Synthesis and Characterization of TiO_2 Nanoparticles via Sol-Gel Method by Pulse Laser Ablation

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Abstract

Nanocrystalline titania powder was prepared at room temperature via sol-gel method; using $TiCl_4$ as precursor and absolute ethanol solution. After mixing, the gel solution was formed. Then the sol-gel dried and calcined at different temperatures. The size of the prepared nanoparticles was reduced by Nd-YAG Pulse Laser Ablation (PLA). The characterization of the TiO_2 Nanoparticles in two phases was carried out by X-ray Diffraction (XRD) to investigate the phase structure. The Transmission Electron Microscope (TEM) result shows the particle size of nanoparticles after laser ablation less than 10 nm. Scanning Electron Microscopy (SEM) to obtain the surface morphological studies Results showed that anatase was the only phase in titanium oxide powders up to 500 °C, when the calcination increased in the region of 900 °C the phase transformation from anatase to rutile occurred in the TiO_2 nanopowders. This paper shows a comparison between two phases of TiO_2 Nanoparticles (anatase and rutile). Fourier Transform Infra-Red (FTIR) to study the vibrational frequencies between the bonds of atoms for synthesized TiO_2 Nanoparticles. The Crystalline size of TiO_2 Nanoparticles obtained was between (15 -70) nm for anatase at 500 °C and rutile at 900 °C. In FTIR analysis, all the peaks observed were around (400-700) cm^{-1} due to stretching and bending vibrations.

Keyword: TiO_2 NPs, Sol-gel method, TiO_2 phases, PLA.

تصنيع وتوصيف جسيمات ثنائي اوكسيد التيتانيوم النانوية بطريقة الصول-جل بالازالة بالليزر النبضي

الخلاصة

تم تحضيرمسحوق جسيمات ثنائي اوكسيد التيتانيوم النانوية االبلورية بدرجة حرارة الغرفة وبطريقة الصول-جل وباستخدام رباعي كلوريد التيتانيوم كمادة اولية والايثانول النقي, بعد الخلط يتكون الجل ثم يجف ويتعرض للاحراق بدرجات حرارة مختلفة. النتائج توضح بان طور الاناتاس هو الطور الوحيد الذي يكون عند 500 درجة سيليزية وعند زيادة درجة حرارة الاحراق الى 900 درجة سليزية يتحول الطور من الاناتاس الى الروتايل وهذا يحدث مع مسحوق ثنائي اوكسيد التيتانيوم . هذا البحث يوضح المقارنة مابين جسيمات ثنائي اوكسيد التيتانيوم النانوية لطوريها الاناتاس والروتايل. تم تقليل حجم

جسيمات ثنائي اوكسيد التيتانيوم النانوية المحضرة باستخدام الازالة بالليزرر الياك النبضي, وتم توصيف للجسيمات النانوية بجهاز حيود الاشعة السينية لمعرفة التركيب الطوري والمجهر الالكتروني النافذ لقياس حجم الجسيمات النانوية بعد الازالة بالليزر والمجهر الالكتروني الماسح لدراسة مورفولوجيا السطح وتحويلات فورير للاشعة تحت الحمراء لدراسة الترددات الاهتزازية مابين اواصر الذرات للجسيمات النانوية المحضرة. الحجم البلوري للجسيمات النانوية وجد انه يقع مابين (15- 70) نانومتر لطور الاناتاس عند 500 درجة سليزية وللروتايل عند 900 درجة سليزية . من تحليلات فورير للاشعة تحت الحمراء معظم القمم تم ملاحظتها مابين cm^{-1} (400-700) نتيجة المط و الاهتزازات الانحنائية.

الكلمات المفتاحية: جسيمات ثنائي اوكسيد التيتانيوم النانوية, طريقة الصول –جل, اطوار ثنائي اوكسيد التيتانيوم, الازالة بالليزر النبضي.

INTRODUCTION

TiO_2 nanoparticles are interesting by scaling because of their unique photocatalyst properties. This increased its role in understanding, creating and improving materials for different applications. TiO_2 has been widely used in many technological and as antibacterial agents applications [1,2,3]. TiO_2 exists in three different crystalline habits: rutile (tetragonal), anatase (tetragonal) and brookite (orthormbic). Both anatase and rutile have tetragonal crystal structure but belong to different phase groups. Anatase has the space group $I4_1/$ amd [4] with four formula units in one unit cell and rutile has the space group $P4_2/$ mnm [5] with two TiO_2 formula units in one unit cell [6]. The low- density solid phases are less stable and undergo transition rutile in the solid state. Rutile TiO_2 has some advantages over anatase phase, such as higher refractive index, higher dielectric constant, higher electric resistance and higher chemical stability. The transformation is accelerated by heat treatment and occurs at temperture degrees in the range of (450-1200) ˚C [7]. This transformation is dependent on several parameters such as initial particle size, initial phase, dopant concentration, reaction atmosphere and annealing temperture [8, 9]. TiO_2 nanoparticles can be synthesized using various methods such as sulfate process [10], chloride process [10], impregnation [11], hydrothermal method [12, 13], direct oxidation of $TiCl_4$ [14], metal organic chemical vapor deposition method, Physical Vapor Deposition (PVD) [15, 16]. Sol-gel method is one of the most convenient ways to synthesize various metal oxides due to low cost, ease of fabrication and low processing temperatures. It is widely used to prepare TiO_2 for films and particles. In general, the sol-gel process involves the transition of a system from liquid "sol" (colloid) in to a solid "gel" phase [17, 18, 19]. The homogeneity of the gel depends on the solubility of reagents in the solvent, the sequence of addition of reactant, the temperture and the pH. In this work TiO_2 nanoparticles were prepared via a sol-gel method in two phases; anatase and rutile using $TiCl_4$ as a precursor. The products were characterized by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Fourier Transform Infra-Red (FTIR). The aim of this work is to prepare TiO_2 NPs

with two phases anatase and rutile via sol-gel method, and try to reduce the particle size by Nd-YAG pulse laser ablation.

Experimental Part :Synthesis and Characterization Techniques

Nanocrystalline SnO_2 powder was prepared by mixing tin(IV) dichloride with distilled water at room temperature:

$$SnCl_4 \cdot 5H_2O(\text{powder}) + H_2O(\text{distilled water}) \longrightarrow SnO_2 + 4HCl + 4H_2O$$

Thus 10 g of $SnCl_4.5H_2O$ (Promchimperm Co,98%) was mixed with 800 mL of distilled water. This mixture was maintained under stirring for 24h (sample a) ,48h (sample b) and 72h (sample c). During this period, the solution remained cloudy and white. The pH of the solution decreased rapidly after a few minutes of stirring to reach pH =2 and it remained almost constant. After 24,48 and 72 hours, the stirring was stopped and the mixture was allowed to settle. The gel at the bottom of the beaker was easily separated from the solution by filtering ,it was then washed five times with distilled water and ethanol. After each washing, the mixture was allowed to settle in order to allow the separation of the gel from the solution by decantation .The gel obtained was dried at 80˚C temperature to yield a white powder.

Phase identification determination was carried out using X-ray diffraction (Shimadzu XRD-6000) with Cu $K\alpha_1$ radiation. The average crystallite size (D) of the powder was estimated from the Scherrer formula. XRD data were collected in the 2θ range of (20–70)º using step scan mode with step width of 0.02°. Rietveld analysis was carried out to calculate unit cell parameters. The powder morphology was observed using a (VEGA\\Easy Probe) scanning electron microscope. The chemical groups of the prepared powders were carried out in Shimadzu equipment (IRAffinity-1 FTIR Spectrophotometer).

Experimental Section

Materials and preparation method

Titanium Tetrachloride $TiCl_4$ 99.99% and absolute ethanol CH_3CH_2OH 99.99% for producing TiO_2 nanoparticles by adding drop wise from $TiCl_4$ in ethanol with 1:10 ratio. The reaction was performed at room temperature while stirring under fume hood due to the large amount of Cl_2 and HCl**.** The solution was left to rest and cool back at room temperature after that measured the pH of the solution in the range of (1-2). The final solution was dried at 80˚C until gel was formed. The obtained TiO_2 powder was calcined for two hours in the box furnace at 500˚C in an ambient atmosphere in this temperature getting TiO_2 nanoparticles in anatase phase when increasing the temperature degree to 900˚C the phase transformation from anatase to rutile in TiO_2 powder.

Pulse Laser Ablation (PLA) Treatment of TiO_2 NPs

Nd-YAG pulse laser using for the ablation method of nanoparticles colloid for minimizing the particle size and get more small size nanoparticles. Pulse Laser ablation (PLA) was used after preparation of the nanoparticles colloid. Nanoparticles colloid irradiated by Q-switched Nd-YAG laser operated at

wavelength of 1064 nm, 7 ns pulse duration, and PRF of 6 Hz. The laser energy was used to ablate nanoparticles colloid was (400) mJ/pulse, the time of ablation was (6) min. The beam laser was focused on colloid using focusing lens of 100mm focal length. Fig. (1) shows the schematic diagram of laser ablation.

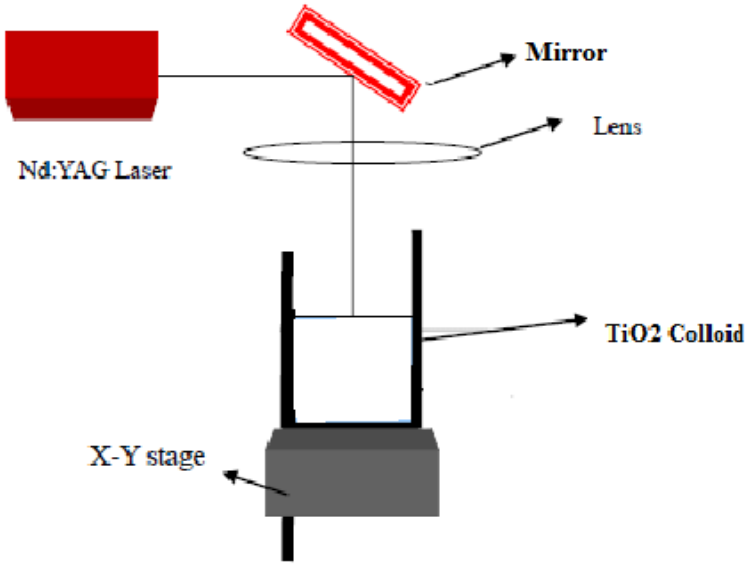


Figure (1) Schematic diagram of laser ablation

Characterization of TiO_2 NPs

X-ray diffraction (XRD-7000 Shimadzu Maxima-a) 40 kV voltage and with current 20 mA was used to identify the crystalline phases and to estimate the crystallite size. The XRD patterns were recorded with 2θ in the range of 10° - 60° by step scanning, employing Cu tube with wavelength of Cu 1.54 A˚. Scanning Electron Microscope (SEM) model (TESCAN-VEGA/USA) with resolution 3nm at 30 kV, Transmission Electron Microscope (TEM) JEOL JEM 1400 were used for investigating the size and shape of nanoparticles and Fourier Transform Infra- Red (FTIR- SHIMADZU/ Japan) Spectroscopy to determine chemical bounds for material at wave number in the range of (400-4000) cm^{-1}.

Results and Discussion

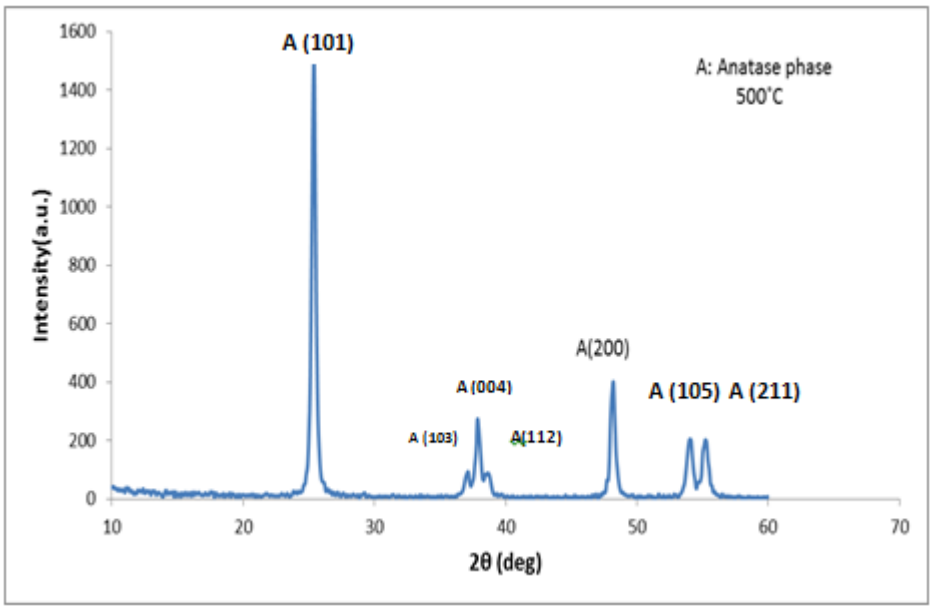
Figure (2a) show almost all of the crystal type is anatase (marked with A). Peaks of TiO_2 nanoparticles in anatase phase with 2θ angle at 25.38˚, 37.90˚, 48.14, 54.026˚ and 55.139 with diffraction plans (101), (004), (200), (105) and (211) respectively. Figure (2b) shows the peaks of TiO_2 nanoparticles in rutile

phase (marked with R) of 2θ angle at 27.5˚, 36.16˚, 39.26˚, 41. 32˚, 44.14˚, 54.42˚and 56.72˚ with diffraction plans (110), (101), (200), (111), (210), (211)

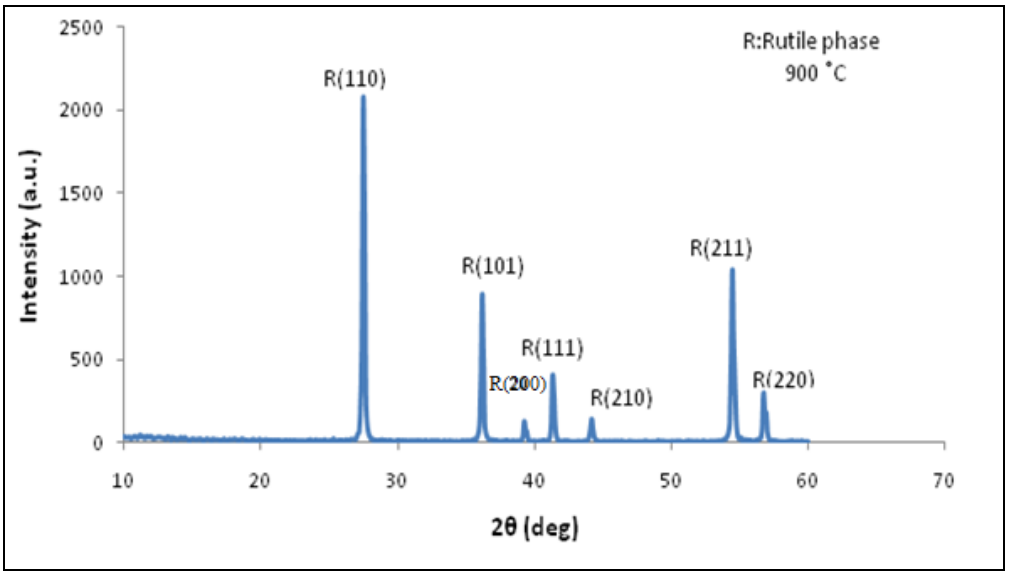
and (220) respectively. The average particle size was estimated from the Scherrer equation on the anatase phase and rutile diffraction peaks (the most intense peaks) [20].

$$D = \frac{K\lambda}{\beta Cos\theta} \qquad \ldots (1)$$

Where D is the crystal size of the catalyst, λ the X-ray wavelength, β the full width at half maximum (FWHM) of the diffraction peak (radian), k is a coefficient (0.89) and θ is the diffraction angle at the peak maximum. The average crystal sizes of anatase TiO_2 nanoparticles were calculated are found to be around 15nm and for rutile TiO_2 nanoparticles it was around 32nm**.**



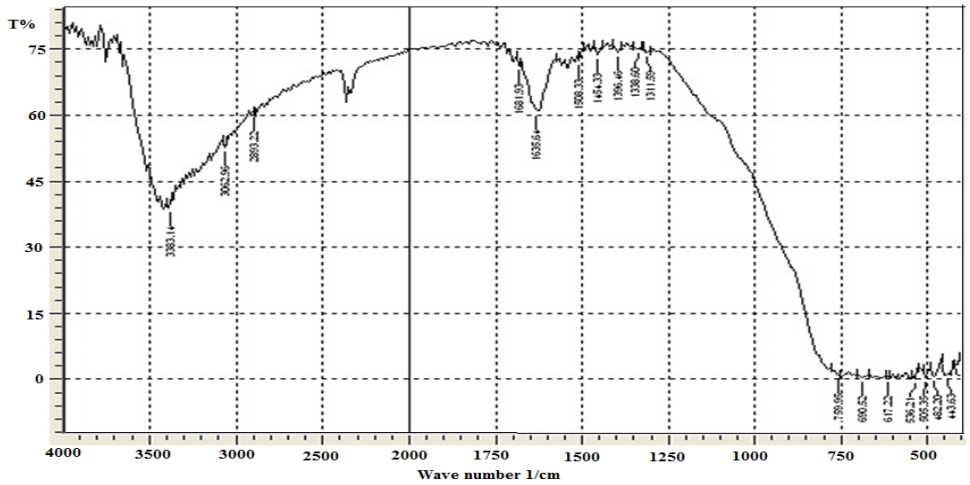
Figure(2a) XRD pattern Anatase phase which have intensity at peak (101), (004), (200), (105) and (211).



Figure(2b) XRD pattern Rutile phase which have intensity at peak (110), (101), (200), (111), (210), (211) and (220).

The infrared spectrum of the synthesized TiO_2 nanoparticles was in the range of 400-4000 cm^{-1} wave number which identifies the chemical bonds as well as functional group in the compound (Figure 3a and 3b). Strong absorption in the frequency region of 400- 1000 cm^{-1} corresponds to Ti-O-Ti bonding and indicates the formation of a titanium oxide. The broad intense band below 1200 cm^{-1} is due to Ti-O-Ti vibrations. Calcination TiO_2 nanoparticles at 500˚C leads to significant sharpening of absorption bands or transmission in the region of 400-700 cm^{-1} and clearly indicates the formation of anatase phase as shown in Figure 2a and the Figure 2b shows the IR-Spectra of TiO_2 nanoparticles calcination at 900˚C clearly shows the absorption peaks at 426.2, 480.2 and 663.51 cm^{-1} characteristic for rutile phaseTEM images for nanoparticles after treated with pulse laser ablation (PLA) are illustrated in Figure (4a) anatase and Figure (4b) rutile after laser treating. Laser ablation was used for treating and minimizing the nanoparticles sizes as a spherical homogeneous nanoparticle in the range of (1-12) nm for anatase and in the range of (3-22) nm for rutile. The TEM results agreed with R.Vijayyalakshmi et.al.[21]. The morphology of calcinated titania powders at 500˚C and 900˚C observed by Scanning Electron Microscopy (SEM) is shown in Figures 5a, 5b, 6a , 6b for anatase and rutile phase respectively. TiO_2 nanoparticles; prepared via Sol-Gel method, exhibited irregular morphology due to the agglomeration of primary particles. The average diameter of anatase phase was about 35nm and for rutile phase was about 65nm. This result shows the particles size of the anatase phase smaller than rutile phase. SEM

micrograph of the calcined (500 ºC) and (900˚C) respectively agreed with Kheamrutai Thamaphat *et.al.* [22], and Kavitha Thangavelu *et.al.* [23].



Figure(3a) FTIR spectra of the TiO_2 nanoparticles (anatase phase) calcined at 500˚C for 2 hours.

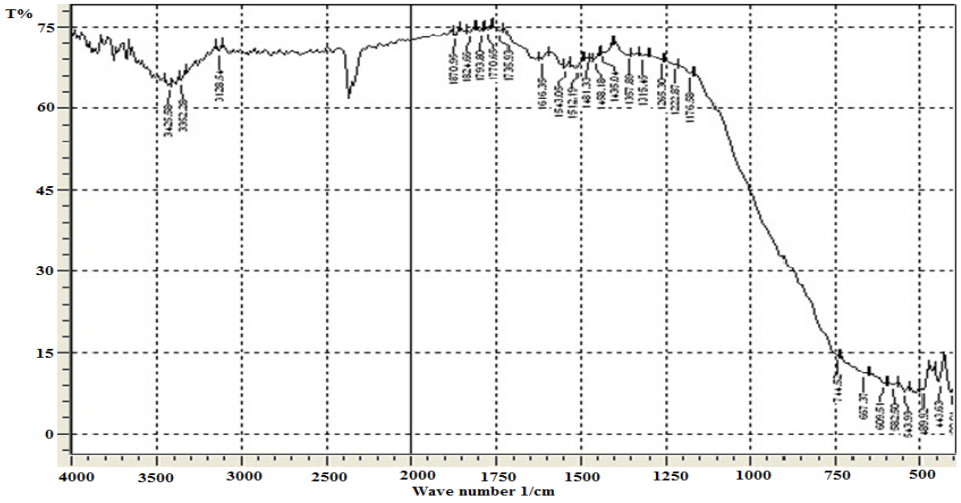


Figure (3b) FTIR spectra of the TiO_2 nanoparticles (rutile phase) calcined at 900˚C for 2 hours.

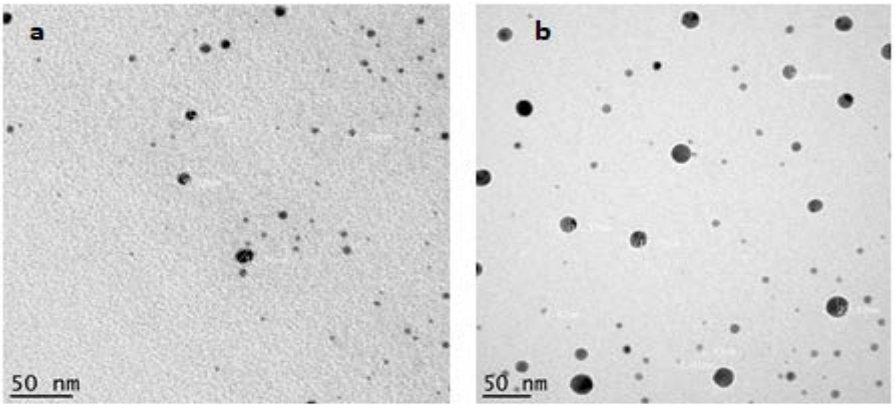


Figure (4a), (4b) Transmission Electron Microscope (TEM) images TiO_2 nanoparticles, (a) anatase and (b) rutile phase after laser ablation treating, respectively.

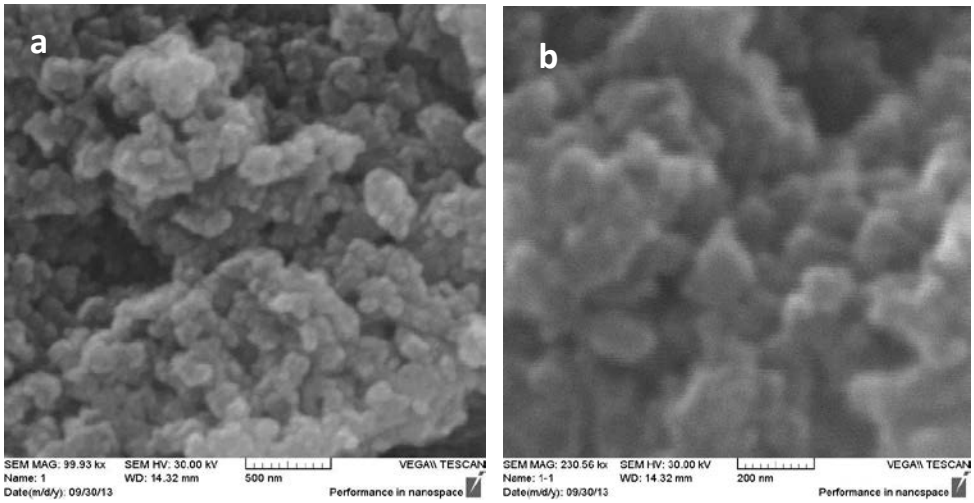


Figure (5a) SEM micrographs showing morphologies of TiO_2 nanoparticles (anatase phase) powder samples made in calcination temperature 500 ˚C for 2 hours with two different magnifications (a) 500nm and (b) 200nm.

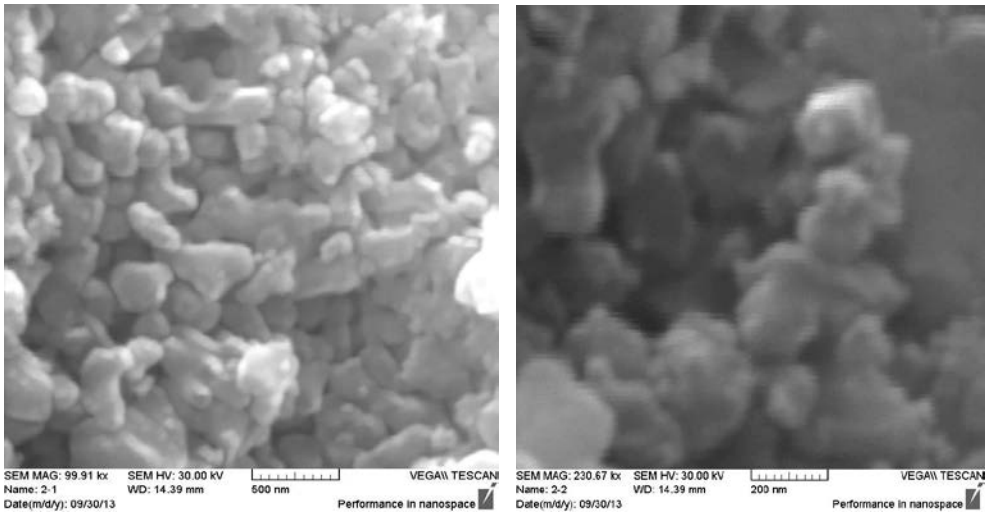


Figure (6) SEM micrographs showing morphologies of TiO_2 nanoparticles (rutile phase) powder samples made in calcination temperature 900 ˚C for 2 hours with two different magnifications (a) 500nm and (b) 200nm.

Conclusion

TiO_2 NPs was synthesized successfully via the sol-gel method, using $TiCl_4$ as a starting material. As a comparison between two phases of TiO_2 NPs; anatase and rutile in preparation and characterization of preparing phases in this work. The diameter size of rutile TiO_2 NPs at 900˚C which characterized by Scanning Electron Microscope (SEM) was 65 nm bigger than diameter size of anatase phase TiO_2 NPs at 500˚C was about 35 nm. X-ray Diffraction (XRD) pattern with sharp peak at $2\theta = 25.38^{\circ}$ with particle size 15 nm calculated by Scherrer equation for anatase phase and with sharp peak at $2\theta = 27.5^{\circ}$ and particle size 32 nm for rutile phase. From the results of SEM and XRD the diameter of TiO_2 NPs increased with increasing calcinations temperature. TEM measurements of nanoparticles after treated by laser ablation in the range (1-15) nm. The FTIR of the TiO_2 NPs in the region between (400-700) cm^{-1} indicated the Ti-O and Ti-O-Ti bonds due to stretching mode of a TiO_2 network which was important for photocatalytic process.

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