Iraqi Journal of Science

ISSN: 0067-2904

Non Linear Optical Properties of Silver Nanoparticles

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Abstract

In the present work, a Z-scan technique was used to study the nonlinear optical properties, represented by the nonlinear refractive index and nonlinear absorption coefficients of the Ag nanoparticles. In this technique, a pulsed second harmonic Nd :YAG laser at wavelength 532 nm was used. The results show that the nonlinear refractive index and nonlinear absorption coefficients of the Ag nanoparticles are found to be dependent on the size these nanoparticles.

Keywords: Silver nanoparticles, Nonlinear refractive index; Nonlinear absorption coefficient.

الصفات البصرية اللاخطية لجسيمات الفضة النانوية

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الخلاصه

في العمل الحالي، استخدمت تقنيه المسح على المحور الثالث لدراسة الخصائص الغير خطية ، والتي تمثل معامل الانكسار اللاخطي ومعامل الامتصاص اللاخطي لجسيمات الفضة النانوية. في هذه التقنية استخدم ليزر النديميوم ياك النبضي عند الطول الموجي 532 نانومتر. اظهرت النتائج ان معامل الانكسار اللاخطي ومعامل الامتصاص اللاخطي لجسيمات الفضة النانوية يعتمد على حجم هذه الجزيئات النانوية.

Introduction

One of the most prominent features of metal nanoparticles (NPs) subjected to the electromagnetic irradiation is their ability to support specific electron excitations, termed localized surface plasmon resonances (LSPR). Noble metal nanoparticles (Au, Ag, Cu) are of prime interest since the frequency of LSPR for those metals occurs at the visible spectral range. Moreover, the resonance frequency can be tuned by varying particles' size and shape as well as the dielectric environment [1]. Unique frequency dependence of the real and imaginary parts of the dielectric function of silver makes the metal more suitable for various applications using nanoparticles, as compared to gold and copper. Indeed, the inter band transition threshold for silver is about 4 eV, while the same for gold and copper occurs at 2.3 and 2.6 eV, respectively. Inter band transitions in latter cases substantially damp LSPR in Au and Cu nanoparticles [2]. Reported studies were performed employing an experimentally simple but powerful *Z*-scan technique [3]. Some authors interpret the results of *Z*-scan measurements by the formation of thermal lens in the medium around metal nanoparticles due to the effective heat transfer from the nanoparticles to the medium [4–7] or by the difference in the refractive index of nanoparticles and the matrix [8].

The Z-scan technique can used to investigate nonlinear optical (NLO) properties of silver nanoparticles. Z-scan technique [9] is a simple and high sensitive method to determine both n_2 (nonlinear refractive index) and β (nonlinear absorption coefficient).

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Experimental Materials

The experimental setup of closed and open aperture Z- scan was used to measure the nonlinear properties of the Ag NPs which prepared by hot chemical reduction method at three different reduction periods as described elsewhere [10] is shown in Figure-1. The laser that is used in the present work is pulsed Laser Nd: YAG at wavelength (532 nm) and intensity (6.794 GW/cm^2). The laser output was divided into two parts by a beam splitter. The reflected part was employed as the reference, representing the incident-light fluence, and the transmitted part was focused by a lens. The sample was placed at the focus. The incident and the transmitted pulse fluences were measured simultaneously by two energy detectors.

The Z-scan technique is based on the intensity-dependent refractive index and measures the variation of the refractive index as a function of intensity of incident beam. The induced lens inside the sample holds different focal lengths for each position of the sample and the focal length depends on the on the intensity of the laser beam. To measure the nonlinear refractive index the laser beam was focused and the sample was scanned along a focused Gaussian–beam (TEM_{00}) through its focal plane. The intensity of the laser beam for each position as a function focus position was measured using finite aperture at far field. To measure the total beam intensity of the laser, the input beam is divided by a beam splitter, and was detected by a suitable detection system. The closed aperture allowed measurements of both sign and value of nonlinear refraction coefficient. Since the light intensity irradiated on the sample is different at each position, therefore a typical peak-valley transmittance curve is obtained when the nonlinear refractive index of the medium is negative. A negative refraction index for the sample means that the sample acts as a concave lens in the vicinity of the focal. As the sample moves closer to the negative position of the Z towards the focal, the focal position shifts to positive Z direction. This suppresses the beam at the aperture plane and the intensity at the detector becomes larger. As the sample becomes near to the positive position of Z to the focal position, the beam spreads at aperture and the intensity becomes larger at positive side.

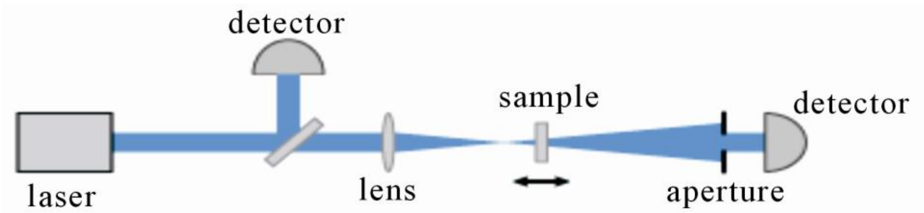

Figure 1- The setup of Z-scan system.

Results and Discussion

Nonlinear Refractive Index measurements (Closed Aperture Z-scan method)

Closed aperture Z-scan was used to investigate the nonlinear refractive index, where a circular aperture with transmissivity (S<1) is placed behind the sample in the far field to control the cross section of the beam coming out of the sample. As the sample is scanned through the beam, the far field profile shows intensity variation across the beam profile, which is recorded through the aperture and the transmission, is recorded as a function of (Z-position). Figure-2 shows the closed aperture Z-scan results for the Ag NPs which is prepared by hot chemical reduction method at three different reduction periods.

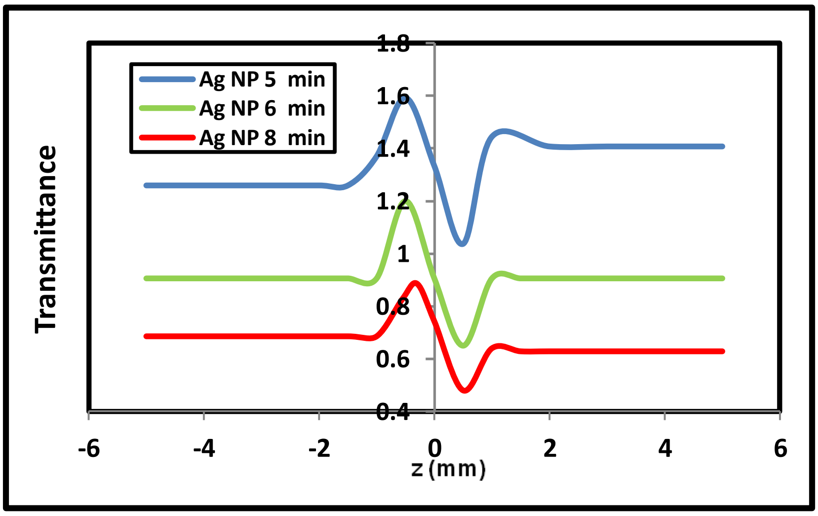

Figure 2- shows the closed aperture Z- scan curves of Ag NPs.

Where this figure indicates a negative z-scan profiles which represent a self-defocusing effect for two all samples. A negative Z-scan profile beginning far from the focus (**Z** < **0**), the beam flounce is low and nonlinear refraction is negligible, in this condition, the measured transmittance remains constant (i.e., z-independent).

In a closed-aperture Z-scan the nonlinear refractive index n_2 can be calculated from the following formula [11]

$$n_2 = \Delta\phi_o / I_o L_{eff}\, k \tag{1}$$

where

$$k = 2\pi / \lambda \tag{2}$$

$\Delta\Phi_o$: nonlinear phase shift
λ : is the wavelength of the beam
I_o : is the intensity at the focal spot
L_{eff} : is the effective length of the sample which can be determined from the following formula [11]:

$$L_{eff} = (1-e^{-\alpha o\, L}) / \alpha_o$$

where
L : the sample length
α_o : linear absorption coefficient
The intensity at the focal spot is given by [12]:

$$I_o = 2P_{peak} / \pi\, \omega_o \tag{3}$$

where
ω_o : the beam radius at the focal point
P_{peak} : the peak power given by [12]

$$P_{peak} = E / \Delta t \tag{4}$$

where
E : the energy of the pulse
Δt : the pulse duration.

The closed-aperture Z-scan defines variable transmittance values, which used to determine the nonlinear phase shift $\Delta\Phi_0$ and the nonlinear refractive index n_2 using the above equations. This can be shown in Ttable-1.

Table 1- The nonlinear refractive index of Ag NPs at three different reduction periods using closed aperture Z-scan with is pulsed Laser Nd: YAG at wave length 532 nm.

Ag NPs reduction periods	*Particles size of Ag NPs [10]*	T_{max}	T_{min}	ΔT_{pv}	n_2 cm^2/GW
5 min	22.33 nm	1.59	1.03	0.56	- 0.2279
6 min	33.49 nm	1.2	0.65	0.55	- 0.271
8 min	48.04 nm	0.88	0.48	0.4	- 0.244

The main reason is thought to be the cause of this, the size of the nanoparticles investigated. In these experiments, the sizes of the nanoparticles investigated are known to be around 22.33 nm in diameter at reduction time of 5min is smaller than Ag NPs of 33.49 nm for reduction time of 6 min and this size is much smaller than 48.04 nm in diameter at reduction time of 8 min. The size of the nanoparticles will directly affect the transmitted laser intensity as it is expected that the cubic nonlinearity will scale with the volume of the particle. The above results are good agreement with the results of R. Gamernyk et al. [13].

Nonlinear Absorption Coefficient measurements (Open Aperture Z-scan method)

Open aperture Z –scan was used to in investigate the nonlinear absorption coefficient β by removing the aperture. This case corresponds to collecting all the transmitted light and therefore it is insensitive to any nonlinear beam distortion due to nonlinear refraction [14].

The coefficients of nonlinear absorption can be easily calculated from such transmittance curves. The total transmittance is given by [11]:

$$T(z) = \sum_{m=0}^{\infty} \frac{\left[\dfrac{\beta I_o L_{eff}}{1+(Z/Z_o)^2}\right]^m}{(m+1)^{3/2}} \quad \textbf{(5)}$$

where

Z : is the sample position at the minimum transmittance

Z_o : the diffraction length

m : integer

T(z) : the minimum transmittance

The two terms in the summation are generally sufficient to determine the nonlinear absorption coefficient β.

Figure-3 show the open aperture Z –scan results for Ag NPs at three different reduction periods.

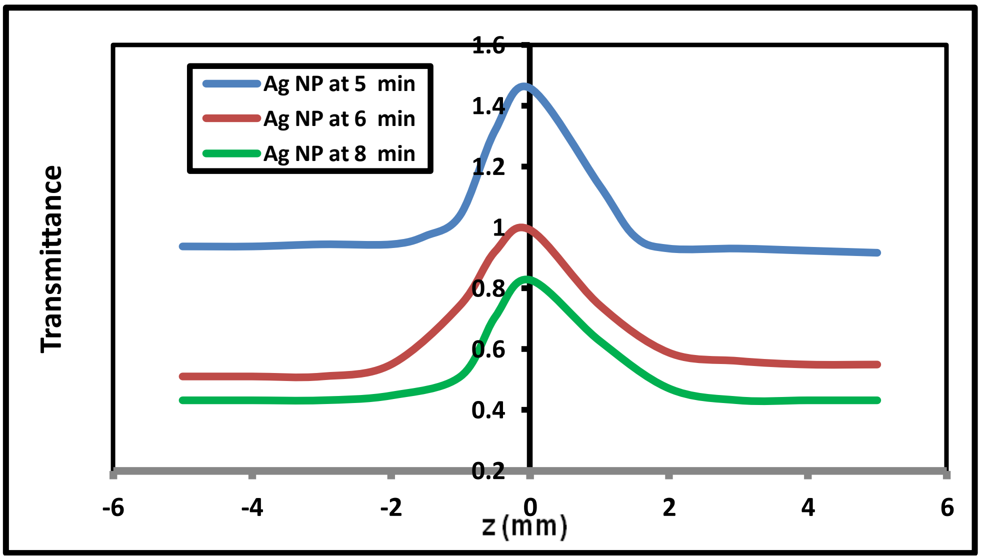

Figure 3- shows the open aperture Z- scan curves of Ag NPs.

The results of open aperture Z- scan indicated that, the Ag NPs at three different reduction periods showed saturable absorption from the broad surface plasmon resonance band, and one has found it to be highly anisotropic and this can be well explained by a simple two-level saturation model. Table-2 can be used to determine β.

Table 2- The nonlinear absorption coefficients of Ag NPs at three different reduction periods using closed aperture Z-scan with is pulsed Laser Nd: YAG at wave length 532 nm.

Ag NPs reduction periods	***Particles size of Ag NPs [10]***	T_{max}	**β cm /GW**
5 min	**22.33 nm**	**1.45**	**66211.22**
6 min	**33.49 nm**	**0.99**	**4673.61**
8 min	**48.04 nm**	**0.82**	**2287.53**

Conclusion

In this paper, the nonlinear optical properties of Ag NPs with different sizes have been investigated using Z-scan technique. The sign of the nonlinear refractive index is found to be negative (self-defocusing effect) for closed aperture Z-scan whiles the Ag NPs exhibits the saturable absorption for open aperture Z-scan.

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