

Synthesis and Characterization of TiO₂ Nanoparticles by Laser Ablation in Liquid

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ABSTRACT

The laser ablation techniques was employed to prepare TiO₂ nanoparticles by pulsed laser ablation of titanium target immersed in the double distilled deionized water using wavelength of 532nm and 1064nm of Nd:YAG laser with energy 500mJ. The as prepared products were characterized by X-Ray diffraction (XRD), Atomic Force Microscope (AFM) and UV-Vis spectrophotometer. The results indicate that the TiO₂ nanoparticles are synthesized at room temperature and the average diameter is about (84.78, 95.96) nm to the wavelength (1064nm, 532nm) respectively. The optical study shows the nanoparticles possesses direct optical transition with band gap (3.82, 3.65) eV to the wavelength (1064nm, 532nm) respectively. A heterojunction photo detector fabricated by drop cast film of colloidal TiO₂NPs (nanoparticles) onto p-type single crystal silicon wafer. *I-V* characteristics of TiO₂NPs/Si heterojunction under dark and illumination conditions have been studied.

Keywords: TiO₂ nanoparticles; laser ablation; heterojunction; band gap.

تحضير وتوصيف الجسيمات النانوية لـ TiO₂ بطريقة الازالة الليزرية في السائل

الخلاصة

طريقة التشظية الليزرية هي الطريقة التي استخدمت للحصول على الجسيمات النانوية لأكسيد التيتانيوم من خلال وضع قطعه من التيتانيوم عالي النقاوة 99.9% في 2 مل من الماء الثنائي التقطير اللابوني. استخدم ليزر النيديميوم ياك Nd:YAG وللتولين الموجيين (1064 و 532 نانومتر) وبطاقه 500 ملي جول. درست خواص المحلول الناتج بواسطة جهاز حيود الاشعه السينيه (XRD)، مجهر القوى الذريه (AFM) وجهاز مطياف الامتصاصيه (UV-Vis). من خلال نتائج الفحوصات التي اجريت للجسيمات النانويه لأكسيد التيتانيوم وجد ان معدل قطر الجسيمات يتراوح بين (84.78 نانومتر، 95.96 نانومتر) للتولين الموجيين (1064 نانومتر، 532 نانومتر) على التوالي. الدرسة البصريه قد بينت ان قيمه فجوة الطاقه هي (3.82، 3.65) eV للتولين الموجيين (1064 نانومتر، 532 نانومتر) على التوالي. للحصول على كاشف ضوئي ثنائي الوصله من المحلول المحضر تم تقطير المحلول بطريقة (drop casting) على سليكون من النوع القابل p-type وقياس التيار - فولتية لثنائي الوصله في الظلام والاضاءة.

INTRODUCTION

Laser ablation of solid target in a liquid environment has been established as a simple, quick, straightforward and environmentally friendly (green) method for the synthesis of nanoparticles (NPs) with desired properties [1-2]. Most importantly, it provides with the

opportunity to synthesis NPs in a surfactant free environment and thus obtain NPs with legend free surfaces (ultrapure colloidal solutions).throughout the years NPs out of a number of different materials such semiconductors , metal and dielectrics have been method nanoparticles of the oxide of the titanium are important nonmaterial for a large number of applications in environmental engineering usually for the oxides of the titanium are important nonmaterial for large number of application in environmental engineering usually for the photo catalytic degradation of water pollutants ,point industry ,as electrically conductive fillers biomedicine and fabrication of organic optoelectronic devices such as hybrid polymer-nanoparticles solar cells [3-5]. Three types of TiO₂ are abundant in nature brookite (orthorhombic), anatase (tetragonal) and rutile (tetragonal).Anatase and rutile have photo-catalytic activity [6-7]. Rutile TiO₂ has some advantage over anatasephase, such as higher refractive index, higher dielectric constant, higher electric resistance and higher chemical stability, rutile TiO₂ has been traditionally used in pigment, plastic, construction and cosmetic fields because of its good light-scattering and light-reflecting effect nontoxicity and chemical inertness. In the electronics industry the rutile tio₂ is used because of the high dielectric resistance and also used in capacitor, filter, power circuit and temperature compensatingcondensers [8-9].Inorganic n-type semiconductor titanium dioxide (TiO₂) particles have good biocompatibility, stability and environment safety [10].

In recent years pulsed laser ablation of metal target in liquid media has attracted great interest because such Pulsed Laser Ablation in Liquid (PLAL) can produce the extreme conditions and lead to the formation of thenovel nanostructures [11-12].The laser Ablation of metal target in liquid media form some special nonmaterial that are difficult to be obtained by the conventional methods.

In this work, we reported successful one-step fabrication TiO₂ nanoparticles by PLAL of titanium plate in double distilled deionized waterat room temperature and fabricated heterojunction photo detector by depositing a thin layer of colloidal TiO₂ nanoparticles on single crystalline p-type silicon.

Experimental

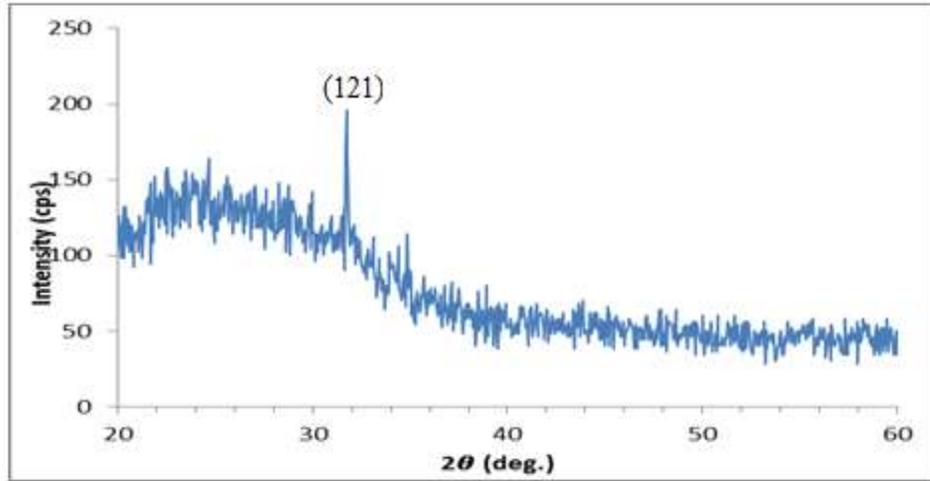
Titanium plate with thickness of 2mm, diameter of 20mm and higher than 99.9% purity was used. The target was immersed in double distilled deionized water (DDDW) (2ml) in glass beaker the target was kept at about 6mm below the liquid surface. Q-switched Nd/YAG laser system type HUAFEI providing pulses of 1064nm and 532nm wavelength with maximum energy per pulse of 1000 mJ, pulse width of 10ns, repetition rate of 10Hz and effective beam diameter of 5mm, was used for laser ablation. The laser is applied with a lens with 110mm focal length is used to achieve laser energy (500mj) at room temperature. (XRD-6000SHIMADZU Japan), was used to analyze thesesamples. (AFM)(type A Solver P-47H (Digital Instruments Nan scope NT-MDT SOLVER P47H-PRO) was used to observed the diameter of the nanoparticles , the optical absorption spectra of the irradiated solution were measured immediately by the UV-Vis double beam spectrophotometer (CECIL C.7200 (France) and SHIMADZU) using optical quartz cell with 1 cm optical path, the wavelength varies from 200 to 800nm and by using drop-casting technique [13],athin film of TiO₂ NPs is deposited on a 3Ω .cm (p-type 111) to calculated ideality factor of Tio2NPs/Si heterojunction.

Results and discussion:

Structure Properties of TiO₂ NPs

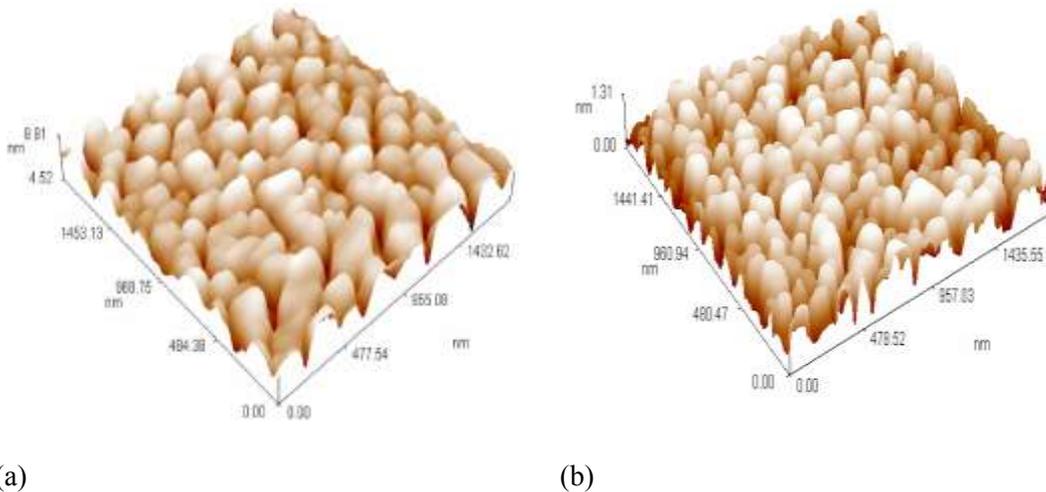
Figure (1)shows XRD pattern of the product prepared in 2ml of DDDW .It is in good agreement with the standard JCPDF data of brookite phases of TiO₂ the dominate peak at 2θ about (31.7)

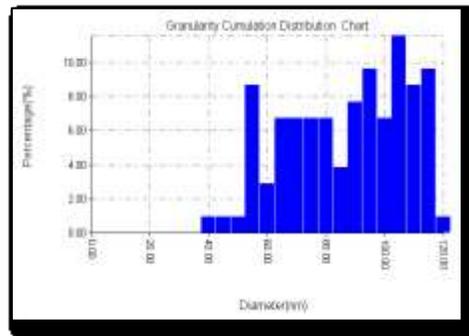
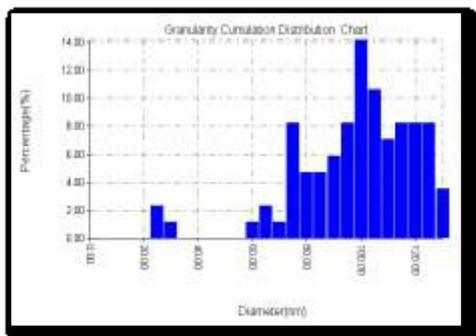
which represent the (hkl) miller indices of (121) correspond to the crystalline structure of TiO₂ (7,8,14,15,16).



Figure(1) XRD pattern of as-prepared sample.

The morphologies of particles were observed by AFM from Fig. (2) the product is nearly spherical shape. The fig (2, a and b) show 3DAFM image of TiO₂NPs to the 1064 nm, 532nm respectively and the particles size distribution is measured from Fig. (2, c and d) shows the particles size distribution histograms for TiO₂ nanoparticles to the 532nm and 1064nm. The average roughness and the average diameter of particles shown in the table (1)





(c)

(d)

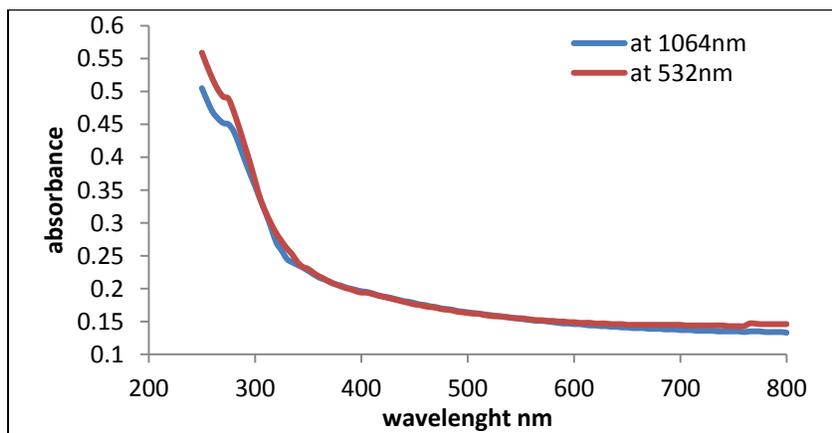
Figure (2): AFM image of samples prepared at the wavelength (a) 532 and (b) 1064nm, the particles size distribution histograms for TiO₂ NPs(c) at 532nm,(d) at the 1064nm

Table (1): The average rough nesses value and the average diameter of particles with the wavelength and energy

Wavelength (nm)	Energy (mJ)	Ave. Diameter (nm)	Ave. Roughness (nm)	RMS (nm)
532	500	95.96	0.667	0.84
1064		84.78	0.266	0.31

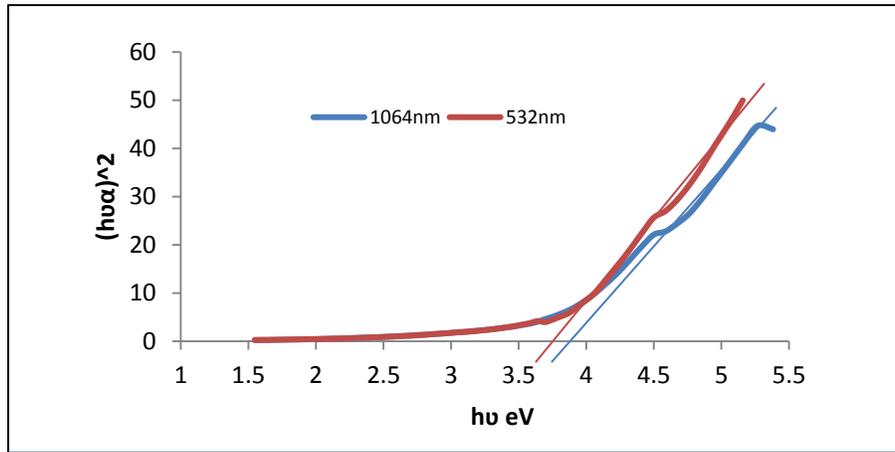
Optical properties of TiO₂ nanoparticles

Fig (3) shows the ultraviolet visible (UV-Vis) optical absorption spectrum of the obtained colloid solutions .A significant increase in the absorption at wavelengths short than 400 nm is observed.



Figure(3) absorpation spectrumforTio2 NPsprepared by PLAL at two wavelength (1064nm ,532nm).

Fig.(4) represent the plot $(\alpha h\nu)^2$ with $h\nu$ the nature of plot suggests direct interband transition .the extrapolation gives E_g (3.65,3.82ev)to wavelength(532,1064 nm) respectively. The band gap energies (E_g) of as-prepared TiO₂ NPs which have larger that the value of 3.2 eV for the bulk TiO₂.This can be explained because the band gab of the semiconductors has been found be particles size dependent .The band gab increases with decreasing particle size (84.78nm, $E_g=3.82\text{ev}$) and (95.96nm, $E_g=3.65\text{ev}$).



Figure(4) variation $(\alpha h\nu)^2$ with photon energy ($h\nu$) for TiO₂ NPs

To study using TiO₂ nanoparticles to fabricate heterojunction of TiO₂NPs/Si by drop-casting technique,I-V curve under illumination condition and reverse bias is presented in Fig(5).It demonstrated the photocurrent increases with biasing voltage .The dark I-V characteristics of TiO₂NPs/Si heterojunction are demonstrated in Fig(6). This junction exhibits a poor rectification with a large series resistance.an ideality factor of 11 calculated from the Fig(6) .

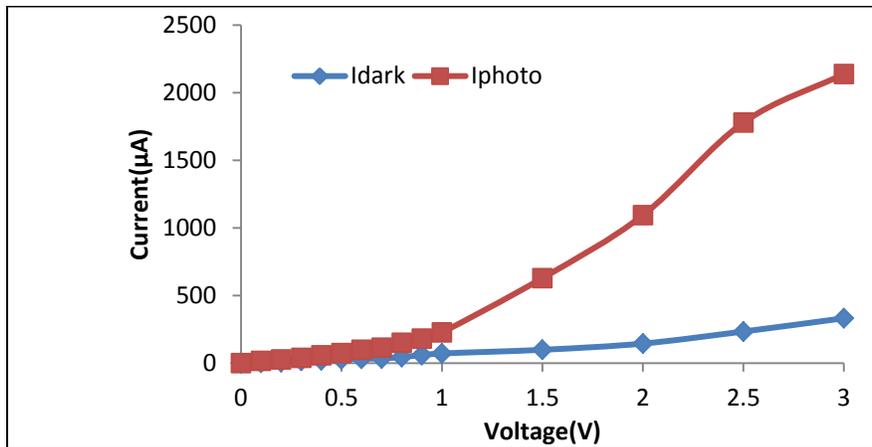


Figure (5): Illuminated $I-V$ characteristics under reverse bias.

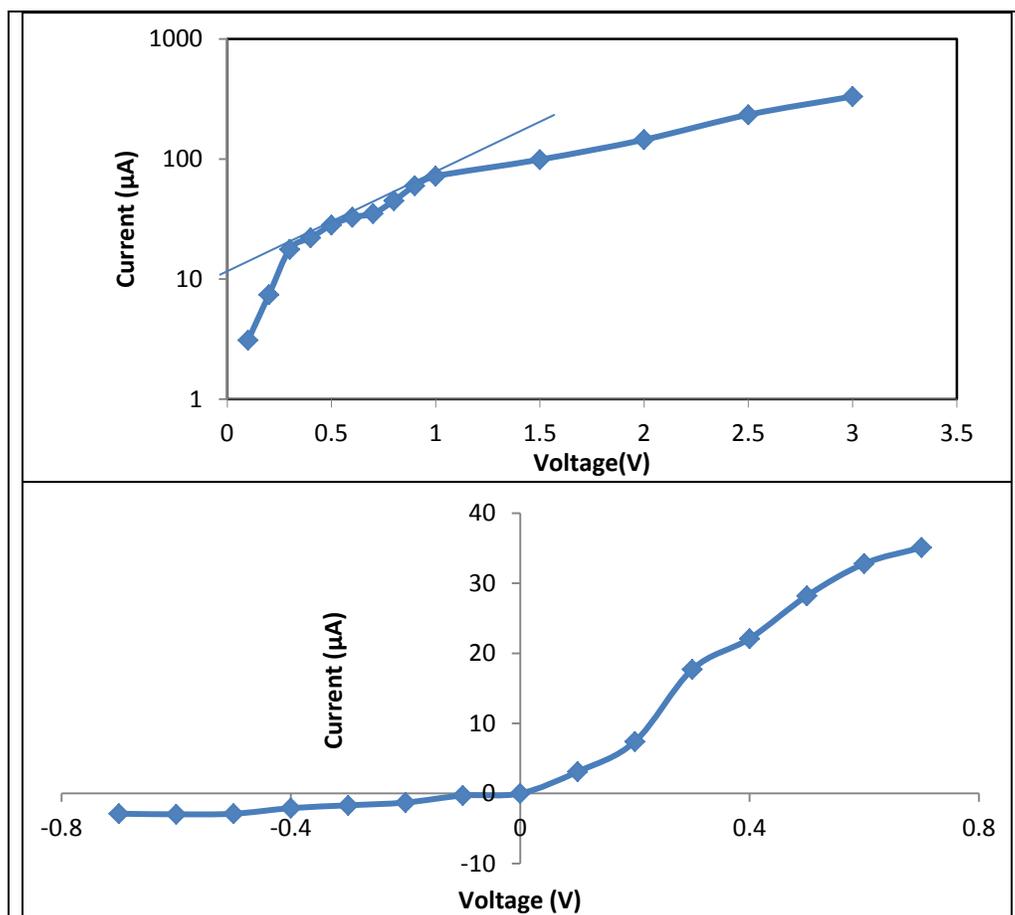


Figure (6):(a)the semi-log I - V characteristics plot(b) I - V dark characteristics of TiO₂/Si heterojunction.

CONCLUSIONS:

TiO₂ nanoparticles have been successfully fabricated by laser ablation at energy of (500 mJ), number of pulses 50 pulse and wavelength (532nm,1064nm) of Ti target immersed in DDDW water. From this result we can see that the wavelength 1064nm is useful than 532nm to fabricated TiO₂ nanoparticles to the same energy and number of pluses. Through the (UV-Vis) it is found that the A significant increase in the absorption at wavelengths short than 400 nm is observed.

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