Synthesis of TiO$_2$ Photocatalyst Nanoparticles by Thermal Plasmas.

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Abstract. This study examined the synthesis of TiO$_2$ nanoparticles by Direct current (DC) thermal plasma system at atmospheric pressure, using Titanium Tetra Iso-Propoxide (TTIP) as Titanium precursor. We investigated the effects of various process variables, such as flow rate of raw materials, supplied power on the particle composition, size and morphology by observing XRD and TEM measurements. The TiO$_2$ nanoparticles collected at the reaction tube were predominantly rutile which was over 50% of weight with the particle size around of 250 nm.

Keywords: Titanium dioxide nanoparticles, thermal plasma, ultrafine powder.

1. Introduction

TiO$_2$ nanoparticles have been widely applied in photovoltaic solar cells, photocatalysis, gas sensors, batteries and pigments, sunscreens, ointments and toothpaste [1-5]. In those applications, the particle size, morphology, size distribution, and, specially, phase composition are key factors, which must be controlled [6]. Studies of TiO$_2$ nanoparticles as a catalyst have shown that rutile is the most efficient phase in sonocatalysis, and anatase mainly contributes the photo-catalytic activity [4]. Therefore, there are many researches aiming to synthesize and improve the catalytic efficiency of TiO$_2$. Recently, our group successfully produced thin film of TiO$_2$ on glass beads and utilized them to remove NO and SO$_2$ completely in gas stream [6].

There are several methods to synthesis TiO$_2$ nanoparticle, such as sol-gel, sputtering, flame synthesis and thermal plasma synthesis [7]. Among them, the thermal plasma process is a promising method to achieve a large-scale production of TiO$_2$ because the high temperature inside reactor will lead to short processing time, even though with high throughput [8]. The fast and high supersaturation of vapor precursor inside thermal plasma reactor provides the driving forces for particle condensation, leading to the generation of ultrafine nanoparticles by the homogeneous nucleation.

In this study, we synthesized TiO$_2$ nanoparticles by using the DC thermal plasma system at atmospheric pressure. We investigated the effects of various parameters, including the flow rate of carrier gas and the supplied power, on the size, morphology, and phase composition of the TiO$_2$ nanoparticles.

2. Experimental

TiO$_2$ nanoparticles was synthesized from TTIP (Ti (OCH(CH$_3$)$_2$)$_4$) 97%, Aldrich) in a thermal plasma reactor. Fig.1 shows the schematic diagram of the DC plasma reactor, which consists of a DC generator, an injection block for source materials, a reaction tube and a quench chamber. The plasma torch consists of a tungsten cathode and a copper anode. It was operated from 100 A to 300 A of input amperage with a flow rate of 10 l/min of Ar gas as the plasma source. The plasma torch, reaction tube and chamber were properly
cooled by water. The reaction time was set at 20 minutes and the process pressure was adjusted to approximately 1 atm. TTIP was carried by N₂ gas through the injection block and the quantity of TTIP was varied by flow rate of carrier gas, which was controlled from 2 l/min to 4 l/min. Oxygen was supplied into the reactor to oxidize TTIP.

![Diagram of DC thermal plasma for synthesis of TiO₂ nanoparticles](image)

**Fig. 1. Schematic diagram of the DC thermal plasma for synthesis of TiO₂ nanoparticles**

The synthesized TiO₂ nanoparticles were collected mostly on the wall of the reaction tube. The phase compositions of particles were analyzed by XRD. The weight fractions of anatase and rutile were calculated by using the following equations [9].

\[
f_A = \frac{1}{1+1.26 I_R/I_A} \quad (1)
\]

\[
f_R = 1 - f_A \quad (2)
\]

Where \( f_A \) and \( f_R \) are the weight fraction of anatase and rutile, respectively. \( I_R \) is intensity of (110) reflection of rutile, and \( I_A \) is intensity of (101) reflection of anatase.

The particle sizes and morphologies of TiO₂ nanoparticles were observed by TEM measurements.

### 3. Results and Discussion

The TTIP precursor is oxidized by oxygen gas and then the oxidation products are evaporated due to the high temperature (~ 10⁴ K) inside plasma region, quickly reach the supersaturation state. TiO₂ clusters were formed by homogeneous nucleation. Those clusters grow by the heterogeneous condensation of Ti precursor in plasma phase on their surface, the coagulation and sintering to generate the spherical particles. Inside the plasma phase, those particles are charged and then collide by the electrostatic force and Brownian motion to obtain the aggregated form. Some aggregated particles quickly deposit on the reactor wall, lose energy and, thus, remain their small sizes and phase compositions. Phase compositions of these particles are mostly anatase. Some particles continue to grow to be bigger when moving along the plasma stream and finally attach each other to be agglomerated shape. It has been noticed that the anatase-to-rutile transformation starts at approximately 600°C and complete at 1000°C [10]. The phase compositions of TiO₂ nanoparticles, therefore, strongly depend on their retention times in plasma region, which also affect on their sizes and shapes. The bigger particles collected in the downstream have longer retention time or longer anatase-to-rutile transformation time, resulting in higher rutile composition.

Table 1 shows all conditions to prepare TiO₂ nanoparticles and their particle sizes, phase compositions.
Table 1. Weigh fractions of anatase and rutile and the average particle size of TiO₂ nanoparticles prepared from various conditions of the carrier gas flow rate and input amperage.

<table>
<thead>
<tr>
<th>Carrier gas (l/min)</th>
<th>Input power (A)</th>
<th>$f_A$ (%)</th>
<th>$f_R$ (%)</th>
<th>Single particle size (nm)</th>
<th>Average particles size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>2</td>
<td>200</td>
<td>46</td>
<td>54</td>
<td>11</td>
</tr>
<tr>
<td>S2</td>
<td>3</td>
<td>200</td>
<td>37</td>
<td>63</td>
<td>9</td>
</tr>
<tr>
<td>S3</td>
<td>4</td>
<td>200</td>
<td>28</td>
<td>72</td>
<td>8</td>
</tr>
<tr>
<td>S4</td>
<td>2</td>
<td>100</td>
<td>49</td>
<td>51</td>
<td>10</td>
</tr>
<tr>
<td>S5</td>
<td>2</td>
<td>300</td>
<td>22</td>
<td>78</td>
<td>12</td>
</tr>
</tbody>
</table>

Fig. 2 shows the XRD patterns of the TiO₂ nanoparticles prepared from various conditions. All the samples showed the typical peaks of anatase and rutile phases. The particles were dominated by rutile with over 50% of weight as a result from the Eq. (1) and (2). The rutile phase increased from 54% to 72% when the flow rate of carrier gas was increased from 2 l/min to 4 l/min. As mentioned above, when the flow rate of carrier gas increased, the number of primary TiO₂ particle increased and finally, the bigger and denser particles were obtained. The retention of those particles inside plasma region might be longer, resulting in longer transformation time, leading more anatase was transformed into rutile.

When the supplied amperage increased from 100A to 300A, the rutile phase increased from 54% to 79%. It can be explained that the increase of amperage could promote the generation of plasma phase, which increased the formation of electrons and ions inside the plasma region and also increase the plasma temperature. The TiO₂ nanoparticles, therefore, became more charged and thus, stayed longer in plasma zone with very high temperature. Hence, more anatase phase could be transformed into rutile phase by increasing the supplied amperage.

Fig. 2. X-Ray diffraction patterns of TiO₂ nanoparticles obtained at the different conditions.
Fig. 3 shows the TEM images of TiO\textsubscript{2} nanoparticles obtained at different conditions. All particles were mainly agglomerated. The primary particle sizes of all samples were almost similar at around 10 nm but their final particle size varied. When the flow rate of carrier gas increased from 2 l/min to 4 l/min (Sample S1-3), the primary particle size slightly decreased from 11 nm to 8 nm but the final particle size increased from 180 nm to 300 nm. When the flow rate of carrier gas increased, more TTIP was supplied into the reactor tube which slightly promoted the nucleation and, thus, more clusters were generated. The primary particles, therefore, could be slightly decreased but the final aggregated particles could be bigger and became denser due to the coagulation of more primary particles. Obviously, by TEM observation, sample S3 corresponding to 4 l/min of carrier gas shows more compact aggregated particles with bigger size than sample S1 and S2, which are corresponding to 2 and 3 l/min of carrier gas, respectively.

When the applied amperage increased from 100 A to 300 A but kept the flow rate of carrier gas at 2 l/min, the primary particle sizes were slightly increased from 10 nm to 12 nm but the final particle sizes were almost similar at 200 nm. Because the amount of Ti precursor was constant due to the same flow rate of carrier gas, the number of primary TiO\textsubscript{2} particles was almost same in all conditions, resulting in the narrow range of the particle size of the final aggregated nanoparticles.
4. Conclusions

TiO\textsubscript{2} nanoparticles have been synthesized successfully by using the DC thermal plasma system. The phase compositions, sizes and morphologies of TiO\textsubscript{2} nanoparticles were investigated with various conditions of the flow rate of carrier gas and supplied amperage. The TiO\textsubscript{2} nanoparticles collected at the reaction tube were predominated rutile phase with over 50% of weight. The final particle sizes increased when increasing the flow rate of carrier gas but varied in a narrow range when changing the supplied amperage.

5. References

This research was performed for the Hydrogen Energy R&D Center, one of the 21st Century Frontier R&D Program which funded by the Ministry of Science and Technology of Korea.

6. References