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# Femtosecond Nonlinear Optical Properties of Laser Ablated Gold Nanoparticles in Water

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**Abstract**Femtosecond third order nonlinear optical (NLO) properties of ultrafast laser ablated gold (Au) colloidsin distilled waterare investigatedusing degenerate four wave mixing technique with 50fs pulses at 800nm wavelength. The estimated value of $\chi^{(3)}$obtained for Au nanoparticles is $1.93\times10^{-14}$ e.s.u. The characterization of the NPs was achieved done using TEM and HR-TEM techniques. We also present the time resolved studies of Au colloids by using DFWM technique in the forward BOXCAR phase matching geometry.

## INTRODUCTION

Noble metal nanoparticles in solution hold great interest due to their superior nonlinear optical (NLO) properties arising from the surface plasmonresonances[1-3], andthe localization of the NPs influences the optical nonlinearities. Unlike the conventional chemical synthesis of NPs ultrafast laser ablation technique provides a captivating way to achieve metal nanoparticles with superior optical properties and applications.This is an environment friendly technique [4-5]. Here we report third order optical nonlinearities of Au colloidal solution, by using degenerate four wave mixing technique [6-7] using femtosecond (fs) laser pulses at 800nm wavelength in the forward phase matching geometry. The time resolved studies provides the dephasing time of surface plasmon oscillations and also the magnitude of $\chi^{(3)}$.

## EXPERIMENTAL DETAILS

The DFWM measurements were performed with an amplified Ti:sapphire laser(LIBRA, Coherent) system which is seeded by a mode locked oscillator (Vittesse) at 800nm central wavelength. All the three beams are derived from the same fundamental beam (from the amplifier) as shown in the figure1, the beams are arranged in a BOXCAR geometry in trapezoid shape followed by an efficient phase matching. The three beams are focused with 20cm focal lens and the generated signal at the fourth corner of the trapezium is collected by using a large-area photo diode which is connected to a lock-in amplifier. A delay stage is used to perform the time resolution studies in one arm of the beams and all the components are synchronized with a LabView programme. The sample is mounted on a sample holder with 5-mm quartz cuvette for an efficient interaction of all the three beams. The signal is also observed at 800nm wavelengthdue to so called the degenerate four wave mixing (DFWM). Before placing the sample the signal is optimized using a thin BBO (β-barium borate crystal) crystal.

Aunanoparticles colloidal solution is prepared with fs laser ablation technique. The gold substrate ($10\times10\times1$ $mm^3$) is placed in waterin a glass beaker and the laser beam is focused with 100mm focal lens with pulse energies up to 250μJ. The water level from the surface of the substrate is 13 mm. The glass beaker is mounted on a X-Y motorized stage (Newport), translated with 500 μm/s up to 20 minutes in both the directions at a beam waist of 100

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μm. The morphological studies were performed with transmission electron microscope (TEM) and high resolution-TEM.

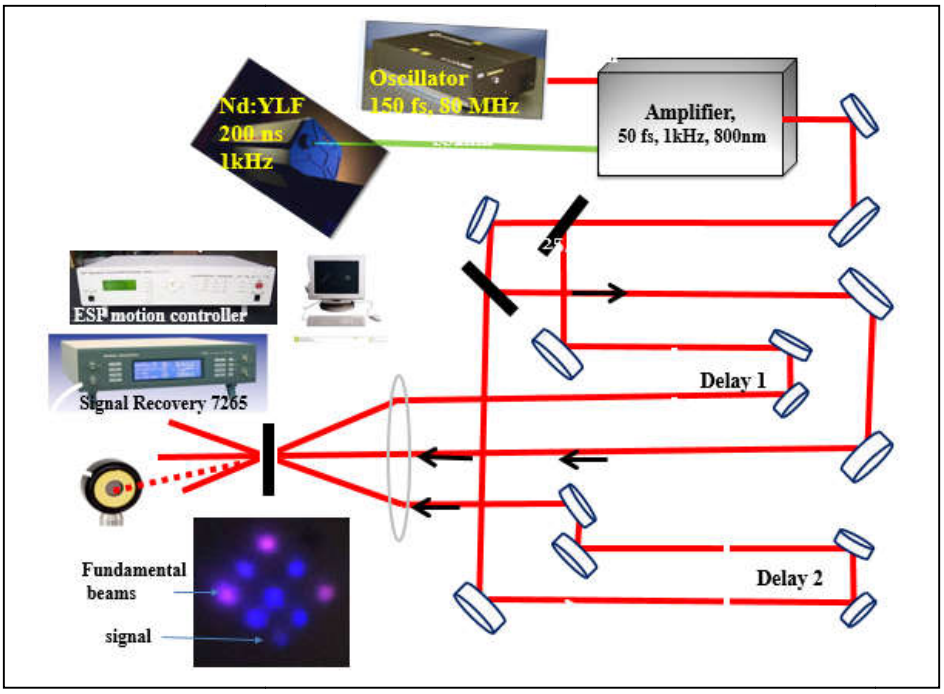


**Figure 1.** Experimental schematic of the fs-DFWM in the BOXCAR geometry. Inset shows the DFWM signal in BBO crystal.

## RESULTS AND DISCUSIONS

Au NPs with spherical shape were prepared at an input energy of 250 μJ. The TEM image depicted the distribution of nanoparticles with an average size varying from 20nm to 50nm as shown in figure 2(left). HR-TEM image shows the well-ordered crystalline phase. Multi-photon absorption is the prerequisite for the formation of Au NPs, the chain like behavior is evident from the laser induced agglomeration suggested by Serkov et al..[8]

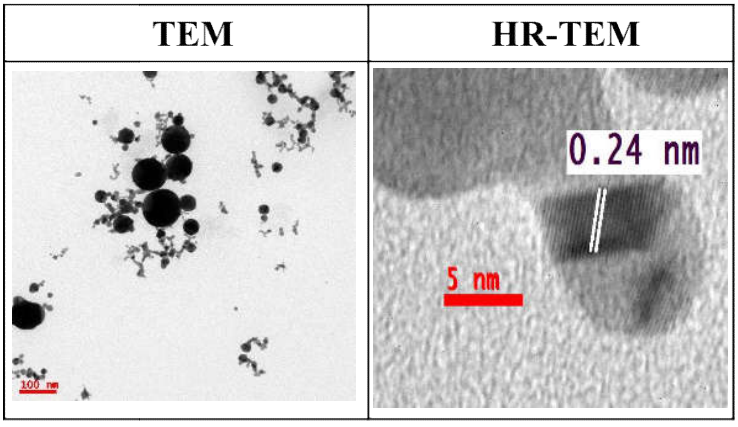


**Figure 2.** TEM(left) and HR-TEM(right) images of the Au NPs.

On laser irradiation dipole interaction between the ablated NPs and the neutral particles lead to the formation of chains (as seen in TEM image). Third-order nonlinear susceptibility measurements were performed with a standard reference sample as $CCL_4$ ($4.4\times10^{-14}$esu). Typical input energies used were ~5μJ, while the time constant was kept at 1 sec in the lock-in system to reduce the fluctuations from the laser as well from the electronics. By placing the sample at zero position and varying the input intensities ($3.1\times10^{11}$W/cm$^2$, $2.4\times10^{11}$ W/cm$^2$,$1.9\times10^{11}$W/cm$^2$, $6.6\times10^{11}$ W/cm$^2$) the DFWM signal is recorded. By plotting theinput intensities versus logarithmic values of DFWM signal as shown in figure 3 the third order nonlinear process was confirmed by fitting with a straight line (with slope of ~3.2).This also ensures that no higher order process are involved in the measurements.

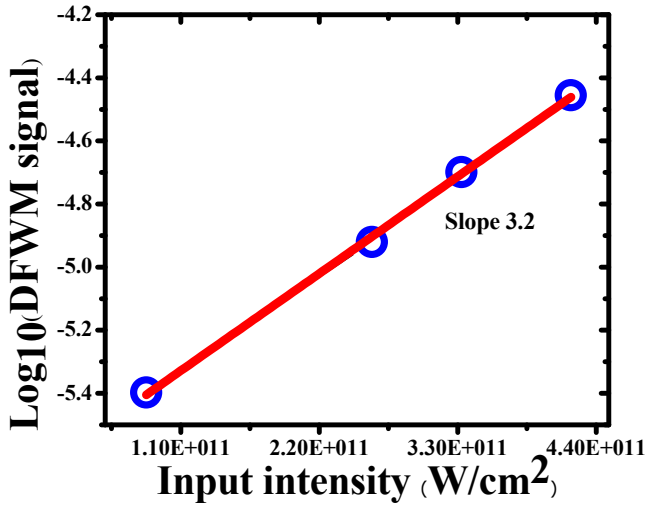


**Figure 3.** Input intensities versus the DFWM signal of Au NPs.

The electronic contribution to the nonlinear susceptibility in the fs domain of $CCL_4$ provides the standard reference to measure the unknown materialNLO susceptibility[6]. The estimated $\chi^{(3)}$ value of Au colloids is achieved by using a reference sample($CCL_4$) at same experimental conditions, the $\chi^{(3)}$ sample is measured by using the relationship[6],

$$\chi^{(3)}_{sample} = \left(\frac{n_{sample}}{n_{ref}}\right)^2 \left(\frac{I_{sample}}{I_{ref}}\right)^{1/2} \left(\frac{L_{ref}}{L_{sample}}\right) \alpha L_{sample} \left(\frac{e^{\frac{\alpha L_{sample}}{2}}}{1-e^{\alpha L_{sample}}}\right) \chi^{(3)}_{ref}$$

Where $n_{sample}$is the refractive index (n =1.4534) of water and $n_{ref}$ is the solvent refractive index(n=1.3280).The estimated $\chi^{(3)}$ value is $1.93\times10^{14}$ esu.

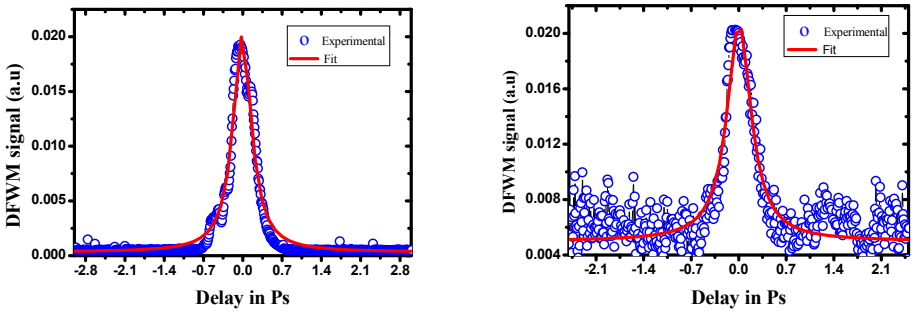


**Figure 4.** Time resolved DFWM traces of chloroform (left) Au colloids in water (right).

The time resolved DFWM signal of Au colloids as a function of probe delay (in ps) is recorded and the data isshown in figure 4. The fitting is done with a Lorenztian function(red, solid curve). The dual peak nature in figure 4 (right) data for Au nanoparticles requires further detailed investigation. The full width half maximum (FWHM <0.38ps) of both the solvent $CCL_4$and the colloidal solution fit was similar and the signal profiles were symmetric about the zero delay which clearly suggests the nonlinear response times are shorter than pulse duration [7]. No decays were observed in the case of Au nanoparticles DFWM response. Such a short response is prerequisite for optical switching applications.

## CONCLUSIONS

Pure Au nanoparticles were prepared in distilled water by using laser ablation technique with an average size of 12-40 nm. HRTEM data provided the crystalline phase of the nanoparticles. Third-order NLO nonlinear susceptibility is measured using the DFWM technique and is found to be $\sim 1.93\times10^{14}$ e.s.u. with $CCL_4$ as standard reference sample, and the time resolved studies confirmed the short response time of the observednonlinear susceptibility.

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