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Pulsed Laser Deposition of Tio_2 Nanostructures for Verify the Linear and Non-Linear Optical Characteristics

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Abstract

The present work aims to achieve pulsed laser deposition ofTiO_2 nanostructures and investigate their nonlinear properties using z-scan technique.The second harmonic Q-switched Nd: YAG laser at repetition rate of 1Hz and wavelength of 532 nm with three different laser fluencies in the range of 0.77-1.1 J/cm^2 was utilized to irradiate the TiO_2 target. The products of laser-induced plasma were characterized by utilizing UV-Vis absorption spectroscopy, x-ray diffraction (XRD), atomic force Microscope (AFM),and Fourier transform infrared (FTIR). A reasonable agreement was found among the data obtained usingX-Ray diffraction, UV-Vis and Raman spectroscopy. The XRD results showed that the prepared TiO_2 thin films were all crystallite structure with no impurity peaks of other elements. Also, their peak intensities were increased with increasing the ablating laser fluency. AFM measurements indicated that,during pulsed laser deposition, as the laser fluency was increased, the average diameter of the prepared TiO_2 nanoparticles (TiO_2 NPs)was decreased from 86 to 57 nm, althoughthe differences were increased with the increase in the laser fluency. The multiphoton absorption was investigated using ultra-fast femtosecond laser with the z-scan method.The impact of thickness of the prepared films on the non-linear absorption coefficient was studied as well.

Keywords: ultrafast laser; femtosecond; z-scan technique; pulsed laser deposition; nanostructure.

الترسيب بالليزر النبضي للتركيب النانوي لثنائي اوكسيد التيتانيوم للتحقق من الخصائص البصرية الخطية واللاخطية

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الخلاصة

يهدف العمل الحالي إلى تحقيق الترسيب النبضي لليزر TiO_2 والبنى النانوية والتحقيق في الخصائص غير الخطية باستخدام تقنية المسح الضوئي z ، بينما التوافقي الثاني المتعلق بليزر Q–switched Nd: YAG بمعدل تكرار يبلغ 1 هرتز وطول موجي 532 نانومتر مع بثلاث نبضات ليزرية مختلفة في حدود 0.77–1.1 جول / سم^2 لإشعاع هدف TiO_2. تم تمييز منتجات البلازما المستحثة بالليزر باستخدام التحليل الطيفي لامتصاص UV–Vis ، وحيود الأشعة السينية (XRD) ، ومجهر القوة الذرية (AFM) ، وتحويل

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فوريه للأشعة تحت الحمراء (FTIR). تم العثور على اتفاق معقول مع البيانات التي تم الحصول عليها باستخدام حيود الأشعة السينية و UV–Vis و Raman الطيفي. أظهرت نتائج XRD أن أغشية TiO_2الرقيقة المحضرة كانت كلها ذات بنية بلورية مع عدم وجود قمم شوائب للعناصر الأخرى. أيضا ، زادت شدة الذروة مع زيادة فلور الليزر. أشارت قياسات AFM إلى أنه في ترسيب الليزر النبضي ، مع زيادة تدفق الليزر ، ينخفض متوسطقطر TiO_2NPs المحضرة من 86 إلى 57 نانومتر ، على الرغم من أن الاختلافات تزداد عندما يزداد تدفق الليزر. تم فحص امتصاص متعدد الفوتونات باستخدام ليزر الفيمتوثانية فائق السرعة بطريقة المسح z ودراسة تأثير سماكة الأغشية المحضرة على معامل الامتصاص اللاخطي.

Introduction

Titanium dioxide (TiO_2) is an important material for many physical applications, including solar cells [1] and heterogeneous catalysis [2-6]. Generally, $TiO_2$was applied in two major forms, namely thin and powder films. The former TiO_2form was majorly utilized for liquid and gas phase catalysis. Normally, its photocatalytic activity was specified via particle size, phase composition [7], and the position of valance and conduction bands in the energy scale [8]. More recently, $TiO_2$was utilized in photovoltaic applications, including photoelectron chemical systemsas well as the dye-sensitized solar cells for the harvesting ofphotons [9].Also, TiO_2 in such form is offering energy alignments between energy positionsofvalance band edge and the redox species in electrolyte, through possible biasing photoanodes. Severaldeposition approaches of TiO_2 thin films were employed, such as metal organic chemical vapor deposition [10], reactive RF sputtering [11], direct current (DC) magnetron sputtering [12], and sol-gel spin-coating [13]. Currently, laser has various applications, one of which being the thin film preparation field which is referred to as pulsed laser deposition (PLD) [14-16],along with other technique used for other applications [17-18]. With such an approach, the thin films were prepared through ablation of at least one of the targets illuminated through focused pulsedlaser beam. In 1965, Smith andTurner initially utilizedthis approach [19] to prepare semiconductorsin addition to dielectric thin films. Moreover,is the approach was developed through the study of Dijkkamp and colleagues in 1987,who described superconductors of hightemperature. Their study indicated major laser induced plasma LIP characteristics, particularly the stoichiometry transfer between deposited and target films, the elevated deposition rate of approximately 0.10 nm for eachpulse, and the occurrence of droplets on substrate surface. The benefit of utilizing PLD, as compared to other techniques of sputtering, is its efficiency and simplicity in producing multi-layered films of a variety of materials through sequential ablation of assorted targets. The thickness of the thin film is controlled by the number of pulses of the laser used, down to the single atom layer.One of the major PLD features is that the target stoichiometry might be retained in the deposited film, while PLD has also some drawbacks. In the present study, TiO_2 thin films with nanostructure were fabricated through thePLD approach which iscommonly utilized for oxide film growth since it allows the stoichiometryof the synthesized material. Also, the structural and optical characteristics of TiO_2thin film were examined.

Experimental Part

Turner and Smith initially utilized the general typical setup for pulsed laser deposition [19]. In the present work, $TiO_2$was utilized as a target, with 2cm diameter and 1cm thickness, and fixed the target at the top chamber. The glass substrate was applied as one of the substrate materials for studying the non-linear and linear characteristics. Substrate cleaning was required for ensuring a surface that is free from contamination films,including absorbed water.Also, the glass substrates were cut into standard sizes (10x10) mm, cleaned ultrasonically in acetone, and then left the glass substrate in an oven to dry. In addition, the effect of laser fluencies of 0.77, 0.91 and 1.1 J /cm^2 on optical and structural characteristics of TiO_2 thin films was examined.Titanium dioxide thin films were grown for 5mins on a glass substrate, while the chamber's base pressure was $2.0x10^{-5}$mbar.LIP is a method of high importance for metal as well as semiconductor deposition, offering uniform coverage, high deposition rate, and dc magnetron sputtering, ultimatelyproviding the capability for rapidly depositing large amounts of material. In the present work, severalcharacterization approaches were utilized for evaluating the structural and optical characteristics of TiO_2thin films. For the purpose of avoiding fast drilling, the target was mounted on a rotating holder located at a distance of45 mm from thesubstrate for improving the film's uniformity.

For the purpose of determining the TiO_2 film thickness, the optical interference fringes measurement was utilized, which is non-destructive, precise and rapid**.**XRD is applied for determining the overall structure of TiO_2 thin films, involving polycrystals orientation, unknown materials grain size, lattice constants, and single crystals orientation. In the current work, the thin films were studied via XRD with Cu-Kα X-ray tube (λ = 01.54056Å). Also, the XRDspectrum was achieved at diffraction angle values 2θ, ranging10°-60°.

The optical measurements of TiO_2 thin films were achieved by utilizing a U.V. mate SP8001 double beam spectrophotometer (Metertech Corporation, Taipei, Taiwan) that coverswavelength values in the range of 190-1100nm .In addition, the investigation of thenon-linear absorption at near resonant regime was conducted utilizing a fully-computerized,single beam, open aperture z-scan femtosecond laser [18]. Femtosecond laser with 100fs and 80 mJ/cm^{2}maximum laserfluencies was utilized as alaser source, while pulse duration was estimated via auto-correlation system.Energy was estimated via apyroelectric energy probe (PDA-36A, Thorlabs) which covers a range of 350-100nm. Beam profilewas adjusted througha spatial filter with a beam quality of $M^2 \approx 1.7$.A convex lens with a focal length of 15 cm was used to produce a waistof 37μm. The sample was movedalong the beam axis (z-axis) via a Rayleigh distance of 2.1mm.

Results and discussion

The PLD is a technique of high importance for synthesizing nanostructuredTiO_2because of the contactless treatment. Nanostructuresof various patterns might simply be achieved on treated surfaceswith no more masking.The thin films'thickness,which was found via optical interference approach,showed values of 200, 250, and 300 nm.XRD is a convenient method for determining thestructure and crystallite size of nanostructures. Figure-1 shows the XRD pattern of the TiO_2nanostructures prepared by LIP.The XRD patternexhibits peaks centered at 2θ = 25.5°, 38.2°, 47.3°, 54.4° and 63.6°, corresponding to (101), (112), (200), (104) and (204) planes, respectively. These planes agreed with the crystal planes that are related to TiO_2 phase, as determinedbased on the data published by theJoint Committee onPowder Diffraction Standards (JCPDS No21-1272). Also, the broadening of the XRD pattern verified the reduction in the size of the generated TiO_2 nanostructures. The values of the crystallite size (D) of the synthesized sample were estimated based on Scherrer's equation shown in Table-1.

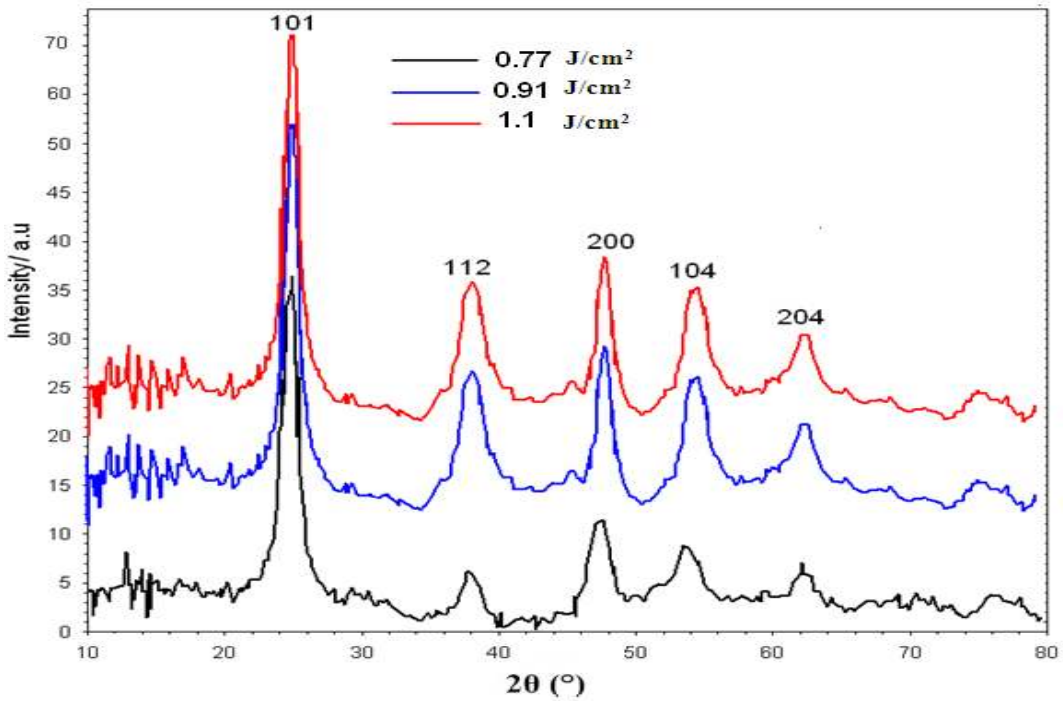

Figure 1-X-ray diffraction (XRD) of TiO_2 nanostructures prepared by laser –induced plasma at different laser fluencies.

Table 1-Structural properties of TiO_2 nanostructures at different laser fluencies

Laser fluencies J/cm^2	*hkl*	*2θ*	*d A^o*	*FWHM*	*D nm*
0.77	*101*	*25.2*	*3.5*	*0.86*	*9.5*
0.91	*101*	*25.6*	*3.24*	*0.94*	*8.8*
1.1	*101*	*25.6*	*2.48*	*0.98*	*8.5*

AFM measurements were carried out to investigate the morphology and size of TiO_2nanostructures synthesized by ablating the TiO_2 metal at different laser fluencies (0.77, 0.91 and 1.1 J/cm^2).. As shownin Figure-2, the morphology and size of TiO_2nanostructures varied with increasing the laserenergy.

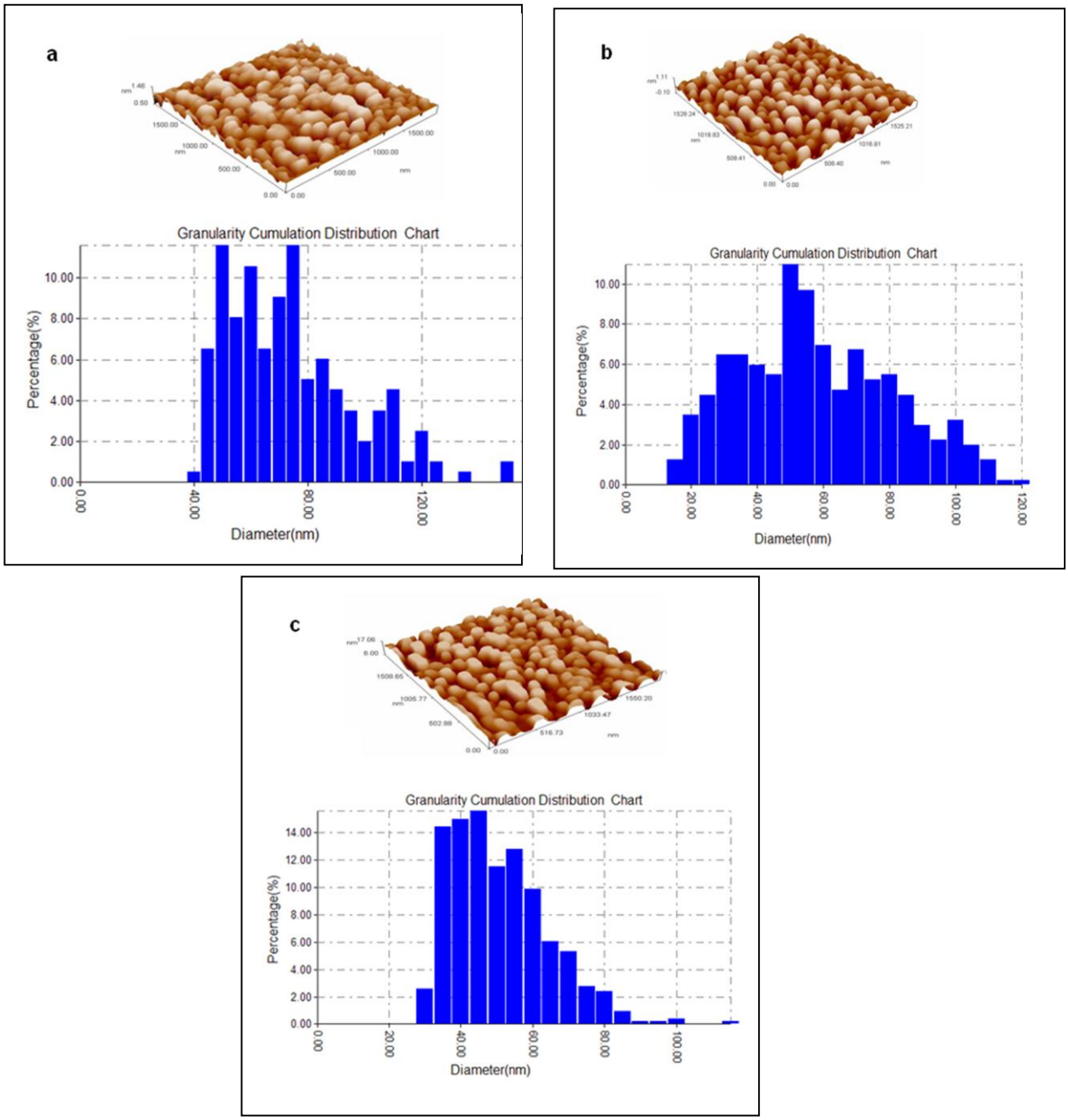

Figure 2-3D AFM images and granularity accumulation distribution chart of TiO_2 nanostructures prepared by laser –induced plasma at different laser fluencies (a) 0.77 J/cm^2, (b) 0.91 J/cm^2 and (c) 1.1 J/cm^2.

The average diameter size was decreased from 86 to 57 nm with increasing the laser energy. The difference in size and morphology are stronglydependent on the characteristics of the generated plasma on the surface of the target, according to the interaction of laser pulse with the solid target. At lowlaser energy, the plasma of low temperature and large nanoparticles size is re-produced. By increasing the energy of laser pulse, a high temperatureplasma plume is generated, leading to larger kinetic energy that increasescollisions among theinitially-formed large nanoparticles.This effect causes a reductionin particle size and probability of adhesion and makes the size of each nanoparticle relatively uniform. Figure-2 presents the3D AFM images of TiO_2nanostructures prepared at different laser fluencies; (a) 0.77 J/cm^2, (b) 0.91J/cm^{2}and (c) 1.1J/cm^2. SEM measurements were carried out at laser fluency equal 1.1 J/cm^2.The nanoparticles appeared in spherical shape and high number. In addition,some aggregations between these nanoparticles could be noted. Once thenano-colloidal solution is synthesized, the nanoparticles can be affectedby the attractive Van der Waals force, which promotes the growth of nanoparticles with aggregation, as shown in Figure-3.

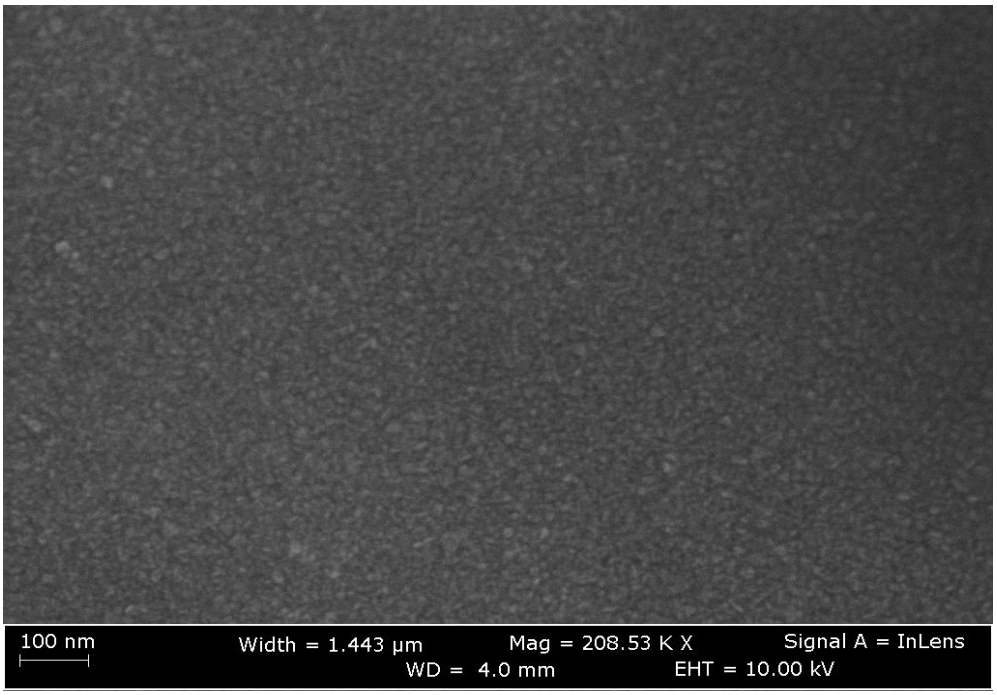

Figure 3-SEM of TiO_2 nanostructures prepared by laser –induced plasma at 1.1 J/cm^{2}laser fluency.

The absorption spectra of the synthesized TiO_2nanostructureswere recorded in the wavelength scan region (200–1100nm).Figure- 4 illustrates the optical absorption spectra of TiO_2nanostructuresthat are prepared at different laser fluencies. A significant increase in the absorption, below 334 nm, was observed and the absorption edge was shifted toward shorter wavelengths with increasing the laser energy. Moreover, the intensity of the absorption peaks is increased with the increase in laser energy, due to the high deposition of nanoparticles. This can beexplained by delivering more energy to the target, which leads to the production of intense plasma plume and the ablation of a larger amount of material so that thenanostructure becomes denser.

FTIR measurement was performed over the range of 400-4000 cm^{-1} for the TiO_2nanostructures to confirm the formation of oxide bonds. Figure-5 shows FTIR spectra of TiO_2 nanostructures prepared at different laser fluencies. The intense peaks centered at 480 cm^{-1}are allocated to the bending vibration related to O-Ti-O bond. The absorption of water molecules observed as broad peaks at 3350cm^{-1}corresponds to the stretching vibrations of O-H bond, while the weak peaks at 1630 cm^{-1} were a result of the bending vibration of H-O-H bond.

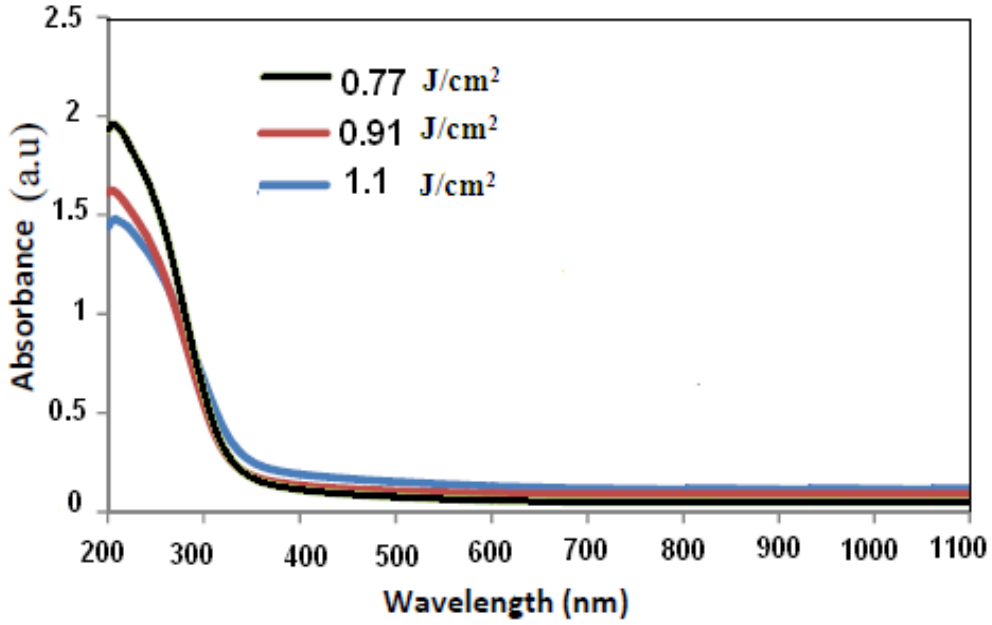

Figure 4-UV-Vis absorbance spectra of TiO_2 nanostructures prepared at different laser fluencies.

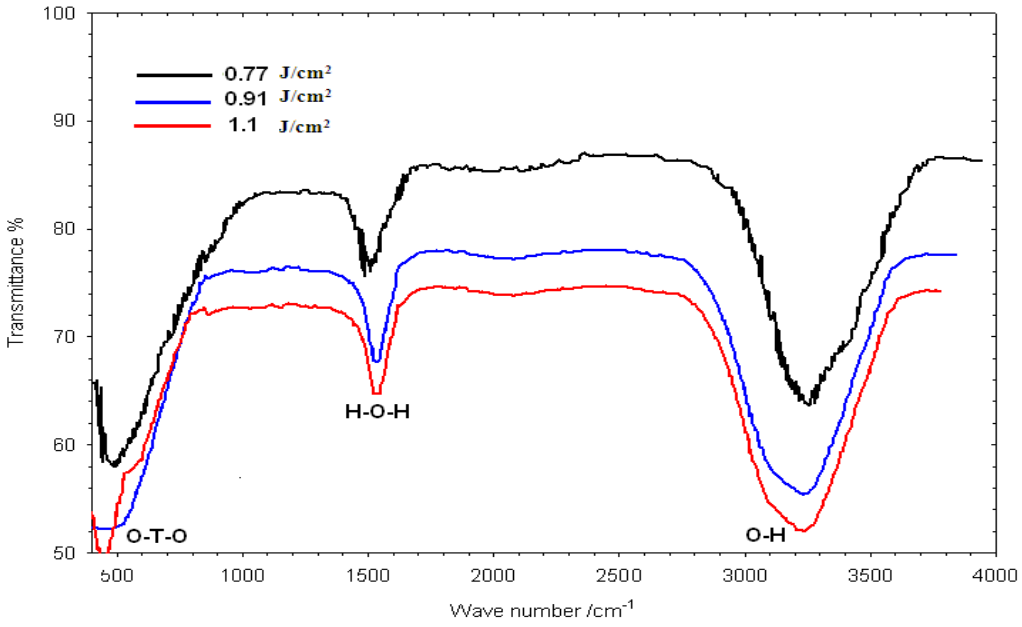

Figure 5-FTIR spectrum of TiO_2 nanostructures prepared at different laser fluencies

Results of the Raman mode of the TiO_2 samples after irradiation at different fluencies are shown in Figure-6. Raman spectra of the synthesized TiO_2 nanoparticles show that, in accordancewith the XRD results, most of the crystalline phaseis anatase, without appreciable amounts of rutile orbrookite phases. As the crystallite size increases, the Raman blueshift and bandwidth decreases, in a total accordance with the phonon confinement model. Another possibility is to look closely at the Raman bands that appear in the low-wavenumber zone due to acoustic-phonon confinement.

Normalized energy transmittance with regard to the three photon absorption valuesof open aperture z-scan is provided by Sutherland *et al*. [20], as follows:

$$T(z) = \frac{1}{\pi^{0.5} P_o} \int_{-\infty}^{\infty} \ln\left\{[1 + P_o^2 e^{-2x}]^{0.5} + P_o^2 e^{-x^2}\right\} dx \qquad ----(1)$$

in which $P_o = (2\gamma I_o^2 L_{eff})^{0.5}$and $I_o = I_{oo}/(1+z^2/zo^2)$ represent the intensity of theexcitation at position z, $zo=\pi\omega o^2/\lambda$, where zo represents Rayleigh's range, ωo represents minimal waist of thebeam at the focal point (z=0), λ represents the laser free-space wavelength, $L_{eff}=[1-\exp(-2\alpha oL)]/2\alpha o$ represents the effective sample length of the 3PA procedures, L represents the length of sample,and αo represents the coefficient of the linear absorption. In addition, thegraphs of the open aperture z-scan were often normalized to linear transmittance; for instance, transmittance at high |z|values. 3PA coefficient might

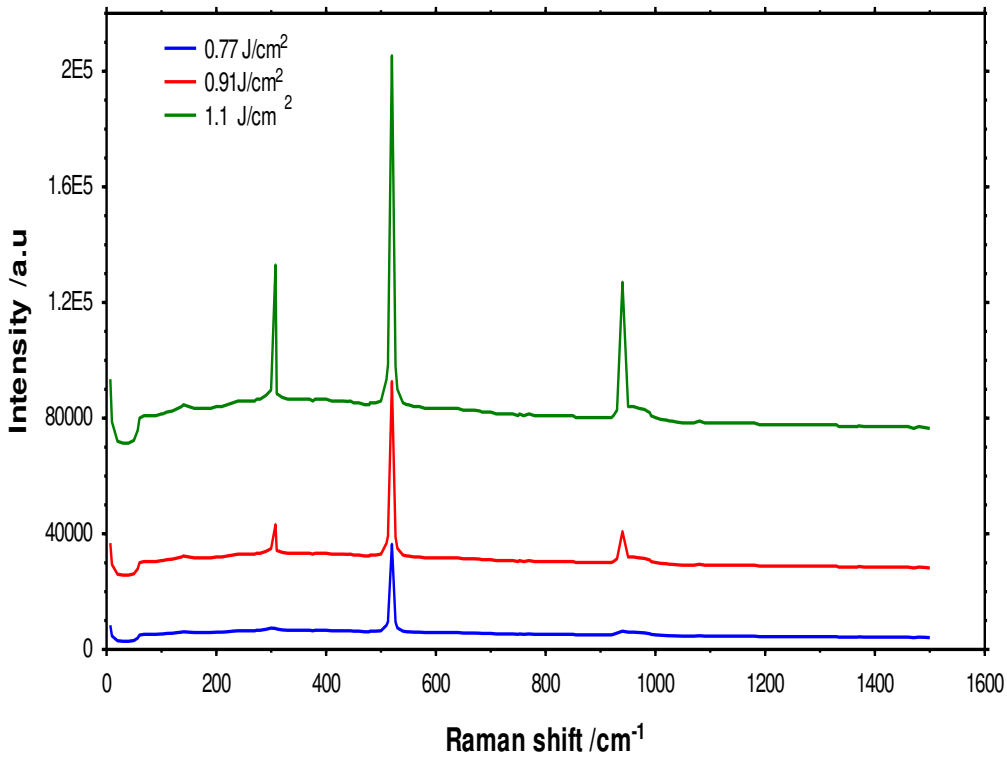

Figure 6-Raman spectra of TiO_2 nanostructures prepared at different laser fluencies.

be obtained from the optimal fit betweeneq2 andexperiment (OA) z-scan curve. In the case when $P_o$is less than 1, eq2might be expanded in Taylor series, asin the following form [20]:

$$T = \sum_{m=1}^{\infty} (-1)^{m-1} \frac{P_o^{2m-2}}{(2m-1)!\,(2m-1)^{0.5}} - \qquad -------(2)$$

In the case when high order terms are ignored, the transmission as incident intensity function is provided as reported by Sutherland [20]:

$$T = 1 - \frac{\gamma I_o^2 L_{eff}}{3^{\frac{3}{2}}} \qquad ----------(3)$$

The curves in Figure-7 were the optimal fit for eq3, which showthe depth of theabsorption dip as linearly proportionate to 3PA coefficient γ.Yet the trace shape was mainly specified byRayleigh's range of focused Gauss beam.

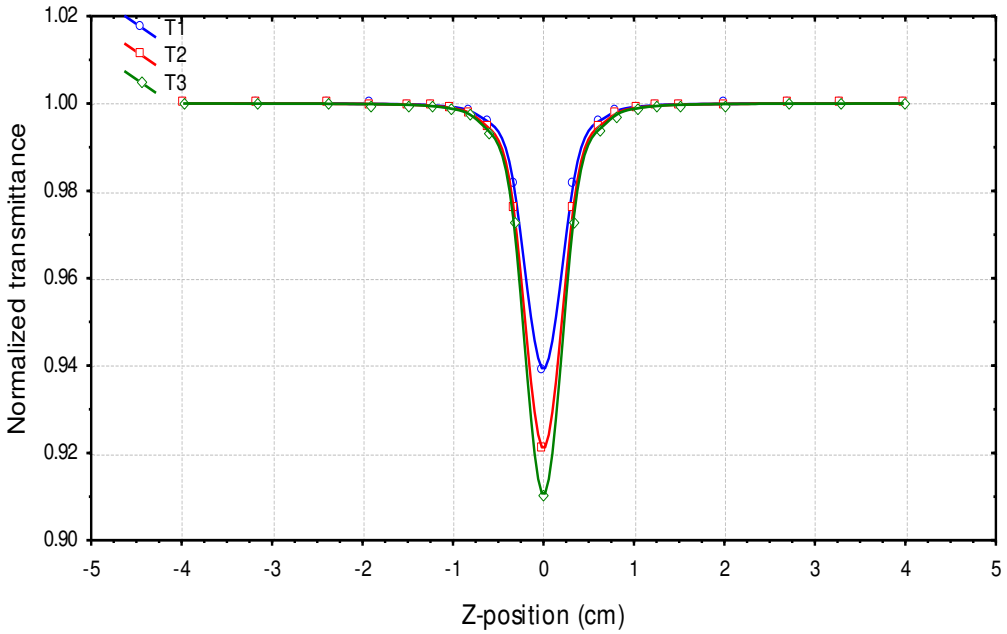

Figure 7-OA z-scan measured at a maximum influence of 80 mJ/cm^2, wavelength of 800 nm, pulse duration of 100 fs, and repetition rate of 10 kHz. Normalized transmittance spectra of TiO_2 nanostructures were prepared at different laser fluencies.

The fitted values of γ are shown in Table -2.It is observed that when thelaser fluenciesincreases, there will be an increase in the prepared film's thickness, and therefore the values of the effective length will increase exponentially, which leads to decreased transmittance and anincrease in the non-linear absorption coefficient.

Table 2-The fitted values of γ with different laser fluencies and thickness of sample

Laser fluencies J/cm^2	$L_{eff\,cm}$	γ cm^3 /GW^2
0.77	0.000843	0.0586
0.91	0.00098	0.0655
1.1	0.00104	0.0780

Conclusions

Through this work, we could conclude that the three-photon absorption was observed in TiO_2nanocrystalline prepared by pulsed laser deposition, byilluminating it with femtosecond Titanium-Sapphire laser. The laser fluencies have considerable effects on thickness of films prepared via pulsed laser deposition, which in turn will change the value of the non-linear absorption coefficient of the films prepared. The proposed synthesis method allows an easy synthesis of TiO_2 nanostructures with a controlled size (range of 86-57 nm), depending on the laser fluencies.

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