Linear and nonlinear optical characterization of gold nanoparticles in polyvinyl alcohol

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The nonlinear optical absorption of gold nanoparticles dispersed in polyvinyl alcohol is investigated using open aperture Z-scan technique. Au:PVA nanocomposite material is synthesized by chemical method. The characterization of the material is done by UV/Vis absorption spectroscopy, transmission electron microscopy and X-ray diffractometry (XRD).

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1. Introduction

Metal nanoparticles exhibiting wide variety of nonlinear optical properties have attracted much attention because of their potential applications including optical switching, chemical and biological sensing, optical limiting and surface enhanced Raman scattering [1]. One of the most characteristic features of metal nanoparticles is the surface plasmon resonance (SPR) due to collective oscillations of the conduction electrons. Plasmons excited by light lead to strong light scattering and absorption together with an enhancement of the local electromagnetic field. In the SPR absorption region, the material exhibits large optical nonlinearities and ultra-fast response time. Many studies reveal that composite materials, which consists of nanoparticles embedded in a dielectric matrix have a large third-order optical susceptibility. The idea is that the cubic optical nonlinearity of materials with delocalized electrons can be enhanced by artificially confining the electrons in regions smaller than their natural delocalization length in the bulk [2]. The intetest on such structures is based on the prospects of the elaboration of optical switchers with ultrafast response, optical limiters and intracavity elements for mode locking [3]. As the dielectric constant of the matrix increases, the SPR band is shifted to the longer wavelength. There have been numerous investigations on the linear and nonlinear optical properties of Au nanoparticles dispersed in different matrices such as TiO_2 [4], SiO_2, ZnO and Al_2O_3 [5]. The third order optical nonlinearities of these composite materials are greatly enhanced at the SPR band, by the giant amplification of the local electric field [6].

In this article we report an experimental investigation of the third order nonlinearity of gold nanoparticles dispersed in polyvinyl alcohol prepared by chemical method. The material characterization was done by UV-Vis absorption spectroscopy, XRD and TEM analysis. The nonlinear optical properties were studied by z-scan technique.

2. Experimental

Gold nanoparticles in polyvinyl alcohol(PVA) was synthesized by the following procedure. 3.0g of PVA was dissolved in 100 ml distilled water and it was kept at 60 ^oC for 5 hours along with stirring and the temperature was increased to 80 ^oC. Also the speed of stirring was increased. After 12 hours, we got a transparent solution when cooled to room temperature. To 50 ml of PVA solution, 0.0152 ml of 1M auric acid (AuHCl4) was added. This amount of AuHCl4 provided 0.2% wt. of Au-PVA suspension. The mixture was kept at 20^oC and stirred for 1 hour. Then, stirring was slowed down and heater was switched off. After 3 hours, we observed that transparent solution turned to purple color indicating the formation of gold nanoparticles. The collective electron resonances induced by electromagnetic radiation denoted as plasmons is the origin of the intense colour [7]. The sample was characterized by optical absorption measurements using a spectrophotometer (Jasvo V-570 UV/VIS/IR). For further analysis a thin film of the sample was prepared by gravity settlement method. The crystal structure of the gold nanoparticles was identi_ed using XRD analysis. Also, average particle sizes were calculated from XRD patterns using Scherrer equation [eq. (2)]. Transmission electron micrograph (TEM) was taken to confirm the size of the gold nanoparticles in polyvinyl alcohol.

In the present investigation, we performed open aperture z-scan to measure the nonlinear optical absorption of gold nanoparticles in polyvinyl alcohol. A Q-switched Nd:YAG laser (Spectra Physics LAB-1760, 532 nm, 7ns, 10Hz) was used as the light source. The laser beam was focused on the sample by a lens of focal length 200 mm.

The radius of the beam ω_0 was calculated to be 42.5 μm. The Rayleigh length, $z0 = \pi \omega_0^2/\lambda$, was estimated to be 1.07 cm, which is much greater than the thickness of the sample cuvette (1 mm), and is an essential prerequisite for z-scan experiments. The sample was translated on both sides of the focal plane over a 30 mm range, using a computer controlled translation stage. The transmitted beam energy, reference beam energy and the ratios were measured simultaneously using an energy ratio meter (Rj7620, Laser Probe Corp.) having two identical pyroelectric detector heads (Rjp735). The z-scan data were analyzed by using the procedure described by Sheik-Bahae et al. [8] and the nonlinear absorption coefficients were obtained by fitting the experimental data with the theoretical plots.

3. Results and discussion

Absorption spectrum of the gold nanoparticles in PVA matrix is shown in Fig. 1. The SPR peak is observed around 534 nm. XRD analysis is carried out to examine the crystal structure in the polymer complex and to calculate the size of dispersed gold nanoparticles [Fig. 2].

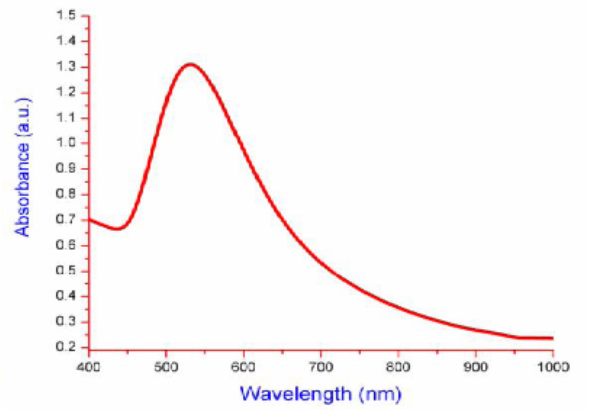

Fig. 1. Absorption Spectrum of gold nanoparticles in PVA.

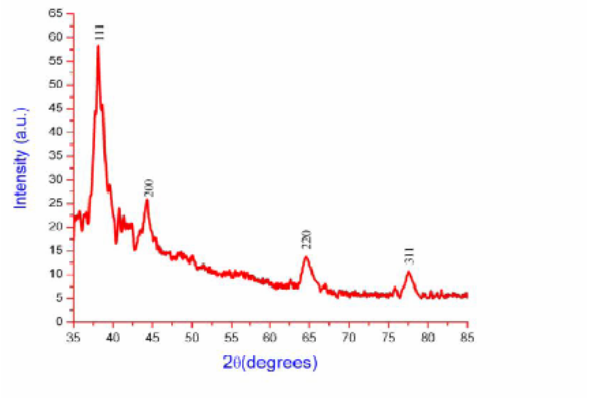

Fig. 2. XRD pattern of the prepared gold film

The XRD pattern indicates that the Au-nanoparticles occur in the usual fcc crystal structure which is similar to the earlier reported crystallites of this type [9]. Average size of the nanoparticles is calculated from the Schrerrer's formula [10].

$$d = 0.89\lambda / B\cos\theta_B \quad (1)$$

where d is the diameter of the particles, λ is the wavelength of the X-ray beam, θ_B is the Bragg angle and B is the full-width at half maxima of the diffraction peak. The estimated particle size is 4 nm corresponding to the [111] peak. For the other peaks, it varies between 3 to 10 nm. Fig. 3 shows the transmission electron micrograph of the sample which indicates that the gold nanoparticle are mono-dispersed and are uniformly distributed in the PVA matrix. TEM image clearly shows that maximum number of particles falls in the size range 4 - 5 nm. The SPR peak of the sample is observed to be at 534 nm. Therefore, 532 nm is capable of exciting the localized plasmons around the metal nano-particles. Fig. 4 shows the open aperture z-scan curve of gold-PVA nano-composite at an input fluence 0.15 GW/cm^2. The curve exhibits a normalized transmitted valley, indicating the presence of induced absorption in the material. When the sample is away from the focus, the weak intensity cannot induce any nonlinearity, and the transmittance is unity. As the sample is moved towards the focus, the transmittance acutely decreases with increasing light intensity to less than unity, resulting in induced absorption [11]. The data are analyzed using the procedures described by Sheik-Bahae et. al for a two-photon absorption (TPA) process [8]. The normalized transmittance T(z) could be written as,

$$T(z) = \sum_{m=0}^{\infty} \frac{[-q_o(z)]^m}{(m+1)^{\frac{3}{2}}} \quad (2)$$

where, $q_0(z) = \beta I_0 L_{eff}/(1 + z^2/z_0^2)$, I_0 is the laser peak intensity, $L_{eff} = (1-\exp(-\alpha L))/\alpha$ is the effective thickness of the sample (L is the sample thickness) and z_0 is the diffraction length of the beam. The solid curves in Fig. 3 are the theoretical fit to the experimental data. The experimental error is estimated to be 1.1%. The imaginary part of the third order susceptibility, Im $\chi^{(3)} = n_0^2 \varepsilon_0 c^2 \beta/\omega$, where n_0 is the linear refractive index of the gold-PVA nanocomposite, ε_0 is the permittivity of free space, c is the velocity of light in vacuum, ω is the angular frequency of the radiation used. In general, induced absorption can occur in metal nanoclusters and nanoparticles due to a variety of processes like, excited state absorption, two-photon absorption, interband and intraband transitions and nonlinear scattering [12]. The theory of two photon absorption process fitted well with the experimental curve infers that TPA is the basic mechanism for induced absorption. It is observed that, the material exhibits induced absorption at 1064 nm (Fig. 9). This could be due to the reason that, as the SPR peak of the material is around 534 nm, there is a high probability for two photon absorption at 1064 nm. The measured values of nonlinear

absorption coefficient β at 532 nm and 1064 nm are, 130.17 cm/GW and 92.7 cm/GW respectively.

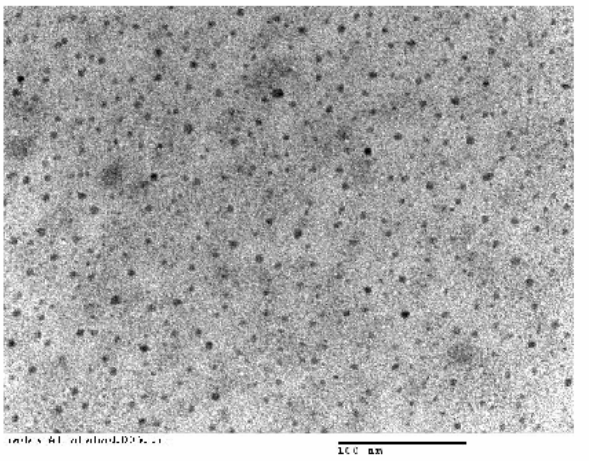

Fig. 3. TEM image of the prepared gold film. Average particle size is 5 nm.

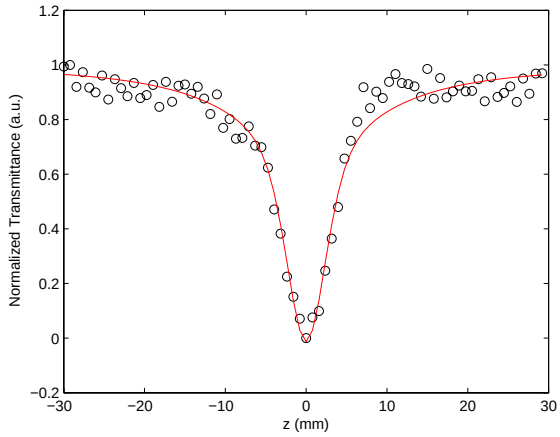

Fig. 4. Open aperture z-scan transmittance of the sample at 532 nm (input fluence – 0.15 GW/cm^2). The solid curve is the theoretical value fitted to the experimental data sing equation (2).

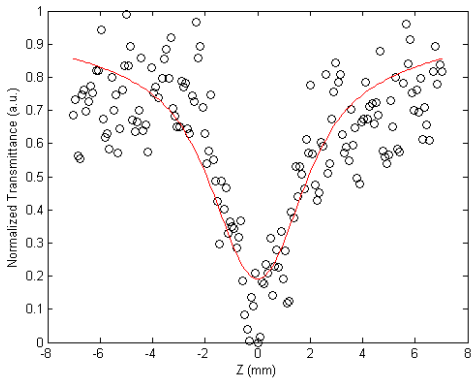

Fig. 5. Open aperture z-scan transmittance of the sample at 1064 nm (input fluence – 0.2 GW/cm^2). The solid curve is the theoretical value fitted to the experimental data using equation (2).

4. Conclusion

We have synthesized nanogold suspensions in PVA which exhibits stable plasmonic band around 534 nm. The average particle size observed from TEM analysis is 4-5 nm. Nonlinear absorption of the sample is done by z-scan technique. Sample exhibited induced absorption at 532 nm and 1064 nm. The possible origin of induced absorption is two-photon absorption.

Acknowledgements

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