

Photocatalytically active titanium dioxide nanopowders: Synthesis, photoactivity and magnetic separation

J-P Nikkanen¹, S Heinonen, E Huttunen Saarivirta, M Honkanen and E Levänen
Department of Materials Science, Tampere University of Technology P.O. Box 589,
FIN-33101 Tampere, Finland

E-mail: juha-pekka.nikkanen@tut.fi

Abstract. Two approaches were used to obtain nanocrystalline titanium dioxide (TiO₂) photocatalyst powders. Firstly, low-temperature synthesis method and secondly, liquid flame spraying. The structural properties of the produced powders were determined with X-ray diffraction, transmission electron microscopy and nitrogen adsorption tests. The photocatalytic properties of the powders were studied with methylene blue (MB) discoloration tests. After discolorations tests, TiO₂ was coagulated with magnetite particles using FeCl₃·6 H₂O at a fixed pH value. Magnetic separation of coagulated TiO₂ and magnetite was carried out by a permanent magnet. The obtained results showed that the particle size of the powders synthesized at low-temperature was very small and the specific surface area high. The phase content of the powder was also shown to depend greatly on the acidity of the synthesis solution. Powder synthesized by liquid flame spraying was mixture of anatase and rutile phases with essentially larger particle size and lower specific surface area than those of low-temperature synthesized powders. The MB discoloration test showed that photocatalytic activity depends on the phase structure as well as the specific surface area of the synthesized TiO₂ powder. The magnetic separation of TiO₂ –magnetite coagulate from solution proved to be efficient around pH:8.

1. Introduction

In 1960s, Fujishima and Honda began to investigate the photoelectrolysis of water using a single crystal TiO₂ electrode. They found that water maybe decomposed using TiO₂ and UV-light into hydrogen and oxygen without an external voltage. The findings of Fujishima and Honda were reported in Nature in 1972 [1]. After that, the semiconductor photocatalysis has been under extensive research as a possible way to purify water, air and surfaces from organic and inorganic impurities [2–4]. Among many oxide semiconductors, TiO₂ has been proved to be the most suitable for environmental applications because its chemical inertness, non-toxicity and strong oxidizing power. Three polymorphs, anatase, rutile and brookite occur in nature [3,4]. In photocatalytic applications, TiO₂ has been used as photocatalyst especially in its anatase form.

However, rutile has a smaller band gap than that of anatase. Due to a smaller band gap rutile has better photo absorption properties in visible light wavelength range [5]. Moreover, the mixture of anatase and rutile phases in TiO₂ powders are commonly used in photocatalytic applications [6,7].

¹ To whom any correspondence should be addressed.



An industrial method to produce crystalline TiO₂ phases is based on sulphate or chloride process at the temperature of the order of 1000° C. At such high temperature, the crystal size typically grows considerably and the surface area subsequently decreases [8]. Because the photocatalysis is a surface controlled reaction, the decrease in the surface area of the photocatalyst is an unwanted process. To avoid the grain growth and to maximise the surface area and photocatalytic activity of TiO₂, low-temperature (LT) synthesis methods have been studied [9–13] and developed [14,15].

In addition of LT synthesis method, also liquid flame spray technique (LFS) has been used to produce TiO₂ nanopowder. In LFS, a liquid precursor solution is fed into a turbulent high-temperature ($T_{\text{max}} \sim 3000$ K) hydrogen-oxygen (H₂-O₂) flame, where the precursor evaporates, decomposes, reacts and finally nucleates to the nanosized particles. LFS method may be used to produce both single and multicomponent nanopowders and functional coatings. Although the temperature of LFS is very high, the residence time of the injected solution in the flame is short, which hinders the crystal growth [16,17].

In this study, titanium dioxide powders were synthesized by two different synthesis methods: firstly, at a relative low temperature (50°C) as a function of acidity and secondly, using liquid flame spray method. To the best of our knowledge, no earlier studies compare photocatalytic activities of the low-temperature and liquid flame spray produced TiO₂ powders. The photocatalytic activities of the synthesized powders were measured in methylene blue (MB) discoloration tests. After discoloration test, the potentiality of magnetic separation of TiO₂ nanopowder from the solution was performed.

2. Experimental

2.1 Low-temperature synthesis (LT)

In this part, three TiO₂ powders were synthesized at low temperature as a function of acidity of synthesis solution. The starting precursors in the syntheses were tetra-n-butyl orthotitanate (denoted as C₁₆H₃₆O₄Ti; > 98%, VWR), 2-propanol (denoted as C₃H₇OH > 99.5 VWR, amount of water ≤ 0.2 %), nitric acid (denoted as HNO₃, 65%, VWR) and ion-exchanged water. All chemicals used in this study were reagent grade and no further purification was done. In the beginning, 1.9 ml (5.5 mmol) tetra-n-butyl orthotitanate liquid was diluted with 6.3 ml (84 mmol) 2-propanol. The solution mixture was stirred for 15 min and then 90 ml of ion-exchanged water and varying amounts of nitric acid were added into the solution container. The amounts of used nitric acid were 1, 3, and 5 ml. The molar ratios of HNO₃/tetra-n-butyl orthotitanate were 2.5, 7.8 and 13. The solution was further stirred in a sealed reflux condenser reaction vessel for 24 h. The temperature of the solution was 50° C. Finally, the obtained precipitates were filtered and dried in an oven at 50° C for 12 h.

2.2 Liquid flame spraying

In LFS, 0.1 mol of tetra-n-butyl orthotitanate (C₁₆H₃₆O₄Ti; > 98%, VWR) was dissolved in 1000 ml 2-propanol (C₃H₇OH > 99.5 VWR, amount of water ≤ 0.2 %) and fed into H₂-O₂ flame. The precursor feed rate was 5 ml/min, while gas flows were 40 ml/min for H₂ and 20 ml/min for O₂. The formed particles were collected by a cylindrical electrostatic precipitator with a diameter of 100 mm and length of 1000 mm, using 6.0 kV voltage on the central rod, and 0.3 mA current from rod to a grounded cylinder.

2.3 Characterization and separation

The crystal structure of TiO₂ powders were determined with a Siemens Kristalloflex D-500 X-ray diffractometer and monochromatized CuKα radiation. The mass fractions of anatase and rutile were determined from XRD peak intensities by Spurr and Myer's method [18]. The specific surface area of powders was measured in a nitrogen adsorption test using a Brunauer-Emmett-Teller (BET) method and a Coulter Omnisorp 100cx device. The morphology of the particles was determined using a JEOL JEM 2010 transmission electron microscope and acceleration voltage of 200 kV.

Photocatalytic measurements were performed in aqueous solution of methylene blue (MB). 10 mg of TiO_2 powder was dispersed into 100 ml of 0.015 mM MB solution in an open beaker and the dispersion was magnetically stirred. In order to reach adsorption equilibrium, the test solutions were first kept in the dark for 60 min after which the UV lamp was turned on. Illumination was done from above with a 75 W/m^2 power using Ledia NIS330U-M UV-Gun (peak maximum at $365 \pm 5 \text{ nm}$). The concentration of methylene blue in the solution was followed by UV-VIS spectroscopy (Shimazu UV-2501PC Spectrophotometer). At one-hour intervals a 3 ml sample was taken and subjected to centrifugation to separate the photocatalyst particles from the solution. After this the absorbance of MB at the wavelength of 665 nm was measured. A dark experiment without any irradiation but under otherwise identical conditions was also conducted for comparison. The discoloration of MB under UV irradiation but without TiO_2 powder was also tested to confirm that irradiation does not decompose MB intrinsically.

After photocatalytic measurements, the possibility to remove TiO_2 powder from MB solution by magnetic separation was examined. For that, 50 mg of magnetite powder (Fe_3O_4 , $> 5 \mu\text{m}$, 98 %, Sigma) and 20 mg of iron (III) chloride hexahydrate ($\text{Fe}(\text{Cl})_3 \cdot 6 \text{H}_2\text{O}$ > 98 %, VWR) was weighed into beaker with TiO_2 powder. After this, the pH value was adjusted by adding 1.0 M NaOH into the solution. Finally a permanent magnet was placed to a side of a beaker. Magnetic separation test was performed for one produced powder from low-temperature synthesized series.

3. Results and discussion

Figure 1 shows the XRD patterns and the specific surface areas (SSA) of the low-temperature synthesized TiO_2 powders. The anatase phase was detected in the powder (a) synthesized with the lowest amount (1.0 ml) of HNO_3 used. When the amount of acid was increased also the rutile phase was obtained (b). Moreover, when the concentration of acid was high enough (c) the product was single-phase rutile without any anatase phase. The mass fraction for the mixed phase anatase/rutile powder (figure 1b) was estimated from XRD to be approximately 50/50.

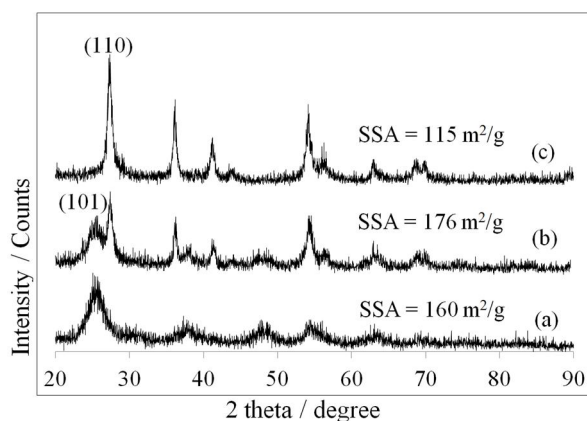


Figure 1. XRD pattern of LT1 (a), LT2 (b) and LT3 (c). SSA is the specific surface area of the powder.

Figure 2 shows TEM micrographs of the low-temperature synthesized powders. The gradual change in morphology and size of the prepared particles was dependent on the conditions of preparation. The micrographs confirm the dependence of the particle morphology on the acid content used in synthesis. As can be seen, the shape of the particles was spherical when the lowest amount of (1 ml) nitric acid was used (figure 2a). With increase in the amount of acid, the shapes of the particles changed. In figure 2b, there were still same spherical particles but also increased amount of rod-like nanocrystals. The rod-like shape is known to be typical for rutile phase synthesized under hydrothermal conditions [9,12]. It can be clearly seen that the powder synthesized with the highest amount of acid consisted only of rod-like nanocrystals without any spherical particles.

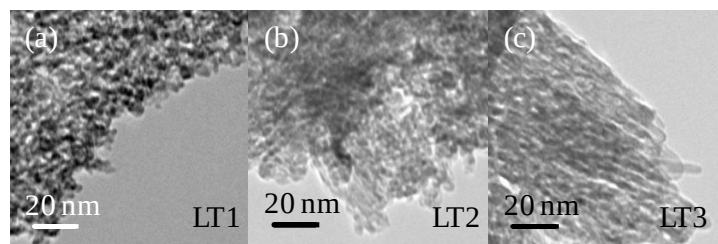


Figure 2. TEM micrograph of LT1 (a) LT2 (b) and LT 3 (c).

Interestingly, the specific surface area of the powder increased as a function of used amount of acid up to a certain point. This is surprising because it is well known that the particle size of rutile is larger than that of the anatase. Due to the larger size of rutile particle it would be reasonable to expect the decrease in the specific surface area when more rutile is formed. However, when the acid content was increased from 1 to 3 ml the specific surface area increased from 160 to 176 m²/g in spite of formation of the rutile. Thus, it is supposed that the increasing acidity of the solution does not only enhance the formation of the rutile phase but also reduce the size of produced anatase particles. This explains the increase in the specific surface area when the amount of acid is increased from 1 to 3 ml. However, when the amount of acid was further increased the specific surface area decreased flatly because the only produced phase was rutile.

The XRD pattern, the determined specific surface area and the TEM micrograph of LFS produced powder are presented in figure 3. Both anatase and rutile phases were detected. The mass fraction for the anatase/rutile mixture was estimated from XRD spectra to be approximately 50/50 like it was for low-temperature synthesized powder LT2. Conventionally, phase transformation from anatase to rutile occurs at temperatures between 550 and 1000° C [19]. However, although the temperature of LFS is very high, the residence time of the injected precursor solution in the flame is very short (few milliseconds). This explains the existence of anatase in the LFS synthesized powder.

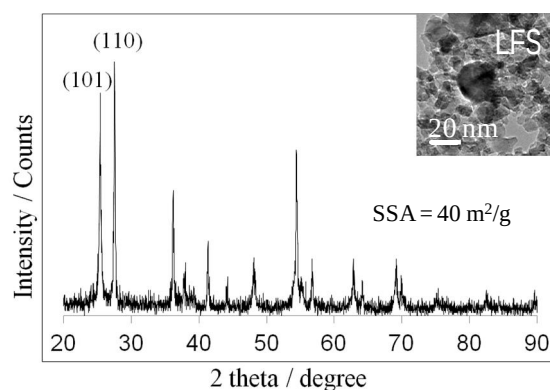


Figure 3. XRD pattern of the powder generated by LFS. TEM micrograph of the powder is inserted.

The experimental results of photocatalytic discoloration of MB with LT and LFS powders are shown in figure 4. The dark experiments showed that there was no significant adsorption of MB on the synthesized powders. In the tests using UV-radiation, the concentration of MB decreased as a function of reaction time in the case of all synthesized powders except for that of low-temperature synthesized rutile powder (LT3). After 2-h of radiation, MB solution was completely discolored in the mixture of anatase and rutile (LT2) indicating best photoactivity. The photoactivity of low-temperature anatase LT1 was slightly lower. However, after 3-h radiation of MB solution with LT1 almost all MB was

discolored. The reasons for the high activity of anatase-rutile powder (LT2) as compared to activity of the anatase phase (LT1) are most probably a higher surface area of LT2 than that of LT1 and the potential synergetic effect between the rutile and anatase phases, in which electron transfer from rutile to anatase trapping sites hinders charge recombination and enhances the photocatalytic activity [6]. In the case of liquid flame sprayed powder (LFS), the concentration of MB degraded about 42 % during a 3-h experiment. However, because the photocatalysis is surface-controlled reaction, the discoloration of MB was also calculated per surface area. These results are shown in table 1. It can be seen that the LFS powder was most efficient in terms of activity/m². The reason for this is probably a higher crystallinity of LFS powder than that of low-temperature LT series.

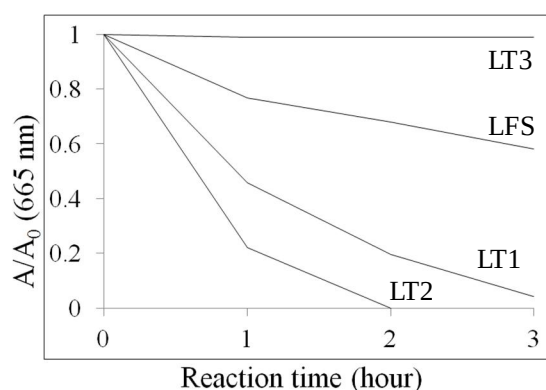


Table 1. Relative discoloration (RDC) of MB expressed per unit of surface area (m²) during a 2-h experiment.

Powder sample	RDC/ m ²
LT1	5.0 x 10 ⁻³
LT2	6.0 x 10 ⁻³
LT3	7.0 x 10 ⁻⁵
LFS	8.0 x 10 ⁻³

Figure 4. Photocatalytic discoloration of MB as a function of reaction time.

Figure 5 presents images from magnetic separation performed for the low-temperature powder LT2 after MB discoloration test. In figure 5a, the MB has discolored after 2 h of irradiation and the solution was milky white. After the addition of magnetite and iron (III) chloride hexahydrate, the solution turned greyish. When the pH value was adjusted to 8, the magnetite and TiO₂ coagulated to ferrihydrite precipitate by an increase in the pH value of solution (figure 5b) [20]. In figure 5c, the solution was transparent and the powder particles were attracted of the decanter glass walls due to an external magnetic field by a permanent magnet. These results findings may find potential use in separation of powders from the solutions. However, further studies are needed to demonstrate quantitatively the removal efficiency and the possibilities to reuse the separated powder as photocatalyst.

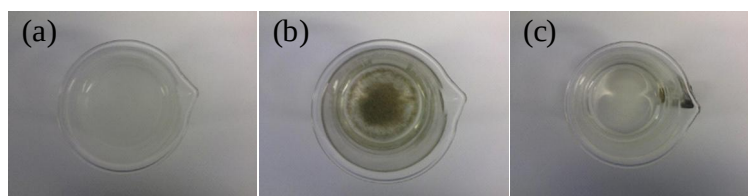


Figure 5. Magnetic separation of LT2 from solution.

Conclusions

In this study, TiO₂ powders were produced by low temperature (LT) and liquid flame spray (LFS) synthesis methods. The characteristics of the synthesized powders were studied and compared. It was found that the acidity of the used solution in LT process determinates the final crystal structure and the specific surface area of the formed powder. In the diluted solution of acid, the anatase phase is formed. When the acid content is increased, the product is a powder mixture of anatase and rutile phases. When acid content is high enough, only rutile phase is formed. The specific surface area increases to the certain point as a function of acidity after which it decreases when more acid is used. In LFS synthesis the mixture of anatase and rutile phases is formed. The specific surface area of LFS powder is much lower than that of low temperature powder. Also the photocatalytic activity per mass is lower than that of low-temperature anatase or powder mixture of anatase and rutile. However, LFS powder shows better activity per unit surface area than the powders produced at low temperature. This is probably caused by higher crystallization of LFS powder compared to powders made at low temperature. In this study, also the potential way to remove powder from the aqueous solution was demonstrated. Although the tentative results were promising, more research effort is needed in the area. However, this study provides a fruitful basis for contributions to compare totally different synthesis methods to produce TiO₂ and ideas for magnetic separation of powder from aqueous solution.

References

- [1] Honda K, Fujishima A 1972 *Nature* 238 37–8
- [2] Fujishima A, Rao T N and Tryk D A 2000 *J. Photochem. Photobiol. C Photocem. Rev.* 1 1–21
- [3] Fujishima A, Hashimoto K and Watanabe T 1999 *TiO₂ Photocatalysis: Fundamentals and Applications, first ed., BKC Tokyo*
- [4] Hashimoto K Irie H and Fujishima A 2007 *AAPPS Bulletin* 17 12–28
- [5] Yin S, Hasegawa H, Maeda D, Ishitsuka M and Sato T 2004 *J. Photochem. Photobiol. A Chem.* 163 1–8
- [6] Hurum D C, Agrios A G and Gray K A 2003 *J. Phys Chem. B* 107 4545–9
- [7] Besca R R and Kiwi J 1998 *Appl. Catal. B Environmental* 16 19–29
- [8] Yang S, Liu Y, Guo J, Zhao H, Xu Z and Wang J 2002 *J. Mater. Chem. Phys.* 77 501–6
- [9] Gobal M, Moherty Chan W J and de Jonghe L C 1997 *J. Mater. Sci.* 32 6001–08
- [10] Wang C C and Yin J Y 1999 *Chem. Mater.* 11 3113–20
- [11] Watson S, Beydoun D, Scott J and Amal R 2004 *J. Nanopart. Res.* 6 193–207
- [12] Nikkanen J-P, Kanerva T and Mäntylä T 2007 *J. Cryst. Growth* 304 179–83
- [13] Nikkanen J-P, Huttunen-Saarivirta E, Kanerva T, Pore V, Kivelä T, Levänen E and Mäntylä T 2011 *J. Ceram. Sci. Tech.* 2 97–102
- [14] Yin S, Li R, He Q and Sato T 2002 *Mater. Chem. Phys.* 75 76–80
- [15] Yin S, Inoue Y, Uchida S, Fujishiro Y and Sato T 1998 *J. Mater. Res.* 13 844–47
- [16] Nikkanen J-P, Keskinen H, Aromaa M, Järn M, Kanerva T, Levänen E, Mäkelä J M and Mäntylä T 2008 *Res. Lett. Nanotech.* Article ID 516478, doi: 10.1155/2008/516478
- [17] Aromaa M, Arffman A, Suhonen H, Haapanen J, Keskinen J, Honkanen M, Nikkanen J-P, Levänen E, Messing M E, Deppert K, Teisala H, Tuominen M, Kuusipalo J, Stepien M, Saarinen J J, Toivakka M and Mäkelä J M 2012 *J. Aerosol Sci.* 52 52–68
- [18] Spurr R A and Myers W 1957 *Anal. Chem.* 29 760–2
- [19] Hanaor D A H and Sorrell C C 2011 *J. Mater. Sci.* 46 855–874
- [20] Karapinar N 2003 *Int. J. Miner. Process* 71 45–54