Synthesis of Spherical TiO$_2$ Made up of High Reactive Facets of (001)

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Recently, TiO$_2$ crystals with high reactive facets of (001) have attracted much attention. However, there is less reports on spherical TiO$_2$ exposing high reactive (001) facets. In this paper, we synthesized spherical TiO$_2$ made up of crystallites with high percentage of (001) facets by a simple one-step hydrothermal template process. The spherical SiO$_2$ were used as templates. The effect of the reaction time on the structures and morphologies were systematically investigated. The structures and morphologies of the as-synthesized samples were characterized by X-ray diffractometer (XRD) and scanning electron microscopy (SEM). Energy-dispersive spectroscopy (EDS) was employed to determine the final stoichiometry of the samples. The results showed that spherical TiO$_2$ were of anatase phase, the spheres were about 1.5µm in diameter and the composed TiO$_2$ (001) facets were of <1µm in length.

Keywords: TiO$_2$; spherical structures; SiO$_2$ template; {001} facets

1. INTRODUCTION

TiO$_2$ in anatase crystal form becomes the most promising photocatalyst for its efficient photocatalytic, nontoxic, low cost and oxidation activity.[1-5] And TiO$_2$ crystals with {001} facets have attracted much attention since Yang et al. [6] reported that anatase TiO$_2$ crystals with a high percentage of {001} reactive facets can be obtained if their surfaces are surrounded by F ions. Many researches had been done on the synthesis of anatase {001} facets. [7-17] As morphology control can effect the photocatalytic activities, hierarchical TiO$_2$ microspheres,[18] anatase TiO$_2$ tubular structures
microcrystallites,[19] anatase TiO$_2$ Sheets[10-12,20,21] have been investigated. However, only a few researches had been reported on the spherical TiO$_2$ made up of \{001\} facets. Liu and coworkers firstly present a feasible strategy for the synthesis of hollow TiO$_2$ microspheres (HTS) consisting of anatase TiO$_2$ nanosheets with a high percentage of \{001\} facets.[22] Chen and coworkers reported a simple synthesis of hierarchical spheres with nearly 100% exposed (001) facets. The anatase TiO$_2$ manifests an unusually high Coulombic efficiency for lithium extraction, excellent capacity retention, and superior rate behavior.[23]

F ions can stabilize the \{001\} facets, in other words, fluorine-terminated surfaces of anatase TiO$_2$ can be dominated by \{001\} reactive facets.[6] Most of the experiments were carried out by using HF as the source of F ions.[6,10,14] However, HF is extremely corrosion and a contact poison. So other source of F ions should be developed. Here, we use (NH$_4$)$_2$TiF$_6$ as the source of both Ti ions and F ions.

In this paper, a facile and green one-step hydrothermal method was employed to synthesize spherical TiO$_2$ with reactive \{001\} facets exposed. The structures, morphologies, and growth procedures were investigated. Moreover, a plausible growth mechanism was proposed.

2. EXPERIMENTAL SECTION

2.1 Synthesis of the Samples

A one step hydrothermal method was employed in this work. (NH$_4$)$_2$TiF$_6$ was used without further purification. Spherical SiO$_2$ with average diameter of 500 nm was used as templates. Firstly, (NH$_4$)$_2$TiF$_6$ was dissolved into distilled water with the concentration of 0.1 mol/L. Secondly SiO$_2$ was put into the above solution and stirred for 2 hours. Then the suspension was transferred into a Teflon-lined stainless-steel autoclaves. And the autoclaves were then kept in an oven at 200 °C for different time. After the reaction, the products were filtered, rinsed with distilled water and ethanol for several times. The products were finally obtained after dried in an oven at 80 °C.

2.2 Characterization of the Samples

The structures and morphologies of our samples were characterized by X-ray diffraction (XRD; Bruker AXS D8 advance powder X-ray diffractometer) and scanning electron microscopy (SEM; Hitachi S4800), respectively. The Energy-dispersive spectroscopy (EDS) was taken on a HORIBA EMAX Energy EX-350 energy dispersive X-ray micro analyzer.

3. RESULTS AND DISCUSSION

3.1 Structure of SiO$_2$ templates

Figure 1 shows the XRD pattern of SiO$_2$ templates. We can see from figure 1 that the SiO$_2$ templates were of amorphous phase. In order to determine the elements and final stoichiometry of the
sample, EDS was employed. The inset shows the energy dispersive spectrum (EDS) of SiO₂, in which only Si and O elements can be found. The ratio of Si: O is 1: 2.83, the excess of O can be ascribed to the system deviation.

Figure 1. XRD pattern of SiO₂ templates and the inset shows the EDS of SiO₂

3.2 Crystal Structure of the as-synthesized samples

Figure 2. XRD patterns of the samples obtained after hydrothermal processing at 200 °C for various reaction times.
XRD patterns of the samples obtained after hydrothermal processing at 200 °C for various reaction times were shown in figure 2. It can be concluded from figure 2 that the crystallinity increased with the increase of reaction time. When the reaction time is 20 min, there is hardly any peak indexed to TiO$_2$ phase. All the diffraction peaks of the as-synthesized samples can be indexed to pure anatase TiO$_2$ phase (JCPDS card 21-1272) when the reaction time exceeds 40 min. The phase structure is in good agreement with the result of Hao et al. where they using ammonium fluoride (NH$_4$F) as a shape-capping reagent.[24] And Tian et al. investigated XRD patterns for the anatase TiO$_2$ with different volumes of hydrofluoric acid (HF), which shows the close phase structure. [25]

3.3 EDS Analysis

Table 1. EDS data of the samples obtained after hydrothermal processing at 200 °C for various reaction times.

<table>
<thead>
<tr>
<th>Atomic % Time</th>
<th>Si</th>
<th>O</th>
<th>Ti</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 min</td>
<td>25.69</td>
<td>73.86</td>
<td>0.44</td>
<td>—</td>
</tr>
<tr>
<td>40 min</td>
<td>22.61</td>
<td>75.69</td>
<td>1.71</td>
<td>—</td>
</tr>
<tr>
<td>1 h</td>
<td>—</td>
<td>68.50</td>
<td>20.13</td>
<td>11.37</td>
</tr>
<tr>
<td>3 h</td>
<td>—</td>
<td>66.12</td>
<td>24.18</td>
<td>9.70</td>
</tr>
<tr>
<td>12 h</td>
<td>—</td>
<td>67.70</td>
<td>25.10</td>
<td>7.20</td>
</tr>
</tbody>
</table>

As SiO$_2$ templates were amorphous, EDS was taken to characterize the content of Si element and determine the elements and final stoichiometry of the as-synthesized samples (see Table 1). The contents of Si element decreased with the increase of reaction time. When the reaction time reaches 1 h, only Ti, O, F atoms are detected from the as-grown TiO$_2$ samples and no Si element can be found, indicating that SiO$_2$ templates had been corroded away completely. The atom content of Ti is only 0.44 percent when the reaction time is 20 min, which is too small to be detected by XRD corresponding to the relevant XRD pattern in figure 2. The ratio of Ti: O increased with the increase of reaction time. After 12 h reaction, the ratio of Ti: O is 1: 2.7, which is close to the respect stoichiometry (1: 2) correspondingly. It can be further conformed that the spheres are composed of TiO$_2$ crystals, which is in consistent with the XRD pattern. The existence of F can be ascribed to the presence of (NH$_4$)$_2$TiF$_6$ in the hydrothermal process.[19]
3.4 Morphology Characterization

SEM images of SiO$_2$ and the samples obtained after hydrothermal processing at 200 °C for various reaction times are shown in Figure 3. SiO$_2$ shows homogenous spheres with average diameter of about 500 nm. SiO$_2$ templates are corroded with holes on the surface as shown in Figure 3 b. TiO$_2$ nanocrystals grew up on the surface of SiO$_2$ spheres (Figure 3 c). And {001} facets appeared when the reaction time reached 1 h. The edge of the {001} facets become more and more obvious with the reaction time increased.

![Figure 3](image)

**Figure 3.** SEM images of SiO$_2$ and the samples obtained after hydrothermal processing at 200 °C for various reaction times (a: SiO$_2$, b: 20 min, c: 40 min, d: 1 h, e: 3 h, f: 12 h).

Finally, spherical TiO$_2$ show well crystallined {001} facets when the reaction time comes to 12 h. The spheres were about 1.5µm in diameter and the composed TiO$_2$ (001) facets were of <1µm in length (Figure 3 f). The results are close to those obtained by Wang et al. where they synthesized TiO$_2$ tubular materials made up of microcrystallites with a high percentage of reactive {001} facets.[19]
3.5 Growth Mechanism

The reactions of the spherical TiO$_2$ synthesized by the hydrothermal process using SiO$_2$ spheres as templates can be occurred as Eqs. 1 and 2. (NH$_4$)$_2$TiF$_6$ was hydolyzed as shown in Eq. 1, while at the same time SiO$_2$ spheres were gradually corroded away (Eq. 2).

\[
\text{Eq. 1:} \quad (\text{NH}_4)_2\text{TiF}_6 + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 2\text{NH}_4\text{F} + 4\text{HF}
\]

\[
\text{Eq. 2:} \quad \text{SiO}_2 + 4\text{HF} + 2\text{NH}_4\text{F} \rightarrow (\text{NH}_4)_2\text{SiF}_6 + 2\text{H}_2\text{O}
\]

Fig. 4 illustrates the schematic diagram of a plausible growth mechanism. Firstly, (NH$_4$)$_2$TiF$_6$ was hydolyzed and SiO$_2$ are corroded at the same time within little reaction time. SiO$_2$ was seen as the nucleus and TiO$_2$ nanoparticles grew up on the surface of SiO$_2$ spheres, while SiO$_2$ spheres gradually corroded with the increase of reaction times. When the reaction time reached 12h, the SiO$_2$ templates are completely corroded away and only spheres composed of TiO$_2$ with reactive {001} facets remains.

![Figure 4. The schematic diagram of a plausible growth mechanism of TiO$_2$.](image)

4. CONCLUSIONS

In summary, we successfully synthesized spherical TiO$_2$ with reactive {001} facets by a facile and green synthetic route. The effect of the reaction time on the structures and morphologies is systematically investigated. The crystallinity is increased and the exposed {001} facets are obvious with the increase of the reaction time. The results showed that spherical TiO$_2$ were of anatase phase and the spheres were about 1.5µm in diameter and the composed TiO$_2$ (001) facets were of <1µm in length. And a plausible growth mechanism was proposed from SEM images.

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