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Rapid Communication

Preparation of titanium monoxide nanopowder by low-energy wet ball-milling

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ABSTRACT

Titanium monoxide (TiO), which is a versatile ceramic material with a low electrical resistivity and an extreme hardness, has received considerable attention for potential applications in decorative and protective coatings, and in microelectronic layered structures. In this study, a green and simple method to synthesize titanium monoxide (TiO) nanoparticles from commercial TiO micro sized powder through low-energy wet ball-milling is presented. The as-milled TiO powder shows good dispersibility in ethylene glycol, indicating a promising material for solution-based production. During annealing in a vacuum at 900 °C, the as-milled TiO powder transforms from monoclinic to cubic structure. The annealed TiO, in the form of a pellet, shows a very low electrical resistivity (2.1 mΩ cm). When dispersed in ethylene glycol, the annealed TiO powder almost preserves the optical property of the as-milled TiO by presenting a gradual increase in absorption from visible range to near-infrared region. Thus, low-energy wet ball-milling is an environmentally friendly and effective method to synthesize TiO nanopowder for a variety of purposes.

1. Introduction

Titanium monoxide (TiO) is a versatile ceramic material with a low electrical resistivity [1], an extreme hardness of 19.6 GP in the face-centered cubic (FCC) crystal structure [2], and a high melting point [3]. At a stoichiometric composition, atomic vacancies of TiO exist at 15% for both Ti and O in equimolar proportions [4]. TiO film exhibits a golden yellow color [2] and has high efficiency as a diffusion barrier against the interdiffusion of Al and Si [5]. Thus, TiO has received considerable attention for use in decorative and protective coatings [1], and in microelectronic layered structures [5].

Several processing techniques have been used to synthesize TiO particles, including the reduction of TiO_2 with Ti at 1500 °C for 70 h in a vacuum [6], the mechanochemical synthesis from high-energy ball-milling [7], laser pyrolysis [8], and laser ablation [9]. Among them, high-energy ball-milling is an effective method due to a true cubic TiO structure obtained after milling of Ti and TiO_2 powders [7]. However, this method has faced some problems, such as contamination from vials and milling ball debris [7], products containing variable phase composition [10], and thermal problems caused by operating the machine at a high speed. Hence, low-energy wet ball-milling [11], which is carried out at a low speed to mix particles and reduce the particle size of the solid part in suspension, is an alternative means of synthesizing TiO nanoparticles.

Commercial TiO powders contain micron-sized particles [12] and many TiO_x polymorphs [8]. Due to an increasing demand for ultra-fine powders in various applications such as pigments, chemical products, pharmaceutics, and ceramic materials, the reduction of particle dimensions to the nanoscale plays an important role in changing size-dependent properties such as dispersibility and optical or electronical properties [12–16]. Moreover, in our previous study [12], the demonstration of the inkjet-printed TiO layer on polymeric substrate echoes the demands of high-quality starting powders. Therefore, this study aims to synthesize TiO nanopowder from commercial TiO powder by using low-energy wet ball-milling and to control its properties during milling and annealing. The main advantages of using wet ball-milling to produce TiO nanopowder are (i) homogeneous TiO nanoparticles are obtained without any contamination from vials and milling ball debris, (ii) deionized DI water is used as a green solvent for TiO suspension during the milling process, (iii) thermal problems are reduced, and (iv) it is easy to operate the machine.

2. Experiment

The raw TiO powder was purchased from Sigma Aldrich with −325 mesh (<44 μm) in particle size. Pluronic F127

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Table 1
Calculated mean crystallite size, BET surface area, and calculated mean particle size of (a) raw TiO, (b) milled TiO, and (c) annealed TiO powders.

TiO powders	Calculated mean crystallite size (nm) from the Scherrer equation	BET surface area (m^2/g)	Theoretical density (g/cm^3)	Calculated mean particle size D_{BET} (nm)
(a) Raw TiO	20	1.1650	4.91	1049
(b) Milled TiO	8	34.7004	4.91	35
(c) Annealed TiO	25	5.7476	5.795	180

Table 2
Compacted density and electrical resistivity of (a) raw TiO, (b) milled TiO, and (c) annealed TiO pellets.

TiO pellets	Thickness (mm)	Weight (g)	Compacting force (MPa)	Compacted density ($g\ cm^{-3}$)	Electrical resistivity ($m\Omega\ cm$)
(a) Raw TiO	0.850	0.204	6.865	3.057	286.8
(b) Milled TiO	1.116	0.204	6.865	2.329	$>10^3$
(c) Annealed TiO	0.997	0.204	6.865	3.397	2.1

(polyethylene–polypropylene glycol) surfactant was added to DI water, followed by TiO powder, which made up 20 wt.% of the suspension. The suspension was then milled in a shaker mixer (TURBULA-T 2F) using zirconia balls (1 mm in diameter) at a mild rotation speed of 72 rpm for 72 h. The milled suspension was dried to obtain milled TiO powder, and then the milled powder was annealed at 900 °C for 15 min in a vacuum to become annealed TiO powder.

The surface morphology and elemental composition of the powders were characterized by a cold field-emission scanning electron microscope and energy dispersive spectrometer (HITACHI, S-4800, FE-SEM/EDS). The crystal structure of the samples was examined by an X-ray powder diffractometer (BRUKER, D2-Phaser, XRD). The mean crystallite size of the powders was calculated using the Scherrer equation [17], as shown in Table 1. Raman spectra of powders were analyzed using a Raman spectrometer (PROTRUSTECH, UniRAM) to determine phase impurity. A field emission transmission electron microscope (JEOL, JEM-ARM200FTH, FE-TEM) was used to determine the crystal structures of the TiO powders at 200 kV, and to record their selected area diffraction (SAED) patterns by preparing a few drops of the diluted dispersion of powders on a standard C-covered Cu TEM micro grid. The specific surface area of powders was measured and calculated by a high-resolution surface area analyzer (MICROMERITICS, ASAP2020) using the Brunauer–Emmett–Teller (N_2-BET) adsorption method. Assuming that the particles have solid, spherical shape with smooth surface, and uniform size, the mean equivalent particle size D_{BET} can be calculated from the BET surface area by the equation D_{BET} = 6000/(BET surface area in m^2/g) × (density in g/cm^3) (in nm) (Table 1) [18]. The optical absorption spectra of the colloidal suspensions, which were dispersed from raw, milled, and annealed TiO powders in ethylene glycol (EG), were analyzed by a UV–visible spectrophotometer (SHIMADZU, UV-1601). For electrical resistivity measurement, pellets (10 mm in diameter) were compacted from raw and milled TiO powders (without a binder) at the compacting force of 70 $kg\ cm^{-2}$ (6.865 MPa). The milled TiO pellet was annealed in the same condition as the annealed TiO powder. The electrical resistivity of each of the 3 pellets – the raw TiO pellet, the milled TiO pellet, and the milled TiO pellet after annealing – was measured by a four point probe system (JIEHAN, SRS-4000), as shown in Table 2.

3. Results and discussion

Fig. 1 shows the SEM images of raw, milled, and annealed TiO powders. The raw TiO powder (Fig. 1a and b) is large and irregular, and some particles reach dimensions of over 50 μm. After 72 h of milling, the particle size of raw TiO powder is remarkably reduced

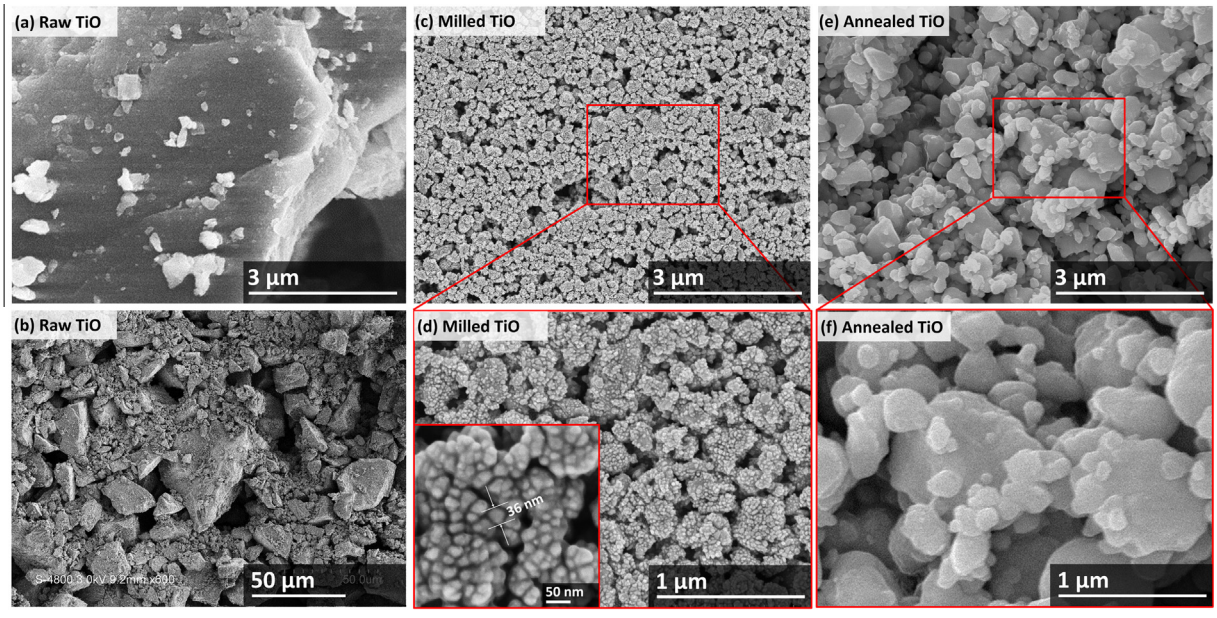

Fig. 1. SEM images shown in low and high magnification of raw TiO powder (a and b), milled TiO powder (c and d), and annealed TiO powder (e and f).