plasmon resonance can be locally enhanced, thus enhancing the yield in nonlinear microscopy. Exploiting this phenomenon, localized THG and 2PF enhancement with the aid of gold nanoparticles has been demonstrated recently.[5] However, due to the requirement of small particle size for membrane penetration and molecular labeling, the plasmon-resonance energy of most nanometer-sized noble metal nanoparticles falls in the near-ultraviolet (NUV) and visible spectral regimes. For most biotissues with a near-infrared penetration window (1200–1300 nm),[4] excitation at the NUV-visible wavelength range encounters the problems of shallower penetration depth and potential photodamage. To satisfy both requirements, instead of fundamental wavelength, it is necessary to employ metal nanoparticles with plasmon resonance at the third harmonic of excitation. This idea has been demonstrated recently on silver[6–8] and gold nanoparticles.[9] Because of the penetration requirement on excitation wavelength,[7] the plasmon-resonant wavelength of the nanoparticle should range within 400–430 nm. This condition makes silver a

better candidate than gold or copper as the contrast agent of THG microscopy in biotissue.[7] Nevertheless, the THG $\chi^{(3)}$ of a single Ag nanoparticle, which is an important parameter for the characterization of material properties,[10] has never been measured. In this letter, we spectrally study the THG generation on the air-quartz interface with dispersed Ag colloids. All Ag colloids have controlled size and polymer encapsulation so that the aggregation-induced plasmon frequency shift and the dipole-dipole interaction among particles can both be reduced. According to the effective medium theory and with a theoretical model for interface THG with a strongly focused Gaussian beam, the ensemble-averaged nonlinear susceptibility of a single 5–7 nm diameter Ag nanoparticle can thus be obtained.

For Ag nanoparticles with a size well below the excitation wavelength, the electric field can be regarded as quasistatic and the effective dielectric constant ε_{eff} depends on the filling factor f and the polarizability α as[11]

$$\varepsilon_{\text{eff}} = \varepsilon_m (1 + 2f\alpha)(1 - f\alpha)^{-1}, \qquad (1)$$

with

$$\alpha = (\varepsilon - \varepsilon_m)(\varepsilon + 2\varepsilon_m)^{-1}, \qquad (2)$$

where ε and ε_m are the intrinsic dielectric constants of silver nanoparticles and their embedded matrix, respectively. For metal particles with size even smaller than one-tenth of the optical wavelength, their intrinsic dielectric constant will be affected by the free path effect. The corresponding dielectric constant ε is simply a modification from its bulk value.[11] With the effective optical linear properties, we can then extract the THG $\chi^{(3)}$ by measuring interface THG. With the normally incident and focused Gaussian beam, the THG power emitted from a multilayered thin film can be formulated as[10]

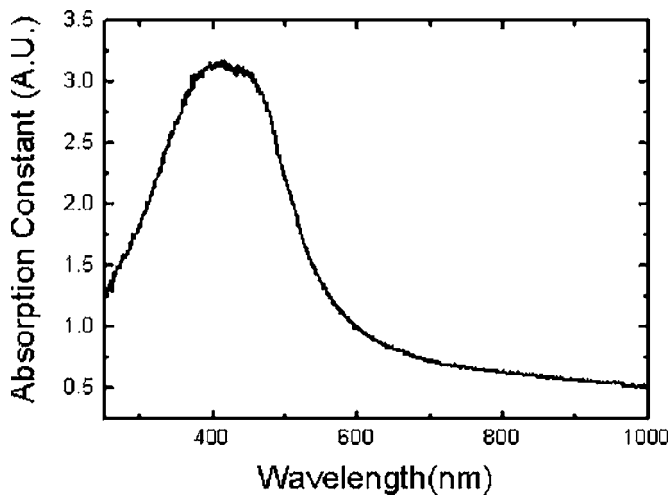[a)]Author to whom correspondence should be addressed; electronic mail: sun@cc.ee.ntu.edu.tw

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FIG. 1. Absorption spectrum of Ag-PVP colloids.

FIG. 2. Measured THG ratio (solid squares) and the fitting curve (solid curve) as a function of third-harmonic wavelength. The inset is the obtained THG $\chi^{(3)}$ of silver nanoparticles at different excitation wavelengths.

$$P_{3\omega} \propto \left| \sum_j \exp(i\Delta\phi_j) \int_{qj}^{rj} \chi_j^{(3)} \exp(i\Delta k_j z)(1 + 2iz/b_j)^{-2} dz \right|^2, \quad (3)$$

where j is the subscript of each layer, Δk is the wave vector mismatch, and b is the confocal parameter of the focused Gaussian beam. For each layer, the integration limits (q and r) and phase correction $\Delta\phi$ at each interface can be determined iteratively.[10] For the Ag colloidal layer, when the third harmonic of the fundamental field coincides the plasmon-resonant frequency, the corresponding THG $\chi^{(3)}$ required in Eq. (3) will be enhanced by a local field factor $L_{3\omega}$ with[8]

$$L_{3\omega} = \varepsilon_m(3\omega)/[\varepsilon_m(3\omega) + (\varepsilon(3\omega) - \varepsilon_m(3\omega))(N - f/3)], \quad (4)$$

where 3ω represents the corresponding value at the third-harmonic and N is the shape-dependent depolarization factor of the nanoparticles. The local field factor $L_{3\omega}$ provides the magnitude enhancement of THG $\chi^{(3)}$ and brings a phase lag between the nonlinear polarization and the third-harmonic field. If we only make one THG measurement on air/Ag/substrate interfaces, it is hard to determine the proportional constant in Eq. (3). This proportional constant can be eliminated by another THG measurement of air/substrate interface.[12] By measuring the dispersion of THG ratio around the plasmon-resonant wavelength, the THG $\chi^{(3)}$ of this colloidal layer can then be extracted from the fitting with Eq. (3).

In our experiments, the nanoparticles we used to enhance THG are 5–7 nm Ag clusters encapsulated with ~2 nm polyvinylpyrrolidone (PVP). Its absorption spectrum (Fig. 1) shows that 410 nm is the plasmon-resonant wavelength, which is highly desired for biological THG applications.[6] Then we dispersed a droplet with ~10^{12} colloids uniformly on the surface of quartz slide within a circular area (1 cm diameter) and let it dry out in room temperature. The average thickness of this Ag colloidal film was 20 ± 2 nm measured by an atomic force microscope. With this colloidal film, we measured its interface THG. The excitation source we used to generate THG was a femtosecond optical-parametrical oscillator, synchronously pumped by a
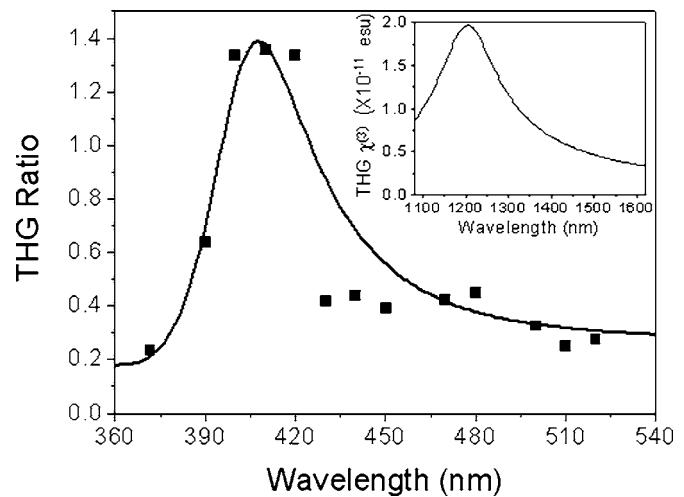
femtosecond Ti:sapphire laser. The laser beam was focused by an objective [(numerical aperture) NA=0.75] on the interface with Ag-PVP colloids. The generated THG was collected by a NA=0.9 UV condenser and detected by a spectrometer with a nitrogen-cooled-charge-coupled device. To induce the plasmon resonance of the silver nanoparticles with the laser THG wavelength (410 nm), we tuned the central excitation wavelength around 1230 nm (from 1110 to 1530 nm). The acquired spectra were then integrated to obtain the total THG power. At each excitation wavelength, we also measured the spectra of the corresponding interface THG without the colloids to eliminate the proportion constant in Eq. (3). As shown in Fig. 2, when the THG wavelength was tuned close to the plasmon-resonant wavelength, we found an obvious enhancement of THG yield with a 1.36 THG ratio. This phenomenon verified that Ag-colloidal film contributed to the THG yield. When the third harmonic was tuned away from the plasmon-resonant wavelength, the emission of interface THG with Ag-PVP colloids reduced to 0.3 of that without colloids. Since the absorption constant of fundamental field is low ($\sim 10^{-4}$ nm^{-1}) in silver colloidal layer, we attribute the off-resonant reduction to the extra interfacial reflection ($\sim 4\%$) and the destructive interference of THG caused by the local field factor $L_{3\omega}$.

In order to fit the dispersion of THG ratio with Eq. (3), we need to calculate related parameters according to Eqs. (1)–(4). Because the Ag colloids were densely dispersed (~ 0.33 filling factor for colloids), the PVP shells surrounded them can be treated as the embedded matrix, whose dielectric constant ε_m is equal to 2.62.[13] For the calculation of intrinsic dielectric constant of Ag nanoparticles,[11] we used the bulk value of Ag in Ref. 14, $R=3$ nm, and related material parameters.[15,16] With $f=0.072$ and these material parameters, we can then obtain the dielectric constant ε_{eff} of the effective Ag-colloidal layer at different optical wavelengths. For the calculation of Eq. (4), we employed the calculated dielectric constants and assumed $N=1/3$, a value for nanoparticles with spherical shape. Finally, we employed the dispersion relation[17] and THG $\chi^{(3)}$ of quartz[18] together with the parameters obtained above to fit the measured THG ratio with Eq. (3) (solid curve in Fig. 2). From the fitting results, the obtained THG $\chi^{(3)}$ of Ag colloidal film at resonance can be

estimated to be $\chi_{film}^{(3)} = 1.4 \times 10^{-12}$ esu with $\pm 10^{-13}$ esu fitting margin. Thus obtained THG $\chi^{(3)}$ was the volume weighting sum of PVP's and Ag-nanoparticles' THG $\chi^{(3)}$. Since the third-order nonlinearity of PVP ($\sim 10^{-14}$ esu) is much smaller than that of colloidal film, its contribution to THG can be neglected.[19] As a result, the THG $\chi^{(3)}$ of Ag nanoparticles is the $\chi_{film}^{(3)}$ divided by the filling factor of Ag nanoparticles. As shown in the inset of Fig. 2, the obtained THG $\chi^{(3)}$ of Ag nanoparticles shows a significant enhancement feature around three times the plasmon-resonant wavelength, 1230 nm, with a peak value of $(2 \pm 0.3) \times 10^{-11}$ esu and a 5.6 local field enhancement. Ruling out the local field enhancement factor $L_{3\omega}$, the intrinsic THG $\chi^{(3)}$ without the local field enhancement is 3.5×10^{-12} esu, which is close to that estimated by Burns and Bloembergen in confined Ag films.[20]

In summary, by exploiting the plasmon-resonance effect, we spectrally measured the enhanced interface THG with dispersed Ag colloids. According to the effective medium theory and the formula for interface THG with focused Gaussian beams, we extracted 3.5×10^{-12} esu intrinsic THG $\chi^{(3)}$ of Ag nanoparticles with a $5-7$ nm diameter. When the third harmonic of the excitation coincides with the plasmon-resonant frequency, the THG $\chi^{(3)}$ was found to be enhanced to $(2 \pm 0.3) \times 10^{-11}$ esu with a 5.6 local field enhancement.

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