

Photo-Catalytic Nanometer Composite-Crystal TiO₂ Powder Synthesized by Two-Step Method

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ABSTRACT: *TiCl₄, ammonia, inorganic salts as raw material, nanometer composite-crystal TiO₂ powders were synthesized by two-step chemical method. Precursors were crystallized with different phase and stable composite-crystal TiO₂ 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, microstructure, morphology were discussed. Applied experiments of photo-degradation organic dyes illuminated by sunshine showed higher photocatalytic activity of composite-crystal than that of pure anatase, pure rutile and mechanical mixture of both, nanometer composite-crystal TiO₂ as photocatalyst.*

KEY WORDS: *Nano-TiO₂, Composite-crystal, Photocatalysis.*

INTRODUCION

Recently, nano-crystalline titania has attracted increasing attention because of its wide applications in pigment, cosmetics, catalyst, solar cell, etc [1-4]. There are seven known polymorphs of titania, six of which have distinct structures [5]. Three of these polymorphs, rutile, anatase, and brookite occur in nature, and TiO₂ shows different applied properties due to different phase structure. There is a lot of research about synthesis method and structure characterization of different structure titania [6-10]. In photo-catalysis research, anatase titania is usually

considered to be more active than rutile phase[11,12] and the enhancement is ascribed to the difference of the *Fermi* level and the extents of hydroxylation on the surface of the solid [12]. 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 antase phase, and it shows better photoabsorption property in visible light wavelength range, and photo-catalytic

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efficiency can be improved when two structure titania are combined. Therefore, composite-crystal (anatase and rutile phase) nano-TiO₂ with larger special surface area and non-agglomeration can possess the advantages of both phases then the photo-catalytic reaction activity will be enhanced.

Our studies were based on those theories, and a series of high active nano-TiO₂ composite-crystal materials were synthesized with control of crystal phase and stable phase composition. Factors including reaction pH, treatment time et al influenced the phase composing, microstructure, morphology and specific surface area have been discussed in detail. The samples showed higher photo-catalytic activity than pure anatase, rutile and mechanical mixture of them in photo-degradation experiments of organic dye with solar illumination. And mineralization of organic molecules was realized completely in some experiments within 30 min.

EXPERIMENTAL SECTION

The preparation of TiO₂ samples

TiCl₄, NH₃•H₂O, C₂H₅OH and other chemicals were analytic grade reagents. The procedure of synthesis was as follows: 22.0mL TiCl₄ was dripped in a flask containing 178.0 mL deionized water and at a rate of 1 drop per second, then a transparent solution of 1.0M Ti⁴⁺ was obtained, subsequently the solution was heated quickly to hydrolyze compulsively at 100°C~101°C at 50°C/min. After the reaction, ammonia solution (1:1 volume ratio) was dripped into the suspension in a time controlled manner with vigorous magnetic stirring. The optimal pH value was 9.0. Then the reactive system was transferred into hydrothermal autoclave (filling rate was 70%), and heated quickly (8°C/min). The hydrothermal reaction was performed at 160°C, and the reaction time was controlled at the same time. After the treatment, the product was filtered and washed with boiling de-ionized water in order to remove NH₄⁺ and Cl⁻, and then washed with anhydrous ethanol for 3~5 times to remove the water in the product to prevent agglomeration, and dried at 60°C~62°C in the vacuum dryer at the pressure of 3kPa for 5h. The composite-crystal nano-TiO₂ powder was obtained after milling.

Characterization techniques

The phase constitution of the products was determined with X-ray diffraction analysis (XRD, Y-2000 China) with

continuous scanning mode at 3.6° min⁻¹ using graphite-monochromized Cu Kα radiation. The molar ratios of anatase and rutile were determined by the XRD peak intensity ratio with *Spur-Myers* method [13]:

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

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

Where W_R, W_A, I_A and I_R are the molar ratio of rutile and anatase, and the 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).

Applied experiments of photo-catalytic reactions were performed in a Pyrex vessel illuminated by sunlight. The experimental process was as follows, First, acid red 3R solutions were prepared at a concentration of 100ppm, and 200.0mL of dye solution was extracted, then transferred to four conical flasks. 0.1000 g composite-crystal product, pure rutile and anatase products and mechanical mixture catalyst powder were added into the solution, respectively, to obtain the concentration of the catalyst which was 0.5g/L suspension. Then the mixture was treated by ultrasonic treatment for 15~20min in the dark place for adsorption balance, subsequently the photo-reactions in the four vessels could be performed with the solar illumination at the same time. The sample was extracted every 15 min during the photoreaction, and the suspension was centrifuged, and the clear solution was analyzed with UV-1200 spectrophotometer, and the maximal adsorption wavelength and adsorption value was determined, and the concentration change of organic acid dye was measured with standard comparison method during photo-reaction, and the decomposition rate was calculated according to following formula:

$$D \% = (A_{\text{starting}} - A_{\text{ending}}) / A_{\text{starting}} * 100\% \quad (3)$$

RESULTS AND DISCUSSION

Reaction pH value played an important role in preparation of composite-crystal nano-TiO₂ by two-steps method. A mass of H₃O⁺ was released due to hydration between Ti⁴⁺ and H₂O molecules during the compulsive hydrolyzation of TiCl₄ at normal pressure. And it is well known that titanium did not exist in the form of Ti⁴⁺ cation, but existed as a sixfold coordinated [Ti (H₂O)₆]⁴⁺ complex [14,15]. It is accepted that both anatase and

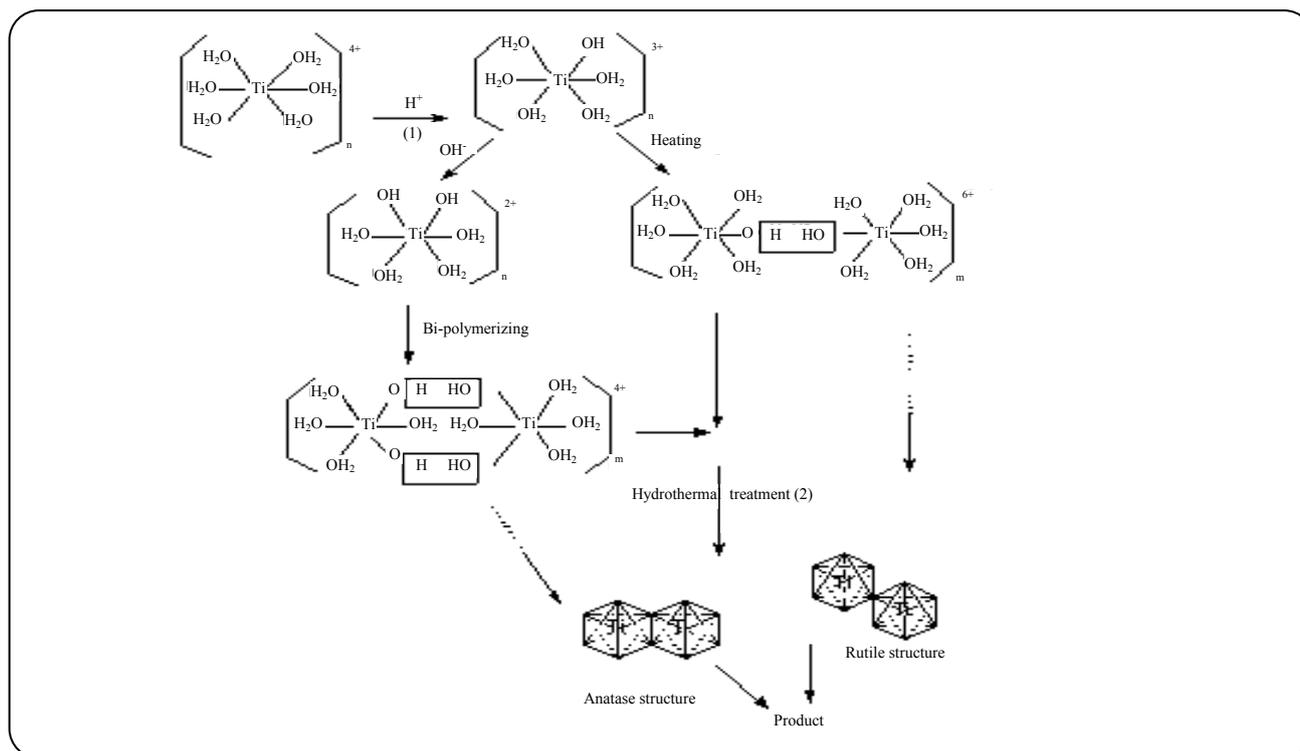


Fig. 1: Formation mechanism of the titania nano-crystals prepared by two-steps method.

(1) Compulsive hydrolyzation process at normal pressure. (2) Hydrothermal treatment process at low temperature.

rutile titania can grow from TiO₆ 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, $[Ti(OH)(H_2O)_5]^{3+}$ was formed from hydration in the compulsive hydrolyzation process, and bi-polymerizing structure of $[(H_2O)_5Ti-O(HO)-Ti(H_2O)_5]^{6+}$ was formed if keeping the acidity sufficient in the reaction system, then the corner-sharing structure of rutile phase cadre. And pH value was adjusted to 9.0 with diluted ammonia, and the excess hydrated Ti^{4+} in the reaction transformed into $[Ti(OH)_2(H_2O)_4]^{2+}$ structure by the effects of the OH^- , and this structure due to a edge-sharing configuration of anatase phase cadre [16]. The product of composite-crystal nano-TiO₂ was synthesized by two-steps method. The Formation mechanism of the titania nanocrystals is shown as Fig. 1.

Fig. 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 this may be ascribed to following reason, amounts of crystal nuclei were formed due to hydrated Ti^{4+} in strong acid conditions after heated quickly, then the nuclei tended to transformed into rutile structure by the influence of H_3O^+ , and this structure transformation would consume the hydrated Ti^{4+} in the reaction system gradually with the time prolonging. The excess of hydrated Ti^{4+} in the solution will transform to octahedral structure of anatase by OH^- effects after the change of pH, and at this moment, the prolonging reaction time could not change the molar ratio between rutile and anatase structure, because rutile phase is more thermodynamically stable than anatase. Thus rutile phase and anatase phase crystallized successively and grew interlaced after hydrothermal treatment, and then nano-composite crystal titania 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

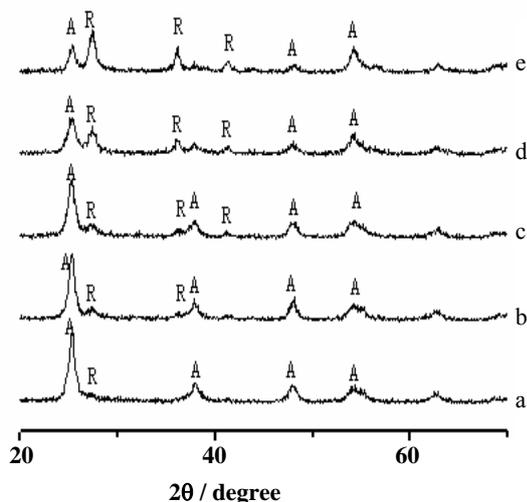


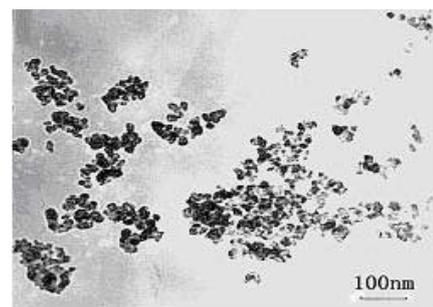
Fig. 2: Effects of compulsive hydrolyzation time on the control of structure phase. a: 10%A 90%R (2min); b: 20%R 80%A (12min); c: 25%R 75%A (48min); d: 30%R 70%A (75min); e: 40%R 60%A (180min) A: anatase ratio R: rutile ratio.

increase, and spherical particles appeared dominating in the product's morphology; the content of anatase phase increased with the decrease of hydrolyzation time, and rod-shape particles dominated in the product's morphology, (see Fig. 3). The reason may be ascribed to crystal lattice constants of rutile and anatase phase which 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 tends to grow along with axial orientation, growth trend of rutile phase along c axis would be stronger than that of anatase phase, thus spherical particles appeared in rutile structure but rod-shape appeared in anatase phase.

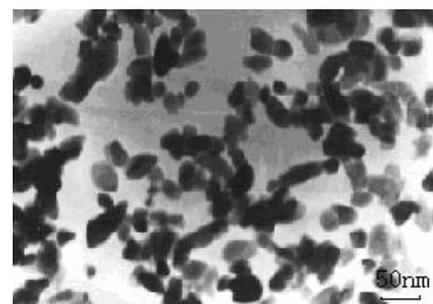
The cooling and drying temperature may affect the crystal phase and particle distribution, as we all know that crystalline will be aged after a long time cooling at a low temperature, and in this work the product had been aged/perfect after the hydrothermal treatment, so the cooling factor was secondary.

Drying temperature is very important in this work, much more agglomeration appeared due to fast water loss at high temperature, and drying efficiency is not enough at low drying temperature, and the further experiment will be affected.

Photo-degradation experiments of organic dyes (acid red 3R) were performed with composite-crystal product (for example anatase:rutile = 7:3 molar ratio) compared with pure anatase and rutile (self-prepared, about 20nm) and mechanical mixture of both in the same ratio



1. TEM for sample "e"



2. SEM for sample "c"



3. TEM for sample "a"

Fig. 3: Effect of the reaction time on morphology.

illuminated by the sun. From Fig. 4 we can find that composite-crystal product possessed the highest photo-catalytic activity among three samples, and it showed that the structure of composite-crystal product was different from mechanical mixture. The enhancement of photo-catalytic activity may be ascribed to adjacent property of crystal structure in the product and more crystal boundary appearance, then transferring efficiency of photoexcited charges was enhanced and recombination of electrons and holes on titania surface was reduced effectively, so photo-catalytic efficiency improved obviously.

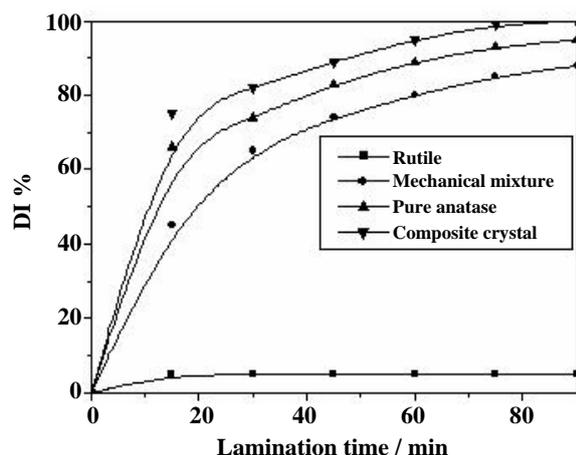


Fig. 4: Degradation experimental results with different photocatalysts.

CONCLUSIONS

1. TiCl₄, ammonia, inorganic salts as raw material, nanometer composite-crystal TiO₂ powders were synthesized by two-step chemical method.

2. Morphologies and crystal phase contents of sample were quantitatively controlled by different reaction time.

3. Composite-crystal sample has higher photocatalytic activity than pure rutile and anatase sample illuminated by sunshine.

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