Applied Surface Science 405 (2017) 183–194

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Effects of ablation energy and post-irradiation on the structure and properties of titanium dioxide nanomaterials

G. García Guillén [a], S. Shaji [a,b,*], M. I. Mendivil Palma [c], D. Avellaneda [a], G.A. Castillo [a], T.K. Das Roy [a], D.I. García Gutiérrez [a,b], B. Krishnan [a,b]

[a] Universidad Autónoma de Nuevo León, Facultad de Ingeniería Mecánica y Eléctrica, San Nicolás de los Garza, Nuevo León 66455, México
[b] Universidad Autónoma de Nuevo León-CIIDIT, Apodaca, Nuevo León, México
[c] Centro de Investigación en Materiales Avanzados (CIMAV), Unidad Monterrey, PIIT, Apodaca, Nuevo León, México

A R T I C L E I N F O

Article history:
Received 25 August 2016
Received in revised form 14 January 2017
Accepted 26 January 2017
Available online 3 February 2017

Keywords:
Pulsed laser ablation in liquid
Titanium dioxide
Nanomaterials
TEM
XPS
Optical and luminescence properties

A B S T R A C T

Nanomaterials of titanium oxide were prepared by pulsed laser ablation of a titanium metal target in distilled water. The ablation was performed at different laser energy (fluence) using a nanosecond pulsed Nd:YAG laser output of 1064 and 532 nm. A post-irradiation of titanium oxide nanocolloids obtained by ablation using 532 nm was carried out to explore its effects on the structure and properties. Analysis of morphology, crystalline phase, elemental composition, chemical state, optical and luminescent properties were performed using Transmission Electron Microscopy (TEM), X-Ray Diffraction (XRD), X-Ray Photoelectron Spectroscopy (XPS), UV–-vis absorption spectroscopy and room temperature photoluminescence spectroscopy. It was found that titanium oxide nanomaterial morphologies and optical properties were determined by ablation wavelength and fluence. Further, nanocolloids prepared by 532 nm ablation showed a crystalline phase change by laser post-irradiation. The results showed that pulsed laser ablation in liquid as well as post-irradiation were effective in modifying the final structure and properties of titanium oxide nanocolloids.

1. Introduction

Titanium dioxide (TiO_2) is a wide band gap semiconductor that commonly exists in rutile (bandgap 3.0 eV) and anatase (band gap 3.2 eV) phases. It has been extensively studied for photocatalytic, hydrophilic, chemical stability properties and for a variety of applications such as in dye-sensitized solar cells, water/air purifier, environmental photo-catalyst, optoelectronic devices and gas-sensors [1–4]. Various chemical preparation methods to synthesize nanostructured titanium dioxide were reported, such as sol–gel [5,6], hydrothermal [7], micro-emulsion [8] and solvothermal method [9]. However, recent studies on pulsed laser ablation in liquid media (PLALM), an environmental friendly process for the fabrication of nanomaterials, have demonstrated as a promising technique for synthesis of chemically pure nanoparticles in solution [10–12]. Several research groups reported the synthesis of crystalline titanium dioxide nanoparticles by different conditions applied in PLALM, such as the use of different liquid media, laser beam focusing conditions and changing the laser parameters (laser wavelength, energy and pulse duration). Nath et al. [13,14] synthesized titanium dioxide nanoparticles with different particle size distributions and phases by changing the focusing conditions of the pulsed laser. Spherical TiO_2 nanoparticles were produced by pulsed laser ablation of a titanium target in various liquid environments such as water, ethanol, 2-propanol, n-hexane [15], and at different concentrations of sodium n-dodecyl sulfate (SDS) [16,17]. Preparation of titanium dioxide nanoparticles with different morphologies and crystalline phases via pulsed laser ablation of a titanium target in water was done by varying the laser fluence [18–20] or the pulse width [21,22]. Also, TiO_2 raw particles dispersed in liquid media were irradiated by a nanosecond pulsed laser [23]. In the present work, we report synthesis of titanium dioxide nanoparticles with different morphology, size and optical properties by varying the laser ablation wavelength and fluence. Also, the effects of post-irradiation on TiO_2 nanocolloids obtained at different fluence of 532 nm ablation are included. Post-irradiation of the titanium oxide nanomaterials produced by PLALM resulted in morphological and structural changes that are reported for the first time.

* Corresponding author at: Universidad Autónoma de Nuevo León, Facultad de Ingeniería Mecánica y Eléctrica, San Nicolás de los Garza, Nuevo León, 66455, México. Tel.: +52 18114920380.
E-mail addresses: sshajis@yahoo.com, sadasivan.shaji@uanl.edu.mx (S. Shaji).

http://dx.doi.org/10.1016/j.apsusc.2017.01.282

2. Experimental

The ablation experiments were performed using the fundamental (λ = 1064 nm) and the second harmonic (λ = 532 nm) of a high power Q-switched Nd:YAG laser system (Model LQ929, Solar Laser Systems) operated at 10 Hz with a pulse width of 10 ns. A laser energy meter (Model PM100D, Thorlabs Inc.) was used to monitor the output energy of the 1064 and 532 nm laser beams; they were 300 and 230 mJ per pulse, respectively.

2.1. Pulsed laser ablation of titanium (Ti) metal

High purity titanium rod (99.99% in purity) was used as the target for the laser ablation. The target was placed at the bottom of a glass vessel filled with 15 ml of distilled water. Laser output (532 or 1064 nm) was focused using a convex lens of focal length 20 cm. In the ablation setup, the distance between the lens and target was varied to obtain different ablation energy (fluence). For the 1064 nm output ablation, the estimated fluence values were 4.7, 8.7, 20.4 and 45.9 J/cm^2. For laser ablation using 532 nm, the estimated fluence were 2.8, 6.0, 19.4 and 27.6 J/cm^2 respectively. Ablation time was 5 min for all the experiments. After the ablation experiment, distilled water turned into a turbid solution due to the presence of nanoparticles.

2.2. Laser post-irradiation of titanium nanocolloids

The colloidal solutions obtained by pulsed laser ablation of titanium rod in distilled water by 532 nm at different laser fluence were subjected to a laser post-irradiation using the unfocused 532 nm laser beam from the Nd:YAG laser. First, 15 ml of each colloidal solution was irradiated for 10 min and another set of colloids were irradiated for 20 min. The colloidal solutions were stirred continuously during post-irradiation to avoid their agglomeration and precipitation. The laser fluence estimated for post-irradiation was 0.23 J/cm^2. For the nanocolloids, 532 nm has better absorption than the fundamental (1064 nm). So 532 nm output was chosen for post irradiation. The absorption coefficient of the TiO_2 nanocolloids at 532 nm was 0.22 cm^{-1}. The nanocolloid used for post-irradiation (15 ml) was 1.2 cm thick.

2.3. Material characterization

Drops of all the colloidal solutions prepared at different ablation conditions were dried separately on carbon-copper grids to characterize their morphology, size and structure using Transmission Electron Microscopy (TEM, Model FEI Titan G2 80-300). Calibration for the TEM is done using a standard Silicon sample. All the samples were dried on conducting copper tapes to perform X-ray photoelectron spectroscopy (XPS) analysis (Thermo Scientific Inc. Model K-Alpha). This analysis was done with a monochromatized Al Kα radiation (E = 1486.68 eV). A fraction of the colloidal solution was centrifuged and dried on a glass substrate to characterize its structure by X-ray diffraction (XRD) using a diffractometer employing Cu Kα1 radiation (λ = 1.5406 Å, Bruker D8 Advance) at normal mode. The scan range (2θ) was 10°–70°. The nanocolloids were subjected to UV–vis absorption analysis using a UV–vis dual beam Spectrophotometer (Shimadzu UV-1800) in the wavelength range of 300–1000 nm. The colloidal solution was taken in a quartz cuvette with 1 cm path length and the reference liquid (distilled water) also. Photoluminescence (PL) spectra of all these nanocolloids were measured using a Fluorescence Spectrometer (LS 55 Perkin Elmer). The results on morphology, structure, chemical composition, optical and luminescence properties of these titanium oxide nanomaterials obtained by pulsed laser ablation at different laser ablation conditions were analyzed.

3. Results and discussion

3.1. Morphology and structure by TEM analysis

TEM analysis was carried out to study the morphology, size and structure of the ablation products. Figs. 1–5 show the TEM images, size distribution of spherical nanoparticles as well as selected area electron diffraction (SAED) analysis of these titanium oxide nanomaterials obtained for different ablation conditions. Size of the nanoparticles was measured using Gatan Microscopy Suite software and the Digital Micrograph for Transmission Electron Microscopy image analysis. For each sample, five TEM images were selected and the diameters of the spherical nanoparticles only were measured using the LineROI tool for length measurement. Then, all nanoparticles diameter data were analyzed in OriginPro 8 software and their frequency counts were made by the statistics tool. The average size and standard deviation for nanoparticles were analyzed by descriptive statistics tool considering the size range of 1–40 nm. The presence of agglomerated tiny particles might have affected the average size evaluated. Average size and size distribution of these nanoparticles are evaluated from different TEM images collected from the same sample grid. Nanomaterials with different morphologies are obtained for the colloids prepared by laser ablation with 1064 nm for different fluence (Fig. 1). Spherical nanoparticles are obtained for the ablation of titanium rod at a fluence of 4.7 J/cm^2 as observed in Fig. 1a. These nanoparticles are agglomerated and their selected area electron diffraction (SAED) pattern in Fig. 1b is indexed for TiO_2 rutile crystalline phase (PDF No. 04-008-7645). Their size distribution histogram is included as inset in Fig. 1a, with an average size of 13 ± 7.2 nm. As the laser fluence is changed to 8.7 J/cm^2, needle-shaped nanostructures with a few spherical nanoparticles are formed, as in Fig. 1c. The rings of electron diffraction points of the needle-shaped nanostructures (Fig. 1d) correspond to the crystalline planes of TiO_2 anatase phase (PDF No. 04-007-0701). When the laser fluence of ablation is increased to 20.4 J/cm^2, needle shaped nanostructures as well as spherical nanoparticles (Fig. 1e) are formed. The SAED rings of these nanostructures (Fig. 1f) are indexed and the interplanar distances measured are in agreement with the (101), (112), (200), (105), (116) and (204) diffraction planes of TiO_2 anatase phase. The average size of those spherical nanoparticles observed in Fig. 1e (20.4 J/cm^2) is 19 ± 7.3 nm. As the fluence is increased to 45.9 J/cm^2, needle shaped nanostructures disappeared and only spherical nanoparticles are obtained (Fig. 1g). Those bigger spherical nanoparticles are surrounded by an agglomerated zone of tiny spherical particles as well as some ablated material. In this case, the average size of the spherical nanoparticles estimated is 12 ± 6.4 nm. The electron diffraction of these nanoparticles is indexed to anatase TiO_2 phase as included in Fig. 1h.

The morphology of nanoparticles obtained by pulsed laser ablation using 532 nm laser wavelength consists of mainly spherical nanoparticles (Figs. 2–5). These nanocolloids were also post-irradiated using 532 nm laser output at a fluence of 0.23 J/cm^2 for 10 and 20 min. Fig. 2 shows the morphologies of nanoparticles obtained at fluence of 2.8 J/cm^2 (Fig. 2a) and its post-irradiation of 10 min (Fig. 2c) and 20 min (Fig. 2e). Spherical nanoparticles with average size of 13 ± 6.1 nm are obtained for the ablation at 2.8 J/cm^2 (Fig. 2a) and their SAED pattern indexed is in agreement with rutile TiO_2 phase as shown in Fig. 2b. When these colloids were irradiated for 10 min with unfocused 532 nm laser beam, larger (average size of 17 ± 7.9 nm) agglomerated spherical nanoparticles are obtained (Fig. 2c). Well dispersed spherical nanoparticles with