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Production of TiO_2 Nanoparticles in Different Phases and Shapes by using PLA and Hydrothermal Method

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Abstract
Titanium dioxide was prepared using pulsed laser ablation (PLA) and hydrothermal method. Scanning electron microscopy images showed that the product from hydrothermal method had a nanotube shape, whereas those from PLA in liquid were nanoparticles. The optical properties in the absorption curve of product from the hydrothermal method were slightly greater than those from the PLA method, and the energy gaps were 3.39 and 3.26 eV for the hydrothermal method and PLA, respectively. XRD results showed that the TiO_2 prepared through PLA showed one phase (rutile), whereas those prepared through hydrothermal method showed two phases (anatase and rutile). Moreover, the product from hydrothermal method had smaller particle size smaller than that from PLA. Furthermore, the product yield and the required reaction time of the hydrothermal method were higher than those of PLA.

Keywords: Nanoparticle, nanorods, Titanium dioxide, PLA, Hydrothermal

الخلاصة

في هذا البحث تم تحضير مادة اوكسيد التيتانيوم بطريقة القشط بالليزر النبظي وطريقة الهايدروثيرمال. اظهرت صور المجهر الالكتروني الماسح بان التشكيل المتكون على السطح بطريقة الهايدروثيرمال هي اشكال انابيب دقيقه ولكن الاشكال الظاهرة بطريقة القشط بالليزر هي اشكال كرويه.
الخصائص البصريه اظهرت من خلال منحني الامتصاص بان الامتصاصيه بطريقة الهايدروثيرمال هي اكبر بقليل من الامتصاص الناتج بطريقة القشط بالليزر وان فجوة الطاقه كانت (3.26 eV 3.39- eV) للنماذج المحضره بطريقة الهايدروثيرمال والليزر على التوالي. نتائج حيود الاشعه السينيه اظهرت بان ثنائي اوكسيد التيتانيوم الناتج بطريقة الليزر كان بطور واحد هو الروتايل بينما كان بطورين هما (الروتايل والاناتاس) بطريقة الهايدروثيرمال اضافة الى ذلك فان حجم الجسيمات الناتجه بواسطة الهايدروثيرمال كان اصغر من حجم الجسيمات الناتجه بطريقة الليزر وكذلك الزمن المطلوب لاتمام التفاعل بطريقة الهايدروثيرمال يكون اطول من الزمن اللازم بطريقة الليزر.

Introduction
Titanium dioxide (Titania, TiO_2) is one of the most important metal oxide semiconductors [1]. Crystalline of the TiO_2 mainly exists in three types: anatase (tetragonal), rutile (tetragonal), and brookite (orthorhombic) [2]. The TiO_2 nanorods without the seed layers are grown in the crystal orientations [101] and [002] [3]. TiO_2 has been applied in different applications, for example in the decomposition of the pollutants, photocatalysis, water splitting, biosensing, and the quantum dot solar cells [4][5]. Nanomaterials received big interest because of their unique characteristics of that renders them different from the bulk materials [6]. Laser ablation of the solid targets in the liquid has attracted attention for a last decade because of its potential to produce small, monodispersed nanoparticles with complex compositions [7]. Pulsed laser ablation (PLA) is process of ablating material from a target surface by using irradiation with ultra-short laser to form the high temperature plasma [8]. Nanotechnology deals with the nanoparticles production, particularly synthesis and processing of metals, metal carbides, semiconductors, and metal oxides [9]. Hydrothermal method is an environment-friendly and powerful technique for the preparation of the high-purity, a high-crystalline, ultra-fine and high homogeneous powder of various oxide components (single or multi-component) [10][11].

Materisls and Methodologies

TiO_2 nanoparticles were produced by PLA in deionized water (DI) with a pulse number of 2000 by using Nd:YAG laser (wavelength = 532 nm) operating at a voltage of 900 V and a frequency of 1 Hz. The laser beam was vertically directed on the target surface. The experimental set-up of liquid phase PLA consists of a laser, focusing lens, a target, and DI. The advantage of PLA in liquid is that this method does not require a vacuum environment and thus is relatively cheap to perform.

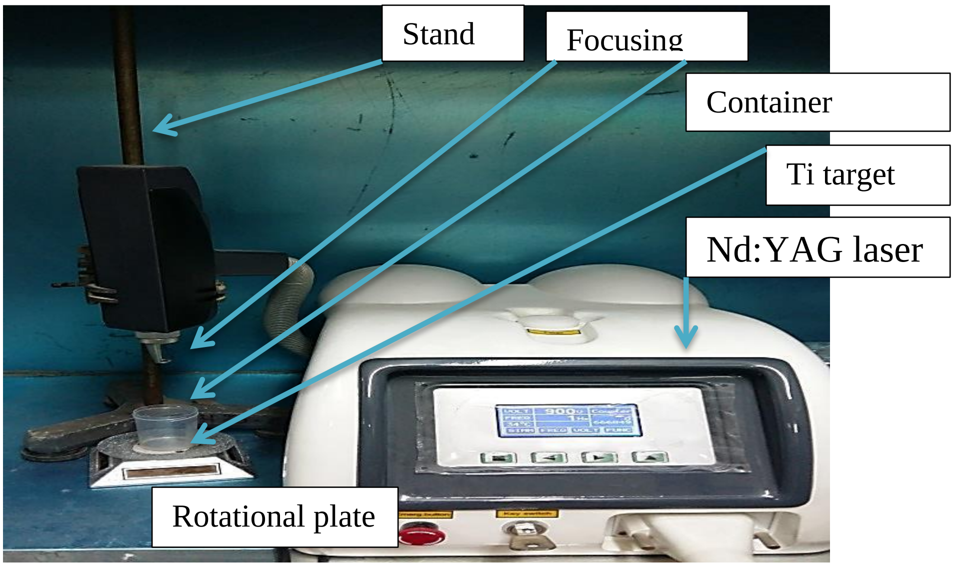

Figure 1: Basic experimental set-up of pulsed laser ablation (PLA) in liquid.

In the second approach, the hydrothermal method is use; the products were synthesized by mixing hydrochloric acid (4mL) and DI (10mL) and placing the mixture in a Teflon-lined hydrothermal synthesis autoclave reactor with continuous stirring for 15min. A specific amount of titanium isopropoxide (97%, Sigma-Aldrich) was drop-wise added in the solution with continuous stirring for 15min at a temperature of 150°C and residence time of 3.5h to produce TiO_2 powder. After completing the hydrothermal residence time, the powder was removed from the cells, rinsed with DI through centrifugation, and dried at room temperature to produce pure powder through drop casting deposition on the substrates. X-ray diffraction (XRD) characteristics and optical properties were subsequently studied.

Results and discussion

Figure 2 presents the XRD characteristics of the particles produced by both PLA and hydrothermal method. Variation in the intensity and position of full width at half maximum depends on the preparation method. According to Scherrer equation [11], the crystal sizes of the samples prepared by PLA and hydrothermal method were 26.5 and 4.6 nm, respectively. XRD analysis indicates that the film prepared by PLA appeared as only one phase (rutile), whereas the file prepared by hydrothermal method showed two phases (anatase and rutile). The product yield and the required reaction time of the hydrothermal method are higher than those of PLA.

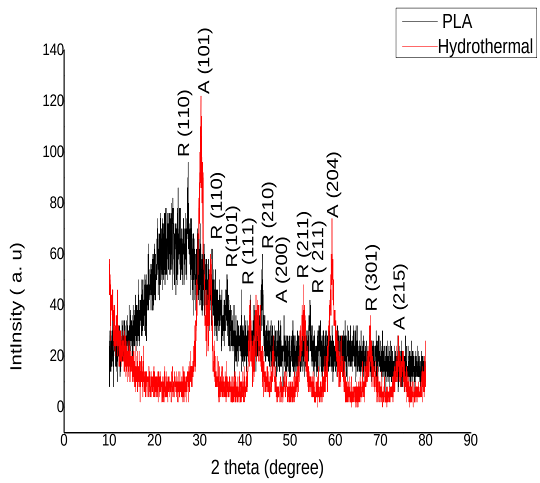

Figure 2: XRD patterns of TiO_2 nanoparticles prepared by different methods.

Figure 3 illustrates the effect of the preparation method on the structure of nanoTiO_2. Both methods produced nanostructured materials but with different particle shapes. PLA produced nanoparticles, whereas hydrothermal method produced nanorods or cluster rods due to the effect of pressure and temperature inside the hydrothermal cells. This confinement effect acts in two dimensions and produces nanorods.

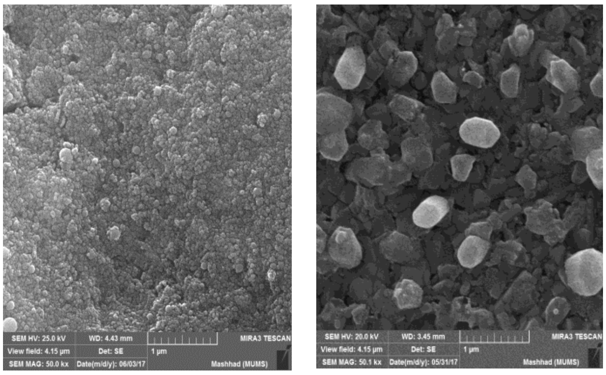

Figure 3: SEM images of TiO_2 nanoparticles (A) prepared by PLA and (B) hydrothermal method.

Figure 4 shows the absorption curve of films prepared by both PLA and hydrothermal method. The absorption peak of the sample synthesized by hydrothermal method is lower than that by PLA. This phenomenon occurred because quantum confinement greatly affects the particles produced by the hydrothermal method. Based on the wavelength cut-off and absorption edge, the energy gaps of TiO_2 were 3.26 and 3.39eV for the samples synthesized by PLA and hydrothermal method respectively. The blue shift in energy gap is due to the different crystal sizes caused by the confinement effect. All material properties depend on the electron distribution on the energy levels.

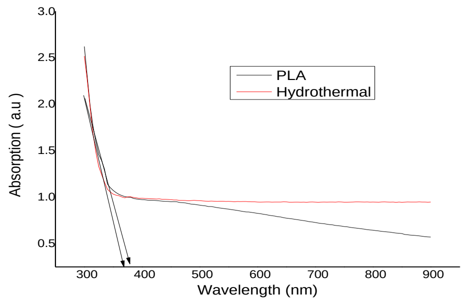

Figure 4: Absorption edge from the relationship between the absorption curve and wavelength.

Conclusion

PLA is affected by laser wavelength, frequency, and power, whereas hydrothermal method depends on process time, pressure, and temperature of the hydrothermal cells. The use of hydrothermal method produces nanorods, whereas the use of PLA produces nanoparticles. The shape and structure of the product strongly depend on the preparation conditions, shape, and size. Controlling the preparation conditions is possible in hydrothermal method but difficult in PLA. In both methods, the prepared films are polycrystalline and exist in two phases (anatase and rutile). The product from the PLA method has larger crystal size than that from the hydrothermal method. Absorption is dependent on crystal size and energy band gap. When the band gap increases, the transmittance also increases, and the grain size subsequently decreases. All these phenomena are caused by the quantum confinement. This process does not involve any chemical for the synthesis of nanoparticles and is environment-friendly because no hazardous and toxic gases are emitted.

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