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## Nanometer composite-crystal TiO<sub>2</sub> powder synthesized by two-step method

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### ABSTRACT

TiCl<sub>4</sub>, ammonia, inorganic salts as raw material, nanometer composite-crystal TiO<sub>2</sub> powders were synthesized by two-step chemical method. Precursors were crystallized with different crystal phase and stable composite-crystal phase TiO<sub>2</sub> with anatase and rutile phase was prepared at low temperature. Quantitative control of crystal phase was realized. Remarkable factors including reaction pH value, reaction time, which affected the phase content, micro-structure, morphology were studied.

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### KEYWORDS

Nano-TiO<sub>2</sub>;  
Composite-crystal;

### INTRODUCTION

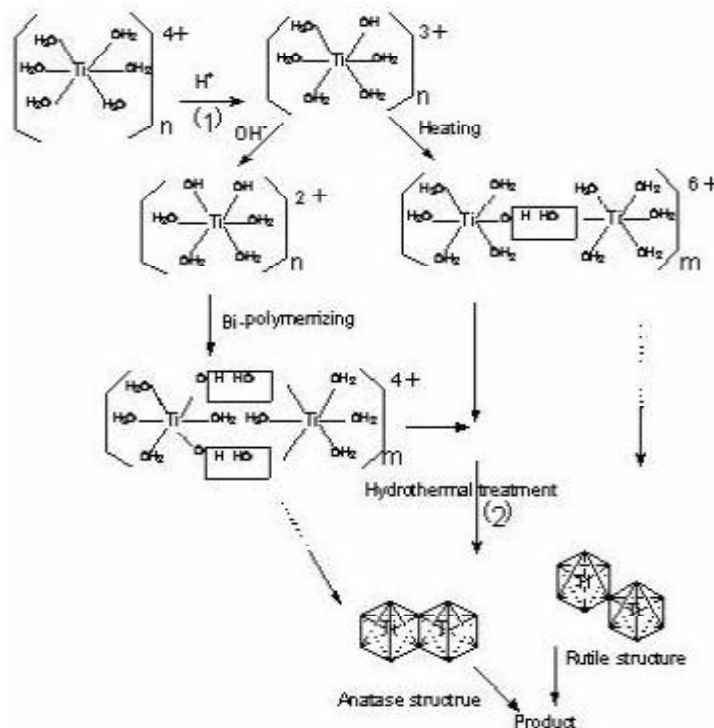
Recently, nano-crystalline titania has attracted increasing attention because of its wide applications in pigment, cosmetics, catalyst, solar cell, etc<sup>[1-4]</sup>. There are seven known polymorphs of titania, six of which have distinct structures<sup>[5]</sup>. Three of these polymorphs, rutile, anatase, and brookite occur in nature, and TiO<sub>2</sub> with different applied properties due to different phase structure. There are many researches about synthesizing methods and structure characterization about different phase structure titania<sup>[6-10]</sup>. In photo-catalysis research, anatase titania is usually considered to be more active than rutile crystalline<sup>[11,12]</sup> and the enhancement is ascribed to the difference of the Fermi level and the extents of hydroxylation on the surface of the solid<sup>[12]</sup>. In addition, rutile usually showed harder agglomeration and larger particle size than anatase since rutile is normally prepared by calcinations of anatase at high temperatures. But rutile structure is thermodynamically

stable phase and possesses a smaller band gap than that of anatase phase and shows better photoabsorption property in visible light wavelength range, and photocatalytic efficiency can be improved after two structure titania are combined. Therefore composite-crystal (anatase and rutile phase) nano-TiO<sub>2</sub> with larger special surface area and non-agglomeration can possess both advantages of both phase then the photo-catalytic reaction activity will be enhanced.

Our studies were based on those theories and a series of high active nano-TiO<sub>2</sub> composite-crystal materials with control of crystal phase and stable phase composition were synthesized. Remarkable factors including reaction pH value, treatment time et al influenced the phase composing, micro-structure, morphology and specific surface area were discussed in detail.

### EXPERIMENTAL

#### Preparation of TiO<sub>2</sub> samples



**Figure 1:** Formation mechanism of the titania nano-crystals prepared by two-steps method- (1) Compulsive hydrolyzation process at normal pressure; (2) Hydrothermal treatment process at low temperature

$TiCl_4$ ,  $NH_3 \cdot H_2O$ ,  $C_2H_5OH$  et al were analytic grade reagents. The procedure of synthesis was as follows: 22.0mL  $TiCl_4$  was dripped in a flask containing 178.0 mL deionized water and at a rate of 1D/s, then a transparent solution of 1.0M  $Ti^{4+}$  was obtained, subsequently the solution was heated quickly to hydrolyze compulsively at  $100^\circ C \sim 101^\circ C$ . After controlling the reaction time, ammonia solution (1:1 volume ratio) was dripped into the suspension with vigorous magnetically stirring. The optimal pH value was 9.0. Then the reactive system was transferred into hydrothermal autoclave, and heated quickly. The hydrothermal reaction was performed at  $160^\circ C$ , and the reaction time was controlled at the same time. After the treatment, the product of white suspension was filtered and washed with boiling de-ionized water in order to remove  $NH_4^+$  and  $Cl^-$  in the product, and then washed with anhydrous ethanol for 3~5 times to remove the water in the product, dried at  $60^\circ C \sim 62^\circ C$  in the vacuum dryer for 5h. The composite-crystal nano- $TiO_2$  powder was obtained after milling.

### Characterization techniques

The phase constitution of the products was deter-

mined with X-ray diffraction analysis (XRD, Y-2000 China) with continuous scanning mode at  $3.6^\circ \text{min}^{-1}$  using graphite-monochromized  $Cu K\alpha$  radiation. The molar ratios of anatase and rutile were determined by the XRD peak intensity ratio with Spur-Myers method<sup>[13]</sup>:

$$W_R = (1 + 0.8(I_A/I_R))^{-1} \quad (1)$$

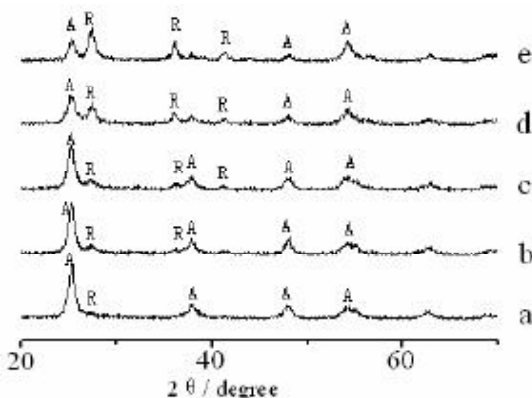
$$W_A = 1 - W_R \quad (2)$$

Where  $W_R$ ,  $W_A$ ,  $I_A$  and  $I_R$  are the molar fractions of rutile and anatase, peak intensity of anatase d (101) and that of rutile d (110) respectively. The microstructure and morphology of the powder were observed by transmission electron microscopy (TEM, JEM-100X Japan) at 200kV, and scanning electron microscopy (SEM, KYKY-1000B Japan).

## RESULT AND DISCUSSION

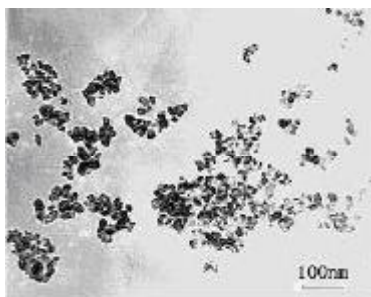
Reaction pH value played an important role in preparation of composite-crystal nano- $TiO_2$  by two-steps method. A mass of  $H_3O^+$  was released due to hydration between  $Ti^{4+}$  and  $H_2O$  molecules during the compulsive hydrolyzation of  $TiCl_4$  at normal pressure. And it is well known that titanium did not exist in the form of  $Ti^{4+}$  cation, but existed as a sixfold coordinated [Ti

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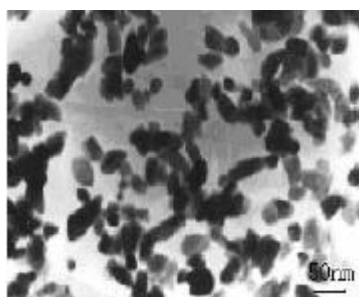


**Figure 2: Effects of compulsive hydrolyzation time to control of structure phase-(a): 10%A 90%R (2min); (b): 20%R 80%A (12min); (c): 25%R 75%A (48min); (d): 30%R 70%A (75min); (e): 40%R 60%A (180min) A: anatase R: rutile**

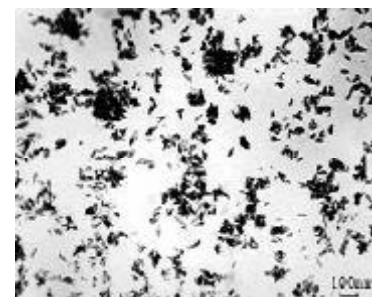
Figure 2 shows that quantitative control of product's structure phase could be realized by controlling the compulsive hydrolyzation time of the first step, the content of rutile phase increased with increase of the hydrolyzation time, when the hydrothermal treatment time was 60 min. A small quantity of rutile phase appeared when reaction time of hydrolyzation was 2 min, while 40 percent of rutile phase appeared when the reaction time of hydrolyzation was 180 min, and the reasons may be: Amounts of crystal nucleuses were formed due to hydrated  $\text{Ti}^{4+}$  in strong acid conditions after heated quickly, then the nucleuses tended to transformed into rutile structure by the influence of  $\text{H}_3\text{O}^+$ , and this structure transformation would consume the hydrated  $\text{Ti}^{4+}$  in the reaction system gradually with the



1. TEM for e sample



2. SEM for c sample



3. TEM for a sample

**Figure 3: Effect of the reaction time on morphology**

$(\text{H}_2\text{O})_6]_n^{4+}$  complex<sup>[14,15]</sup>. It is accepted that both anatase and rutile titania can grow from  $\text{TiO}_6$  octahedra, and the phase formation proceeds by the rearrangement of the octahedra. In the present research, the formation of the anatase and rutile phase in the product is correlated with pH value closely. Firstly,  $[\text{Ti}(\text{OH})(\text{H}_2\text{O})_5]_n^{3+}$  was formed from hydration in the compulsive hydrolyzation process, and bi-polymerizing structure of  $[(\text{H}_2\text{O})_5\text{Ti}-\text{HOHO}-\text{Ti}(\text{H}_2\text{O})_5]_m^{6+}$  was formed if keeping the acidity sufficient in the reaction system, then the corner-sharing structure of rutile phase cadre. then pH value was adjusted to 9.0 with diluted ammonia, and the excess hydrated  $\text{Ti}^{4+}$  in the reaction transformed into  $[\text{Ti}(\text{OH})_2(\text{H}_2\text{O})_4]_n^{2+}$  structure by the effects of the  $\text{OH}^-$ , and this structure due to a edge-sharing configuration of anatase phase cadre<sup>[16]</sup>. The product of composite-crystal nano- $\text{TiO}_2$  was synthesized by two-steps method. The Formation mechanism of the titania nano-crystals was showed as figure 1.

time prolonging. The excess of hydrated  $\text{Ti}^{4+}$  in the solution will transform to octahedral structure of anatase by  $\text{OH}^-$  effects after the change of pH, and at this moment, and the prolonging reaction time could not alter the molar ratio between rutile and anatase structure because rutile phase is more thermodynamically stable than anatase under this condition. Thus rutile phase and anatase phase crystallized successively and grown interlaced after hydrothermal treatment, and then nanocrystal titania with special configuration was formed.

Reaction time affects the microstructure and morphology of the product to some extent. Experimental results proved that the content of rutile phase increased with time increase, and spherical particles appeared dominating in the product's morphology; the content of anatase phase increased with hydrolyzation time decrease, and rod-shape particles dominated in the product's morphology, (see figure 3). The reason may be that crystal lattice constants of rutile and anatase

phase were  $a = b = 0.4584$  (nm)  $c = 0.2953$  (nm) and  $a = b = 0.3733$  (nm)  $c = 0.937$  (nm) respectively, and if crystal formation tend to grow along with axial orientation, growth trend of rutile phase along  $c$  axis stronger than that of anatase phase, thus spherical particles appeared in rutile structure but rod-shape appeared in anatase phase.

### CONCLUSIONS

$TiCl_4$ , ammonia, inorganic salts as raw material, nanometer composite-crystal  $TiO_2$  powders were synthesized by two-step chemical method: Morphologies and crystal phase contents of sample were quantitatively controlled by reaction time.

### ACKNOWLEDGMENT

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### REFERENCES

- [1] F.A.Cotton, G.Wilkinson; Advanced Inorganic Chemistry, 5<sup>th</sup> edition, Wiley, New York, 654-655 (1988).
- [2] A.Fujishima, K.Honda; Nature, **238**, 37-38 (1972).
- [3] B.O'Regan, M.Gratzel; Nature, **355**, 737-740 (1991).
- [4] A.Mills, S.L.Hunte; J.Photo-Chem, Photobiol., **A108**, 1-35 (1997).
- [5] J.F.Banfield, D.R.Veblen, D.J.Smith; Am.Miner., **76**, 343-353 (1991).
- [6] Dong-Seok Seo, Jong-Kook Lee, Hwan Kim; Journal of Crystal Growth, **229**, 428-432 (2001).
- [7] C.S.Fang, Y.W.Chen; Materials Chemistry and Physics, **78**, 739-745 (2003).
- [8] K.D.Kim, H.T.Kim; Colloids and Surfaces, A: Physicochemical and Engineering Aspects, **207**, 263-269 (2002).
- [9] R.H.Chu, J.C.Yan, S.Y.Lian; Solid State Communications, **130**, 789-794 (2004).
- [10] Y.Q.Wang, G.Q.Hu, X.F.Duan; Chemical Physics Letters, **365**, 427-431 (2002).
- [11] Augustynski; Electrochem.Acta, **38**, 43 (1993).
- [12] R.I.Bickley, T.Gonzalez-Carreno, J.S.Lees, L. Palmisano; J.Solid State Chem., **92**, 178-180 (1991).
- [13] R.A.Spur, W.Myers; Anal.Chem., **29**, 760-762 (1957).
- [14] T.Maki; Nippo Kagaku Kaishi, **8**, 45-50 (1978).
- [15] Y.Zhang, E.Shi, Z.Chen; J.Mater.Chem., **11**, 1547-1551 (2001).
- [16] S.Yin, Hitoshi Hasegawa, Daisaku Maeda; J. Photochem.Photobiol., **A63**, 1-8 (2004).