



Full length article

# Anatase TiO<sub>2</sub> powder: Synthesis, characterization and application for photocatalytic degradation of 3, 4-dihydroxy benzoic acid



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## ABSTRACT

White, crystalline TiO<sub>2</sub> powder has been synthesized in a large scale by a single-step chemical reaction between oleic acid and titanium (IV) isopropoxide. The crystal structure of the powder was evaluated by X-ray diffraction and transmission electron microscopy and the BET surface area was estimated by nitrogen adsorption-desorption technique. The structure of TiO<sub>2</sub> strongly depends on the synthesis temperature. The powder synthesized at 400 °C is purely anatase, that prepared at 600 °C is mainly rutile and those synthesized at 450 °C, 500 °C and 550 °C are mixtures of anatase and rutile TiO<sub>2</sub>. The powder synthesized at 450 °C contains 68% anatase and 32% rutile TiO<sub>2</sub> with an effective surface area of 78 m<sup>2</sup> g<sup>-1</sup>. The photocatalytic activity of the above powder has been studied with photodegradation of commercial 3, 4-dihydroxy benzoic acid. The recyclability of the catalyst has been tested after heat treatment of the used TiO<sub>2</sub>.

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## 1. Introduction

The environmental pollution can be effectively curbed by detoxification and degradation of harmful organic compounds in both aqueous and gaseous media. Photocatalysis with the help of semiconductor nanoparticles is considered to be one of the robust techniques for mineralization and removal of major environmental pollutants. Oxide semiconductors such as TiO<sub>2</sub>, ZnO, SnO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> are in great demand for photocatalysis because they are highly stable and non toxic. Among the above, TiO<sub>2</sub> offers additional advantage in that it is low cost, chemically inert, highly photoactive and has a suitable band gap ( $E_g = 3.2$  eV) in which its redox potential of H<sub>2</sub>O/\*OH couple ( $-2.8$  eV) lies. It is also self regenerating and recyclable. TiO<sub>2</sub> occurs in three crystalline polymorphs: rutile, anatase and brookite, out of which the rutile is the most stable phase in bulk [1]. TiO<sub>2</sub> nanocrystals have anatase phase because when the crystallite size is less than 30 nm, the surface energy for the anatase phase is lower than those for rutile and brookite [2,3]. Moreover, the structure of TiO<sub>2</sub> nanocrystal depends on synthesis conditions and precursor chemistry [4]. The band gap of anatase TiO<sub>2</sub> is 3.2 eV whereas that of rutile is 3.0 eV. The adsorptive affinity of anatase TiO<sub>2</sub> nanocrystal for organic molecule is higher than that of the rutile TiO<sub>2</sub> [5]. Again, the rate of carrier recombination in anatase TiO<sub>2</sub> is much lower than that of rutile TiO<sub>2</sub> because the rate of hole trapping in anatase is 10-fold greater than that in rutile [6]. Due to the above reasons, the anatase TiO<sub>2</sub> nanocrystals are more photochemically active and are most suitable for photocatalytic applications [7,8]. Bacsa et al. [9] reported that the photocatalytic activity of

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mixed-phase TiO<sub>2</sub> (anatase + rutile) was higher than that of either pure anatase or pure rutile. Similarly, Hurum et al. [10] explained the enhanced photocatalytic efficiency of commercial, mixed-phase TiO<sub>2</sub> powder (P25, Degussa, 70% anatase + 30% rutile) using electron paramagnetic resonance. They explained that due to its lower band gap (3.0 eV) the rutile TiO<sub>2</sub> works as an antenna for visible absorption and rutile/anatase interface is responsible for effective charge separation that leads to higher photocatalytic activity. Although there are several reports showing TiO<sub>2</sub> powder-assisted photocatalytic degradation of model water pollutants such as methylene blue, the reports about degradation of protocatechuic acid is still infrequent. Protocatechuic acid (3, 4-dihydroxy benzoic acid (DHBA)) is one of the biorecalcitrant polyphenolic compounds typically found in the sewage of olive oil industry and wine distillery. The complications involved in the study of photocatalysis of powder TiO<sub>2</sub>-DHBA mixture are (i) it is difficult to remove highly-dispersed TiO<sub>2</sub> powder and reuse the same after photocatalysis, (ii) the absorption peaks for aqueous DHBA solution occurs in the wavelength range of 200–400 nm and since the anatase TiO<sub>2</sub> band gap corresponds to a wavelength of 387 nm, it is difficult to eliminate the absorption feature due to TiO<sub>2</sub>. Florence et al. [11] studied the photocatalytic degradation of DHBA with TiO<sub>2</sub> Degussa P25 powder. Poulis et al. [12] reported oxidation of DHBA with ZnO and TiO<sub>2</sub> powder. However, in all above reports it was difficult to separate the TiO<sub>2</sub> powder after the reaction and there was no such discussion related to recyclability of the used catalyst. In this article, we report a large scale production of mixed-phase TiO<sub>2</sub> powder for photocatalytic degradation of aqueous solution of commercial DHBA. In order to avoid the complications involved in the process of separation of TiO<sub>2</sub> powder from DHBA solution, the TiO<sub>2</sub> powder was immobilized in form of porous thin film on glass substrates by doctor-blade coating. We have observed that the above porous thin film can be recycled after heat treatment at 70 °C, without any loss of the catalytic efficiency.

## 2. Experimental

Titanium (IV) isopropoxide (97%), oleic acid, ethyl cellulose, 3, 4-dihydroxy benzoic acid were purchased from Aldrich, South Korea. Absolute ethanol and  $\alpha$ -terpinol were purchased from Samchun and Kanto chemicals, respectively. In a typical synthesis, 8 ml of titanium tetra isopropoxide (TTIP, 97%) was added to 30 ml of oleic acid at room temperature. The mixture was stirred for five minutes to form a yellow solution. The above solution was heated in a regular laboratory oven in air at 270 °C for two hours. The rate of raising the temperature was 6 °C. min<sup>-1</sup>. After 2 h, the liquid turned deep red. A brown precipitate was obtained with excess ethanol. The precipitate was separated by centrifugation at a speed of 3500 rpm for 30 min and subsequently fired at 450 °C in air for 3 h in order to remove the organic byproducts. All organic ligands were burnt away and about 3 g of white powder was obtained which was dispersed in 100 ml of absolute ethanol taken in a 200 ml beaker. The dispersion was sonicated with a 30 W horn ultrasonicator for at least 30 min. The bigger crystallites settle down at the bottom of the beaker. The smaller crystallites get uniformly dispersed in ethanol which was transferred to another beaker and vacuum dried at 90 °C till complete evaporation of the solvent takes place. Then, the dry powder was scratched off the wall of the beaker, ground in an agate mortar and collected for characterization.

The XRD patterns were recorded with a PANalytical's X'PERT-PRO X-ray diffractometer operating under optimized condition of 30 mA, 40 kV using CuK $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). The transmission electron microscopic study was carried out with a JEOL JEM 2011 model with acceleration voltage of 200 kV. The BET (Brunauer Emmette Teller) surface area of the TiO<sub>2</sub> powder was estimated from the N<sub>2</sub> adsorption-desorption data recorded with the help of an ASAP 2020 V3.04G system. The sample was degassed at 300 °C before measurement and the adsorption-desorption was studied at 77 K. The surface area and pore sizes were calculated by BET and BJH methods.

In order to determine the band gap of TiO<sub>2</sub> powder, 0.015 g of powder was mixed with 10 ml of deionized water and the mixture was sonicated for one hour to give a uniform white suspension. 3.0 ml of the above suspension was sampled out for uv-vis absorption measurement. The absorption spectrum was recorded with an Optizen 3220 spectrophotometer.

In order to study the photocatalytic properties, the above powder was coated on glass plates by the doctor-blade technique. In a typical paste preparation process, 0.1 g of ethyl cellulose was dissolved in 2.5 ml of  $\alpha$ -terpineol diluted with 5 ml of absolute ethanol. 0.5 g of TiO<sub>2</sub> powder was added to the above mixture with continuous stirring in order to form a homogeneous mixture. The mixture was stirred at 50 °C for 24 h for complete evaporation of ethanol. About 2 g of white colored paste with appropriate rheological properties was obtained. Thin films of the above paste were deposited on ultrasonically cleaned glass plates by doctor-blade technique. For a typical sample, the area of the film was  $5 \times 2 \text{ cm}^2$  and the size of the glass plate was  $6 \times 3 \text{ cm}^2$ . The film was dried at room temperature for 24 h and then sintered in a muffle furnace for 30 min at 450 °C in air. A uniform, semi-transparent, white thin film was observed on glass plate after cooling to room temperature. Similar paste preparation process and doctor-blade coating was repeated for commercial P25 powder (Degussa, BET surface area  $60 \text{ m}^2 \cdot \text{g}^{-1}$ ) with exactly same amount of powder and the area of deposition was same ( $5 \times 2 \text{ cm}^2$ ).

In order to study the photocatalytic degradation of the DHBA, doctor-bladed thin films (thickness = 10  $\mu\text{m}$ , area =  $5 \times 2 \text{ cm}^2$ ) were immersed in 10 ml aqueous solution of DHBA (three different concentrations, i.e., 35  $\mu\text{M}$ , 52  $\mu\text{M}$  and 71  $\mu\text{M}$ ) taken in a  $8 \times 7 \times 5 \text{ cm}^3$  size glass box with top side open. The above system was irradiated with a 254 nm, 15 W UV-lamp. The irradiation was switched off in every 10 min interval in order to check the concentration of the solution by UV-vis spectrometry with an An Optizen 3220 spectrophotometer.

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