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A novel method for preparation of nanocrystalline rutile TiO_2 powders by liquid hydrolysis of $TiCl_4$

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Nanocrystalline rutile TiO_2 with average crystal sizes of 6.9–10.5 nm and specific surface areas of 70.3–141.0 m^2g^{-1} were prepared by hydrolysis of $TiCl_4$ aqueous solution at lower temperatures. The presence of small amounts of nano rutile TiO_2 as crystal seed could obviously accelerate the crystallization of TiO_2, make nanocrystalline rutile TiO_2 well dispersed and make the reaction of formation of rutile more kinetically favorable than that of formation of anatase in the liquid hydrolysis of $TiCl_4$.

Introduction

Nanosized titania has received much research attention because of its unique physicochemical properties in the applications of pigments, cosmetics, fine ceramics, photocatalysts for environmental purification, catalyst supports and dielectric materials.[1–4] Titania exists in three main crystallographic form *i.e.* anatase, rutile, and brookite. Each structure exhibits different physical properties. Rutile TiO_2 has higher relative permittivity, refractive index, ultraviolet ray absorption rate and stronger resistance against powdering. Each application of titania requires a specific structure and, usually, also a specific size.[5,6] Thus, it is important to develop synthetic methods in which the size, morphology, and the structure of nano titania could be controlled. In the past two decades, great efforts have been devoted to studying the preparation of nanosized anatase titania at low temperatures.[7,8] However, few results concerning the preparation of nano rutile TiO_2 with higher specific surface areas at low temperatures have been available. The conventional method for preparation of rutile TiO_2 powders is the phase transformation of TiO_2 from anatase to rutile at temperatures higher than 450 °C.[7,9] Rutile TiO_2 can also be directly prepared by flame oxidation of $TiCl_4$.[10] These two methods usually result in large titania particles with low surface area. The only way to obtain small rutile titania particles reported so far involves the use of $TiCl_4$ and mineralizers, like $SnCl_4$, NH_4Cl, NaCl or SnO_2.[11,6] The particles obtained using mineralizers by hydrothermal methods were rod-like or broom-like aggregates with sizes 100 by 10 nm.[12,13] Recently, Aruna *et al.*[14] developed a new method of preparation of nanosize rutile titania by hydrothermal synthesis from titanium isopropoxide. Zhang *et al.*[15] reported the preparation of nanosized TiO_2 by hydrolysis of $TiCl_4$ solution at 70 °C for several hours, but the rate of nucleation at room temperature was so slow that the powder was predominantly amorphous.[16] Pedraza *et al.*[17] prepared rutile TiO_2 with a higher surface area through direct oxidation of $TiCl_3$ by O_2 at room temperature, but the samples contained 5% anatase after pretreatment at 80 °C. Obviously, developing a method for one-step preparation of nanocrystalline TiO_2 powders with pure rutile structure at lower temperatures is of significance. In this work, we report a novel method for the preparation of nanocrystalline titania with pure rutile structure by hydrolysis of $TiCl_4$ solution at lower temperatures.

Experimental

Preparation

Commercial titanium tetrachloride (98% $TiCl_4$, Shanghai Chemical Agent Co.) was used as the main starting material without further purification. Known amounts of $TiCl_4$ were added dropwise into 200 ml portions of distilled water. Then the above aqueous solutions were kept at different temperatures for hydrolysis of $TiCl_4$ in a temperature-controlled bath. In order to promote crystallization of titania, a small amount of nano rutile TiO_2 (*ca.* 70 mg) with an average crystal size of 6.9 nm and a specific area of 141.0 $m^2\ g^{-1}$ was added into the above solutions. After hydrolysis and crystallization for several days, the precipitates formed in the solutions were filtered and washed thoroughly with distilled water, and then dried at 150 °C in air for 24 h.

Characterization

The as-prepared samples were characterized by using X-ray diffraction (XRD), transmission electron microscopy (TEM), and surface area measurements, and UV absorption. XRD measurements were carried out on a Shimadzu XD-3A X-ray diffractometer using CuKα radiation. TEM images were taken using a JEM-100CX electron microscope. The BET surface areas of samples were measured on a Micrometrics ASAP 2000 instrument using N_2 adsorption at −196 °C. UV absorption spectra were recorded on a UV-240 UV–visible Recording Spectrophotometer; the titania colloid solution for UV absorption measurements was prepared by ultrasonically dispersing 0.0200 g of sample into 200 ml distilled water.

Results and discussion

Table 1 summarizes the properties of as-prepared TiO_2 prepared by hydrolysis of $TiCl_4$ at lower temperature (note: content of rutile by XRD (%) is estimated from the respective integrated XRD peak intensity using the following equation: $\chi = (1 + 0.8I_A/I_R)^{-1}$, and the average crystal size is determined from the broadening of the corresponding X-ray spectral peaks (at 27.3°) by the Scherrer formula: $L = 0.89\lambda/\beta\cos\theta$).[15] As can be seen from Fig. 1, four intense diffraction peaks appeared at 2θ = 27.3, 35.9, 41.2, 54.4°, which can be assigned to the diffraction peaks of rutile TiO_2, indicating that the as-prepared TiO_2 sample (No.3) has a rutile structure. For the samples

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Table 1 The properties of as-prepared TiO_2 prepared by hydrolysis of $TiCl_4$ aqueous solution at lower temperature

No.	$TiCl_4$ concn./ mol L^{-1}	Hydrolysis time/d	Hydrolysis temp./°C	Crystal seed	Yield of product (%)	Rutile content by XRD (%)	Crystallite size of rutile/nm	Anatase	Surface area/ m^2 g^{-1}
1	0.28	6	20	Rutile	75.6	100	8.4		118.7
2	0.28	8	20	No	66.7	100	7		139.3
3	0.28	3	40	Rutile	89	100	6.9		141
4	0.28	3	40	No	80.1	100	8.7		115.6
5	0.28	2	60	Rutile	91.2	100	8.3		120.5
6	0.28	2	60	No	84.5	46.8	10.9	5.7	162.9
7	0.28	1	80	Rutile	93.4	100	8.1		122.7
8	0.28	1	80	No	86.7	27.5	11.6	5.5	200.4
9	0.28	0.5	95	Rutile	95.6	35.5	12	6.1	156.8
10	0.28	0.5	95	No	88.9	6.2	19.6	6	186
11	0.66	8	20	Rutile	73.2	100	8.8		110.4
12	0.66	8	20	No	15	100	8.3		120.7
13	1.13	9	20	Rutile	6.6	100	10.5		70.3
14	1.13	9	20	No	0				

obtained by calcining No.3 at 300 °C, 400 °C and 500 °C, no diffraction peaks of anatase were observed (curves b, c and d), which suggests that amorphous TiO_2 does not exist in the as-prepared sample as the amorphous–anatase transformation may be complete in the temperature range from 350 °C to 400 °C.[18] It can be seen from Table 1 that the other as-synthesized titania samples such as No. 1, 2, 4, 5, 7, 11, 12, 13 also have pure rutile structures with average crystal sizes in the range of 6.9–10.5 nm.

Fig. 2 shows the morphology of as-prepared rutile titania samples. As can be seen from Fig. 2, the particles obtained in the presence of a crystal seed are well-dispersed nano needle-shaped titania with sizes of 50–70 by 5–12 nm, and the particles obtained in the absence of crystal seed are aggregates of needle-shaped titania. The formation of the nano needle-shaped rutile titania is attributed to the strong HCl acid conditions in which the formation of needle-shaped titania with an appropriate ratio of length and diameter is thermodynamically favorable.[19] The diameters of these needle-shaped rutile titania particles are in good agreement with the average crystal sizes estimated by XRD.

All of the as-synthesized nano needle-shaped rutile titania have very high specific surface areas, as high as more than 110 m^2 g^{-1}, except for No.13. Fig. 3 presents the effect of thermal treatment on the specific surface area of nano needle-shaped rutile TiO_2 (No.3). It can be seen that with increasing thermal treatment temperature the surface area decreases gradually, indicating that thermal treatment at higher temperatures results in the sintering of nanocrystalline TiO_2 particles. After calcination at 400 °C in air for 3 h, the specific surface area of the rutile titania sample was still as high as 44.1 m^2 g^{-1}. The high surface area is very important for its applications such as rutile-based dye-sensitized solar cells,[13] solar reflecting shields,[5] gas sensing,[11] and catalysis.[6]

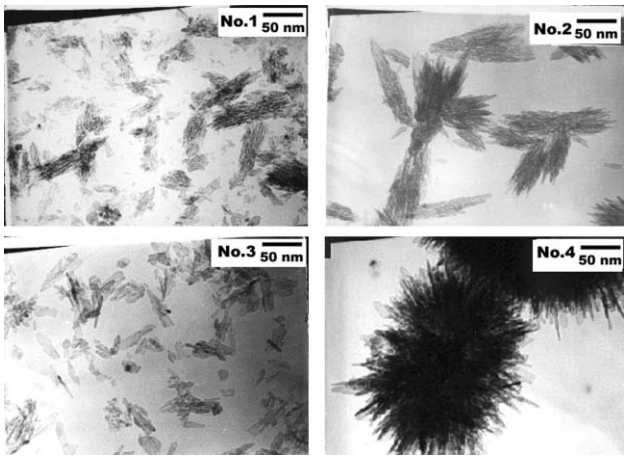

Fig. 2 Morphology of as-prepared TiO_2 powders (No. 1, 2, 3, 4).

Fig. 4 shows the XRD patterns of as-synthesized TiO_2 samples prepared with or without nano rutile TiO_2 as crystal seed. The nano rutile additive has very important effects on the rate of crystallization, yield of TiO_2 product, and the crystalline structure. In the presence of crystal seed in the solution, the crystallization of TiO_2 is obviously accelerated, and the yield of TiO_2 product is improved. In the absence of crystal seed in the $TiCl_4$ solution, the anatase TiO_2 appears in the products when the temperature is above 50 °C; the higher the temperature of hydrolysis, the more the content of anatase TiO_2 in the products. If there is a small amount of nano rutile TiO_2 as crystal seed in the $TiCl_4$ solution, only if the temperature of hydrolysis is below and/or equal to 80 °C does the TiO_2 product still have a pure rutile structure. Therefore it can be concluded that the

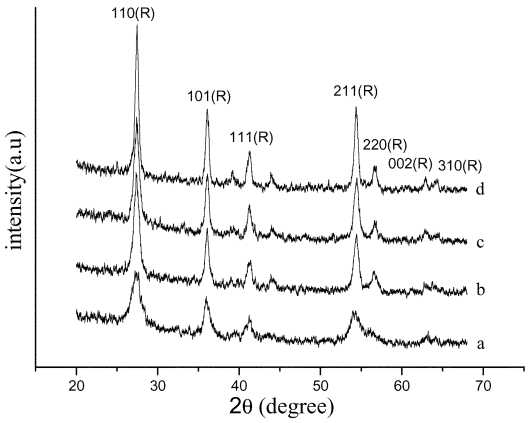

Fig. 1 XRD patterns of the TiO_2 sample (No. 3) dried at 150 °C (a) and calcined at 300 °C (b), 400 °C (c) and 500 °C (d).

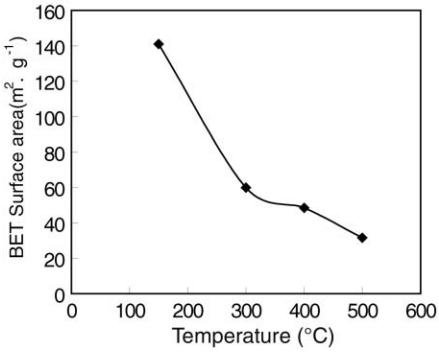

Fig. 3 Effect of thermal treatment on the surface area of nano sized rutile TiO_2 (No.3).

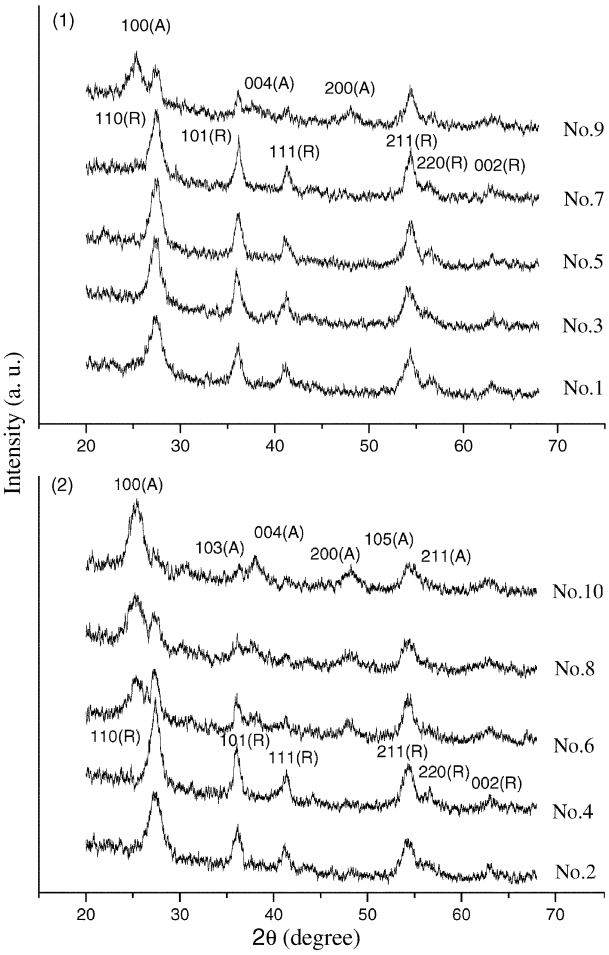

Fig. 4 XRD patterns of the TiO_2 samples: (1). with nano rutile TiO_2 as crystal seed; (2)without nano rutile TiO_2 as crystal seed.

presence of crystal seed in the $TiCl_4$ solution makes the reaction of formation of rutile more kinetically favorable than that of formation of anatase in the liquid hydrolysis of $TiCl_4$, that is to say, nano rutile TiO_2 as crystal seed decreases the activation energy of the reaction of formation of rutile in the liquid hydrolysis of $TiCl_4$.

At lower temperatures (below 50 °C), the concentration of $TiCl_4$ has little effect on the crystalline structure of the TiO_2 product; whether there is crystal seed or not and whether the concentration of $TiCl_4$ is high or low, the final product always has a rutile structure after enough ageing time of the $TiCl_4$ solution. However, the concentration of $TiCl_4$ has an important effect on the rate of hydrolysis and the yield of TiO_2 product. When the concentration of $TiCl_4$ is below 0.28 mol L^{-1} or so, the rate of hydrolysis and the yield of TiO_2 product increase at elevated $TiCl_4$ concentration, but with further increase in the $TiCl_4$concentration, the rate of hydrolysis and the yield of TiO_2 product decrease. At 20 °C, when the concentration of $TiCl_4$ solution is above 1.13 mol L^{-1}, in the absence of crystal seed (rutile TiO_2), no TiO_2 product is formed even after ageing for 9 days. Fig. 5 shows that the relationship between concentration of $TiCl_4$ and BET surface area of TiO_2 product exhibits a volcano pattern. When the concentration of $TiCl_4$ is below 0.28 mol g^{-1} or so, with increasing concentration of $TiCl_4$, the BET area of the TiO_2 product increases, but when the concentration of $TiCl_4$ further increases, the BET area of the TiO_2 product decreases.

From Fig. 4 and Table 1, it can be seen that the temperature of hydrolysis plays a major part in determining the crystal structure of the TiO_2 product and the rate of hydrolysis; with increasing temperature of hydrolysis of the $TiCl_4$ solution, the rate of hydrolysis is increased rapidly and the yield of TiO_2

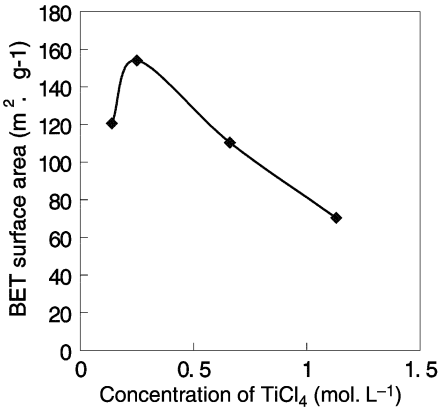

Fig. 5 Relationship between concentration of $TiCl_4$ and BET surface area of the TiO_2 product prepared at 20 °C.

product is improved. When the temperature of hydrolysis is below 50 °C, no matter whether there is crystal seed or not in the $TiCl_4$ solution, the final TiO_2 product always possesses a rutile structure. But when the temperature of hydrolysis is above 80 °C, no matter whether there is crystal seed or not, anatase TiO_2 is formed as the product.

The overall reaction is:

$$TiCl_4 + 2H_2O \rightarrow TiO_2\ (\text{rutile}) + 4HCl \qquad (A)$$

or

$$TiCl_4 + 2H_2O \rightarrow TiO_2(\text{anatase}) + 4HCl \qquad (B)$$

The Gibbs free energy of reaction (A) and reaction (B) at 25 °C is −59.32 kJ $mol^{-1}$and −54.29 kJ mol^{-1}, respectively, therefore the two reactions can take place spontaneously, and reaction (A) is more thermodynamically favorable than reaction (B). At same time, at lower temperatures, whether there is crystal seed or not, whether the concentration of $TiCl_4$ is high or low, the final product always has a rutile structure. From this observation, it can be deduced that reaction A is much more kinetically favorable than reaction B. That is to say, reaction A has a lower activation energy than reaction B. Therefore, at lower temperatures (below 50 °C), reaction A is both more thermodynamically and kinetically favorable than reaction B. Consequently, only reaction A takes place at lower temperatures (below 50 °C), which gives a reasonable explanation for the samples 1, 2, 3, 4, 11, 12, and 13 with pure rutile structures. With increasing hydrolysis temperature, reaction B is accelerated more rapidly than reaction A. If there is no crystal seed in the solution, when the temperature of hydrolysis is above 50 °C, anatase TiO_2 is formed. The higher the temperature of hydrolysis is, the higher the rate of reaction B, therefore, the higher the content of anatase in the TiO_2 product.

At lower concentrations of $TiCl_4$ solution (below 0.28 mol L^{-1} or so), with increasing $TiCl_4$ concentration, the hydrolysis of the $TiCl_4$ solution is accelerated, the rate of nucleation and supersaturation of the solution increase, and the number of nuclei increases. Therefore, the average size of the TiO_2 particles decreases with increasing concentration of $TiCl_4$. On the other hand, at higher concentrations of $TiCl_4$ solution (above 0.28 mol L^{-1}or so), the concentration of H_2O in the $TiCl_4$ solution is so low that the hydrolysis of $TiCl_4$ is decreased. That is to say, the rate of nucleation and the number of nuclei decrease with further elevation of the $TiCl_4$ concentration. Therefore, the average size of the TiO_2 particles increases with increasing concentration of $TiCl_4$. So, the relationship between concentration of $TiCl_4$ and BET surface area of the TiO_2 product exhibits a volcano pattern as the BET

Table 2 The relationship between initial $TiCl_4$concentration and pH of the $TiCl_4$ solution after hydrolysis for a certain time

Concentration of $TiCl_4$/mol L^{-1}	0.14	0.28	0.66	1.13
pH of $TiCl_4$ solution after ageing for:				
3 h	0.61	0.13	0.63	0.99
28 h	0.40	0.07	0.50	0.60
48 h	0.30	0.005	0.43	0.56

surface area of the TiO_2 product increases with decreasing average size of the TiO_2 particles. As can be observed in Table 2, the concentration of H^+ increases as the hydrolysis reaction goes on; when the initial $TiCl_4$ concentration is below 0.28 mol L^{-1} or so, the pH value of the $TiCl_4$ solution decreases at elevated $TiCl_4$ concentrations. However, when the initial $TiCl_4$ concentration is above 0.28 mol L^{-1}or so, the pH value of the $TiCl_4$ solution increases at elevated $TiCl_4$ concentrations. These results demonstrate that the $TiCl_4$ solution with 0.28 mol L^{-1} of initial $TiCl_4$ concentration has the highest rate of hydrolysis and crystallization as the pH value is indicative of the degree of hydrolysis, which further confirms that the above explanation is correct.

The additive nano rutile plays two main roles as follows. Firstly, it provides more interface (0.07 g as-used nano rutile can provide an interface of 9.9 m^2 g^{-1}), which can greatly accelerate the crystallization as crystallization on a solid–liquid interface is much easier than nucleation in a liquid phase.[20] Secondly, as a crystal seed, it could induce titania nuclei to crystallize to rutile with more structure and thermodynamic stability than anatase, and decrease the activation energy of reaction A. The rate of reaction A or B is determined by two main factors *i.e.* temperature and activation energy. The increase in the rate of reaction A caused by the decrease of the activation energy in the presence of rutile seeds is much more rapid than that of reaction B caused by the elevation of hydrolysis temperature. Therefore, in the presence of rutile seeds, only reaction A takes place, provided that the hydrolysis temperature is not more than 80 °C. With a further increase in hydrolysis temperature, reaction B begins to take place. This is the reason why a certain amount of anatase is formed in the TiO_2 sample in the presence of rutile crystal seeds when the hydrolysis temperature is above 80 °C.

One of important applications of nano rutile TiO_2 is as UV absorbent in cosmetics, pigments and plastics instead of organic UV absorbents because of its high absorbance for ultraviolet rays (400–190 nm) and because it is not toxic. Fig. 6 shows the UV absorption spectra of No. 3, 7, 10 and commercial nano rutile TiO_2 (No.15) with a specific area of 87.0 m^2 g^{-1} and an average crystallite size of 13.0 nm (provided by the Taixing Nano Materials Factory of the Chinese Academy of Science). From Fig. 6, it can be seen that anatase and the anatase–rutile mixture have different UV absorption patterns from rutile TiO_2. The as-synthesized nano rutile TiO_2 has a similar UV absorption pattern to the commercial nano rutile TiO_2 product, but shows a blue shift of about 14 nm in maximum absorption in comparison with the commercial nano rutile TiO_2. This blue shift is attributed to the well-known quantum-size effect for semiconductors[21] as the as-synthesized nano rutile TiO_2 has an average crystal size of 6.9 nm smaller than the commercial nano rutile TiO_2 (13.0 nm). Further, it exhibits higher UV absorbance from 400 nm to 190 nm than the commercial nano rutile TiO_2 product.

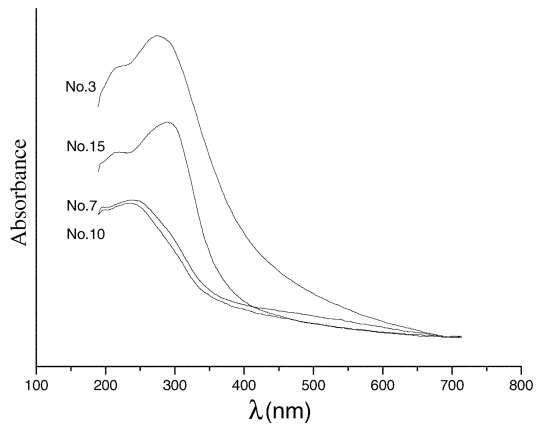

Fig. 6 UV absorption spectra of No. 3, 7, 10 and commercial nano rutile TiO_2 (No.15).

Conclusions

In summary, a novel method for the one-step preparation of nano rod-like rutile TiO_2 powders at lower temperatures has been developed. By this method, nano rod-like titania with pure rutile structure and high specific surface areas can be easily prepared by liquid hydrolysis of $TiCl_4$ at lower temperatures by using nano rutile TiO_2 as crystal seed. The presence of the crystal seed in the $TiCl_4$ solution can accelerate greatly the crystallization of TiO_2 and make the formation of rutile more kinetically favorable than the formation of anatase in the liquid hydrolysis of $TiCl_4$.

Acknowledgement

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