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The Effect of the Concentration of Colloidal Silver Nanoparticles on Optical Limiting Reliability

Shahad M. Naji   Mohamed K. Dhahir and **Sally A. Al-Ani**

Institute of Laser for Postgraduate Studies, University of Baghdad, Baghdad, Iraq, modratk@yahoo.com

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Abstract: The effect of the concentration of the colloidal nanomaterial on their optical limiting behavior is reported in this paper. The colloids of sliver nanoparticles in deionized water were chemically prepared for the two concentrations (31 ppm and 11ppm). Two cw lasers (473 nm Blue DPSS laser and 532 nm Nd:YAG laser) are used to compare the optical limiting performance for the samples. UV–visible spectrophotometer, transmission electron microscope (TEM) and Fourier Transformation Infrared Spectrometer (FTIR) were used to obtain the characteristics of the sample. The nonlinear refractive index was calculated to be in the order of 10^{-9} cm^2/W. The results demonstrate that the observed limiting response is significant for 532nm. In addition, the more concentrated of short optical path length has better optical limiting performance which gets the sample is attractive for optical limiting applications.

Keywords: Optical limiting, Ag nano particles, Self defocusing effect.

Introduction

Optical limiting is an effect to keep the power, irradiance, energy, or fluence transmitted by an optical system below the maximum value, regardless of the magnitude of the input. It must do this while maintaining high transmittance at low input powers (1). The devices used for sensor protection against laser pulses are called optical limiters (2). An ideal optical limiter, by definition, is a device that exhibits a linear transmittance below a threshold and clamps the output to a constant above it, thus providing safety to sensors and eyes. It is well known that optical limiting devices rely on one or more of the nonlinear optical effects such as excited state absorption, free carrier absorption, two-photon absorption(TPA), thermal defocusing/scattering, photo refraction, nonlinear refraction, and induced scattering with enhancement in limiting performance by coupling two or more of such effects (3-5). Due to of their relatively large third-order nonlinearity and ultra- fast response time, silver nanoparticles have wide applications as nonlinear materials for optical switching, optical limiting and beam flattening (6).Different methods have been reported for synthesizing silver nanoparticles (AgNPs), either physical or chemical methods (7). Chemical reduction is the most frequently adopted method for the synthesis of Ag-NPs as colloidal silver dispersion in water is stable. The reduction of silver ions in aqueous solution generally yields colloidal silver with size of particles being several nanometers in diameter (8-11). It involves reduction of an ionic salt in the presence of surfactant as a reducing agent.

Chemical mediated synthesis is cost effective, easily scaled up for bulk synthesis without the use of high pressure, energy and temperature (12). In this work, we report the experimental measurements of the optical limiting behavior for colloidal silver nanoparticles, under the excitation of two wavelengths 473 nm and 532 nm through a self- defocusing effect.

Materials and method

The chemical compounds used are Silver nitrate ($AgNO_3$) obtained from (SIGMA CHEMICAL CO.assay 99 %) , sodium borohydride ($NaBH_4$) (Chemical Point Germany ,assay 99.9 %), Poly-vinylpyrrolidone (PVP) ,assay 99%) and De-ionized Water (DI) were used.

Currently, many methods have been reported for the synthesis of Ag-NPs. Each method has advantages and disadvantages. Among these methods we chose the chemical one because it provides an easy way to synthesize Ag-NPs in solution, low costs and high stability. Colloidal Nanoparticles were prepared by dissolving 0.002g of $AgNO_3$ in 20ml of DI and stirring it for 15 minutes while cooling 0.015g of $NaBH_4$ in 15 mL DI in an ice bath until its temperature reach (0°C).

After preparing the PVP stock solution (1% PVP in DI) ,by using drop wise adding the $AgNO_3$ solution to the $NaBH_4$ solution on magnetic stirrer with ice bath. Finally, the PVP solution was added rapidly to the mixed solution by a syringe while stirring till the colorless solution turned to yellowish indicating the formation of silver nanoparticles.

Characterization of silver nanoparticles

The characterization of the sample was performed using UV- visible Spectrophotometer, Transmission Electron Microscope (TEM) and Fourier transform infrared spectroscopy (FTIR).

UV.Visible spectrometer is quite sensitive to the presence of silver colloids because these nanoparticles exhibit an intense absorption peak. The absorption band in the 350 nm to 450 nm region is typical for the silver nanoparticles (13). As shown in Figure1. The (TEM) image of the silver synthesized is represented in Figure 2.

Figure 2 shows the presence of spherical particles. The average size of these particles is in the range of 15 to 25 nm in size.
(FTIR) is used to confirm the presence of colloid silver nanoparticles.

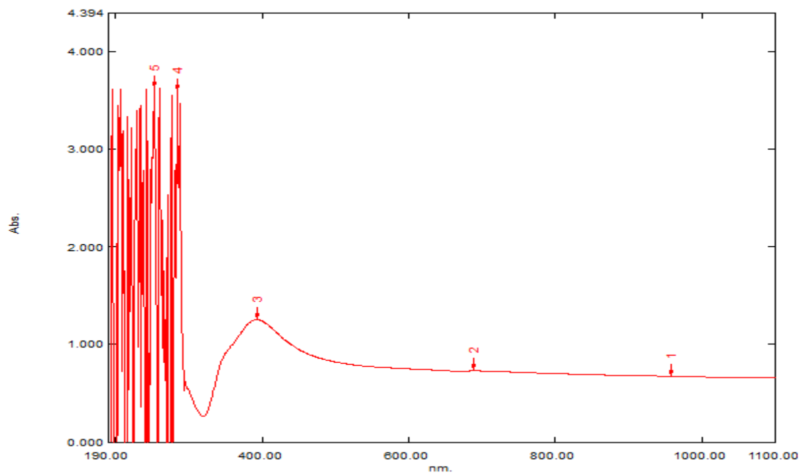

Fig. (1): UV–Vis absorption spectrum of yellow colloidal silver nanoparticles shows the peak at 393 nm.

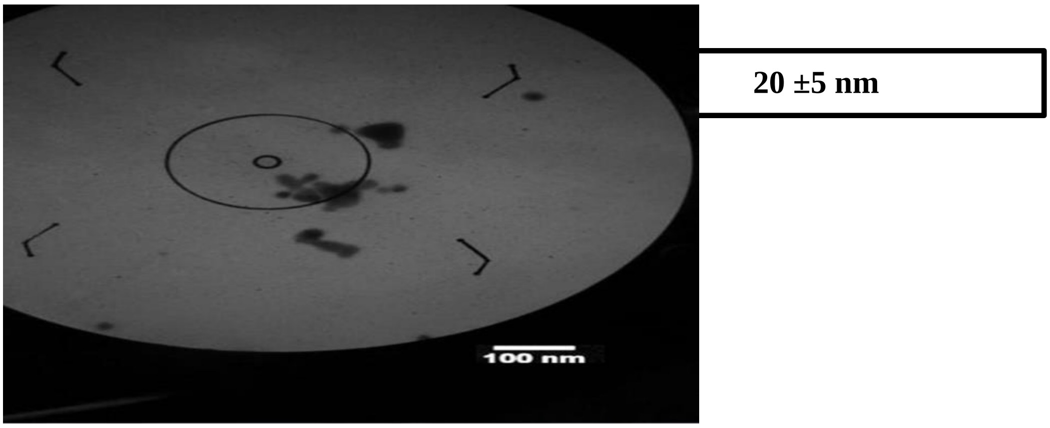

Fig.(2): TEM image for the sample prepared by the reduction of NaBH4 to AgNO3 in the presence of PVP, The particle size 20 ±5 nm is dominated.

Two bands appeared at 700 cm^{-1} and 750 cm^{-1} corresponding to metal–oxygen (M–O) bond due to (C-O^- Ag^+) bonds. There was also new band at 1234 cm^{-1}due to the (C-NO_3) bonds. The absorption bands of (C-H) appeared at 1375 cm^{-1} and 1450 cm^{-1}. The (C-H) aliphatic absorption band appeared at 2990 cm^{-1} .This clear observation is because of some additional peaks and shifts in frequencies. This confirms silver particles as dispersed materials inside the solution as shown in Figure 3.

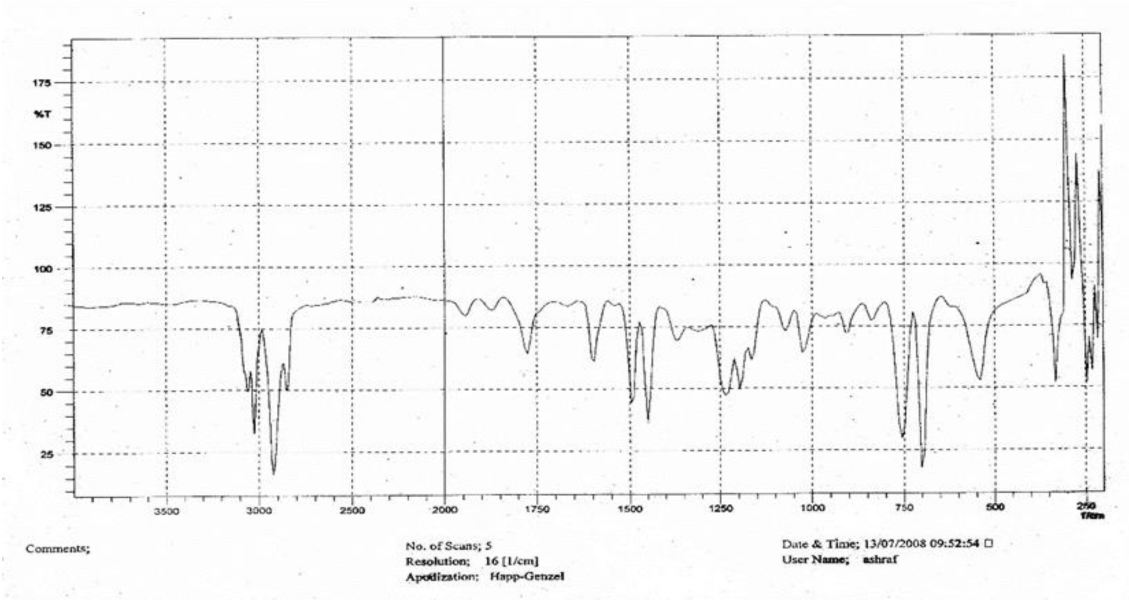

Fig.(3): FTIR spectra of the colloidal silver nanoparticle.

Experimental Details

The self-defocusing technique was often used to study the nonlinear properties but in the current research is used to study the optical limiting performance. This performance and the nonlinear properties for the colloidal silver nanoparticles were demonstrated by using a (DPSS) 473nm cw laser at and compared with 532 nm (Nd:YAG) cw laser. The experimental setup is shown in Fig 4. The first step is to focus the two lasers separately on the same sample through a lens of 5 cm focal length, the effect of the wavelength on the optical limiting and the resulted far-field diffraction ring pattern was recorded by CCD camera(model Beamage – CCD12, gentec-EO,Canada). An attenuator was used to control the incident power which was measured by a laser powermeter (model UNO-200982,gentec-EO,Canada). Second, the effect of the concentration on the optical limiting and the related nonlinear properties were studied by changing the sample from the concentration (11 ppm to 31 ppm).

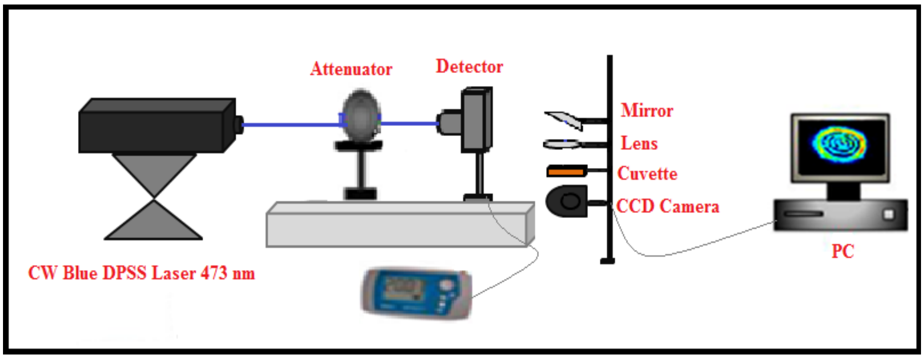

Fig (4): The experimental set up

Result and discussion

The silver colloid in concentration (11 ppm)

Figure 5 illustrates the images of the diffraction patterns by CCD camera for the sample at the concentration of 11 ppm, and a comparison between the wavelengths 473nm and 532 nm and their effect on optical limiting behavior were recorded. As shown form the Figure the number of rings were increased gradually with the laser intensity increasing till they reached (3) rings at the wavelength of 473 nm for the intensity of (638W/cm^2) and (4) rings at 532 nm for the intensity (240 W/cm^2), after that the number of rings would stay constant even in increasing the intensity as the colloidal sample behaves like an optical limiter.

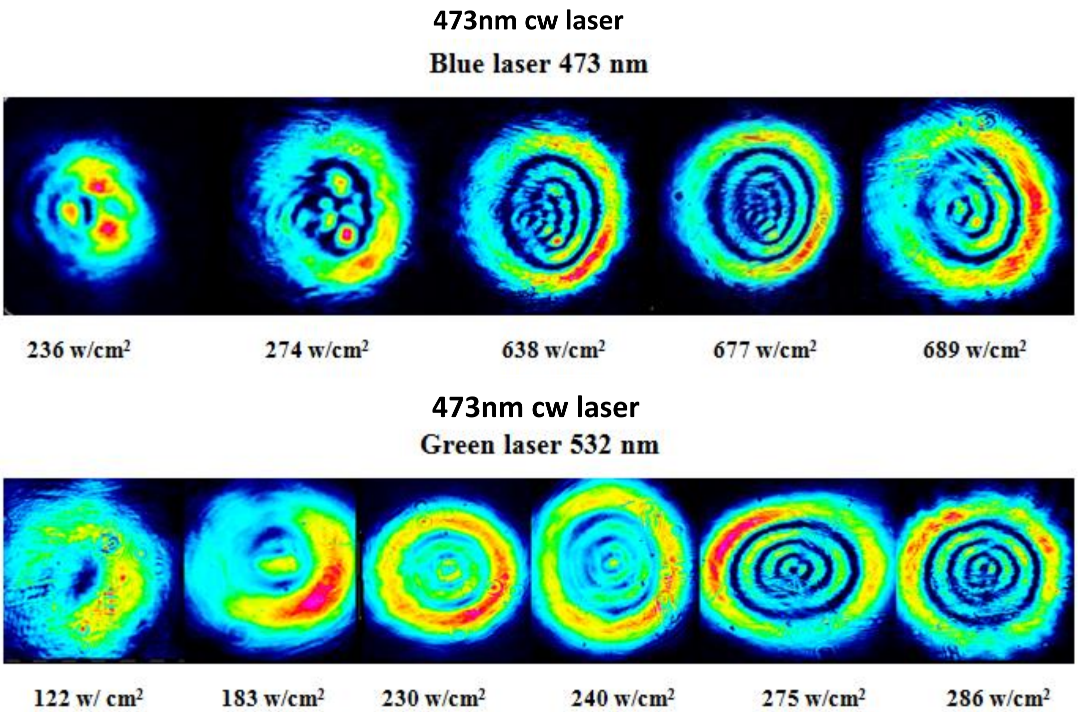

Fig. (5): CCD camera photographs for the sample at the concentration of 11 ppm.

The silver colloid in concentration (31 ppm)

The same process could be done for the sample in concentration of (31 ppm), seen in Fig.6. Here the number of rings reached to (5) at the intensity of (633W/cm^2) at 473nm laser, while (4) rings at the intensity of (238W/cm^2) for 532nm cw laser .It's clear that the performance of the optical limiting is better for the 473nm.

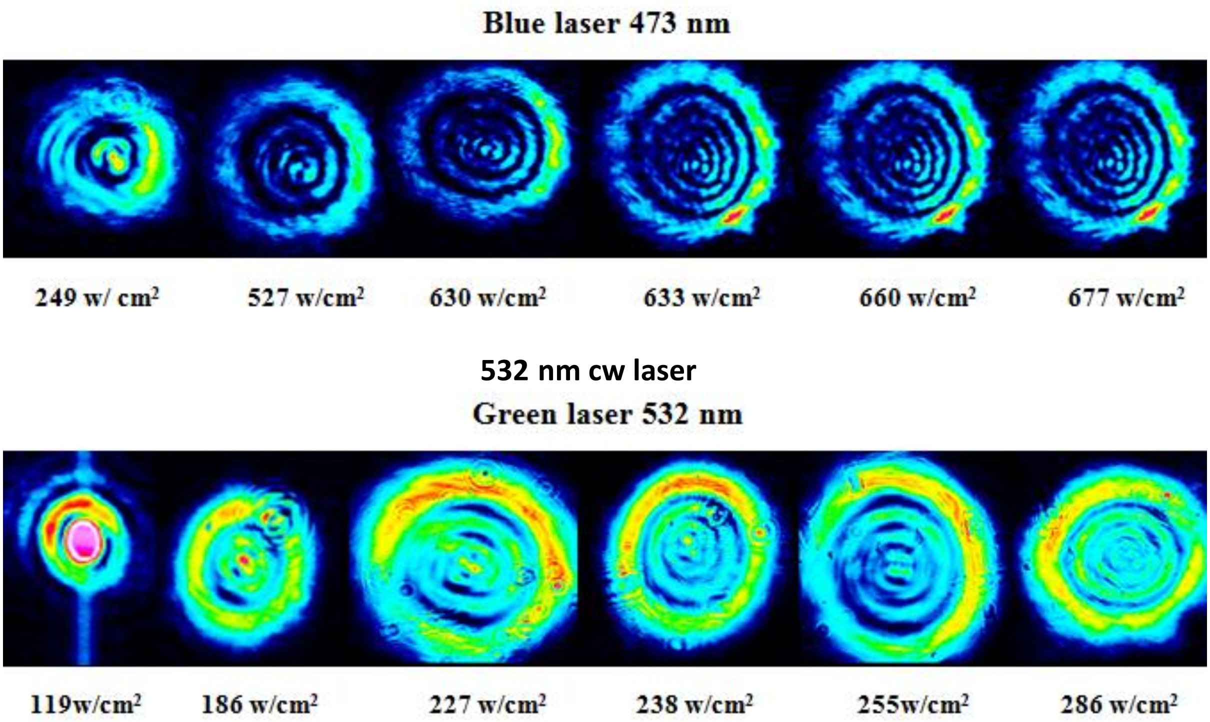

Fig. (6): CCD camera photographs for the sample at the concentration of 31 ppm**.**

Nonlinear optical properties

The maximum change of nonlinear refractive index for the colloidal silver was calculated using the equation (14)

$\Delta_{nl,max} = (\lambda \text{ beam} / L \text{ material}) * N \text{ rings}$

$\Delta_{nl,max}$ is the maximum change of nonlinear refractive index, λ is the wave length of laser and L is the thickness of material (5 mm) in the experiment. While the nonlinear refractive index N_2 can be calculated form the equation (14):

$N_2 = \Delta_{n\ nl,max} / I$

which illustrated in Table 1:

Conclusions

The preparation of stable colloidal Ag NP's has been described. The absorption in silver nanoparticles is confirmed using UV-VIS absorption spectroscopy and the particle size is determined using TEM. The optical limiting behavior and the nonlinear properties are investigated. To the best of our knowledge, this is regarded the first observation using self defocusing technique. The performance of the optical limiting is wavelength depented. The results indicate that the prepared colloidal silver nanoparticles could be used as an optical limiter.

Table 1: The values of the maximum change of nonlinear refractive index ($\Delta_{nl,max}$) and the related nonlinear refractive index type for the sample at the optical limiting intensity .

Laser wavelength nm	Concentration of the sample Ppm	Number of rings	The optical limiting Intensity w/cm^2	$\Delta_{nl,max}$*10^-4	N2 (cm^2/W)$^{-1}$ *10^-9
473	11	3	638	2.83	4.43
473	31	5	633	4.73	7.47
532	11	4	240	4.25	17.73
532	31	4	238	4.25	17.88

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تأثير تركيز جسيمات الفضة النانوية الغروية على موثوقية الحد البصري

شهد مهند ناجي محمد كريم ظاهر سالي العاني

معهد الليزر للدراسات العليا، جامعة بغداد ، بغداد ، العراق

الخلاصة: ان مدى تأثيرعامل التركيز للمواد النانوية على سلوك الحد البصري لها قد تم تدوينه في هذا البحث. واستنادا الى ظاهرة اللاتبؤر الذاتي قد تم تسجيل الحلقات البصرية باستخدام كاميرا حرارية . حيث تم استخدام نوعين من الليزر المستمر الاول بطول موجي 473 نانومتر والثاني 532 نانومتر لمقارنة اداء الحد البصري للعينات .ان مادة الفضة النانوية الغروية المذابة بالماء الايوني قد تم تحضيرها بالطريقة الكيميائية لكل من التركيزين 11 و 31 جزء في المليون . وقد تم استخدام عدة اجهزة فحص منها مقياس الطيف الضوئي للاشعة المرئية- فوق البنفسجية والمجهر الالكتروني النافذ ومطياف فورير لاظهار المواصفات الخاصة بالعينات حيث وجد ان معامل الانكسار اللاخطي الذي تم حسابه بحدود 10^{-9} cm^2/W كذلك حددت النتائج ان الاستجابة الحدية تزداد مع زيادة الطول الموجي بالاضافة الى ان المحلول الغروي الاكثر تركيزا ضمن المسار الخطي الاقصر يمتلك افضل اداء للحد البصري مما يجعل هذا النموذج مناسب لتطبيقات الحد البصري .