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Nonlinear Optical Properties of Pure and Ag/Polyaniline Nanocomposite Thin Films Deposited by Plasma Jet

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Abstract

In present work, the nonlinear optical properties of pure polyaniline and Ag/polyaniline nanocomposite thin films, deposited by plasma jet on glass substrate, were studied through open and closed Z-scan technique using pulse second harmonic Nd:YAG laser of wavelength 532nm, pulse duration of 30 ns and input energy 30mJ. The nonlinear optical properties of pure polyaniline thin films and silver polyaniline nanocomposite thin films prepared at constant gas flow rate $1lm^{-1}$ and different silver weight concentration 4, 5, and 10% were studied. The closed aperture Z-scan data indicates that the sign of the refraction nonlinearity is negative for pure polyaniline thin films $n_2 = 11\times10^{-3}$ cm^2/MW and positive nonlinearity for Ag/polyaniline nanocomposite thin films, $n_2=72\times10^{-3}$, 66×10^{-3} and 96×10^{-3} cm^2/MW for silver weight concentration 4, 5, and 10% respectively. The open Z-scan measurements show two photons absorption $\beta=75\times10^3$ cm/MW for 4%wt silver concentration and show saturated absorption for pure polyaniline, 5 and 10%wt silver concentration. The transmission spectra obtained by UV-Visible absorption spectra exhibit interference fringes, for the samples with 4% and 5%wt silver concentration which is an indication of the good uniformity and homogeneity of the films.

Keywords: Thin films, nonlinear optical properties, Ag/polyaniline nanocomposite.

الخواص البصرية غير الخطية لاغشية متعدد الانلين النقي ومتراكبات فضة متعدد الانلين الرقيقة النانوية المرسبة ببلازما النفث

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الخلاصة

في هذا العمل تم دراسة الخواص البصرية غير الخطية لاغشية متراكبات فضة متعدد الانلين النقية ومتراكبات فضة متعدد الانيلين الرقيقة النانوية التي رسبت ببلازما النفث على قواعد من الزجاج ،هذه الخوص انجزت باستعمال تقنية المسح بالبعد الثالث بوجود حاجز وبدون حاجز وقد استعمل لهذا الغرض ليزر نديميوم ياك عند التردد التوافقي الثاني ذو الطول الموجي 532 نانو متر، وزمن نبضة 30 نانوثانية وطاقة 30 ملي جول. حيث درست الخواص البصرية غير الخطية للاغشية الرقيقة لمتعدد الانلين النقي ولمتراكبات فضة متعدد الانلين الرقيقة النانوية المحضرة عند معدل جريان ثابت للغازمقداره واحد لتر لكل دقيقة وتراكيز وزنية مختلفة من الفضة هي 4 و 5 و 10٪. نتائج المسح بالبعد الثالث بوجود حاجز بينت أن اشارة الانكسار غير الخطي سالبة لأغشية البولي آنلين النقية $n_2 = 11\times10^{-3}$ cm^2/MW وموجبة لاغشية متراكبات فضة متعدد الانلين الرقيقة النانوية $n_2=72\times10^{-3}$, 66×10^{-3} ، 96×10^{-3} cm^2/MW عند تراكيز الفضة 4 و5 و10% على التوالي. ونتائج المسح بدون وجود الحاجز بينت امتصاص فوتونين حيث $\beta=75\times10^3$ cm/MW عند

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تركيز للفضة 4% واظهرت امتصاص مشبع لتركيزي الفضة 5 و10% ولمتعدد الانلين النقي. طيف النفوذية الذي انجز باستعمال مطياف الاشعة فوق البنفسجية والمرئية احتوى على اهداب تداخل للنموذجين الذي فيهما تركيز الفضة 4 و5% مما يدل على ان هذه الاغشية عالية الانتظام والتجانس.

Introduction

In recent years organic materials exhibiting strong nonlinear optical (NLO) properties it has attracted considerable interest because of their promising applications in optical limiters, optical switches and optical modulators [1,2]. A variety of organic materials, including conjugated molecules, polymers and dyes, have been investigated for their NLO responses [3]. Conjugated organic polymers like polyaniline have emerged as a promising class of NLO materials because of their large nonlinear responses associated with fast response time, in addition to their structural variety, processability, high mechanical strength, and excellent environmental and thermal stability [4]. Among various conjugated materials, aniline based polymers are currently under intensive investigation as materials for nonlinear optics because of their large third-order nonlinear response, and chemical stability [5].

Due to their distinctive chemical, electrical and thermal conductivities properties silver nanocomposites have attracted much attention. Ag nanoparticles due to its surface plasmon resonance (SPR) exhibit strong absorption of electromagnetic waves in the visible range [6]. Plasma polymerization plays a significant role due to its cost effectiveness and simplicity, and it's also offer good quality, pinhole free and homogeneous films. Plasma polymerization deposition is now became as an important technique for direct film deposition of entirely new kinds of polymeric films, which are hardly possible to obtain by the conventional methods, and the plasma polymerization deposition is easily integrated into existing manufacturing processes, and it offers the advantage of solvent-free operation. Thus, there is no solvent to be removed after deposition [7].

Z-scan technique is a simple and effective tool to determine the nonlinear properties [8]. It has been widely used in material characterization because it provides the magnitudes of the real and imaginary part of the nonlinear susceptibility and the sign of the real part. The nonlinear refraction (closed aperture Z-scan) and nonlinear absorption (open aperture Z-scan) of samples can be measured easily by Z-scan technique, which use the change of transmittance of nonlinear materials [9].

In this work, the nonlinear optical properties of pure polyaniline and Ag/polyaniline nanocomposite thin films deposited on glass substrate by plasma jet polymerization at atmospheric pressure were studied through Z-scan technique under pulse solid state laser excitation at 532 nm with an output power of 1 MW/cm^2.

Experimental

The films were deposited via a plasma jet. The plasma was generated downstream to the substrate which was positioned at fixed distance from the plasma torch end. The jet was generated via Argon gas flow (flow rate of 1l/min) as in our previous work [10]. The plasma was ignited by using alternating high voltage power supply, generates high voltage of sinusoidal shape of 7.5 kV peak to peak and fixed frequencies of 28 kHz[11]. The films deposition was carried out for 5min. In order to obtain homogeneous films thickness along the substrate area, the substrates were mounted on a movable x - y stage. Silver nanoparticles from Nanjing nano Technology co, ltd, China were used. Its particle size was 50nm and purity of 99.9%, with concentration of 4, 5 and10wt% were mixed with aniline monomer product from Vertex-Dental Netherlands. The mixer dispersed by ultrasonic to ensure a homogeneous distribution of nanoparticles. Then silver polyaniline nanocomposite thin films deposited by plasma jet system on ultrasonically cleaned glass substrate of size 10 x 10 mm. UV-Visible absorption spectra of pure polyaniline and Ag/polyaniline nanocomposite thin films were obtained by using a double beam UV-Vis-NIR 210A spectrophotometer. The thickness of the films was measured by optical interferometric method. The nonlinear optical properties were measured by Z-scan technique with open and close aperture using pulse second harmonic Nd:YAG laser of wavelength 532nm and pulse duration of 30 ns finally collimated lens of focal length 10 cm, input energy 30mJ, the transmitted energy were monitored by the optical detector type (DPSS 1830C).

Results and Discussion

Figure-1 shows the absorbance (A) spectra of Ag/PMMA nanocomposite thin films and pure polyaniline thin films. Table-1 shows the thin films preparation conditions and its thickness. The absorbance spectra of Ag/polyaniline films shows the effect of Ag nanoparticles and the enhancement of SPR which is represented by the peak near 400nm while pure polyaniline films have absorption peak around 300nm and transparent from 500 to 1100nm. This effect is characteristic for metal/dielectric nanocomposites when collective resonant oscillations of electronic gas in metals (plasmons) are excited upon interaction with electromagnetic field [6]. The increase of silver content leads to intensification of the absorption.

Figure-2 shows plots of transmittance versus wavelength for pure polyaniline and silver\polyaniline nanocomposite thin films prepared at different silver concentration, (4, 5 and 10%wt) and gas flow rate 1l/min at room temperature. It is observed that all films showed low transmittance in UV region while the thin films absorbs less energy at long wavelength in the range between 600-1100nm. The optical transmittance was decreased slightly with increasing the silver concentration of the films. The four samples show good transparency in the visible region and exhibit a sharp drop near the band edge, indicating the presence of direct optical transition in the films. Also from Figure-2, it can see that the transmission spectra exhibit interference fringes, for the samples with 4% and 5%W silver concentration which is an indication of the good uniformity and homogeneity of the films [12] and this interference fringes disappear for pure sample and 10% silver concentration.

The nonlinear optical absorption characteristics of the Ag/polyaniline nanocomposite thin films have been investigated by performing Z-scan measurements by launching pulse second harmonic Nd:YAG laser of wavelength 532nm and pulse duration of 30 ns onto the silver \ polyaniline nanocomposite thin films. The incident beam is focused by a lens of focal length 10 cm to provide the beam waist radius $\omega_0 = 60\mu m$, the diffraction length $z_o = k\omega_0^2/2$ of 16 mm. Since the sample thickness is much smaller than the diffraction length, so the thin film approximation has been used to simulate the Z-scan data.

Table 1- The thin films preparation conditions and its thickness

Sample	Thickness (nm)	Gas flow rate l min^{-1}
Pure	177	1
4% Ag	213	
5% Ag	198	
10% Ag	175	

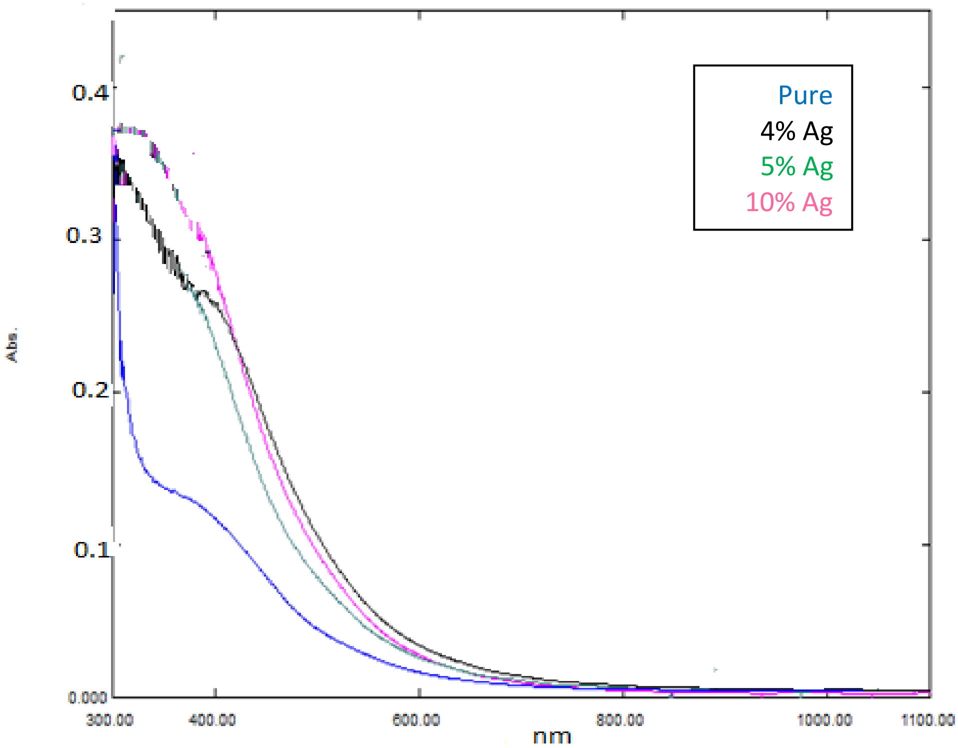

Figure 1- The variation of absorbance with wavelength for pure polyaniline and silver polyaniline nanocomposite thin films at different silver concentrations.

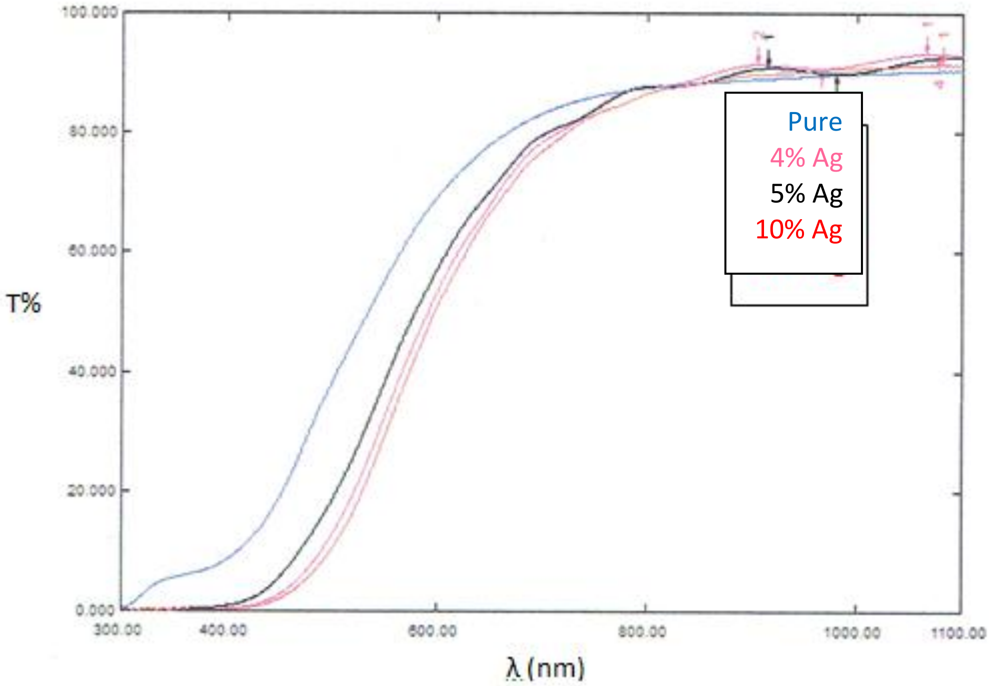

Figure 2- The variation of the transmittance with wavelength for pure polyaniline and silver polyaniline nanocomposite thin films at different silver concentrations at room temperature.

In the nonlinear regime, the intensity (*I*) dependent refractive index *n(I)* and absorption coefficient *α(I)* are given by [13],

$$n(I) = n_0 + n_2 I$$

$$\alpha(I) = \alpha_0 + \beta I$$

where n_0 the linear refractive index and α_0 the absorption coefficient, respectively, n_2 the nonlinear refractive index and β the nonlinear absorption coefficient respectively. Open aperture (OA) Z-scan were performed when the irradiance at the sample is varied by translating the sample. This mode of operation is sensitive to nonlinear absorption (β), as any deviation in the transmitted intensity must be due to two or multi-photon absorption. Closed aperture (CA) arrangement is placing a limiting aperture past the focus of the lens and before the detector. The detector is now become sensitive to nonlinear refraction in the sample. Any focusing or defocusing of the sample may express him as either beam broadening or narrowing in the far field and this leads to a shaped dispersion curve from which nonlinear refraction n_2 is easily estimated.

The normalized change in the OA transmittance is given by the expression [9].

$$T = 1 - \frac{\beta I_0 L_{eff}}{\left[1 + \left(\frac{Z}{Z_0}\right)^2\right] 2^{\frac{3}{2}}}$$

where, the effective thickness of the sample denoted as L_{eff} is defined by the expression:

$L_{eff} = \frac{1-e^{-\alpha_0 I}}{\alpha_0}$ with α_0, I being the linear absorption coefficient and sample thickness, respectively. I_0 is the on-axis power density of the laser beam at the waist. Typical OA scan of silver\polyaniline nanocomposite thin films was shown in Figure-3. Table-2 shows the nonlinear absorption for pure polyaniline and silver \ polyaniline nanocomposite thin films with different silver concentration.

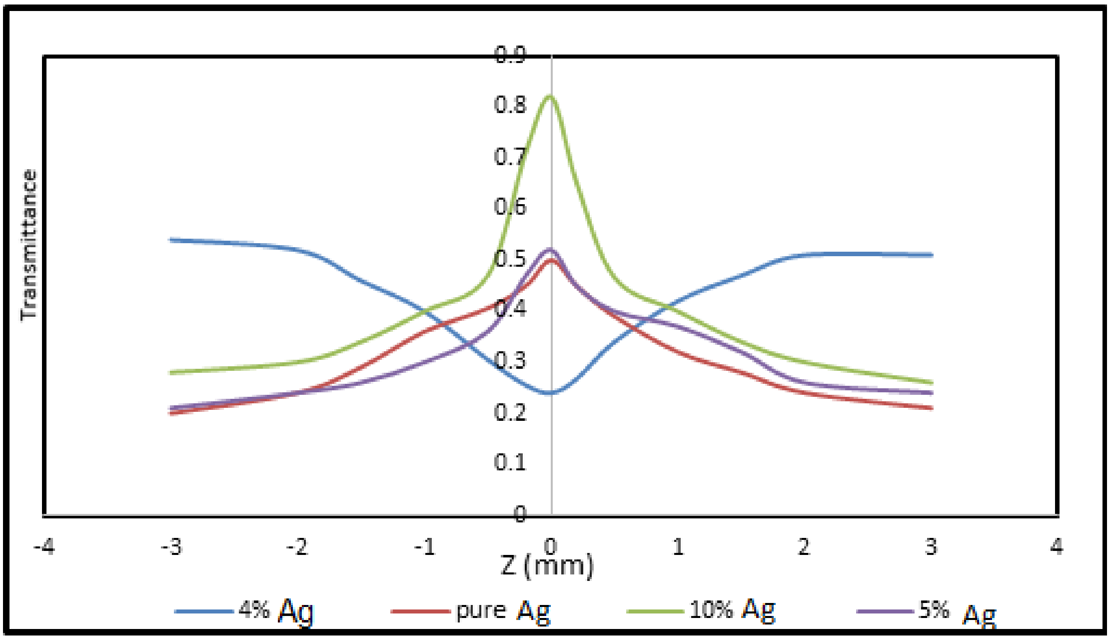

Figure 3- Open Aperture Z-Scan measurement for pure polyaniline and silver \ polyaniline nanocomposite thin films with different silver nanoparticles weight concentration (4, 5 and10%) at constant gas flow rate using pulse laser at 532 nm

Table 2- The nonlinear absorption for pure polyaniline and silver\polyaniline nanocomposite thin films with different silver concentration

Sample	T_{min}	β (cm/MW)×10^3
Pure polyaniline	5.0	151
4% Ag\polyaniline	2.4	75
5% Ag\polyaniline	5.2	144
10% Ag\polyaniline	8.2	250

For an optical beam at wavelength (λ), the light induced nonlinear refractive index n_2 is related to the nonlinear phase shift ($\Delta\Phi_0$) by the relation, $\Delta\Phi_0 = \frac{2\pi}{\lambda} n_2 I_0 L_{eff}$. The sign of n_2 is thus determined by $\Delta\Phi_0$. An important feature of CA Z-scan is that the sign of $\Delta\Phi_0$ and n_2 are determined from the relative position of the peak and valley. A pre-focal transmittance maximum (peak), followed by a post-focal transmittance minimum (valley) is a Z-scan signature of a negative nonlinearity. An inverse Z-scan curve a valley followed by a peak characterize is a positive nonlinearity [9].The relative on-axis transmittance of the sample measured at the small aperture of the far-field detector is given by [8].

$$T = 1 - \frac{4\Delta\Phi_0(\frac{Z}{Z_0})}{\left[1+\left(\frac{Z}{Z_0}\right)^2\right]\left[9+\left(\frac{Z}{Z_0}\right)^2\right]}$$

Figure-4 represents the CA scan of the pure polyaniline and silver\ polyaniline nanocomposite thin films with different silver concentration. And the nonlinear absorption for the silver \ polyaniline nanocomposite thin films with different silver concentration and pure polyaniline showed in Table-3. From the valley-peak configuration, it is clear that the silver\polyaniline nanocomposite thin films with different silver concentration acts as self-focusing lens of variable focal length and the pure polyaniline thin film act as defocusing lens of variable focal length. The nonlinear refractive index n_2 cm^2/W where calculated at 532 nm for pure polyaniline and silver\polyaniline nanocomposite thin films shown at Table-3. From the difference between the peak and valley transmittances (ΔTp-v) in CA scan it is evident that cubic nonlinearity overbear in the present case. Moreover, at irradiance of 8.15 GW/cm^2 it is expected that the changes in the index of refraction is due to the third-order enharmonic motion of the bound electrons [14]. From Figure-4 and Table-3 also note that silver nanoparticles changed the behavior of the pure polyaniline thin films from defocusing lens of variable focal length to self-focusing lens. This change happened because of the silver nanoparticles may have changed in the way of the atoms link in the polyaniline that polymerized by plasma as well as the silver nanoparticles SPR it's able to enhance optical processes. The enhancement effect of (SPR) is based on the excitation of localized surface plasmons (LSP) giving enhanced electromagnetic fields. The molecules placed inside this enhanced field will be excited more often due to intensity enhancement of the incoming light. The ability of silver nanoparticles to convert light to LSP has caused them to be referred to as nanoantennas. So it can be collected light from a large volume and confine it to a smaller volume much smaller than the wavelength, like antennas on the macroscale. In doing that, the electromagnetic field in these regions was highly enhanced [15].

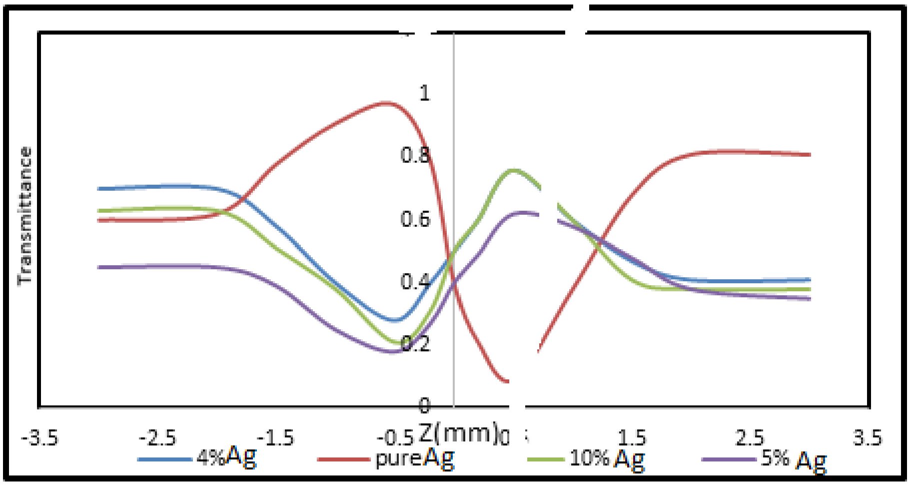

Figure 4- The experimental data for CA scan of the pure polyaniline and silver \ polyaniline nanocomposite thin films with different silver concentration

Table 3- Some of the linear and nonlinear optical parameters for pure polyaniline and silver \ polyaniline nanocomposite thin films using pulse laser at 532 nm

Sample	Thickness (nm)	Linear absorption coefficient $\alpha_0 10^3$ cm^{-1} at 532nm	ΔT_{p-v}	$\Delta\Phi_0$	n_2 (10^{-3}) (cm^2/MW)	n_0 for 532nm
Pure polyaniline	177	14.3	0.07	0.172	-11	2.16
4% Ag\polyaniline	213	20.1	0.48	1.182	+72	1.77
5% Ag\polyaniline	198	16.5	0.44	1.083	+66	2.06
10% Ag\polyaniline	175	21.4	0.55	1.354	+96	1.94

Conclusions

The plasma polymerization method for preparing silver polyaniline nanocomposite thin films simple and cheap method, and features by the possibility of control the non-linear optical properties of the silver \ polyaniline nanocomposite thin films through the variation of the silver nanoparticles concentration. The SPR of the silver nanoparticles enhanced the non-linear optical properties of the prepared thin films. Also it can be concluded that the pure polyaniline and the silver polyaniline nanocomposite thin films polymerized by plasm are a promising material for applications in nonlinear optical devices.

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