

Morphology Control of Anatase TiO₂ by Surfactant-assisted Hydrothermal Method*

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Abstract By hydrolysing titanium isopropoxide in a long hydrocarbon chain surfactant-containing solution, TiO₂ fine particles with a diversity of well-defined morphologies was synthesized in this study by a hydrothermal route. The structural change during the formation process was monitored by scanning electron microscopy, transmission electron microscopy and X-ray diffraction analysis. TiO₂ with various morphologies such as particle, sheet, rod, tube and flower-like shape was obtained by carefully controlling the preparation conditions. The experimental results show that the pH value is crucial for shape control of the produced TiO₂ because it can change the charge state of the surfactant in the solution and the adsorption potential of the surfactant on the TiO₂ surface. The shape evolution of anatase TiO₂ was elucidated by quenching the reaction at different stage and the formation mechanism of different shaped TiO₂ was suggested.

Keywords morphology control, titanium dioxide, charged state, anatase

1 INTRODUCTION

Since the discovery of carbon nanotubes[1], nanostructures and nanomaterials have attracted great interest. Nanomaterials with different morphologies may have some specific properties, and new applications of such materials are considered to be related to their shape and size. Synthesis of nanomaterials with specific shape and size and the clarification of their formation mechanism are important topics for material science and technology. TiO₂, an exceptionally important material for application in photocatalysis, ceramic material, filler, coating, pigment and cosmetics, has been attracting attention in both fundamental research and practical development work. Reports of TiO₂ with different shape such as nanoparticles[2], thin films[3], nanorods[4], nanowires[5,6] and nanotubes[7,8] have spurred a great interest in studies on TiO₂ nanostructure synthesis and their application. Although TiO₂ with different shape has been synthesized by different methods, the formation mechanisms of titania with different shape remain a challenge to the scientists in this field. Moreover, the available titanium precursors, such as alkoxide or chloride have very high reactivity toward water, making shape control of TiO₂ more difficult.

Many techniques such as chemical vapor deposition (CVD)[9] and thermal pyrolysis[10] have been developed to make nanostructured materials, among which the wet chemical methods such as the hydrothermal method and sol-gel method show many advantages such as mild reaction conditions, less energy consumption, simple equipment required and large number of variable factors to control the sample morphology. In the course of hydrothermal synthesis, the reaction path is very sensitive to the experimental conditions, e.g., temperature, pH and duration of the hydrothermal treatment[11]. Also, it is of practical

importance to select suitable surfactant molecules, which act as templates or shape controllers, directing the formation of a structure toward a desired target arrangement[12]. Such a surfactant-assisted templating approach has been used in preparation of many mesoporous transition metal oxides[13,14]. As to the preparation of TiO₂ with specific nanostructure, not only ammonia but also diamine and triethanolamine have been identified by Sugimoto *et al.*[4] as shape control agents and the amino groups are expected to show affinity to specific surfaces of the particles, reducing the normal growth rate on the adsorbed planes and resulting in anisotropic shape.

Among the different shapes of TiO₂, low dimensional materials such as one dimensional (1-D) nanostructures including nano-wires, nanorods as well as nanotubes and 2-D nanostructures such as nanosheet or nanoflakes have aroused substantial research interest not only because of their specific quantum-confinement effects[15] but also because of their ability in conducting electrons, which makes them especially promising for future application in nanoelectronics and photovoltaic cells[16]. Usually the formation of 1-D nanorods and nanowires by the solution-phase route occurs mainly due to the anisotropic growth process, in which the choice of suitable templating agent is sometimes crucial to the success of synthesis. There are so many unpredictable and possible parameters that are influential in the nucleation and growth processes in solution-phase synthesis that it is usually difficult to clearly interpret the intrinsic mechanism involved in the phase and morphology formations.

In this study, we introduced variable hydrophobicity by dodecanediamine (DDA) to the shape controlling system and succeeded in formation of different shaped titania such as nanoparticles, nanorods,

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nanotubes, sheets and flower-like shape in the same system by carefully control the reaction condition and the formation mechanisms were elucidated.

2 EXPERIMENTAL

2.1 Preparation

Experimental procedures were as follows: titanium isopropoxide (TIPT) was mixed with triethanolamine (TEOA) at a molar ratio of [TIPT] : [TEOA]=1 : 2 to form a compound of Ti(IV) which is stable against hydrolysis of Ti(IV) at room temperature[4]. Then distilled water was added to make an aqueous stock solution with the concentration of Ti(IV) fixed at 0.5mol·L⁻¹ (solution 1). Another solution (solution 2) was prepared by mixing DDA with distilled water and the concentration of DDA was fixed at 0.1mol·L⁻¹ throughout the experiment. Then 25ml of solution 1 was mixed with the same volume of solution 2. The pH of the mixed solution was adjusted by adding HClO₄ or NaOH solution. The mixed solution was then transferred into a 100ml Teflon autoclave without stirrer, sealed with a stainless steel lid, and aged at 100 °C for 24h and then an elevated hydrothermal temperature for desired period to nucleate and grow the titania particles. The pH value was almost no change before and after the reaction. The resulting white solid products were centrifuged and washed with distilled water and ethanol to remove the ions possibly remaining in the final products, followed by drying at 80 °C in air.

2.2 Characterization

The obtained samples were characterized by X-ray powder diffraction (XRD) using a Rigaku Goniometer (PMG-A2, CN2155D2) X-ray diffractometer with Cu-K_α radiation ($\lambda=0.154178\text{nm}$) at a scan rate of 2°·min⁻¹. The morphology and features of the product were examined using transmission electron microscope (TEM, JEOL 200CX) with acceleration voltage 200kV and scanning electron micrograph (SEM, JEOL, JSM-6500FE).

3 RESULTS

3.1 Structure and morphology under different pH

Figure 1 shows the SEM and TEM images of the samples obtained after 72h of hydrothermal reactions at 140 °C under different pH. Under acidic condition of pH 5.6, the produced sample showed sphere-like structure with particle size of about 30 to 60nm. With increase of pH of the solution, the shape of the prepared particles changed from ellipsoids to nanorods with large aspect ratio, which showed that pH of the solution had tremendous effect on the morphology of the produced nanosized titania. When pH of the solution was adjusted to above 11, hydrolyzing of TIPT in this system gave a new structure, flower-like TiO₂ with an average size of 1.5 μm , as shown in Figs.1(d) and (e). The definition of the flower-like TiO₂ nanostructures comes from the geometrical similarity to flowers. Each small crystal in the typical flower-like TiO₂ routes from the individual crystalline nucleus.

The selected area electron diffraction (SAED) pattern shown in Fig.1(f) indicates the single crystalline

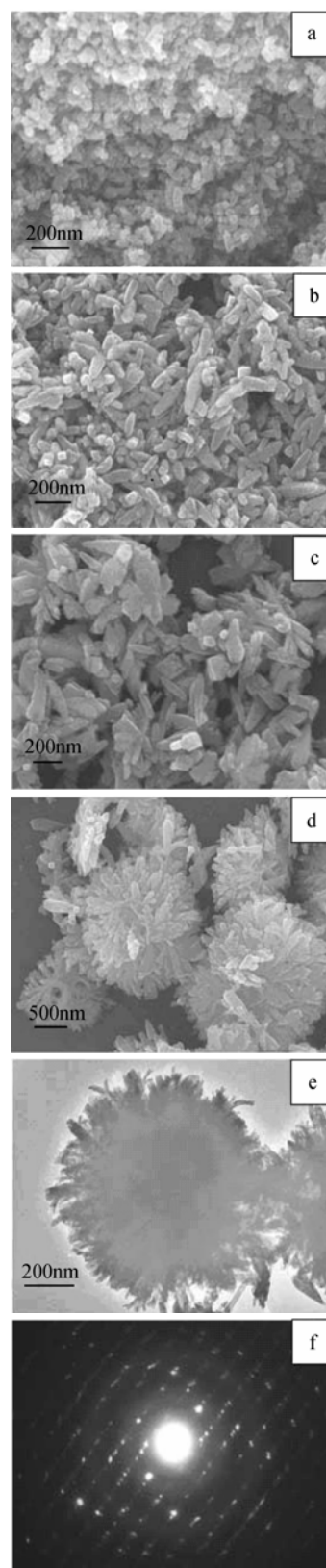


Figure 1 SEM micrographs of the sample formed under pH of (a) 5.6, (b) 10.4, (c) 10.7, (d) 11.1 and (e) TEM micrographs of the sample formed under pH of 11.1 and (f) SAED pattern of the same sample as (e)

nature of the branch of the flower-like sample. From the SAED pattern, it is also concluded that the flower-shaped TiO_2 is composed of monocrystallines of nanorods growing homocentrically, instead of a simple aggregation of small crystallites.

The XRD pattern of the flower-like TiO_2 nanostructure is shown in Fig.2. All the diffraction peaks are well assigned to anatase TiO_2 with lattice constants $a=0.37852\text{nm}$ and $c=0.95139\text{nm}$, which are consistent with the values in the standard card (JCPDS 21-1272). Compared to the standard card, the [004] peak is stronger. The relative intensity has increased from 20% to 30%, revealing the [001] oriented growth of the TiO_2 nanorods. No characteristic peaks of other impurities were observed, indicating that the product has high crystallinity and purity. Fig.3(a) shows the high-resolution transmission electron microscopy (HRTEM) image of an individual TiO_2 nanorod obtained from the flower-like TiO_2 nanostructure treated by long time ultrasonication. The surface profile image of the nanorod shows stepped terraces on the [101] surface, which are marked with arrows. Its height is

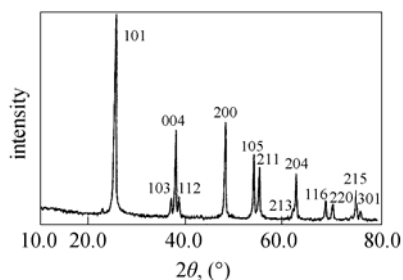


Figure 2 XRD patterns for the flower-like TiO_2 nanostructures prepared by DDA-assisted hydrothermal process at pH of 11.1

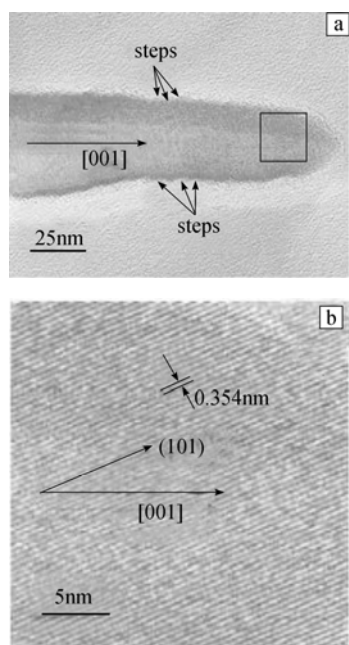


Figure 3 HRTEM image of individual TiO_2 rod (a) and (b) magnified image of selected square in (a)

measured as a multiple of 0.354nm , in accordance with $d_{[101]}$ of anatase. This structural feature has been observed by Chemseddine and Moritz[17] who explained these as the consequence of cluster-cluster growth and condensation of skewed octahedra in the case of anatase. Fig.3(b) shows a magnified image of the selected square area indicated in Fig.3(a). The image clearly reveals that the fringes of [101] planes with a lattice spacing of about 0.354nm can be observed, indicating that the TiO_2 nanorod is single crystal in nature which is in accordance with the SAED pattern shown in Fig.1(f). It was also observed that the crystal growth is not in [101] but in the [001] direction, which is well consistent with the XRD results.

When the pH of the system was adjusted to 12.8, the flower-like structure can also be obtained, as shown in Fig.4. Fig.4(a) indicates a high yield of the flower-like structure. The detailed structure of the sample prepared in this condition is shown in Fig.4(b). From this image it can be seen that the flower-like

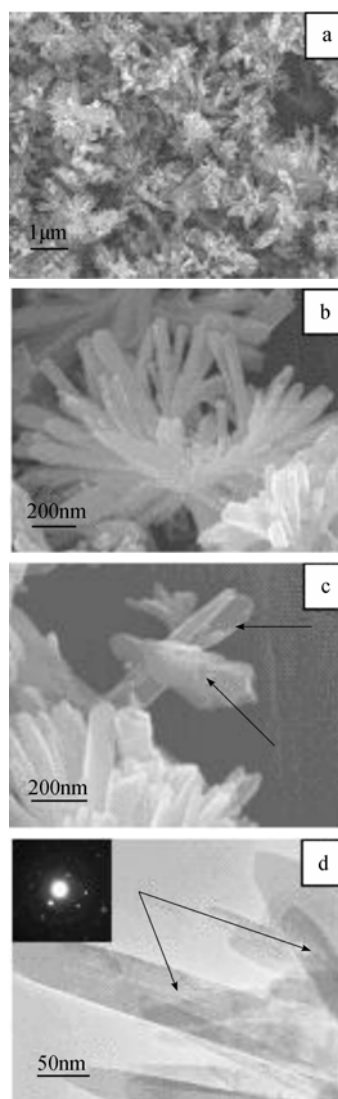


Figure 4 SEM (a), (b), (c) and TEM (d) micrographs of samples formed under pH of 12.8

structure prepared at pH of 12.8 is different from those prepared under pH of 11.1. The flower-like structure prepared under this condition was composed of nanotubes which can be seen very clearly in Figs.4(b) and 4(c). From the high magnification SEM image [Fig.4(c)], one can see some sheets roll to form tubes. Some nanotubes show their multilayer structure very clearly [Fig.4(c), indicated by arrows]. TEM observation [Fig.4(d)] demonstrates that a narrow stripe was observed when the nanotube was not completely closed. The diameter of the nanotubes ranges from about 30nm to 60nm. The SAED pattern [inset of Fig.4(d)] showed that the single crystal nature of the nanotubes and the preferred growth orientation of nanotube TiO₂ was along the C axis of anatase phase.

When the pH value of the solution was adjusted higher than 13, the titanium oxide crystalline could not be formed even after 4d of second aging. That may be due to the inhibited nucleation of TiO₂ by strong adsorption of DDA and TEOA onto the embryos of TiO₂. This result is very similar to the findings of Sugimoto *et al.*[4].

3.2 Shape evolution

To pursue the growth mechanism of the produced TiO₂ with different shape, experiments with different reaction time were carried out to monitor the evolution of particle shape by recording the shape of the sample at suitable interval. Under acidic condition of pH 5.6, the SEM images of the samples at reaction time of 1h and 30h are shown in Fig.5. It can be seen very clearly that spindle-like particles formed first and then the particle grew and eventually larger quasi-spherical particles formed [Fig.1(a)]. Under the basic condition of pH 10.7, a disk-like structure formed after 1h of reaction [Fig.5(c)], and then a sheet structure was observed. The sheet on the surface rolled up and the sheet thickness was shown to be about 20 to 50nm

[Fig.5(d)]. After 72h, an irregular rod-like structure was formed as shown in Fig.1(c).

The shape evolution under pH of 11.1 is shown in Fig.6. The nanodisk-like structure was formed first after 1h of reaction [Fig.6(a)] and then the multisheet structure which was very similar to the lamellar phase of surfactant [Fig.6(b)]. Some sheets on the outer surface were rolled into nanorods [indicated by an arrow in Fig.6(b)]. Fig.6(c) showed flower-shaped aggregates composed of many orderly aligned rods. Some half-flower shaped structures can also be seen in Fig.6(c), and the original multilayer sheets [Fig.6(b)] were completely rolled into many rods which orderly aligned and turned into flower-shaped aggregates. The low magnification SEM image [Fig.6(d)] shows that almost all TiO₂ showed the same flower-like shape with standing or flat arrangement, indicating the high yield of this structure. Under higher pH of 12.8, the shape evolution was similar to that under pH of 11.1 at which the sheet structure formed first and then the sheet rolled to form nanotubes. As further evidence, two TEM images of the sample in the process for nanotube formation are shown in Fig.7[18]. Fig.7(a) showed the rolling sheet and Fig.7(b) showed the rolled sheet forming a nanotube. From these images it was concluded that the anatase TiO₂ nanotubes were formed from the rolled sheets.

4 DISCUSSION

From the present work, one can see that the nanorods and nanotubes are resulted from the rolling growth of the sheet structure. pH of the solution is the most important factor for the shape control of anatase TiO₂. This important effect of pH resulted from the variation in the charge state of DDA versus pH as shown in Fig.8: H₃⁺N(CH₂)₁₂NH₃⁺ being present under pH lower than 8, H₃⁺N(CH₂)₁₂NH₂ between pH = 8 and 11, and H₂N(CH₂)₁₂NH₂ when pH

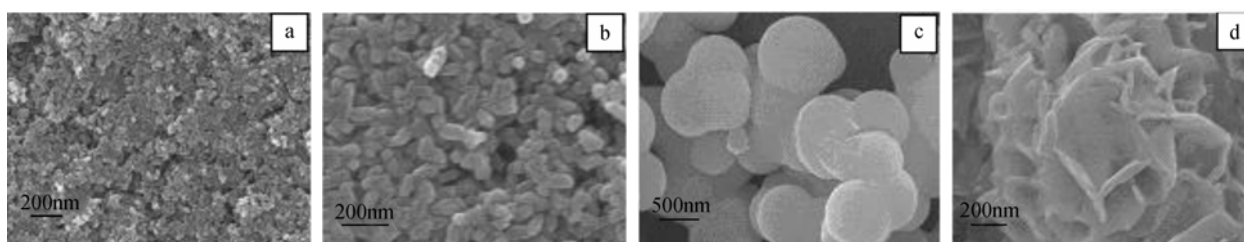


Figure 5 SEM micrographs of samples formed under pH of 5.6 (a), (b) and 10.7 (c), (d) at different hydrothermal time of (a), (c) 1h or (b), (d) 30h

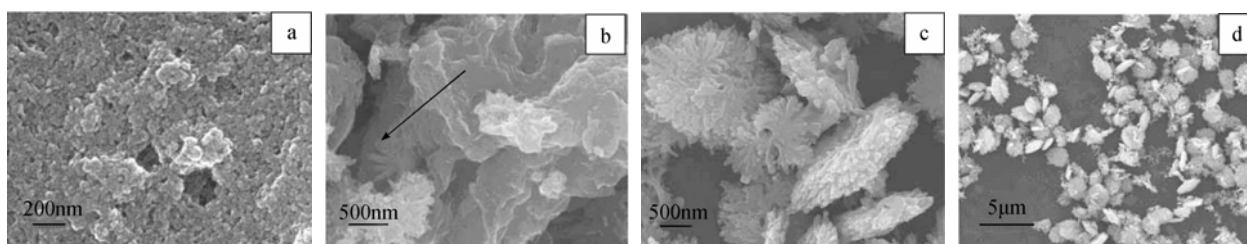


Figure 6 SEM micrographs of samples formed under pH of 11.1 at different hydrothermal time of (a) 1h, (b) 30h (c) 72h and (d) low magnification image of (c)

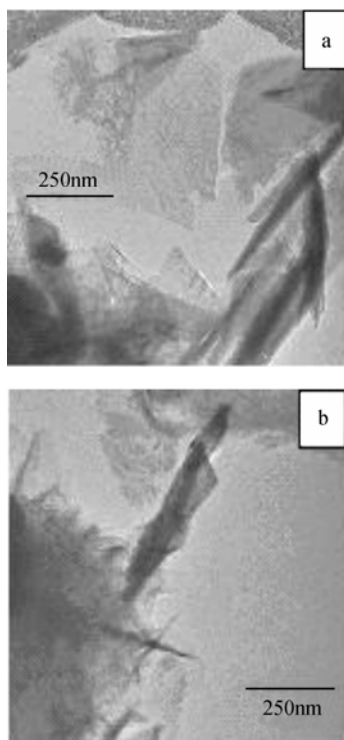


Figure 7 TEM image of the samples during the process for nanotube formation under pH=12.8

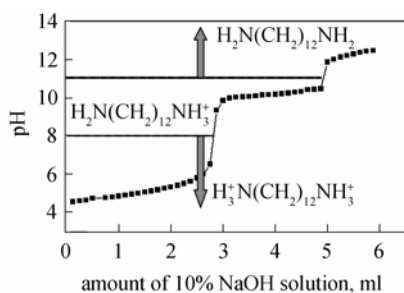


Figure 8 Titration curve for $0.1 \text{ mol}\cdot\text{L}^{-1}$ DDA solution ($0.1 \text{ mol}\cdot\text{L}^{-1}$ DDA, solution 20ml)

higher than 11.

Double charged DDA under pH below 8 is expected to be hydrophilic. Therefore, only particles of TiO_2 can be formed under this condition. When pH of the solution was adjusted to between 10 and 11, most of DDA existed as $\text{H}_2\text{N}(\text{CH}_2)_{12}\text{NH}_3^+$ which is expected to become hydrophobic and make lamellar phase. The small-angle X-ray scattering (SAXS) results shown in Fig.9 indicate that 10min after DDA contacts with water, the lamellar structure has formed at the interface. By using the very thin layer of water as the nanoreactor, the two-dimensional structure can be expected to form easily. Thus, the lamellar structure in this case was inferred to be a loose structure. When the pH value was adjusted to above 11, most of DDA exists in its nonionic state, in which more stable inorganic/organic hybrids of titanium dioxide-DDA lamellar mesostructures are formed. Hydrolysis reaction of TIPT produces isopropyl alcohol which can penetrate and intercalate into the lamellar structure

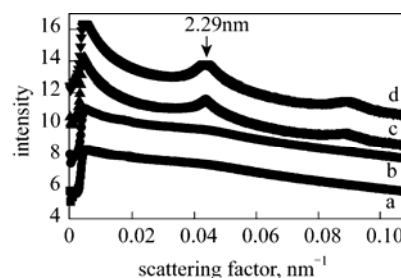


Figure 9 SAXS patterns for DDA-water system detected after contact for (a) 5s, (b) 50s, (c) 2min, (d) 10min

and expel DDA away, resulting in rolling of the TiO_2 nanosheets. Under lower pH values, the nanosheets have high percentage of Ti-OH group on the surface, and the rolling of the sheets results in the condensation reaction between two adjacent Ti-OH groups, Ti-O-Ti bonds are generated and the nanorods formed at last. Under higher pH values, the nanosheets have high percentage of Ti-O^- groups. The highly negatively charged TiO_2 sheets could not fuse into nanorods during rolling but made nanotubes due to electrostatic repulsion.

5 CONCLUSIONS

TiO_2 samples with a diversity of well-defined morphologies such as sphere, sheet, rod, tube, and flower were synthesized by a surfactant-assistant hydrothermal method. Higher pH is preferable for nanotubes formation, whereas lower pH usually leads only to sphere-like structure. The results show that nanotubes and nanorods are formed by rolling sheets which are created by the lamellar structure of DDA. The hydrophobic property of surfactant DDA under basic condition promotes the lamellar structure, the isopropyl alcohol produced in the hydrolysis reaction of TIPT can remove DDA from the gap between the two TiO_2 layers and provide the driving force for sheet rolling. Whether the rolling sheet produces a rod or tube depends mostly on the charge state of the TiO_2 sheet surface.

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