Synthesis and Characterization of TiO₂ Nanoparticles via Sol-Gel Method by Pulse Laser Ablation

The 5th International scientific Conference on Nanotechnology & Advanced Materials Their Applications (ICNAMA 2015) 3-4 Nov, 2015

Dr. Adawiya J. Haider
Nanotechnology and Advanced Materials Research Center, University of Technology / Baghdad
Email: adawiyahaider@yahoo.com

Dr. Zainab N. Jameel
Nanotechnology and Advanced Materials Research Center, University of Technology / Baghdad

Dr. Samar Y. Taha
College of Science for Women, University of Baghdad / Baghdad

Abstract
Nanocrystalline titania powder was prepared at room temperature via sol-gel method; using TiCl₄ 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 TiO₂ 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 TiO₂ nanopowders. This paper shows a comparison between two phases of TiO₂ Nanoparticles (anatase and rutile). Fourier Transform Infra-Red (FTIR) to study the vibrational frequencies between the bonds of atoms for synthesized TiO₂ Nanoparticles. The Crystalline size of TiO₂ 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: TiO₂ NPs, Sol-gel method, TiO₂ phases, PLA.

تصنيع وتوصيف جسيمات ثنائي أوكسيد التيتانيوم النانوية بطريقة الصول-جل باللازالة بالليزر النبضي

تم تحضير مسحوق جسيمات ثنائي أوكسيد التيتانيوم النانوية البوليفية بدرجة حرارة الغرفة وبطريقة الصول-جل باستخدام رباعي كلوريد التيتانيوم كمادة أولية والإيثانول النقفي. بعد الخلط يكون الجل ثم يخف ويتم للاحراق بدرجات حرارة مختلفة. النتائج توضح بيان طور الانناس هو الطور الوحيد الذي يكون عند 500 درجة سيليزية وعند زيادة درجة حرارة الحرق إلى 900 درجة سيليزية يتحول الطور من الانناس إلى الروتالي. هذا يحدث مع مسحوق ثنائي أوكسيد التيتانيوم. هذا البحث يوضح المقارنة المابين جسيمات ثنائي أوكسيد التيتانيوم النانوية لطوريها الانناس والروتالي. تم تقليل حجم
Synthesis and Characterization of TiO₂ Nanoparticles via Sol-Gel Method by Pulse Laser Ablation

INTRODUCTION

TiO₂ nanoparticles are interesting by scaling because of their unique photocatalyst properties. This increased its role in understanding, creating and improving materials for different applications. TiO₂ has been widely used in many technological and as antibacterial agents applications [1,2,3]. TiO₂ exists in three different crystalline habits: rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic). Both anatase and rutile have tetragonal crystal structure but belong to different phase groups. Anatase has the space group I₄₁/a md [4] with four formula units in one unit cell and rutile has the space group P₄₂/mnm [5] with two TiO₂ formula units in one unit cell [6]. The low-density solid phases are less stable and undergo transition rutile in the solid state. Rutile TiO₂ 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 temperature 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 temperate [8, 9]. TiO₂ nanoparticles can be synthesized using various methods such as sulfate process [10], chloride process [10], impregnation [11], hydrothermal method [12, 13], direct oxidation of TiCl₄ [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 TiO₂ 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 temperature and the pH. In this work TiO₂ nanoparticles were prepared via a sol-gel method in two phases; anatase and rutile using TiCl₄ 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 TiO₂ 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 SnO₂ powder was prepared by mixing tin(IV) dichloride with distilled water at room temperature:

\[
\text{SnCl}_4 \cdot 5\text{H}_2\text{O} (\text{powder}) + \text{H}_2\text{O} (\text{distilled water}) \rightarrow \text{SnO}_2 + 4\text{HCl} + 4\text{H}_2\text{O}
\]

Thus 10 g of SnCl₄.5H₂O (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 Kα₁ 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)° 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 TiCl₄ 99.99% and absolute ethanol CH₃CH₂OH 99.99% for producing TiO₂ nanoparticles by adding drop wise from TiCl₄ in ethanol with 1:10 ratio. The reaction was performed at room temperature while stirring under fume hood due to the large amount of Cl₂ 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 TiO₂ powder was calcined for two hours in the box furnace at 500°C in an ambient atmosphere in this temperature getting TiO₂ nanoparticles in anatase phase when increasing the temperature degree to 900°C the phase transformation from anatase to rutile in TiO₂ powder.

**Pulse Laser Ablation (PLA) Treatment of TiO₂ 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 20 in the range of 10 - 60˚ by step scanning, employing Cu tube with wavelength of Cu 1.54 Å. 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 20 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 20 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].

\[
D = \frac{K \lambda}{\beta \cos \theta}
\]  

(1)

Where \(D\) is the crystal size of the catalyst, \(\lambda\) the X-ray wavelength, \(\beta\) the full width at half maximum (FWHM) of the diffraction peak (radian), \(k\) is a coefficient (0.89) and \(\theta\) 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).](image)

*Figure 2a* XRD pattern Anatase phase which have intensity at peak (101), (004), (200), (105) and (211).
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 phase TEM 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 °C) and (900°C) respectively agreed with Kheimrutai 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 TiO₂ nanoparticles, (a) anatase and (b) rutile phase after laser ablation treating, respectively.

Figure (5a) SEM micrographs showing morphologies of TiO₂ 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 20 = 25.38° with particle size 15 nm calculated by Scherrer equation for anatase phase and with sharp peak at 20 = 27.5° 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.

Acknowledgments

The authors would like to thank the University of Technology, Nanotechnology and Advanced Materials Research Center (Iraq) for helping to work on a part of the experimental section and characterization measurements. In addition, Zainab N. Jameel greatly thanks the University of Missouri-Columbia / Department of Electrical and Computer Engineering for the opportunity to perform most of the measurements.
References


