Preparation of Controllable Crystalline Nano-TiO_2 by Homogeneous Hydrolysis

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The crystal-form-controllable nanosize TiO_2 was obtained using homogeneous hydrolysis method by the addition of toluene-*p*-sulfonic acid (TSA). Two processes of the rutile phase formation were proposed. The sample with 0.2 mole ratio of toluene-*p*-sulfonic acid was a mixed crystal of anatase and rutile, and characterised that the size of nano-crystalline was 19.5 nm for rutile, and 13.5 nm for anatase, the specific surface area was 72.7 m^2/g, and the energy of band gap was 2.83 eV. The mechanism of development of rutile nanosize TiO_2 was presented in homogeneous hydrolysis system with TSA.

Since the discovery of photoelectrochemical splitting of water on *n*-TiO_2 electrodes,[1] photocatalysis of TiO_2 has attracted extensive interest. Some groups reported that anatase TiO_2 had high photocatalytic efficiency,[2] and some efforts showed that a mixed crystal TiO_2 containing rutile and anatase had superior photocatalytic properties. The study on the photocatalytic properties of rutile TiO_2 was little reported mainly because ultrafine rutile TiO_2 was difficult to be synthesized.[3] Preparation of ultrafine TiO_2-containing rutile involves following methods. Generally speaking, amorphous TiO_2 prepared by sol-gel, hydrothermal reaction, forced hydrolysis, intense light ion-beam evaporation method, etc. is calcinated at high temperature to obtain TiO_2 with rutile. Preparation of TiO_2 containing rutile with additives had been reported previously, such as inorganic additives ZnO/Fe_2O_3,[4] AlO_3,[5] ZrO_2,[6] and the organic additive hexylene glycol.[7] In this study, a novel homogenous hydrolysis process was developed to prepare crystal-form-controllable nanosize TiO_2 using $TiCl_4$ as the precursor by addition of toluene-*p*-sulfonic acid. By adjusting different addition ratio of TSA, crystal pattern of TiO_2 could be controlled at will.

$$\begin{array}{ccc} CH_3COOH + CH_3OH & \longrightarrow & H_2O + CH_3COOCH_3 \\ & & \downarrow \\ & & TiCl_4 + H_2O \longrightarrow Ti(OH)_4 + HCl \end{array} \qquad (1)$$

Preparation of nanosize TiO_2 in liquid phase involves two procedures,[8] which are nucleating and growing up. And that nucleating rate overmatches growing rate is the prerequisite for preparation of uniform nano-crystalline TiO_2. Under the conventional sol-gel procedure, however, the water needed for the hydrolysis of titanium precursors such as $TiCl_4$ or alkyl titanate was added directly to the reaction system. In the homogeneous hydrolysis process reported in this paper, however, the water used for the hydrolysis was homogenously produced in the mixed solution by the esterification of organic acid and aliphatic alcohol, which provided a superior atmosphere for the nucleation and growth of the primary particles in solution. The mechanism of homogeneous hydrolysis is shown in Eq 1. Expectably, nucleating rate can be controlled soundly in the homogeneous hydrolysis system. And in fact, nanoscale TiO_2 with evenly-distributed particle size have been prepared anticipatively.

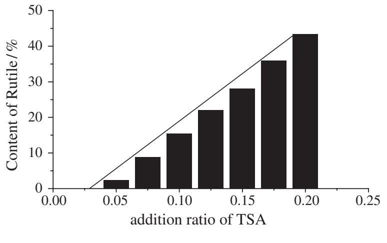


Figure 1. The influence of addition ratio of TSA on content of rutile.

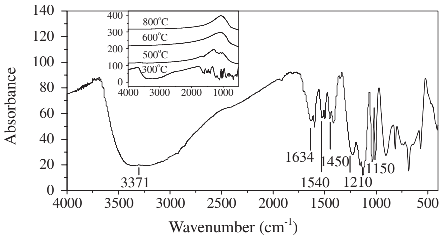


Figure 2. FT-IR spectra of TiO_2 calcinated under 300 °C

The experimental procedure employed here is described as follows. Titanium tetrachloride (98%, $TiCl_4$, Shanghai Chemical Agent Co.) was used as a starting material without further purification. The mole ratio of reactants was 0.25:1:1:0.2 ($TiCl_4$:acetic acid:methanol:TSA). And aftermentioned sample TSA02 represented that the mole ratio of TSA: acetic acid was 0.2:1, and was dried at 110 °C. Similarly, TSA02C implicated the sample with 0.2 mole ratio TSA was heat-treated at 110 and 500 °C orderly. At the beginning of the process, the appropriate amount of $TiCl_4$ was added dropwise into the mixture of acetic acid and methanol in the ice-water bath under N_2 protection and vigorous stirring until forming evenly-distributed solution. Then, TSA was added into this solution followed by transferring the reaction system into lukewarm bath at 60 °C under N_2 protection and vigorous stirring. This process lasted 2 h, and then the intermediate products were dried at 110 °C, ground, and calcinated. The morphologies of the samples were observed through TEM (JEM-1200EX, Japan). The products were characterized by X-ray powder diffraction (XRD, Rigaku D/max 2550VB/PC, Japan) with Cu Kα radiation ($\lambda = 0.154056$ nm). The specific surface area was measured by BET (Micromeritics ASAP 2010, USA). The TG–DTA curves were tested by thermal analysis measurement (851^e model, Switzerland). The characteristics of samples were tested on the Fourier

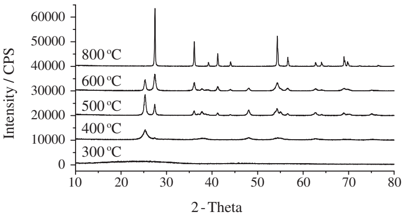


Figure 3. XRD patterns of TiO_2 nano-crystallite under different temperature of heating treatment with TSA.

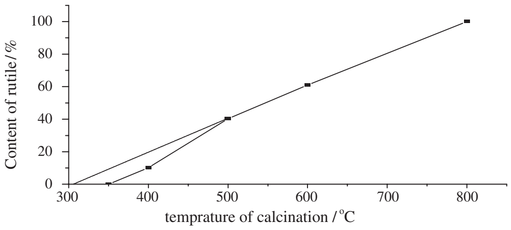


Figure 4. Influence of heat treatment temperature on content of rutile.

infra-red spectrum instrument (Nicolet Magna-IR550).

The sample in the absence of TSA (A1) showed uniform anatase (Figure 1). When the addition ratio of TSA exceeded 0.05, rutile TiO_2 was appeared, and content of rutile was growing linearly with increase of TSA. Content of rutile in mixed crystal was calculated using the typical formula.[9] The fact mentioned above illustrated that the addition of TSA induced the development of rutile phase.

FT-IR spectra (Figure 2) shows that for the sample treated at 300 °C, the bonds at around 1634 cm^{-1} and 3371 cm^{-1}, due to –OH, emerged. And the emergence of CH_3COO–Ti– (1540 and 1450 cm^{-1}) was in accord with the reference reported.[10] The bonds at around 1210 and 1150 cm^{-1}, assigned to –S=O group, could be attributed to sulfonic acid group uneliminated at 300 °C. The sample calcinated at 500 °C had no such bonds, –OH, CH_3COO–Ti–, and –S=O, which illustrated these groups were removed at 500 °C. And the typical bond of TiO_2 was appeared, which accounted for the fact that the nano-crystalline TiO_2 was developed at 500 °C. Consequently, 500 °C was the optimal heat treatment temperature for preparation of nano-crystalline TiO_2 in the homogeneous reaction system.

XRD patterns (Figure 3) shows that the crystalline of the samples treated at different temperature, which were amorphous at 300 °C, anatase at 400 °C, mixed crystal of anatase and rutile at 500 and 600 °C, and pure rutile at 800 °C, respectively. This fact was in agreement with Figure 2. Figure 4 indicates that the growth rate of rutile in mixed crystal with the increasing heat treatment temperature had a turning point at 500 °C. Before the turning point (350–500 °C), the content of rutile increased quickly, and the slope became gentle after 500 °C. This could be explained by the different mechanism for the formation of rutile phase. The bonding effect of $Ti(OH)_4$ with sulfonic acid group accounted for the faster rate. And the transfer of anatase to rutile by heat treatment gave a slower rate.

TEM images (Figure 5) is the morphologies of sample TSA02C calcinated in different temperature, 400 °C (a) and 500 °C (b), respectively. Picture (a) shows the mixture of anatase and amorphous TiO_2, where cubiform shape is anatase, and rod-like one is amorphous TiO_2 surface-covering TSA. And the sample TSA02C calcinated in 500 °C (b) shows obvious cubic form with little bigger crystalline size. The mechanism of the development of rutile nanosize TiO_2 in the process is shown in Scheme 1. In the course of hydrolysis, hydrogen bond is developed between TSA and titanic acid. And steric effect induced from it give the support for difficult agglomeration between the particles. In comparison the co-point oxygen structure between two crystal cells in anatase, titanium atoms between two crystal cells of rutile share two oxygen atoms. The structure of titanic acid shown in Scheme 1 is similar to that of rutile. That mentioned above accounted for the mechanism of formation of rutile. And the further research work for the mechanism will be proceeded.

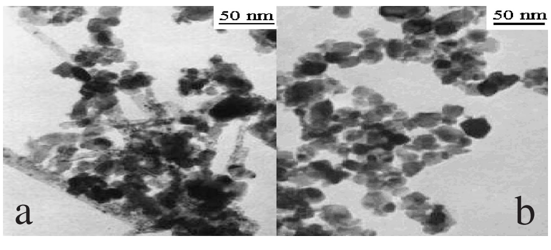
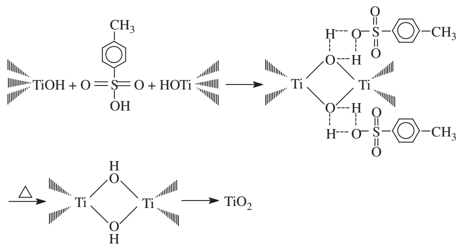


Figure 5. TEM images of sample calcinated at 400 and 500 °C.



Scheme 1.

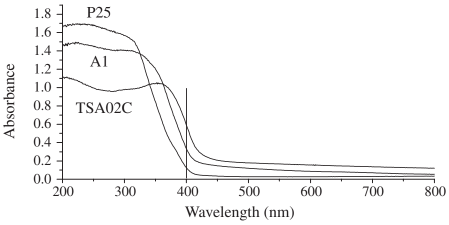


Figure 6. UV–vis curves of TSA02C, A1 and P25.

The border of absorption band can be influenced by the defect of TiO_2 crystal lattice, crystal form, and the size of crystalline. From Figure 6, the superior absorption in the visible light region (over 400 nm) of sample TSA02C containing 43.4% rutile and 56.6% anatase, and red shift of the border of absorption band imply that it could be excitated by the visible light. The band gap values were calculated using the UV–vis spectra from the Eq 2[11] by extrapolation method, which of TSA02C, A1 and P25 were 2.83, 2.94, and 3.03 eV, respectively. Of the three samples, TSA02C had the lowest value of band gap. The addition of TSA also accounted for the change of the band gap energy.

$$\alpha(h\upsilon) = A(h\upsilon - E_g)^{m/2} \qquad (2)$$

The crystal-form-controllable nanosize TiO_2 could be obtained using homogeneous hydrolysis method by the addition of toluene-*p*-sulfonic acid. It can be expected that this process for preparation of crystal controllable nanosize TiO_2 will be meaningful and valuable for scientific research and industry application as well.

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