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Short Communication

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 $(NH_4)_2TiF_6$ 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. $(NH_4)_2TiF_6$ was used without further purification. Spherical SiO_2 with average diameter of 500 nm was used as templates. Firstly, $(NH_4)_2TiF_6$ 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 ^oC 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 ^oC.

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 SiO_2, 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.

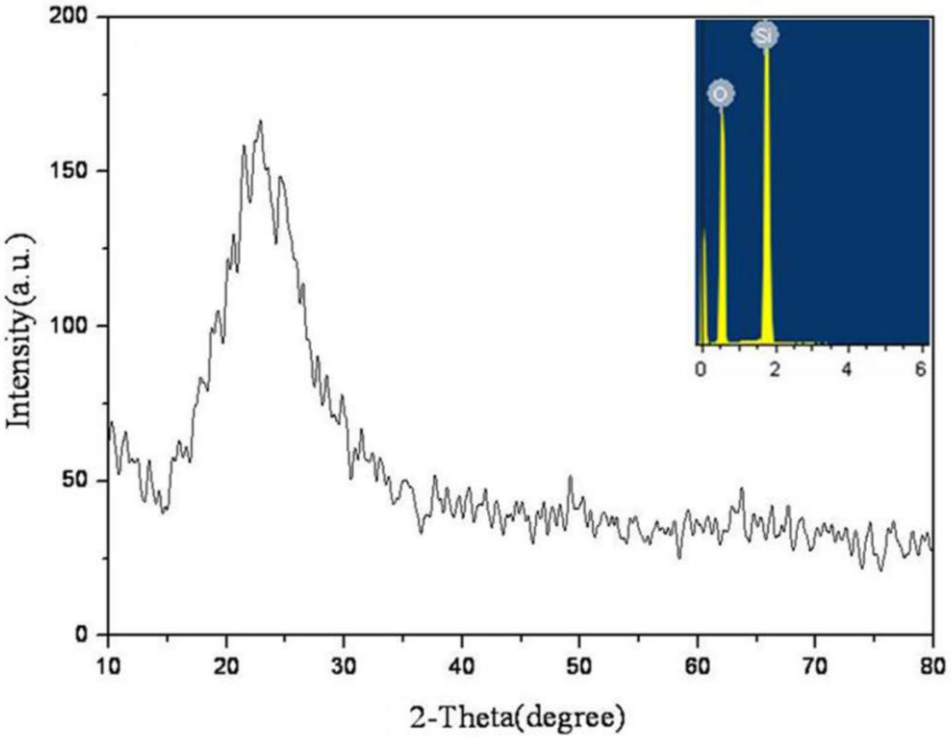

Figure 1. XRD pattern of SiO_2 templates *and t*he inset shows the EDS of SiO_2

3.2 Crystal Structure of the as-synthesized samples

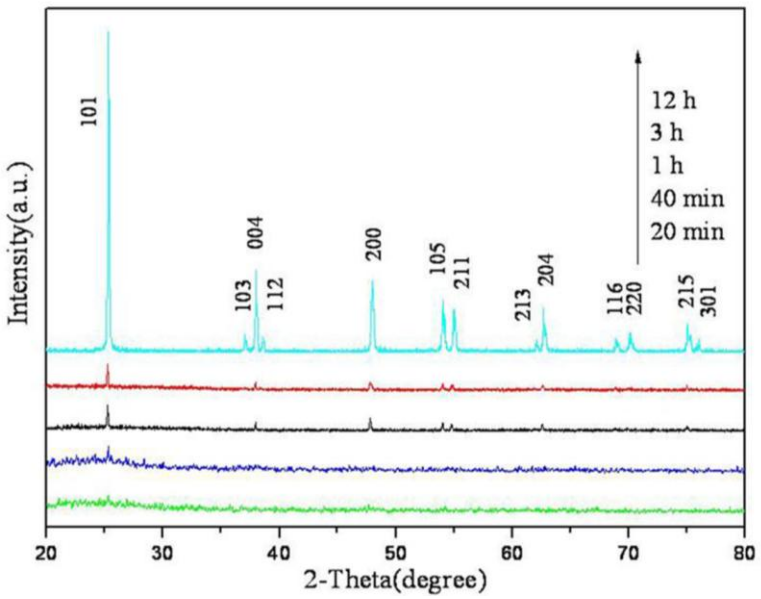

Figure 2. XRD patterns of the samples obtained after hydrothermal processing at 200 ^{o}C for various reaction times.

XRD patterns of the samples obtained after hydrothermal processing at 200 ^{o}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_4F) as a shape-capping reagent.[24] And Tian et al. inestigated XRD patterns for the anatase TiO_2 with different volumes of hydrofluoric acid (HF), which shows the close phae structure. [25]

3.3 EDS Analysis

Table 1. EDS data of the samples obtained after hydrothermal processing at 200 ^{o}C for various reaction times.

Element / Atomic% / Time	Si	O	Ti	F
20 min	25.69	73.86	0.44	—
40 min	22.61	75.69	1.71	—
1 h	—	68.50	20.13	11.37
3 h	—	66.12	24.18	9.70
12 h	—	67.70	25.10	7.20

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 $(NH_4)_2TiF_6$ in the hydrotheral process.[19]

3.4 Morphology Characterization

SEM images of SiO_2 and the samples obtained after hydrothermal processing at 200 ^oC 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 crroded 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.

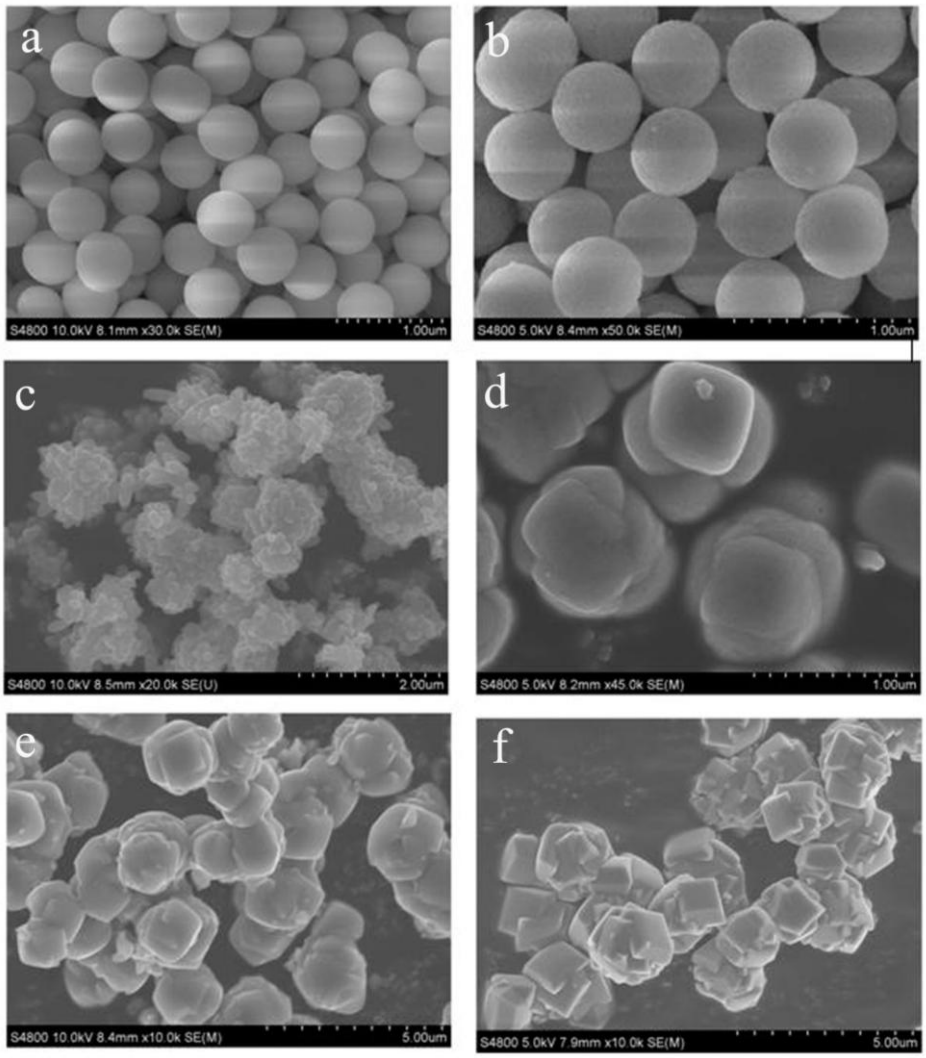

Figure 3. SEM images of SiO_2 and the samples obtained after hydrothermal processing at 200 ^oC for various reaction times (a: SiO_2, b: 20 min, c: 40 min, d: 1 h, e: 3 h, f: 12 h).

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. $(NH_4)_2TiF_6$ was hydolyzed as shown in Eq. 1. while at the same time SiO_2 spheres were gradually corroded away (Eq. 2).

$$(NH_4)_2TiF_6 + 2H_2O \rightarrow TiO_2 + 2NH_4F + 4HF \quad (1)$$

$$SiO_2 + 4HF + 2NH_4F \rightarrow (NH_4)_2SiF_6 + 2H_2O \quad (2)$$

Fig. 4 illustrates the schematic diagram of a plausible growth mechanism. Firstly, $(NH_4)_2TiF_6$ 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 gradurally 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.

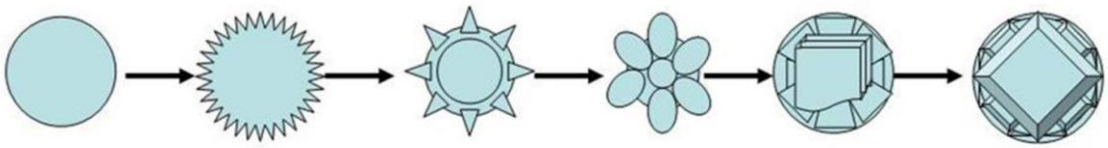

Figure 4. The schematic diagram of a plausible growth mechanism of TiO_2.

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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