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The Synthesis of Titania Nanoparticles by Pulsed Laser Ablation Method

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Abstract
Titania nanoparticles have recently attracted much attention due to their pronounced effects on optical and electronic properties. In this work, titania nanoparticles were synthesized by pulsed laser ablation method with the immersion of metal titania in liquid media using neodymium-doped yttrium aluminium garnet (Nd:YAG) laser. Four different parameters which were the time of ablation process, frequencies of laser, focus points of laser, and input energy of laser were studied to find the optimum condition to synthesize the preferred titania nanoparticles. Afterward, titania nanoparticles were characterized by transmission electron microscopy (TEM), field emission scanning electron microscope (FESEM) coupled with energy dispersive X-ray (EDX) spectroscopy and Fourier transform infrared (FTIR) spectroscopy. The results showed that the optimum condition to synthesize titania nanoparticle was at 30 minutes for ablation time, 1 Hz for the frequency of laser; on the focus point of the laser, and 900 V for the input energy of the laser. FESEM image showed that titania nanoparticles were spherical in shape with no agglomeration and uniform distribution. The TEM image proved that the titania nanoparticles were in the size range of 30-200 nm. The EDX results confirmed the presence of high percentages of titanium and oxygen. The FTIR spectra showed the presence of hydroxyl group, Ti–O vibration, and C–C stretching. It is proven that simple laser ablation of titanium metal plates with a certain set of parameters successfully synthesized uniform spherical titania nanoparticles.
Keywords: Neodymium-doped yttrium aluminium garnet; Laser ablation in liquid; Spherical titania; Optimum parameters

1. Introduction

Titania, also known as titanium(IV) oxide, is the naturally occurring oxide of titanium (K. Palanivelu et al., 2007). Rutile (tetragonal), anatase (tetragonal), and brookite (orthorhombic) are the main crystallographic phases of titania (M.S.P. Francisco & V.R. Mastelaro, 2002). Photocatalysis, photoelectric conversion in solar cells, antimicrobial coating or gas sensors, and food colouring are among the well-known applications of titania (S. Mahshid et al., 2009). Titania nanoparticles have recently attracted much attention due to their pronounced effects on optical and electronic properties. There are several methods to synthesize titania nanoparticles such as hydrothermal, sol-gel, direct oxidation, and pulsed laser ablation methods (M.M. Byranvand et al., 2013). Pulsed laser ablation is a process in which the laser beam is focused on the sample surface to remove material from the irradiated zone (B. Rethfeld et al., 2017). Laser ablation of solid in liquid media has been developed as a promising method for producing nanoparticles due to the advantages such as the ability to obtain high purity nanoparticles, economical, green methodology that avoids the use of chemicals reagents and reactions, not to mention the ability to rapidly synthesize nanoparticles for a large variety of materials (M. Boutinguiza et al., 2013).

Pulsed laser ablation of solid in a liquid is applicable for industrial purposes because of the high ablation rate and the limited poly-dispersion (C. L. Sajti et al., 2010; D. Werner et al., 2012; A. Pyatenko et al., 2016). However, there are some controversial issues concerning the ablation of titanium targets

in water since some authors claimed that the ablation process resulted in the formation of metallic titanium nanoparticles (N. G. Semaltianos et al., 2010) while others obtained TiO_x particles (C. N. Huang et al., 2010) or a mixture of amorphous and crystalline phases (M. Boutinguiza et al., 2013). Apparently, the experimental set up and the details of the ablation process have a strong impact to the properties of the nanoparticles.

Hence, in this work, the optimum condition parameters for the ablation process to obtain the preferred titania nanoparticles were studied in detail. The parameters included are the duration of ablation, frequencies of the laser, the height of the laser's focus point, and the input energy of the laser. The chemical composition of the nanoparticles was investigated by energy dispersive X-ray (EDX) spectroscopy and Fourier transform infrared (FTIR) spectroscopy, while the morphology and the particle size of the nanoparticles were characterized by the field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM).

2. Materials and methods

2.1 Preparation of titanium metal plate

Titanium in the form of a metal plate (purchased from Proceil Enterprise in Skudai, Johor) with a thickness of 5 mm, length of 150 mm, and width of 150 mm was used as the main material in this study. The titanium metal plate was cut into smaller pieces by using an angle grinder (GWS 060, Bosch) in the dimensions of 20 x 20 mm. The top layer of the titanium target was removed by grinding and polishing with sandpaper. The titanium metal plates were then washed with acetone (99.8%, ACROS Organic™) using an ultrasonic cleaner by immersing them into a beaker containing acetone so the dirt and other contaminants could be removed. After washing, the titanium metal plates were left to dry.

2.2 Pulsed laser ablation of titanium metal plate with different time durations

The ultrasonically cleaned titanium metal plate was fixed inside the cuvette at its base and then filled with distilled water such that the thickness of the water film above the target was 5 mm. Then, the target was irradiated with the Nd:YAG laser (Bransonic 221) from the top perpendicular to the plane of the target. The titanium metal plate was ablated for 15 minutes. After the ablation, the sample was centrifuged and dried in an oven at 100 °C overnight. These procedures were repeated for 30 and 45 minutes of laser ablation.

2.3 Pulsed laser ablation of titanium metal plate with different frequencies of laser

The ultrasonically cleaned titanium metal plate was fixed inside the cuvette at its base. Then, the cuvette was filled with distilled water such that the thickness of the water film above the target was 5 mm. The target was irradiated with the laser from the top perpendicular to the plane of the target at the optimum duration using a 1 Hz frequency of the laser. After the ablation, the sample was centrifuged and dried in an oven at 100 °C overnight. These procedures were repeated using a 10 Hz frequency laser.

2.4 Pulsed laser ablation of titanium metal plate with different heights of the focus point of laser

The ultrasonically cleaned titanium metal plate was fixed inside the test cuvette at its base. Then, the cuvette was filled with distilled water such that the thickness of the water film above the target was 5 mm. The target was irradiated with the laser from the top perpendicular to the plane of the target at the optimum duration and frequency of the laser on the focus point of the laser. After the ablation, the sample was centrifuged and dried in an oven at 100 °C overnight. These procedures were repeated for 100 cm below the focus point of the laser.

2.5 Pulsed laser ablation of titanium metal plate with different input energies of laser

The ultrasonically cleaned titanium metal plate was fixed inside the cuvette at its base. Then, the cuvette was filled with distilled water such that the thickness of the water film above the target was 5 mm. The optimum duration and frequency of the laser were used throughout this experiment. The target was irradiated with the laser from the top perpendicular to the plane of the target on the focus point at 700 V input energy of the laser. After the ablation, the sample was centrifuged and dried in an oven overnight at 100 °C. These procedures were repeated using 800 and 900 V input energies of the laser.

2.6 Characterization

The physicochemical properties of the synthesized titania nanoparticles were characterized using field emission scanning electron microscopy (FESEM) coupled with energy dispersive X-ray (EDX) spectroscopy, transmission electron microscopy (TEM) and Fourier-transform infrared (FTIR) spectroscopy. Prior to the characterization, the samples were centrifuged and dried in an oven overnight at the temperature of 100 °C. Although some bogus effects can arise during and after the drying due to the particle-particle and particle-surface interactions, the morphology and size of the nanoparticles are expected not to be influenced by these effects (M. Zimbone et al., 2015).

The morphology as well as the composition were described by the FESEM coupled with EDX using a Hitachi SU8020 unit. The samples were mounted over stubs using double-sided tapes and then coated with a layer of platinum. The stubs were placed in the field emission scanning electron microscope and vacuumed under a pressure of 5 bar. All the scanned images were made with the magnification of 60000 times and 5.0 kV of scanning voltage.

The FTIR spectra of the synthesized titania nanoparticles were recorded using a Perkin Elmer Spectrum 100 Fourier Transformation Infrared Spectrometer. The KBr technique was used for the sample preparation. The sample was mixed with KBr with the ratio of KBr to sample of 100:1. The mixture was ground in the mortar before being mounted and pressed with 8 tons of pressure for 4 minutes to form a transparent pellet with a diameter of 13 cm. The sample pellet was then put in the sample holder and the spectrum was recorded from the infrared range of 400 to 4000 cm-1 at room temperature.

TEM images were taken on a Hitachi HT7700 transmission electron microscope. The samples for TEM analysis were immediately prepared after ablation to reduce the agglomeration effects. The samples were carefully prepared by pipetting a few drops of the ablated suspension on the carbon-coated copper grid. The prepared samples were then left to dry for 24 hours in a desiccator.

3. Results and discussion

3.1 Laser ablation with different time durations

In this study, the titania nanoparticles were synthesized using pulsed laser ablation in liquid media with different time durations, which were 15, 30 and 45 minutes. Fig. 1 shows the observation of the volume of the solution and the colour change. When the titanium metal immersed in the water was irradiated with the laser, the volume and colour of the solution changed because of the formation of small titania nanoparticles (A. Pérez del Pino et al., 2004). At the ablation time of 15 minutes, the solution was light blue-greyish in colour (Fig. 1a). The volume of the solution was not much changed because more time was needed to ablate the titanium metal plate to produce titania nanoparticles. For 30 minutes, the colourless solution turned into a darker blue-greyish colour, and the volume was much higher than that of 15 minutes. Meanwhile, the titania nanoparticles synthesized for 45 minutes changed the solution from colourless to blue-greyish colour. However, the volume of the titania nanoparticles obtained was lower than that of 30 minutes although the ablation time is prolonged. This result is in agreement with Baladi and Mamoory that reported the ablation rate decreases if the ablation duration is longer (A. Baladi et al., 2010). With the increase of the ablation time, the finer titania nanoparticles with narrower size distribution were obtained. However, when the nanoparticles produced in the colloidal solution achieved the maximum concentration, they blocked the pathway of the laser beam from hitting the titanium metal plate to produce more titania nanoparticles. Therefore, it is no use to prolong the ablation time as the laser energy will only be absorbed by the formerly synthesized nanoparticles. In this study, the optimum ablation time of the titanium metal plate was set to 30 minutes.

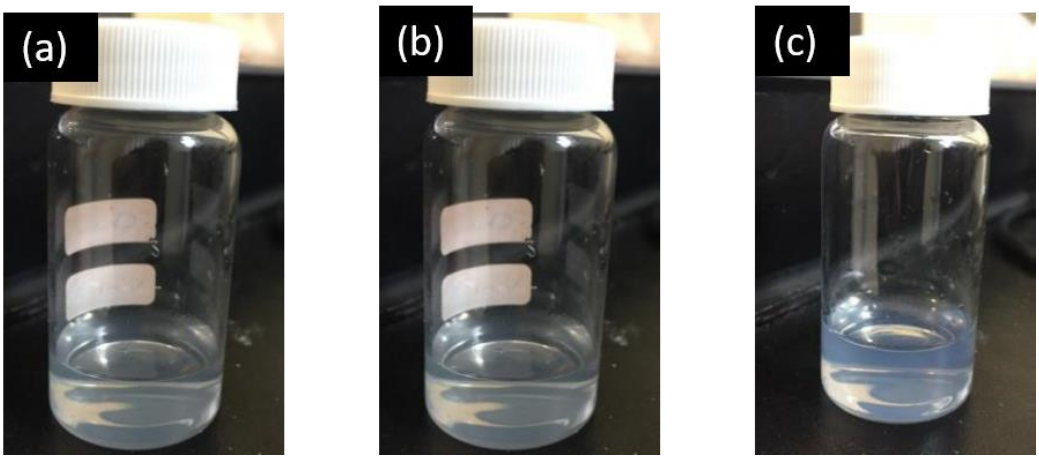

Figure 1 Titania nanoparticles synthesized using laser ablation with different durations; (a) 15 minutes, (b) 30 minutes, and (c) 45 minutes.

3.2 Laser ablation with different frequencies of laser

The titania nanoparticles were synthesized with the 30-minute optimum ablation time but at different frequencies of the laser. Fig. 2 shows the colour change when the titanium metal plate ablated by the laser in 1 and 10 Hz. When the titanium metal plate was ablated at 1 Hz for 30 minutes, the colourless solution turned into blue-greyish colour. However, when 10 Hz was used, the solution remained unchanged because there was no dispersion of titania nanoparticles inside the solution. Chen et al. reported that the change in the colour of the solution resulted from the dispersion of the titania nanoparticles (L. Chen et al., 2014). In this study, the optimum frequency of the laser is 1 Hz because it resulted in the dispersion of titania nanoparticles.

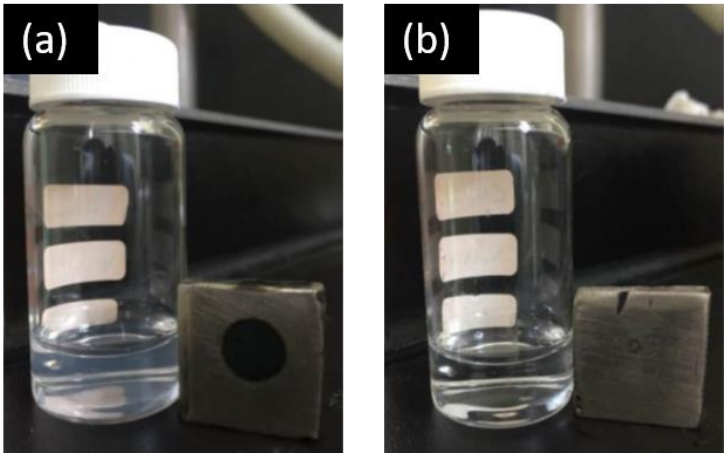

Figure 2 Titania nanoparticles synthesized using laser ablation with different frequencies of laser; (a) 1 Hz and (b) 10 Hz.

3.3 Laser ablation with different heights of the focus point of laser

The titania nanoparticles were synthesized based on the optimum ablation time and optimum frequency of the laser but with different heights of the focus point of laser. Fig. 3 shows the colour change for laser ablation of titanium metal plate on the focus point and 100 cm below the focus point. The colourless solution turned into blue-greyish colour when the titanium metal plate was ablated on the focus point of the laser. However, there was no change in colour of the solution when the titanium metal plate was ablated 100 cm below the focus point of the laser because the laser energy that reached the titanium metal target was reduced (H. Imam et al., 2103). Thus, in this study, the optimum height of the laser is on the focus point.

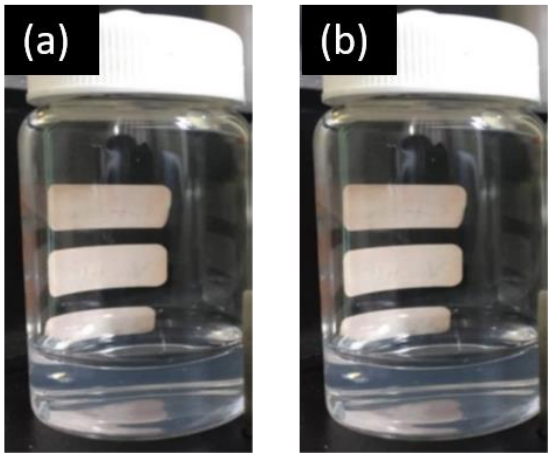

Figure 3 Titania nanoparticles synthesized using laser ablation with different heights of the focus point of laser; (a) on focus point, and (b) 100 cm below focus point.

3.4 Chemical composition

The successful synthesis of the titania particles and the distribution of the elements present in the synthesized titania was proven by EDX analysis. Table 1 shows the atomic composition of elements present in the synthesized titania nanoparticles that were ablated with different input energies of lasers. All of the samples show Ti species as the highest percentage compared to other elements. The presence of Ti and O confirmed that the titania nanoparticles were successfully obtained in the form of titanium oxide. The presence of other elements such as carbon (C), silicon (Si), aluminium (Al), and calcium (Ca) at low percentages was due to the impurities of the cuvette as there is a chance of the laser beam hitting the cuvette.

Table 1 The atomic composition of elements present in the titania nanoparticles synthesized in different input energies of the laser.

Laser Ablation with Different Input Energies of Laser	Atomic Ratio (%)					
	Ti	O	C	Si	Ca	Al
700 V	56.0	41.1	2.2	0.3	0.2	0.2
800 V	61.1	35.8	2.9	0.2	-	-
900 V	63.5	31.7	4.0	0.4	0.4	-

Fig. 4 shows the FTIR spectra of the titania nanoparticles that were ablated using different input energies of the laser. The spectra showed a similar pattern although the laser input energy is different. The intense peaks at about 3450 cm^{-1} wavelengths were ascribed to the stretching vibration of hydroxyl groups (A. Leon et al., 2017,). Meanwhile, the sharp peaks observed at about 1630 cm^{-1} were attributed to C–C stretching. The broad peaks observed at 600 to 400 cm^{-1} corresponded to the Ti–O vibration (M. Khan et al., 2015).

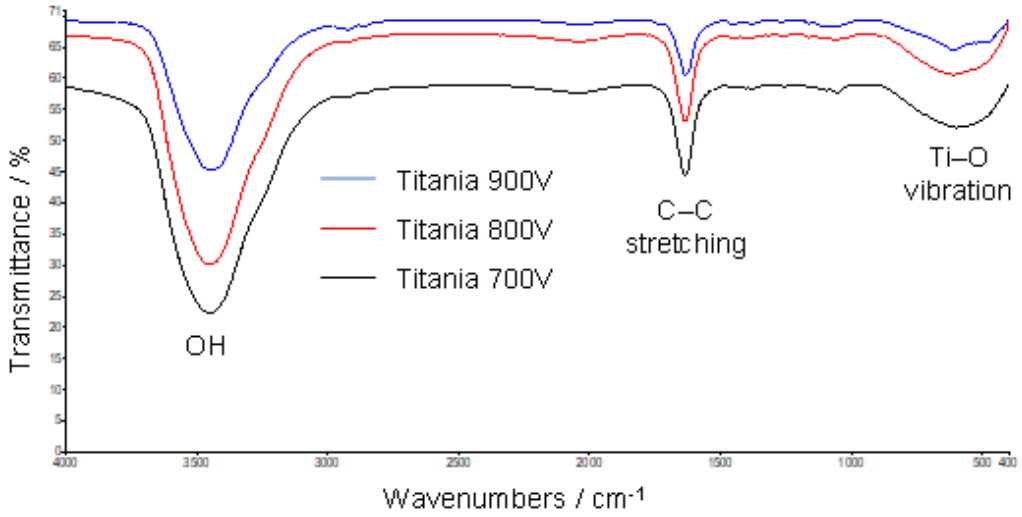

Figure 4 FTIR spectra of the titania nanoparticles ablated with 700 V, 800 V, and 900 V input energies of the laser.

3.5 Morphology and particle size

The morphology and the particle size of the synthesized titania nanoparticle were characterized by the FESEM and TEM. Fig. 5 (a) shows the TEM image of titania nanoparticles that were synthesized with 900 V of laser input energy while Fig. 5 (b-d) shows the FESEM images of titania nanoparticles with different input energies of laser which were 700, 800 and 900 V. From the FESEM image of 700 V laser input energy (Fig. 5 (b)), the titania nanoparticles obtained were spherical in shape with the size range of 70 - 150 nm. However, very few titania nanoparticles can be detected. Meanwhile, Fig. 5 (c) shows the FESEM image of the titania nanoparticle with 800 V of laser input energy. The titania nanoparticles are also spherical in shape but with a size range of 70 - 200 nm. On the other hand, Fig. 5 (d) shows the FESEM image (c) titania nanoparticle with 900 V of input energy. The titania nanoparticles were spherically shaped with a size range of 40 - 120 nm. The sizes of the particles are different as the laser coverage did not equally hit the titanium metal plate. Laser ablation of titanium metal plate with 900 V input energy of laser was chosen as the best energy as it gave the smallest particle size range and the most uniform distribution of titania nanoparticles in comparison to the other two input energies of the laser. The morphology and the size of the titania nanoparticle of 900 V laser input energy shown by the FESEM image in Fig. 5 (d) were further emphasized by the TEM image. The TEM image in Fig. 5 (a) shows that the synthesized titania was spherical with a diameter range from 30 - 200 nm.

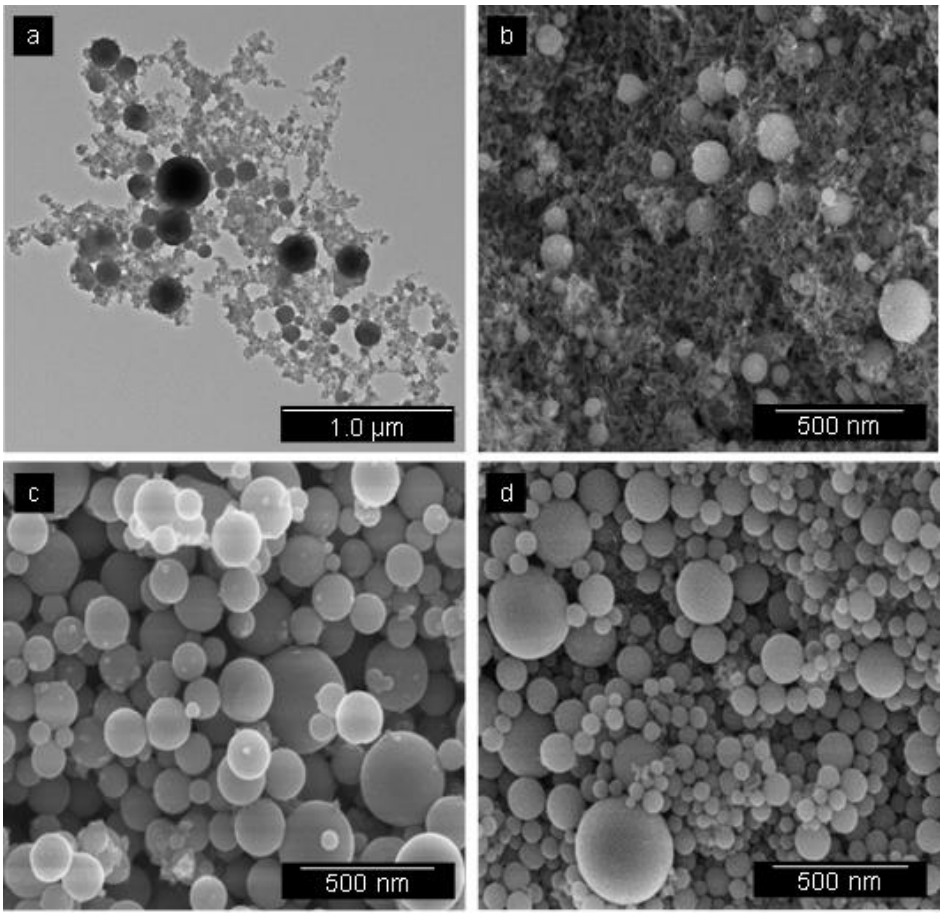

Figure 5 (a) TEM image of titania nanoparticles ablated in 900 V of input energy of laser and FESEM images of (b) 700 V, (c) 800 V, and (d) 900 V of input energy.

4. Conclusion

In order to get the preferred spherical nanoparticle titania, the pulsed laser ablation method should be set to certain parameters. In this work, the optimum condition of the parameters was set as 30 minutes of ablation time, 1 Hz of laser frequency, on the focus point for the height of the focus point laser, and 900 V of laser input energy. The synthesized titania was in the nanosize range and spherical shape, as proven by TEM and FESEM analyses. Furthermore, EDX and FTIR analyses confirmed that the chemical composition of the ablated nanoparticles was titanium oxide. The results showed that with optimum duration, frequency of the laser, height of focus length of laser, and input energy, uniform spherical titania nanoparticles can be synthesized by simple laser ablation of titanium plates. This simple method shows high potential to be utilized in the synthesis of other metal oxides.

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