Controlled crystal phase of TiO$_2$ by spray pyrolysis method

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Abstract: TiO$_2$ in powder form was preferred due to its flexibility and easy handling. TiO$_2$ powders with controlled crystal phase were successfully synthesised by ultrasonic spray pyrolysis from titanium tetraisopropoxide (TTIP) precursor. The effect of various acid solvents (nitric acid, acetic acid and citric acid) in relationship with crystal compositions have been well-studied. This experimental study suggested that the ratio of anatase phase achieved from TiO$_2$ prepared by nitric, acid acetic acid and citric acid solvent are 85%, 39% and 27% respectively. Spurs-Myers equation used to determine the anatase-rutile phase. Crystal sizes were calculated using Scherer equation. Both of ratio and crystal size were estimated from corresponding X-ray diffraction pattern. Precipitation and chelating process were the keys to determine the last composition of TiO$_2$.

1. Introduction
Titanium dioxide (TiO$_2$) was known as a semiconductor material with unique properties. In powder form, it offers major flexibility uses in catalyst [1], self-cleaning agent [2], fuel cell [3], and solar cell [4]. It has a proper band gap that allows electron-hole transfer which results in a strong oxidation features when illuminated with UV light [5]. Degussa P25 is widely known as a commercial TiO$_2$ powder which consist of 20% rutile and 80% mixed anatase and brookite phase [6]. Recent studies reported, anatase phase in TiO$_2$ enhances higher activity than pure phase of rutile structure [7]. Major constituents of anatase phase in a TiO$_2$ structure permit low energy in visible light absorption which can be a future alternative for solar cell applications [8]. Nevertheless, rutile phase is also preferred for a synthetized TiO$_2$ structure since it could be used to enhance the photocatalystic performance of TiO$_2$. However, there were insufficient results about controlling the composition ratio of anatase and rutile phases in a TiO$_2$ structure. Controlling the temperature process [9], and manipulation of hydrolysis rate [10] were the possible methods to control the crystal phase formation of TiO$_2$.

Spray pyrolysis is considered as a promising method since it can combine these methods from the preparation of metals, metal oxides, non-oxides and composite powders until produce particles with controlled composition and morphology, good crystallinity, and uniform size distribution, simply in one-step only [11]. Doeuff et. al reported carboxylic acids addition influence relate to the crystal phase, particle morphology and the particle size distribution [12]. The effect of various acids addition...
study could give better understanding in one-step TiO$_2$ synthesis. In this study, we conduct TiO$_2$ synthesis using ultrasonic spray pyrolysis with various acids addition as an additive solution.

2. Experimental

2.1. Powder preparation

TiO$_2$ powders from TTIP (98%, Ti(OC$_3$H$_7$)$_4$, Acros, US) precursor with various acid; nitric acid, acetic acid and citric acid (C$_6$H$_8$O$_7$) were prepared using a laboratory-scale SP electrostatic deposition system. The whole SP system has the same process with our previous work [13]. Initially, for TiO$_2$ with nitric acid solution, the TTIP was dissolved in the mixture of de-ionized water and nitric acid that instantly form a clear solution. For the second solution, TTIP was dissolved separately in de-ionized water with acetic acid and was stirred for 4 H to form clear solution. For the third solution, TTIP was dissolved in mix of citric acid and de-ionized water for 24 H to form clear solution. All solution were prepared for same concentration of 0.05 M. Afterwards, each solution will undergo ultrasonic SP process at 800°C.

2.2. Characterization

X-ray diffractometer (D2 Phaser, Bruker, Germany), with Ni-filtered Cu Kα radiation, was used to characterize the crystallographic structure of the TiO$_2$ and to determine the ratio of anatase-rutile phase. Field-emission scanning electron microscopy (FESEM, JSM-6500F, JEOL, Japan) was used to investigate the surface of TiO$_2$ particles and to determine the particles distribution. The particle distribution was conducted by measuring the average diameter of approximately more than 250 particles using the Image J software.

3. Results and Discussion

3.1. Crystallographic structure

Figure 1 shows XRD patterns for TiO$_2$ powders prepared using various acids solution. It can be seen that all samples show dual anatase-rutile phases of TiO$_2$ complex microstructure.
Prepared powder with nitric acid has the sharpest XRD anatase pattern peaks that show composition dominantly consists of anatase phase as listed in table 1. Calculation of anatase-rutile phase use the Spurr’s-Myerss equation. By using Origin (version 8.1) software, the Spurr’s-Myerss equation calculated from the selected areas under the highest normalized peak intensities of a diffraction pattern which represent anatase and rutile phase, are apply the Spurr’s-Myerss equation calculation [14]. As shown in table 1 ratios of anatase phase formed with acid additives of nitric acid, acetic acid and citric acid were 85 %, 39%, and 27 %, respectively.

Table 1. Physical properties of prepared TiO₂ powders vs various acids additive.

| Acid additive | Crystalline Size (nm) | % anatase | % rutile |
|---------------|-----------------------|-----------|----------|
| Citric acid   | 28.3 ± 1.9            | 27        | 72       |
| Acetic acid   | 34.6 ± 7.1            | 39        | 61       |
| Nitric acid   | 10.0 ± 3.5            | 85        | 15       |

In the previous work, it found that TTIP with acetic acid fully decomposed with a temperature reaction at 700°C [15]. Either the temperature reaction or the hydrolysis rate can be applied in order to control the crystal phase. As reported by Birnie et al, Acetic acid can prevent early precipitation of titanium particle due to reduce rate of hydrolysis relevant as below reaction [16].

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\text{Ti(OC}_3\text{H}_7)_4 + 4\text{CH}_3\text{COOH} \rightarrow \text{Ti(CH}_3\text{COOH)}_4 + 4\text{C}_3\text{H}_7\text{OH}
\]

Formation of TiO₂ in solutions is distinguished into three steps, hydrolysis, condensation, and solvent evaporation [17]. In the case of acid as additive, acids can act either as catalyst to accelerate the hydrolysis, or as chelating agent to prevent hydrolysis rate. Carboxylic acids such as acetic acid and citric acid, play role in chelating process. During hydrolysis, chelating agent will prevent precipitation but due to ligand effect, formation of particle nucleus will also get slower than condensation process. It makes atom sharing and dissolution only occurs after a colloidal formation in the stable phase. Atom sharing in TiO₆ octahedran via hydrolysis mainly occurs at atomic surface and will effect in anatase phase formation. Meanwhile, shared atom via chelation is processed at edge position and contributes to rutile phase formation.

3.2. Particle morphology

Generally, TiO₂ powders prepared various acid additives have similar shapes. Theory of one-droplet-per-particle fulfilled with the spherical shape formation. It was identified during the particles formation that the solution has high solubility therefore solid particles could be formed. The use of acid was proposed since its enhance precursor solubility in an aqueous solution. The solubility also means ability of dispersed particles in the solution.

For the case of acetic acid addition, it seems that prepared powder has a spherical shape with smooth surface and narrow size as shown in figure 2 (b). The narrow size of this powder is due to formation of acetates ligand which is stable and serve monodisperse particle [12]. The effects of citric acid on TiO₂ powder is also shown in figure 2 (c). It seems that TiO₂ particles also have spherical shape with several fractal particles. The presence of fractal particles explains that the particles were formed in early precipitation due to chelating process. Chelating process in TiO2 preparation promotes the formation of rutile phase than anatase since polycondensation did not occurs [18]. As a conclusion, these acids have different roles. In nitric acid case, the acid was acted as catalyst that accelerates the polycondensation-precipitation reaction. The acidity of nitric acid provide a controlled
transformation of anatase phase. Rather than as a catalyst, citric acid and acetic acid were preferred to act as the chelating agent, where during hydrolysis reaction the ligand change the behavior of TiO$_2$ particle formation at molecular level.

![SEM images of TiO2 particles prepared from (a) TTIP + nitric acid, (b) TTIP + acetic acid, and (c) TTIP citric acid.](image)

**Figure 2.** SEM images of TiO2 particles prepared from (a) TTIP + nitric acid, (b) TTIP + acetic acid, and (c) TTIP citric acid.

3.3. **Particle size distribution**

SEM images were examined in order to determine the particles surface morphologies and to get information of the TiO$_2$ particles size distribution.

In this study, the particle sizes were polydispersed in submicron to micron size scale. Figure 3(a) and (c) show similar behavior that particle size distributions have a normal distribution. Its reveals clear information that no significant effects between nitric and citric acids addition, particle growth has the same rate for both acids. However, in the case used acetic acid as shown in figure 3(b), histogram shows a right skewed distribution that means particle was formed due to “natural force”. As reported by Matijevic, acetates ligand was effectively control the precipitates of anion that promote monodisperse particles [19]. In our case, the particle sizes are mostly in micron size, which only refer to one-particle-per-droplet mechanism.
Figure 3. Particle size histograms of TiO2 particles prepared from (a) TTIP + nitric acid, (b) TTIP + acetic acid, and (c) TTIP citric acid.

Conclusion
Controlled crystal phase of TiO2 has been successfully prepared from titanium (IV) isopropoxide (TTIP) precursor within series of acids as additive solution. It suggested that, in one-step TiO2 synthesis both of temperature and hydrolysis contributes in transformation the anatase to rutile phase. The acidity property of nitric acid is the main reason that allows TiO2 particles precipitation due to accelerated the hydrolysis reaction. Meanwhile, for citric acid and acetic acid, chelating process mainly determine the final product.

Acknowledgment
The authors acknowledge the financial support from the National Science Council of Taiwan (Grant No. MOST 104-222-E-011-017).

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