Preparation of TiO_2 nanoparticles by laser ablation in methanol solution

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الخلاصـة

في هذا البحث تم تحضير الجسيمات النانوية من اوكسيد التيتانيوم TiO_2 المحضر بواسطة الترسيب الفعال بالليزر النبضي بأستخدام ليزر ND:YAG الذي يعمل بطول موجي 532 نانو متر تم عملها بضربات ليزر مختلفة (2000،1500،1000) بأمد نبضة 10 نانو ثانيه وقطر حزمة 4.8mm كوسيلة إقتلاع من سطح الهدف (التيتانيوم) ذو نقاوه 99.99% .تم دراسة تأثيرمحلول الميثانول وعدد ضربات الليزر على خصائص التركيبة و التشكيلية وبينت الدراسه من خلال قياسات الاشعة السينية وجود 4 قمم عند الزوايا 2Ө=27.160 بالمستوى (110) ، وقمة ايضآ عند الزاوية 2Ө=36.2 بالمستوى (101) ، وكذلك عند الزاويه 2Ө=54.7 بالمستوى (211) وأخيرآ عند الزاوية 2Ө=69.02 بالمستوى (301) عند الشرط المثالي وهو 2000 ضربة بطاقة 900 بدرجة حرارة $85\ c^{\circ}$ لـ 45 ثانيه.

Abstract

In this work, TiO_2 nanoparticles prepared by pulse laser ablation(PLA) of titanium target (purity of 99.99%) immersed in methanol solution by focused beam of 532 nm pulsed used Nd:YAG laser operating at different laser pulses in range (1000, 1500, 2000) pulses with 1Hz repetition rate, effective beam diameter 4.8 mm and 10 ns pulse width. Laser energy was kept constant at (900) mJ. The effects of methanol solution and number of laser pulses on the structural properties (XRD) and morphology (FESEM) was study. From XRD measurment have been revealed that 4peaks with 2θ values of 27.160, 36.2, 54.7 and 69.02 degree, corresponding to TiO_2 crystal planes of (110), (101), (211) and (301) respectively at 2000 pulses in methanol solvent after heating at temperature 85 ^{o}C for 45 minute.

Keywords: TiO_2 nanoparticles, X-ray diffraction, Morphology, FESEM.

1. Introduction

TiO_2 is important material for several applications, such as, photo-catalysis, cosmetics, solar cells and smart pigments [1]. Properties are greatly enhanced when material reduced to nanoscale, an efficient route for production of stable and unprotected TiO2 nanoparticles (NPs) in pure solvents is pulsed laser ablation in liquids [2]. Laser ablation is typical example of top-down approach to fabrication TiO_2 nanoparticles in liquid media and promising technique for controlled fabrication of nonmaterial via-rapid reactive quenching of ablated species at interface between plasma and liquid [3]. Therefore, PLA used for prepared various kinds of NPs such as noble metals, alloys, oxides and semiconductors, moreover, PLA is inexpensive technique for controlling the ablation atmosphere and crystallized NPs can easily obtained in one step without subsequent heat treatment, because of high energetic state of ablated species [4]. Three main steps contribute in laser ablation synthesis method and formation nanoparticles, first, heats up the target surface to boiling point and plasma plume containing vapor atoms of target is generated, second, plasma expands adiabatically and ,finally, nanoparticles generated when condensation occurs, during, condensation step nucleation takes place; then fine nuclei either collide or stick to each other or new materials precipitate on them which result in growth [5]. In this paper, we prepared and developed low-cost technique for fabrication TiO_2 nanoparticles using PLA method without need to chemical modification and expensive materials.

2. Experimental work

Figure (1) shows experimental setup for laser ablation Nd-YAG (Type HUAFEI) of 532 nm, frequency (1 Hz) and energy per pulse of 900 mJ at room temperature. To preparation TiO_2 nanoparticles target of (Ti) (purity of 99.99%) immersed in methanol solvent and fixed at bottom of glass vessel container. Then, number of laser pulses (1000-1500-2000) are ablation surface of target and TiO_2 collidal get. Also, methanol solution is stirred during ablation with magnetic stirrer for 0.5 h and solution drop cast on clean glass with temperature (85˚C) at hotplate stirrer.

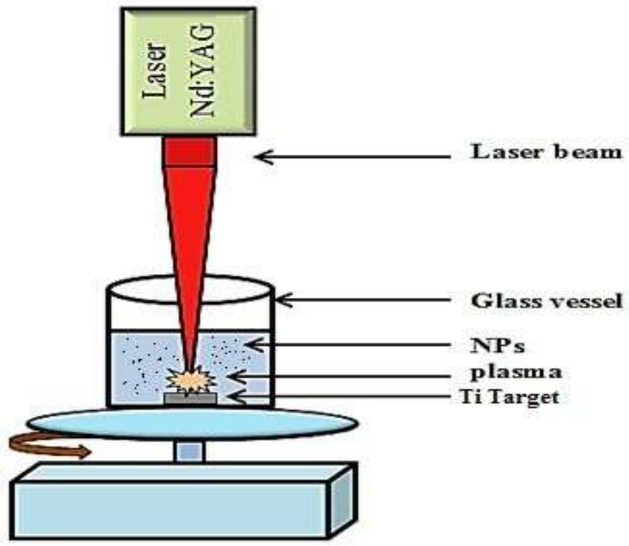

Figure 1: Experimental setup of TiO_2 nanoparticles synthesis by PLA method.

3. Results and Discussion

X-ray diffraction (XRD) patterns of TiO_2 NP_S prepared by pulsed laser ablation in (methanol) on cover glass substrates and evaporating the liquid media at room temprature . Figure (2) reveale (3) peaks with (2θ) values of 27.410, 36.0850 and 69.0083 degree, corresponding to TiO_2 crystal planes of (101), (111) and (301) respectively at 1000 pulses in methanol solvent after heating at temperature 85 ^oC for 45 minute.
Figure (3) revealed that (3) peaks with (2θ) values of 27.18, 45.76 and 54.39 degree, corresponding to TiO_2 crystal planes of (110), (210), and (211) respectively at 1500 pulses in methanol solvent after heating at temperature 85 C^o for 45 minute. Figure (4) revealed that (4) peaks with (2θ) values of 27.160, 36.2, 54.7 and 69.02 degree, corresponding to TiO_2 crystal planes of (110), (101), (211) and (301) respectively at 2000 pulses in methanol solvent after heating at temperature 85 ^oC for 45 minute.

A matching of the observed and standard (hkl) planes confirmed that the product is of TiO_2 having a polycrystalline in nature with tetragonal structure. XRD peaks also reveale that TiO_2 nanoparticles prefer to grow in the (301) direction since the maximum intensity appeared on this direction. The crystal size of the crystalline material has an important effect in determining the properties of the material and can be estimated through the X-ray spectrum display half way to the middle of the peak (FWHM) which is given to (Debye-Scherrer relation):

$$\boldsymbol{D_g = \frac{0.9\,\lambda}{\beta\,cos\theta_B}} \quad \ldots\ldots\ldots\ (6)$$

Where D_g: is the crystal size, 0.9 is the Scherrer constant, λnm , λ is the X-ray wavelength is = 1.54 nm , β; is the full width at half maximum of the diffraction peak, and θ_B; is the Bragg diffraction angle of the diffraction peaks.

It has been found that the crystal size is affected by heat, As the mobility holes in the films (TiO_2) much lower than the mobility of electrons, the increase in particle size will not lead to reducing the resistivity But lead to the removal of stresses, homogeneity as well as re-crystallization of the metal particles.

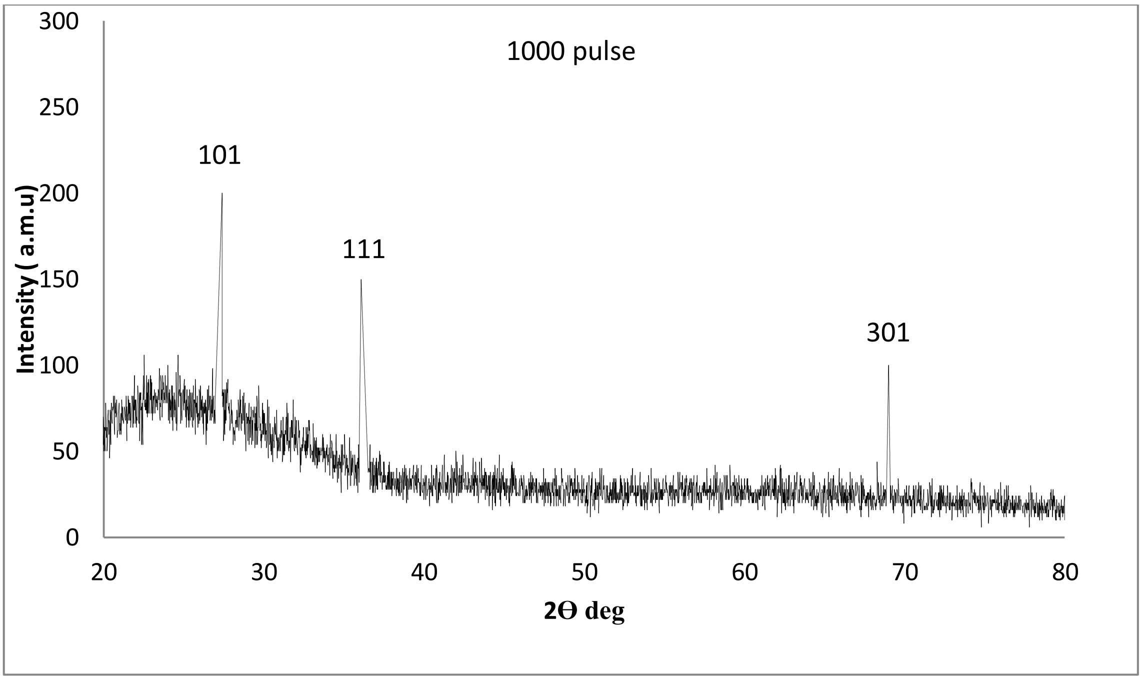

Figure 2 : XRD peaks of TiO_2 NPs at 1000 pulses after heating at temperature 85 ^oC for 45 minute.

Table 1: FWHM, (D) crystal size and (d) interplane distance of TiO_2 NPs after heating at temperature 85 ^oC for 45 minute and 1000 pulses

2θ (deg.)	Plane (hkl)	FWHM (deg.)	Crystal size (Dg) (nm)	d (A)
27.410	**(101)**	**o.46000**	**17.5336**	**3.23199**
36.0850	**(111)**	**0.53000**	**14.89391**	**2.48727**
69.0083	**(301)**	**0.30000**	**22.80881**	**1.35360**

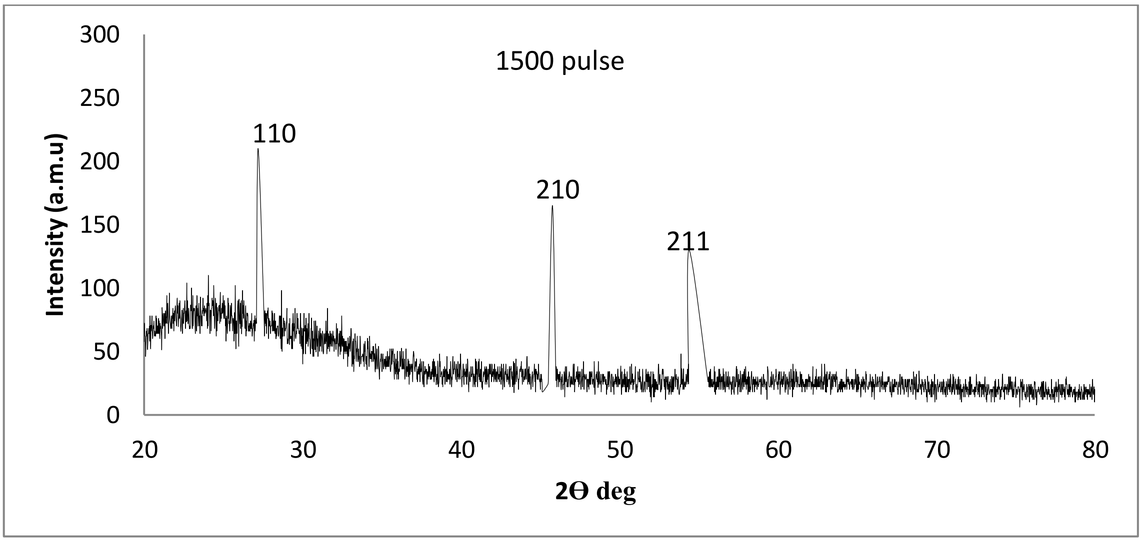

Figure 3: XRD pattern of TiO_2 NPs at 1500 pulses after heating at temperature 85 ^oC for 45 minute.

Table 2: FWHM, (D) crystal size and (d) interplane distance of TiO_2 NPs after heating at temperature 85 C^o for 45 minute and 1500 pulses.

2θ (deg.)	Plane (hkl)	FWHM (deg.)	Crystal size (Dg) (nm)	d (A)
27.18	(110)	0.26000	31.036	3.21373
45.76	(210)	0.06000	12.748	1.97305
54.39	(211)	0.04000	18.462	1.69133

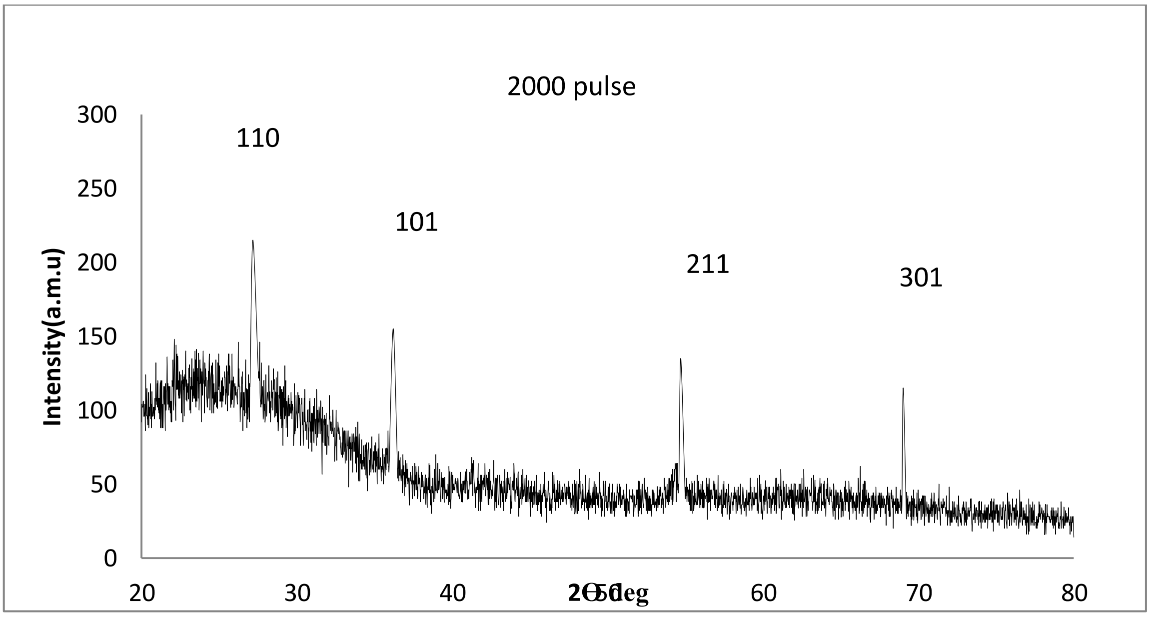

Figure 4 : XRD pattern of TiO_2 NPs at 2000 pulses after heating at temperature 85 ^oC for 45 minute.

Table 3: FWHM, (D) crystal size and (d) interplane distance of TiO_2 NPs after heating at temperature 85 ^oC for 45 minute and 2000 pulses

2θ (deg.)	Plane (hkl)	FWHM (deg.)	Crystal size (Dg) (nm)	D (A^0)
27.160	110	0.78000	10.3458	3.22512
36.2	101	0.50000	15.78239	2.47898
54.7	211	0.64000	11.52269	1.68387
69.02	301	0.28000	24.43629	1.35720

FESEM images of TiO_2 nanoparticles prepared in methanol at optimmaum conditions are shown in figures (5). In these figure, the agglomerates are assemblies of aggregates held together by weak bonds that may be due to van der waals forces or by ionic/covalent bonds operating over very small contact areas. From figure (a, b, c) result shown that nanoparticles seem to irregular shape due to low number of pulses that leads to low fragmentation mechanism at initial stage from laser light. Also methanol density Play an important role in formation of TiO_2 nanoparticles structure,the particle size of (TiO_2) NPs decrease with increased laser pulsed,and the nanoparticle of TiO_2 was sphyrical shape , it was seen homogenouse surface and uniformly covered.

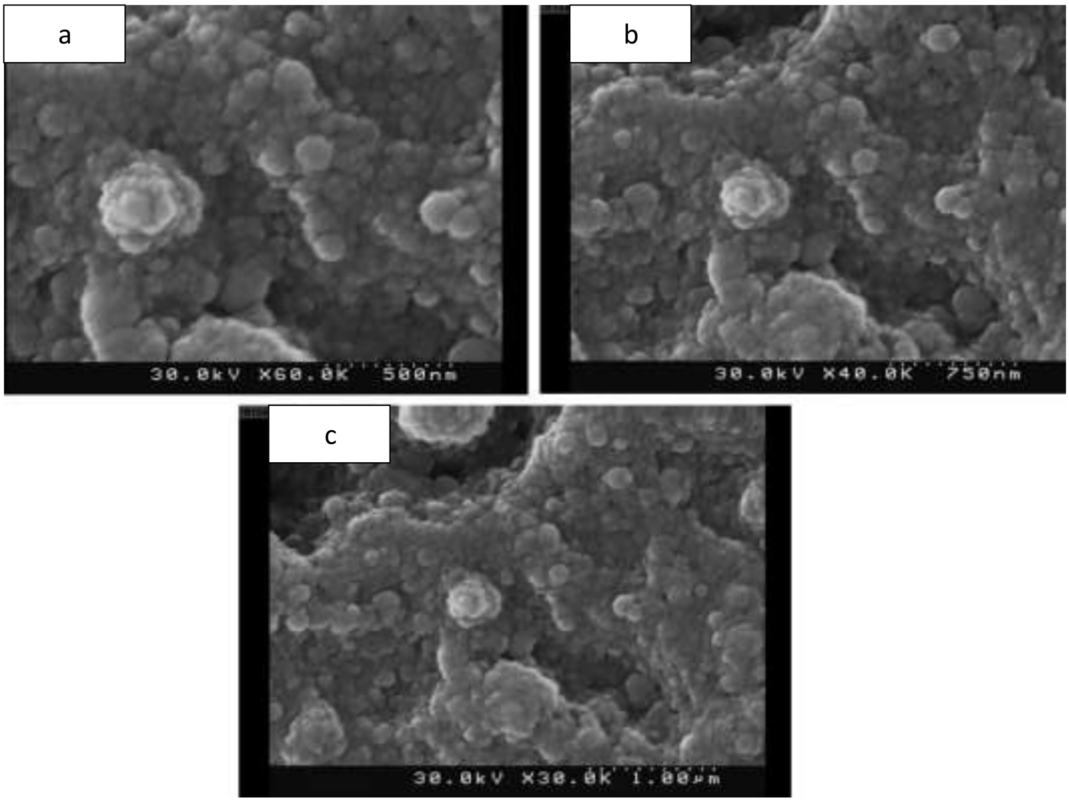

Figure 5 :FESEM of methanol preperd with 2000 pulse at (a) 500 nm (b) 750 nm (c) 1 µm.

4. Conclusions

Laser ablation in liquid provides a simple, flexible, controllable process and less expensive way for fabrication of TiO_2 nanoparticles.From the x-ray characteristics for as-prepared samples show that amorphous structure of TiO_2 NPs films, but after annealing film show that is polycrystalline with tetragonal structure without any trace of an extra phase with preferential orientation in the (110) direction.From FESEM technique the formation rate TiO_2 nanoparticles suspensions, mean particle size could be controlled by proper selection of the laser parameters and liquid media.
The NPs in liquids have an almost perfect spherical shape, agglomerated and some presented chains of welded particles, the particle size of (TiO_2) NPs decrease with increased laser pulsed.

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