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Third-Order Optical Nonlinearity of Au-Ag core-Shell Nanoparticle at 532 nm

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Abstract: ***Au-Ag core-shell nanoparticles in aqueous solution for the various molar ratio of Au and Ag has been synthesized using simple chemical reduction method. The TEM image of the Au-Ag nanoparticles sample gives the confirmation of core-shell structure. The average particle size of Au-Ag core-shell is 10 nm. The Au-Ag colloidal core-shell nanoparticle samples characterized by UV-VIS absorbance and Z-scan technique. The nonlinear refractive index (n_2), the nonlinear absorption coefficient (β), and third order susceptibility (χ3) have calculated for an increase in molar ratio of Au and Ag. The results show that concentration of the reactants can directly affect and alter the nonlinear parameters. As a photonics application is a concern, Au-Ag core-shell nanoparticles optical limiting behavior is also observed. As expected, the sample which has higher nonlinearity shows quickly saturated for input intensity.***

Keywords: Au-Ag core-shell nanoparticles, Z-scan technique, Nanophotonics, Optical limiting.

1. Introduction

The expected outgrowth of the long-standing research about nonlinear optical materials leads to the importance in various fields such as optical communication, signal processing, computing, holographic recording, optical information storage and optical limiting applications. The emerging technology of photonics has drawn lots of interest in searching for nonlinear optical materials. To find the appropriateness of any optical material for a variety of photonic applications, it requires knowing the optical characteristics such as nonlinearity, its significance and response time spectrum. There are varieties of experimental techniques for determining the features of any nonlinear material. Since the development of nanotechnology, synthesis of nanoparticles has received much consideration due to the feasibility of improvement in the nonlinear optical properties for usage in photonic devices application. Recently, CdS-coated Ag nanoparticle has been synthesized using the reverse micelle technique and studied the nonlinear optical response [1]. When covering of the nanoparticle on the material can provide the much higher value of third-order optical nonlinearity also has been investigated [2] for bismuthate glasses doped with silver nanoparticles. The cause behind high refractive index of bismuthate glass, surface plasmon resonance (SPR) of Ag nanoparticles is increased to 1400 nm. The UV-VIS absorption peak show red shift when increasing Ag nanocubes size [4-3] has been reported, but the linear and nonlinear optical properties have improved. Year by year nanotechnology growing fast enough, the exploitation of nanostructured materials [4] needed to study in all possible ways. Recently this field has provided solutions for many technological challenges, e.g., solar cell, medicine, water treatment [5]. When pulse laser excitation based nonlinear study of metal colloid been reported, but same time there have been some nonlinear studies that have investigated using CW laser excitation [6-8]. To study nonlinear characteristic study of material, Z-scan is a very easy method. The Z-scan technique which was anticipated by Sheik-Bahae [9,10] is a modest and sensitive single-beam method for determination of the third-order nonlinear optical coefficients. This approach also supports to find the sign of nonlinear refractive index [11]. When look into the nonlinear study using Z-scan Method, one could observe numerous work in the last 20 years. Using CW 632 nm illumination [12], Jia et al. studied the nonlinear optical properties of gold and silver colloidal solution by Z-scan. When looking deep into the nonlinear study of the nanoparticle, bimetallic nanoparticles are of broad interest since they lead to many interesting size-dependent electrical, chemical, and optical properties. They are of particular importance in the field of catalysis since they often show better catalytic properties than their monometallic counterparts. Gold is very suitable as an alloying metal due to its relatively low reactivity. Recently, bimetallic Au/Ag core–shell nanoparticles have been synthesized by biological methodologies using Neem leaf broth which show that the rates of reduction of the metal ions by Neem leaf extract are much faster than chemical methods [13]. Bimetallic silver and gold nanoparticles, a core–shell type structure, have been prepared by NaBH4 chemical reduction method has been reported [14]. Also, researchers have been published about the gold-coated silver, and silver-coated gold composite nanoparticles are prepared by a seeding growth method to study their SERS-active properties [15]. The structure of Au–Ag is either a core–shell or an alloy phase, depending on the preparation conditions. The high surface-to-volume ratios of nanoparticles lead to dramatic changes in their properties. As the size and the dimension of particles are reduced, their electronic properties change drastically because the density of states and the spatial length scale of the electronic motion reduce with decreasing size. Alloy nanoparticles, on the other hand, have mainly been studied because of their catalytic effects. Depending on the synthesis method, the resulting bimetallic particles can exhibit either alloy behavior or core–shell system behavior. The alloy nanoparticles homogeneously distributed over the whole volume on an atomic scale; however, the core–shell

nanoparticles constitute the core of the structure, and the other one the external shell. Bimetallic nanoparticles can be prepared by simultaneous reduction or by progressive reduction of two metal ions in the presence of suitable stabilization strategies such as steric hindrance and static electronic repulsive force. The above reduction methods may obtain a particle structure of homogeneous alloy, while the latter are for the production of core–shell structure particles. Au and Ag have very similar lattice constants and are completely miscible over the entire composition range. Hence, single-phase alloys can achieve with any desired composition. Plasmonic nanoparticles may even be designed as "core-shell," with a dielectric core and a metallic shell. By the specific figuration of parameters like core diameter and shell thickness, the absorption spectrum of these particles is widely tunable. Researchers reported detailed review on nonlinear optical mechanisms of the inorganic nanostructures for optical limiting applications [16]. An optical limiter is a device that strongly attenuates optical beam to a threshold level of high intensity while shows linear transmittance at low power. The key factor about a typical optical limiter the material should have high optical nonlinearity, and decreasing transmittance with increasing input irradiance to facilitate the transmitted energy never exceeds the damage threshold for the optical sensor [17]. Recently, broadband optical limiting has been reported [18] for nanostructured films of silicon carbide β-SiC (3C) using the ns laser radiation in VIS-NIR spectral range. Also, Graphene Oxide (GO), Ag@TiO2 core-shells and GO-Ag@TiO2 compounds synthesized and it is for optical limiting application [19]. In the present work, Au-Ag core-shell nanoparticles are synthesized, and TEM image of the sample of Au-Ag nanoparticles sample gives the confirmation of core-shell structure. The average particle size of Au-Ag core-shell is 10nm. The Au-Ag core-shell nanoparticles samples are optically characterized by UV-VIS absorbance and Z-Scan technique. Under CW 532nm excitation, Z-scan measurements showed that the Au-Ag nanoparticles exhibited large thermal induced refractive index n2. Due to the large nonlinear refractive index of the Au-Ag core-shell structure was exploited for the optical limiting application. In the present manuscript, section 2 illustrate about the analytical methodology of Z-Scan measurement and followed by the method of optical limiting in a very short manner. Section 3, 4 gives the synthesis and optical, nonlinear characteristics studies of Au-Ag nanoparticles. In Section 5 provides the detailed discussion about the experimental finding and optical limiting studies.

2. Methodology

The nonlinear polarization when the applied field E(t) is monochromatic and is given by [20]

$$P^{(3)}(t) = \frac{1}{4}\chi^{(3)}E^3\cos(3\omega t) + \frac{1}{4}\chi^{(3)}E^3\omega t \qquad (1)$$

The first term in equation (1) describes a response at frequency 3ω due to the interaction of applied field at frequency ω. This frequency ω leads to the process of third-harmonic generation. The second term in equation (1) describes a nonlinear contribution to the polarization at the frequency of the incident field. This term hence leads to a nonlinear contribution to the refractive index experienced by a wave at frequency ω. The phenomena of the self–focusing of an intense Gaussian beam in the nonlinear medium is considered as the starting point for Z-scan analysis which was improved by Sheik-Bahae. It is assumed that a Gaussian TEM00 beam is incident on a thin nonlinear medium and traveling in the +z direction, (i.e., L<< ZR, where ZR is the Raleigh range of the beam in air). In general, for a cubic nonlinearity, the index of refraction n is expressed regarding nonlinear indices n_2 (esu) or n2(m2/W) expressed as

$$n = n_0 + \frac{n_2}{2}|E^2| = n_0 + n_2 I \qquad (2)$$

Where n_o is the linear index of refraction, E is the peak electric field (cgs), and I denotes the irradiance (MKS) of the laser beam within the sample. The quantity n_2 (esu) and n_2 (m^2/W) are related through the conversion formula

$$n_2(esu) = \frac{cn_0}{40\pi}n_2(m^2/W) \qquad (3)$$

where c (m/s) is the speed of light in vacuum.

Assuming a TEM_{00} Gaussian beam of waist radius ω_0 traveling in the +z direction, the magnitude of the electric field E can be written as,

$$|E(r,Z,t)| = |E_0(t)|\frac{\omega_0}{\omega(Z)}\exp\left[-\frac{r^2}{\omega^2(Z)}\right] \qquad (4)$$

Where $\omega^2(Z) = \omega_0^2\left(1+\frac{Z^2}{Z_R^2}\right)$ is the beam radius at z, $Z_R = k\frac{\omega_0^2}{2}$ is the diffraction length of the beam (Rayleigh range), k = 2π / λ is the wave vector, and λ is the laser wavelength, all in free space. E_o denotes the radiation electric field at the focus and contains the temporal envelope of the laser pulse. If the sample length is small enough such that changes in the beam diameter within the sample due to either diffraction or nonlinear refraction can be neglected, the medium is regarded as thin. For such an assumption, the amplitude and nonlinear phase change Δϕ of the electric field within the sample are given by,

$$\frac{d\Delta\varphi}{dZ'} = \Delta n(I)k \qquad (5)$$

And

$$\frac{dI}{dZ'} = -\alpha(I)I \qquad (6)$$

Where Z' is the propagation depth in the sample and $\alpha(I)$ includes the linear and nonlinear absorption terms. Equations (5) and (6) are solved to give the phase shift $\Delta\phi$ at the exit surface of the sample, which simply follows the radial variation of the incident irradiance at a given position of the sample *z*:

$$\Delta\varphi(Z,r,t) = \frac{\Delta\phi_0(t)}{1+\frac{Z^2}{Z_0^2}}\exp\left[-\frac{2r^2}{\omega^2(Z)}\right] \qquad (7)$$

The on-axis phase shift at the focus is defined as

$$\Delta\phi_0(t) = k\Delta n_0(t)L_{eff} \qquad (8)$$

where L_{eff} = $(1- e^{-\alpha L}) /\alpha$, with *L* the sample length and α the linear absorption coefficient.

$L_{eff} \rightarrow L$ for αL << 1 and $L_{eff} \rightarrow 1/\alpha$ for αL >> 1.

Here $\Delta n_o = n_2 I_o(t)$ with $I_o(t)$ being the on-axis irradiance at focus (i.e. z = 0). One can ignore the Fresnel reflection losses

such that $I_o(t)$ is the irradiance within the sample.The change in the refractive index can be evaluated by use of the difference in the peak-valley normalized transmittance T_p-T_v, which is given by,

$$\Delta T_{p-v} = 0.406(1-S)^{0.25}|\Delta\phi_0| \quad (9)$$

Where S is the aperture linear transmittance (S = 0.4) and $|\Delta\phi_0|$is the on-axis phase shift. The nonlinear refraction (n_2) is given by [21],

$$n_2 = \frac{\lambda\Delta\phi_0}{2\pi L_{eff} I_0} \quad cm^2/W \quad (10)$$

The nonlinear absorption coefficient (β) is given by [47],

$$\beta = \frac{2\sqrt{2}\,\Delta T}{L_{eff} I_0} \quad cm/W \quad (11)$$

Experimentally determined nonlinear refractive index n_2 and nonlinear absorption coefficient β can be used in finding the real and imaginary parts of the third-order nonlinear optical susceptibility $\chi^{(3)}$ according to the following relations [21].

$$Re(\chi^{(3)})\ (e.s.u) = 10^{-4}\frac{\varepsilon_0 c^2 n_0^2}{\pi} n_2 \quad (cm^2/W) \quad (12)$$

$$Im(\chi^{(3)})\ (e.s.u) = 10^{-2}\frac{\varepsilon_0 c^2 n_0^2 \lambda}{4\pi^2}\beta \quad (cm/W) \quad (13)$$

Where,ε_0 is the vacuum dielectric constant, c is the vacuum speed of light, n_o is the linear refractive index and λ is the laser wavelength. Using equations (12) and (13), $\chi^{(3)}$ can be calculated. The absolute value of the third-order nonlinear optical susceptibility $\chi^{(3)}$ is given by the relation [21].

$$|\chi^{(3)}| = \{[Re(\chi^{(3)})]^2 + [Im(\chi^{(3)})]^2\}^{0.5} \quad (14)$$

The methodology behind optical limiting is a nonlinear optical process in which transmittance of a material decreases with increased incident light intensity. Optical limiters are one of the most important types of devices used to control the amplitude of high-intensity optical pulses. These devices operate by the intrinsic properties of the materials used for their fabrication. An ideal optical limiter has linear transmittance at low input intensities, but above the threshold power, its transmitted energy remains constant. Various nonlinear optical effects can be employed for the performance of optical limiting. Some of the mechanisms responsible for optical limiting are: 1) Reverse Saturable Absorption (RSA) which translates into increased optical absorption with increased incident optical intensity. 2) Nonlinear Refraction (due to molecular reorientation, electronic Kerr effect, excitation of free carriers, photorefraction, and optically induced heating in the material). 3) Induced Scattering (optically induced heating or plasma generation in the medium).4) Thermal Blooming. 5) Multiphoton Absorption (e.g. Two-photon absorption). In general, materials that exhibit optical limiting behavior use these five mechanisms in any combination, although sometimes one or more processes are predominant in the material used.

3. Synthesis and Optical Characterizations

Many techniques, including chemical and physical means, have been developed to prepare metal nanoparticles, such as chemical reduction using a reducing agent. There are comfortable and convenient chemical methods that use dilute aqueous solutions and simple equipment. At first, Au - Ag alloy nanoparticle of molar ratio 1:1 has been prepared using simple chemical reduction method. In this process, silver nitrate ($AgNO_3$) and chloroauric acid ($HAuCl_4$) has used for gold and silver nanoparticles. In the synthesis process, sodium citrate ($C_6H_5O_7Na_3$) used as a capping agent and $NaBH_4$ used as reducing agent. The absorption spectrum is collected using a Shimadzu model 2401 PC UV-VIS-NIR scanning spectrophotometer, over wavelengths from 300 to 1300 nm. The sample is measured against water as a reference. The absorbance peak for 1:1 is found to be 421 nm. Further Au: Ag nanoparticles of molar ratio 1:2, 1:3, 2:1, 3:1 has prepared in the same manner which is depicted in Fig. 1. By varying the concentration of the reactants such as Au, and Ag, the surface plasmon peaks exhibits a shift in the UV-VIS absorption spectrum.

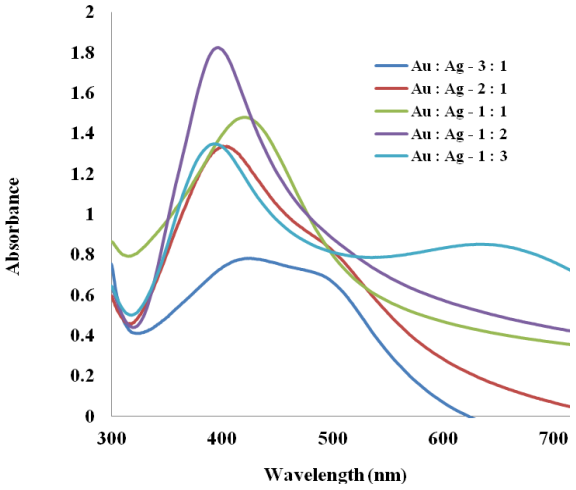


Figure 1: UV- VIS absorbance of the sample for molar ratio 1:1, 1:2, 1:3, 2:1 and 3:1 are observed on Shimadzu model 2401 PC UV–VIS -NIR scanning spectrophotometer

The surface Plasmon absorbance peak for the molar ratio for 1:2 397 nm, for 1:3 molar ratio observing at 390.5 nm and other, for, 2:1 has absorbance peak is at 403 nm and 3: 1 are found to be 420 nm. To know about the structure of Au-Ag nanoparticles, the sample is allowed for imaging using HRTEM. High-resolution transmission electron microscopy (HRTEM) is an imaging mode of the transmission electron microscope (TEM) that enables the imaging of the crystallographic structure of a sample at an atomic scale. The image of the Au-Ag nanoparticles sample is obtained from the HRTEM instrument with operating voltage of 200kV. The TEM image of the sample is depicted in figure 2

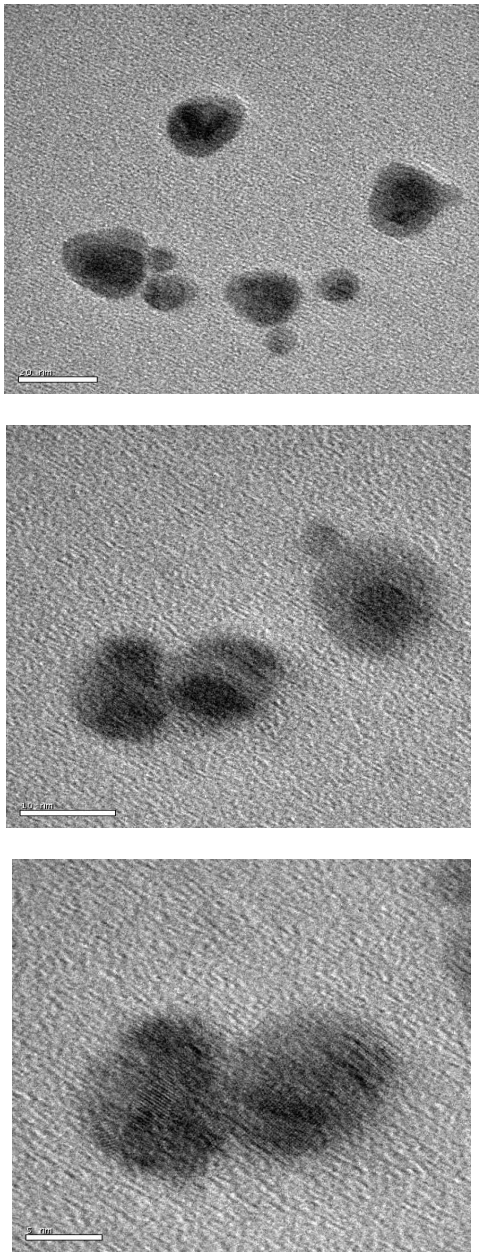


Figure 2: TEM images of the Au-Ag colloidal nanoparticles for molar ratio 1:1 for the three different scales 20 nm, 10 nm and 5 nm. The average particle size of Au-Ag core-shell is 10nm

The TEM image of the Au-Ag nanoparticles in colloidal gives the confirmation of core-shell structure. In the core-shell structure, the core belongs to gold. It appears to be high dense because it has high electron density than silver. The average particle size of Au-Ag core-shell is 10nm.

4. Experimental results

The nonlinear optical measurements have been performed using a single beam Z-scan technique. The Z-scan experiments are carried out using continuous wave of SHG of Nd-YAG laser (COHERENT – Compass 215M diode-pumped laser) at a wavelength of 532 nm, which is focused by 3.5 cm focal length lens. The laser beam waist ω_o at the focus is measured to be 18.1 μm and the Rayleigh length Z_R = 3.7 mm. The Z-scan experiment is performed for Au-Ag nanoparticles, with intensity I_o = 9.314 kW/cm^2 of Nd-YAG laser and it exhibited substantial nonlinearity in the wavelength 532 nm. The schematic diagram of single beam Z-scan technique set up is shown in Figures 3.

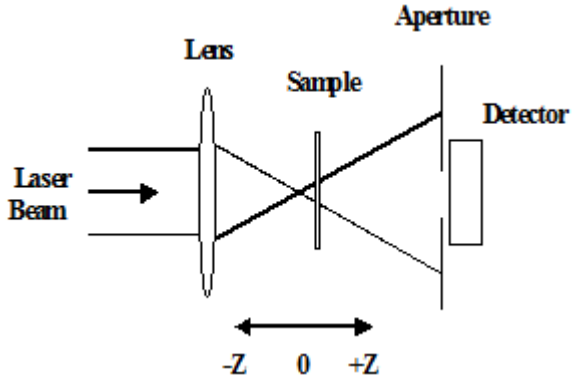


Figure 3: Schematic diagram of Z-scan experiment

A 1 mm wide optical cell (quartz cuvette) containing the Au-Ag nanoparticles in colloidal form are translated across the focal region along the axial direction, i.e. the direction of propagation of laser beam. The transmission of the beam through an aperture placed in the far field is measured using a photodetector (LM2, Coherent Inc.). The output is fed to the digital power meter (Field Master Gs-coherent). For an open aperture Z-scan, the aperture is removed, and a lens is used to collect the entire laser beam transmitted through the sample.

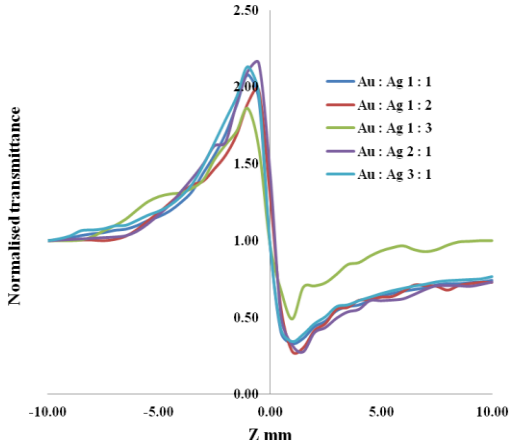


Figure 4: Closed-aperture Z-scan curve of Au-Ag nanoparticles of a) molar ratio (1:1) molar ratio (1:2) , molar ratio (1:3) , molar ratio (2:1) and molar ratio (3:1)

The closed aperture Z-scan is sensitive to both nonlinear absorption and nonlinear refraction. Such Z-scan trace is expected to have maximum transmittance (peak), followed by minimum transmittance (Valley), which corresponds to a negative nonlinearity i.e. self-defocusing. An inverse Z-scan curve (i.e., a valley followed by a peak) characterizes a positive nonlinearity i.e. self-focusing. Z-scan with a fully open aperture (S = 1) is insensitive to nonlinear refraction. Such Z-scan traces with no aperture are expected to be symmetric on the focus (Z = 0) where they have a minimum transmittance (e.g., two-photon or reverse saturation absorption) or maximum transmittance (e.g., saturation of absorption). The change in the refractive index can be evaluated by use of the difference in the peak-valley normalized transmittance T_p-T_v (Eqn.9), from the figure 4, estimated the nonlinear refractive index, nonlinear

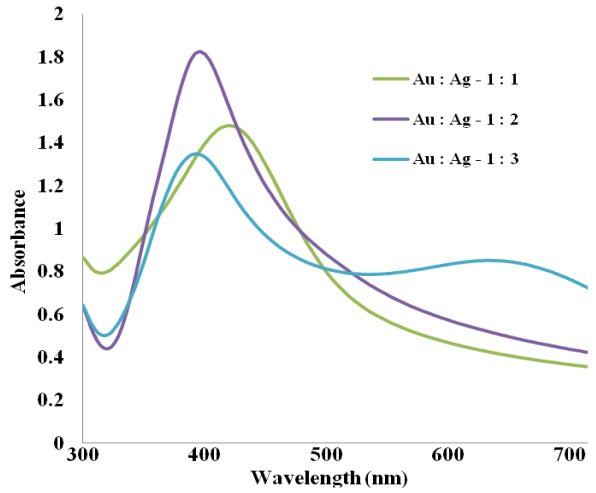
absorption coefficient, and third-order susceptibility is depicted in Table 1. The fractional change in the measured parameters shows that reactants concentration of the material can directly affect the nonlinearity.

Table 1: The measurement results of optical nonlinearity of the Au-Ag colloidal nanoparticles for molar ratio 1:1, 1:2, 1: 3, 2:1 and 3:1

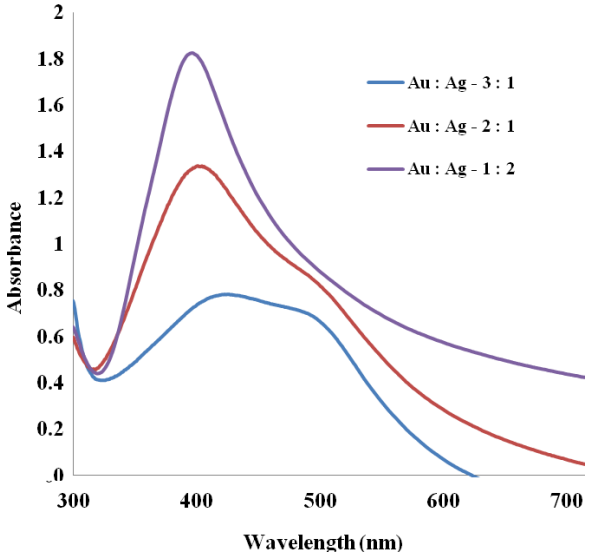
Au-Ag Molar ratio	Absorbance	T_{p-v}	$\Delta\varphi_0$	n_2X 10^{-8} cm^2W^{-1}	β X 10^{-3} cm W^{-1}	$\chi^{(3)}$ X 10^{-10} e.s.u.
1:01	1.4791	1.74	4.888	4.3176	1.467	2.7397
1:02	1.8253	1.7	4.759	4.2048	1.428	2.6682
1:03	1.347	1.37	3.838	3.3899	1.151	2.151
2:01	1.3351	1.87	5.253	4.6398	1.576	2.9442
3:01	0.7753	1.79	5.02	4.4324	1.506	2.8126

5. Discussion

The synthesis of the Au-Ag nanoparticles via chemical reduction is a pretty easy method. The colors of the sample in solution indicate the presence of nanoparticle formation, and it can be confirmed through UV-VIS absorbance.



(a)



(b)

Figure 5: a) UV- VIS absorbance of the sample for an increase in a molar ratio of Ag, absorbance peaks are 421 nm (1:1), 396.5nm (1:2) and 392.5nm, 647 nm (1:3). b) UV-VIS absorbance of the sample for an increase in a molar ration of AU, absorbance peaks are 421 nm (1:1), 402.5 nm, 495 nm (2:1) and 416 nm, 498 nm (3:1).

A blue shift in the surface plasmon peaks is expected, when the molar concentration of Ag increases, as shown in figure 5 (a). However, scrutiny of the UV-VIS absorption peaks indicates in the case of molar ratio 1:3, there is an addition of absorption peak at a higher wavelength. It might be due to the improper monomerization of the Au-Ag alloy sample. Herein present manuscript, contain the HRTEM image for the molar ratio 1:1. In the same manner, if the molar ratio of the Au increases, the absorption peaks shift towards the right, redshift (see Fig 5.(b)). However, the straightway there is no such indication, but careful examination of UV-VIS absorbance in the molar ratio 2: 1, and 3:1 shows two absorption peaks, one corresponds to Au, and other may account for Au. When look into the second peak of the UV-VIS absorbance can able to say that the absorbance peak shift towards the right for an increase in Au concentration. Under CW 532nm excitation, Z-scan measurements showed that the Au-Ag colloidal nanoparticles exhibited substantial thermal induced refractive index (n_2). Due to the large nonlinear refractive index, it can be used for optical limiting. The experiment layout for optical limiting is shown in figure 8. Optical limiting measurements are performed using a CW laser beam of diode pumped neodymium-doped yttrium aluminum garnet (Nd: YAG) laser (Compas^{TM} 215M-50) from (COHERENT) with an output power of 50mW at wavelength 532nm. Optical limiting based on nonlinear refraction is performed by keeping an aperture in front of the detector, which reduces the cross section of the beam entering the power meter. The beam is focused using a lens of focal length f=3.5 cm and pass through a 1mm path length sample cell (Quartz cuvette) contains the Au-Ag nanoparticles in aqueous solution. The beam is focused using a lens of focal length f=3.5 cm and pass through a 1mm path length sample cell (Quartz cuvette) contains the Au-Ag nanoparticles in aqueous solution.

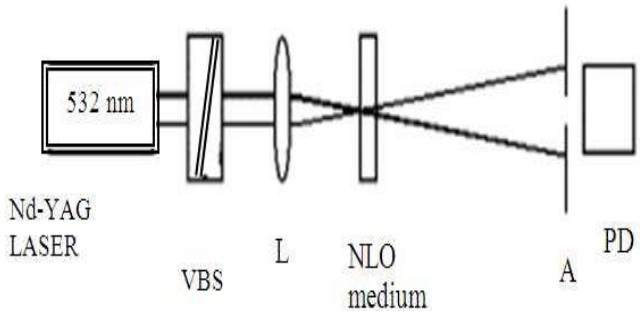


Figure 6: Experimental setup for optical limiting

The beam is focused using a lens of focal length f=3.5 cm and pass through a 1mm path length sample cell (Quartz cuvette) contains the Au-Ag nanoparticles in aqueous solution. The mounted sample cell on translation stage moved back and forth along the optic axis to change the position of the sample on the lens. An aperture of 2mm diameter fixed in front of the photodetector is used to collect the beam coming out of the sample cuvette. This beam is then made to fall on a photodetector which is connected to the digital power meter. The size of the focused spot in the sample is approximately 25.1 µm. The input laser intensity is varied systematically, and the corresponding output intensity

values are measured by the photodetector so that the characteristic curve of the output power as a function of input power can be obtained. The variable beam splitter is used to vary the power/intensity. The sample which has higher third order nonlinearity was promptly saturated with input power. But here there are no drastic nonlinearity differences between the five samples since the concentration of the reactants are small.

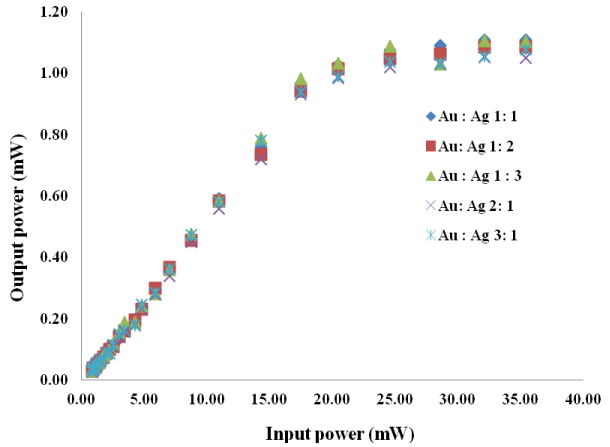


Figure 7: The optical limiting behavior exhibited by Au-Ag nanoparticle for different ratios.

The good performance of optical limiting behavior of the Au-Ag nanoparticles sample, the sample is moved along the direction of the laser beam at various positions around the focus of the lens (Z=0) forward and backward. It is found that the limiting occurs when the sample is placed beyond the focus of the lens i.e. valley point of the Z-scan curve.

6. Conclusion

In this investigation, Au-Ag core-shell nanoparticles in the various molar ratio of Au and Ag had been synthesized using simple chemical reduction method. The TEM image of the Au-Ag nanoparticles sample gives the confirmation of core-shell structure. In the core-shell structure, the core belongs to gold. It appears to be high dense because it has high electron density than silver. The average particle size of Au-Ag core-shell is 10nm. The Au-Ag colloidal core-shell nanoparticle samples characterized by UV-VIS absorbance and Z-scan technique. Under CW 532nm excitation, Z-scan measurements showed that the Au-Ag nanoparticles exhibited large thermal induced refractive index n_2. The nonlinear refractive index, nonlinear absorption coefficient, and third order susceptibility had determined for the various molar ratio of Au and Ag. The results show that concentration of the reactants can alter the nonlinear parameters. Due to the large nonlinear refractive index of the Au-Ag nanoparticles, their optical limiting performance also witnessed.

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