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The synthesis of nanosized TiO_2 powder using a sol-gel method with $TiCl_4$ as a precursor

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Nanosized TiO_2 powder with anatase structure was synthesized by a sol-gel method using $TiCl_4$ ethanol solution as a precursor. The grain size of TiO_2 powder was homogenous and was about 10 nm after the precursor was calcined at 500 °C for 1 hour. Anatase TiO_2 powder formed after the precursor was calcined at a temperature ranging from 300 °C to 550 °C. The gelatinizing mechanism of $TiCl_4$ in ethanol solution can be described as followings. When mixed with ethanol, $TiCl_4$ reacted with ethanol to form $TiCl_x(OCH_2CH_3)_{4-x}$ species and HCl gas. During gelatinizing process, $TiCl_x(OCH_2CH_3)_{4-x}$ species absorbed water from atmosphere to form $Ti(OH)_4$ precursor, which was polymerized to be an inorganic polymer. The formation of inorganic polymer of $Ti(OH)_4$ was intensified with gelatinizing time. In contrast, the organic component was removed from the precursor. The formation of anatase TiO_2 can also be promoted by increasing gelatinizing time. The influence of alcohol on the reacting progress and dispersivity was also studied. The size and activity of alcohol molecule were found to have influence on the polymerization and mineralization degree of the precursor and the dispersivity of TiO_2 powders.

1. Introduction

As an excellent photocatalyst, TiO_2 has a good prospect in environmental purification [1] and can be used as a kind of solar energy cell [2, 3]. When irradiated with UV light, TiO_2 nanosized powder shows strong oxidizability and reducibility [4, 5]. Recently, the photocatalyst of TiO_2 has been utilized for various fields of environmental purification, such as degradation of hazardous volatile organic and malodorous compound, decolorization of dyeing waste water, direct decomposition of NO_x, SO_x and purification of air and water [6–9]. With the decrease of particle size of TiO_2, the catalytic activity can increase dramatically [10]. The energy conversion efficiency of solar cell using TiO_2 as photocatalyst can be as high as 33% [2]. In general, nanosized TiO_2 can be prepared by using a sol-gel method with $Ti(OBu)_4$ as a precursor [11, 12], by which expensive chemicals must be used and the hydrolysis process is not easy to control. In this study, nanosized TiO_2 powders were synthesized using $TiCl_4$ as a precursor due to the cheapness and easier control of hydrolysis. The results confirmed that it is a good way to prepare nanosized anatase TiO_2 powder. The mechanism of gelatinization of $TiCl_4$ ethanol solution and the formation of nanosized TiO_2 power was also revealed.

2. Experimental

All of the chemicals were analytical grade. 1.5 ml $TiCl_4$ was slowly added dropwise into 15 ml ethanol at room temperature. A large amount of HCl gas was exhausted during the mixing process. A light yellow solution was obtained and gelatinized for several days to form sol-gel. Then, the sol-gel solution was vaporized at 80 °C until a dry-gel was obtained. The dry-gel precursor was calcined at different temperatures for definite time in air to form TiO_2 powders. In order to promote the decomposition of organic components in the precursor, the initial heating rate was maintained at 5 °C/min. To study the influence of alcohol on the reacting progress and product, the reactant of ethanol was replaced with CH_3OH and $i\text{-}C_3H_7OH$. The TiO_2 powders were obtained in the same way.

IR spectra of the precursor solution gelatinized for various time and the dry-gel prepared with $TiCl_4$ and different alcohol were obtained in Perkin-Elmer 2000 FT-IR. XRD experiments were carried out in Rigako DMAX-2400 diffractometer using Cu K_α radiation. The topography and particle size were measured using a Hitachi H-800 Transmission Electron Microscopy (TEM). The accelerating voltage of electron beam was 200 kV. TGA and DTA analyses were performed on a Dupond 1090 thermal analyzer. The atmosphere was air, and the heating rate was maintained at 10 °C/min.

3. Results and discussion

3.1. The formation of sol-gel

The gelatinizing process of $TiCl_4$ in ethanol solution was investigated *in-situ* using IR analysis. As shown in Fig. 1, the IR spectra of $TiCl_4$ precursor varied with gelatinizing time. After $TiCl_4$ was mixed with

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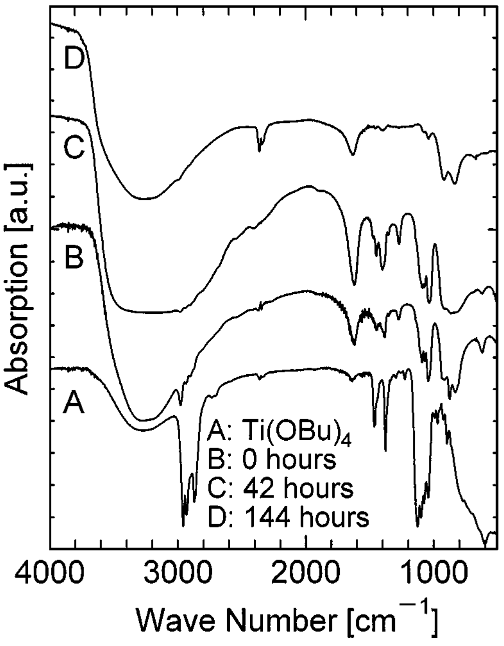


Figure 1 The IR spectra of precursor with different gelatinizing time.

ethanol, a strong absorption peak at 3240 cm^{-1} appeared, which can be attributed to —OH bond, implying that $TiCl_4$ reacted with residual water in ethanol to form Ti-OH bond. The absorption peak at 1623 cm^{-1} also confirmed the existence of —OH bond in the precursor. The peaks at 2978, 2930, 2890, 1456 and 1390 cm^{-1} were attributed to $-CH_2$ and CH_3 groups in $TiCl_x(OC_2H_5)_{4-x}$ species, implying that $TiCl_4$ reacted with ethanol to form $TiCl_x(OC_2H_5)_{4-x}$ species. A weak peak at 621 cm^{-1} can also be observed, which was a characteristic peak of Ti-O-C bond according to the IR spectrum of $Ti(OBu)_4$. This result also confirmed the formation of $TiCl_x(OC_2H_5)_{4-x}$ species in the precursor solution. With the increase of gelatinizing time, the peak at 3240 cm^{-1} intensified, which suggests the increase of hydrolysis degree of $TiCl_x(OC_2H_5)_{4-x}$ species. The peak at 3240 cm^{-1} also became broad, which suggests that the increase of polymeric degree of $Ti(OH)_4$ species. The absorption peaks corresponded to $-OCH_2CH_3$ group weakened with the gelatinizing time, indicating the $Ti-OCH_2CH_3$ group was hydrolyzed into Ti-OH group. The weakening of the peak at 621 cm^{-1} also proved the disappearance of Ti-O-C bond in precursor species. When the gelatinizing time increased to 144 hours, the IR spectrum of precursor kept unchanged with time. This result indicated that equilibrium was reached and $TiCl_x(OC_2H_5)_{4-x}$ species was completely hydrolyzed. The precursor was light yellow at the beginning and become colorless after a certain time (above 120 hours).

Based on the results above, the gelatinizing process of $TiCl_4$ in ethanol solution can be described as followings. At first, $TiCl_4$ reacted with ethanol to form $TiCl_x(OEt)_{4-x}$ species. Simultaneously, $TiCl_4$ also reacted with residual water in ethanol to form $TiCl_x(OH)_{4-x}$ species. This process was very rapid and almost completed after the mixing process. In the gelatinizing process, Ti-OEt, Ti-Cl bonds in $TiCl_x(OH)_{4-x}$ species absorbed water from atmosphere to form Ti-OH. The Ti-OH bond was polymerized into -Ti-O-···-Ti-OH forming inorganic polymer. The hydrolysis process of $TiCl_x(OH)_{4-x}$ precursor was easily controlled due to the existence of HCl in the precursor. The $-OCH_2CH_3$ group was removed more easily from the precursor than —OBu group due to its higher activity for water.

When mixing:

$$TiCl_4 + C_2H_5OH \rightarrow TiCl_x(OC_2H_5)_{4-x} + (4-x)HCl \qquad (1)$$

$$\begin{aligned} &TiCl_x(OC_2H_5)_{4-x} + H_2O \\ &\quad \rightarrow Cl_x(C_2H_5O)_{3-x}Ti\text{-}OH + C_2H_5OH \qquad (2) \end{aligned}$$

During gelatinizing:

Polymerizing:

$$\begin{aligned} &Cl_x(C_2H_5O)_{3-x}Ti\text{-}OH + HO\text{-}TiCl_x(OC_2H_5)_{3-x} \\ &\quad \rightarrow Cl_x(C_2H_5O)_{3-x}Ti\text{-}O\text{-}TiCl_x(C_2H_5O)_{3-x} + H_2O \qquad (3) \end{aligned}$$

$$\begin{aligned} &Cl_x(C_2H_5O)_{3-x}Ti\text{-}OH + TiCl_x(OC_2H_5)_{4-x} \\ &\quad \rightarrow Cl_x(C_2H_5O)_{3-x}Ti\text{-}O\text{-}TiCl_x(C_2H_5O)_{3-x} \\ &\quad + C_2H_5OH \qquad (4) \end{aligned}$$

Hydrolysis:

$$\begin{aligned} &Cl_x(C_2H_5O)_{3-x}Ti\text{-}O\text{-}\cdots + H_2O \\ &\quad \rightarrow Ti(OH)_3\text{-}Ti\text{-}O\cdots Ti\text{-}O\text{-}Ti(OH)_3 \qquad (5) \end{aligned}$$

3.2. The thermal decomposition of the precursor

Fig. 2 shows a typical TGA and DTA results of $TiCl_4$ precursor gelatinized for 24 hours. Three weight-loss regions were observed on the TGA curve. The weight-loss region from 25 °C to 120 °C resulted from the removing of —OH group; the region from 125 °C to

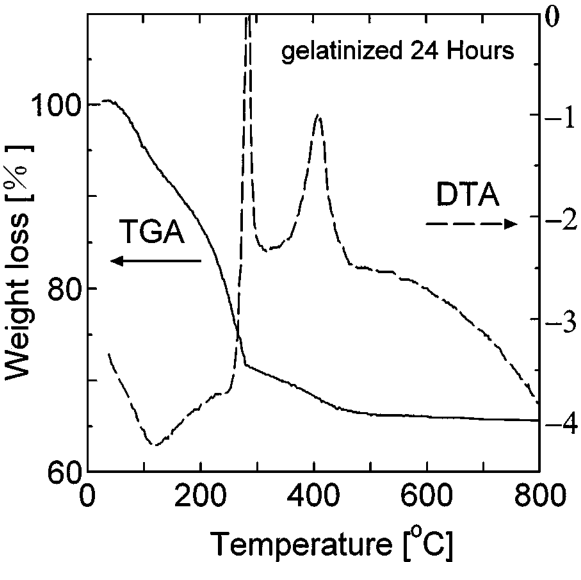


Figure 2 A typical TGA and DTA result of precursor gelatinized for 24 hours.

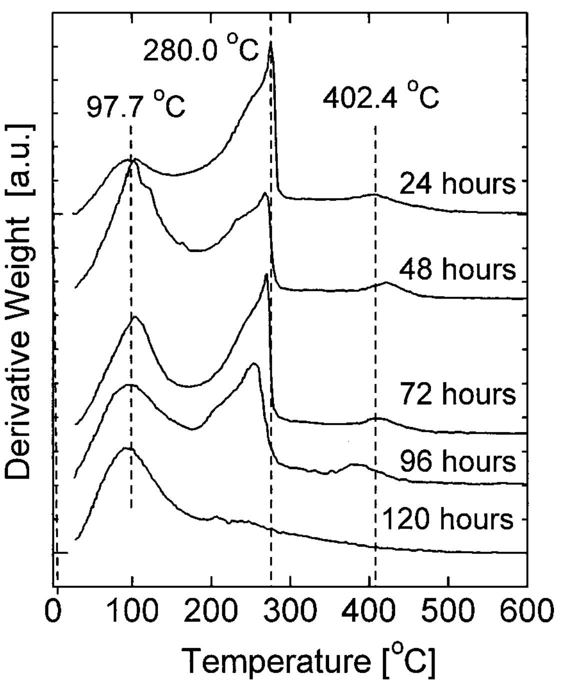


Figure 3 The TGA results of precursor with different gelatinizing time.

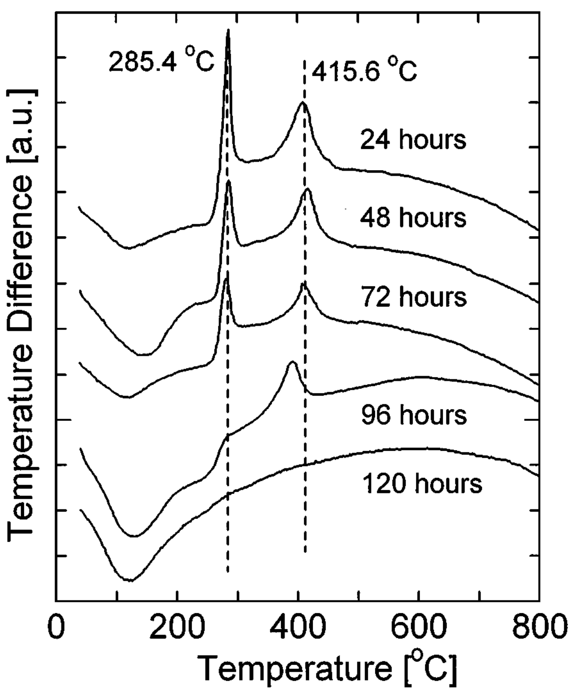


Figure 4 The DTA results of precursor with different gelatinizing time.

280 °C was attributed to the oxidation of organic component in the precursor, and the region from 280 to 500 °C was attributed to the exhaust of HCl from the precursor. The derivative weight curve indicated the quantitative weight-loss for each region. The exothermal region at 100 °C was corresponded to the decrease of H_2O and $Ti(OH)_4$. The exothermal peaks at 280 °C and 450 °C resulted from the oxidation of organic component and the exhaust of -Cl from the precursor, respectively.

The derivative weight curves of TiO_2 precursor gelatinized for various time are shown in Fig. 3. With the increase of gelatinizing time, the peak at 97.3 °C intensified and the peak at 280.0 °C became weakened gradually. The peak at 402.4 °C changed un-obviously. This result indicated that the number of —OH group was increased as gelatinizing time increased while the organic components were decreased. When the gelatinizing time increased to 120 hours, these two peaks disappeared, which suggested that the precursor consisted of inorganic components. The DTA curves of precursor gelatinized for various time are shown in Fig. 4. The isothermal region from 25 °C to 120 °C resulted from the evaporation of solvent and water. The exothermal peak at 285.4 °C was attributed to the decomposition of residual organic component, and the exothermal peak at 415.6 °C resulted from the removing of -Cl. With the increase of gelatinizing time, these two peaks became weakened gradually. When gelatinized for 120 hours, these two peaks disappeared. This result suggested that the gelatinizing time could promote the removing of organic component and Cl.

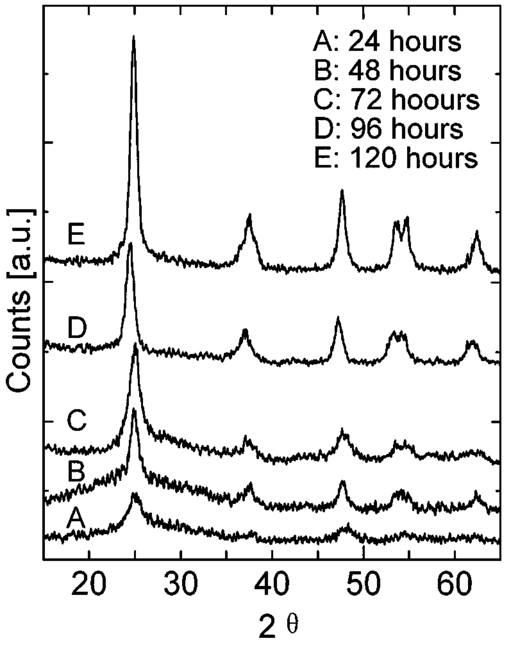


Figure 5 The influence of gelatinizing time on the structure of TiO_2 powder calcined for 1 hour at 400 °C.

3.3. The influence of gelatinizing time on the crystalline of TiO_2 powder

The gelatinizing process can influence the structure of precursor and the formation of anatase TiO_2. Fig. 5 shows the XRD patterns of TiO_2 powder annealed at 400 °C for 1 hour. The precursor gelatinized for 24 hours formed an amorphous TiO_2 after being treated at 400 °C for 1 hour. The formation of amorphous TiO_2 could be attributed to the existence of organic components in the precursor and the low polymerization of the precursor. After the gelatinizing time increased to 48 hours, the characteristic diffraction peaks of anatase TiO_2 can be observed in XRD pattern, indicating the formation of crystalline TiO_2 with anatase structure. The broad background indicated that most TiO_2 still existed as amorphous. With the increase of gelatinizing time, the characteristic peaks of anatase TiO_2 became intensified and sharpened, indicating that the crystalline of TiO_2 powder became much more perfect, which

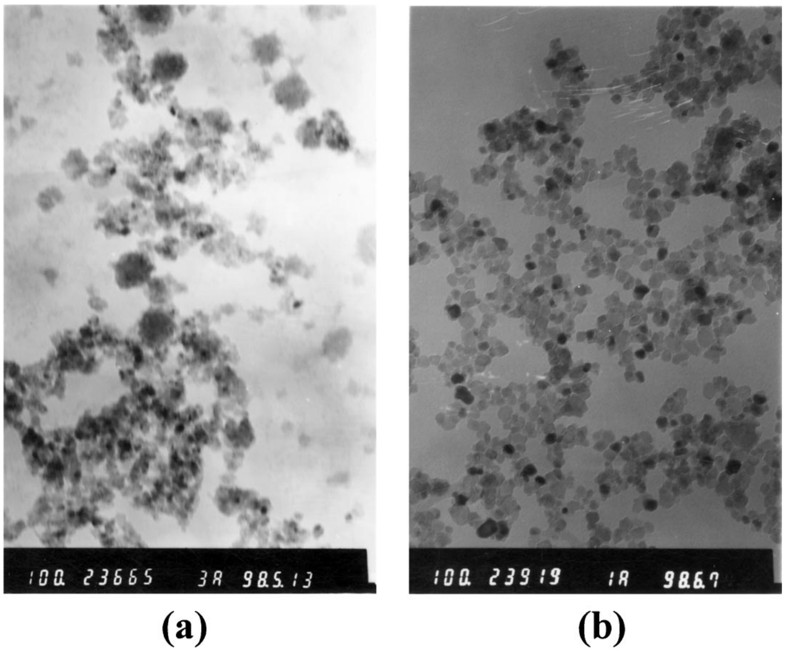


Figure 6 The typical TEM photographs of TiO_2 powder gelatinizing for various time and calcined for 1 hour at 400 °C. (a) gelatinizing for 24 hours, conglomeration, (b) gelatinizing for 120 hours, high dispersivity.

resulted from the hydrolysis and polymerization of the precursor. TEM indicated that the sample existed as palate form when the gelatinizing time was short (24 hour). The longer the gelatinizing time was, the better the dispersivity of TiO_2 powders became. When gelatinized for short time, the TiO_2 powder was gray, indicating the existence of carbonized carbon, which was also confirmed by XPS results. With the increase of the gelatinizing time, the color of sample became superficial. After the gelatinizing time reached 120 hours, the color of TiO_2 was white. The results above revealed that the formation of anatase TiO_2 could be promoted by increasing the gelatinizing time.

3.4. The influence of gelatinizing time on grain size of TiO_2 powder

Fig. 6 shows the TEM photograph of TiO_2 powder which gelatinized for various time. When the gelatinizing time was about 24 hours (in Fig. 6a), TEM indicated the particle was very small and about 4 nm. The dispersivity of TiO_2 particles was not good. With the increase of gelatinizing time, the size of particle increased and the dispersivity was improved. When the time increased to 120 hours, the particle size increased to 10 nm (Fig. 6b). The dispersivity was much better than that of short gelatinizing time. The increase of the gelatinizing time can improve the dispersivity and increase the particle size.

3.5. The influence of thermal treatment on the formation of anatase TiO_2 nanosized particle

The calcination process can also influence the formation of anatase TiO_2. The influence of calcination temperature on the structure of TiO_2 powder is shown in Fig. 7. The XRD patterns showed that the anatase TiO_2 was formed after the precursor was calcined at 300 °C for 1 hour. With the increase of calcination temperature, the peaks became narrower, indicating that calcination temperature can promote the crystallization of TiO_2 significantly. With the increase of calcination time, the characteristic peaks became narrower, indicating that calcination time can promote the crystallization of TiO_2, too. TEM indicated when the calcination temperature increased from 300 °C to 500 °C, the grain size increased from 4 nm to 12 nm.

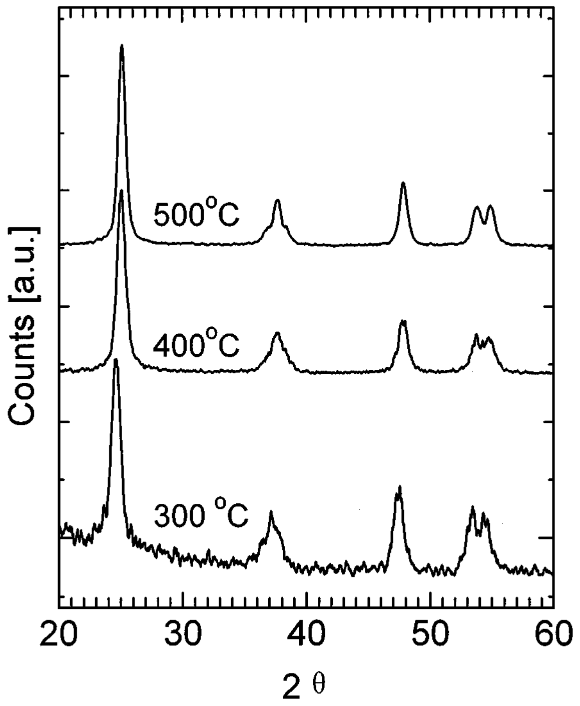


Figure 7 The influence of calcination temperature on the structure of TiO_2 powder.

3.6. The influence of alcohol on the reacting progress

As shown in Fig. 8, the broad peak ranging from 400 to 800 cm^{-1} which is the characteristic resonance of

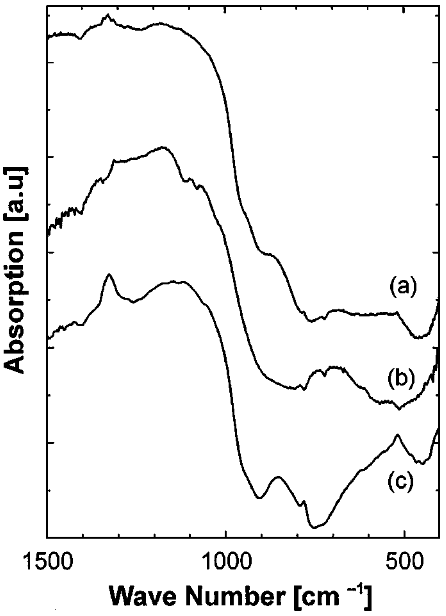


Figure 8 The IR spectra of precursors prepared with different alcohol molecules. (a) CH_3OH, (b) C_2H_5OH, (c) i-C_3H_7OH.

$(Ti\text{-}O)_n$, was obviously broadened in width and increased in intensity from (c) to (a), which indicated that the polymerization degree was gradually increased. Moreover, the intensity of peaks representing the resonance of organic groups was decreased from (c) to (a), which implied the increase of mineralization degree. The size and activity of alcohol molecules can explain the result above. Having a smaller size and a more active —OH and -OCH_3 group, CH_3OH can react with $TiCl_4$ more easily to form a polymer precursor with a higher polymerization degree and the —OCH_3 group in the precursor is much easier to be removed by H_2O than -OC_2H_5 and -i-OC_3H_7, while i-C_3H_7OH can't react quickly due to its bigger size and lower activity of -OH, consequently forming a precursor with a lower polymerization degree and mineralization degree. As to the ethanol, the situation is neutral compared with CH_3OH and i-C_3H_7OH. Thus the size and activity of alcohol molecules have obvious influence on the reacting progress.

3.7. The influence of alcohol on the TiO_2 powders

Fig. 9 shows the TEM photograph of TiO_2 powders prepared with $TiCl_4$ and different alcohol. As shown in Fig. 9, the powders prepared with CH_3OH and C_2H_5OH (Fig. 6b) had a better dispersivity. While those prepared with i-C_3H_7OH existed in small or big conglomeration. It's because the precursor prepared with i-C_3H_7OH is lowly mineralized, the powders can't separate completely due to the interaction between the remaining organic groups. XRD result shows that these three samples are typical anatase TiO_2 after annealed for 1hour at 400 °C. Moreover, the width of peaks are almost the same, which implies that these three samples have similar crystal size.

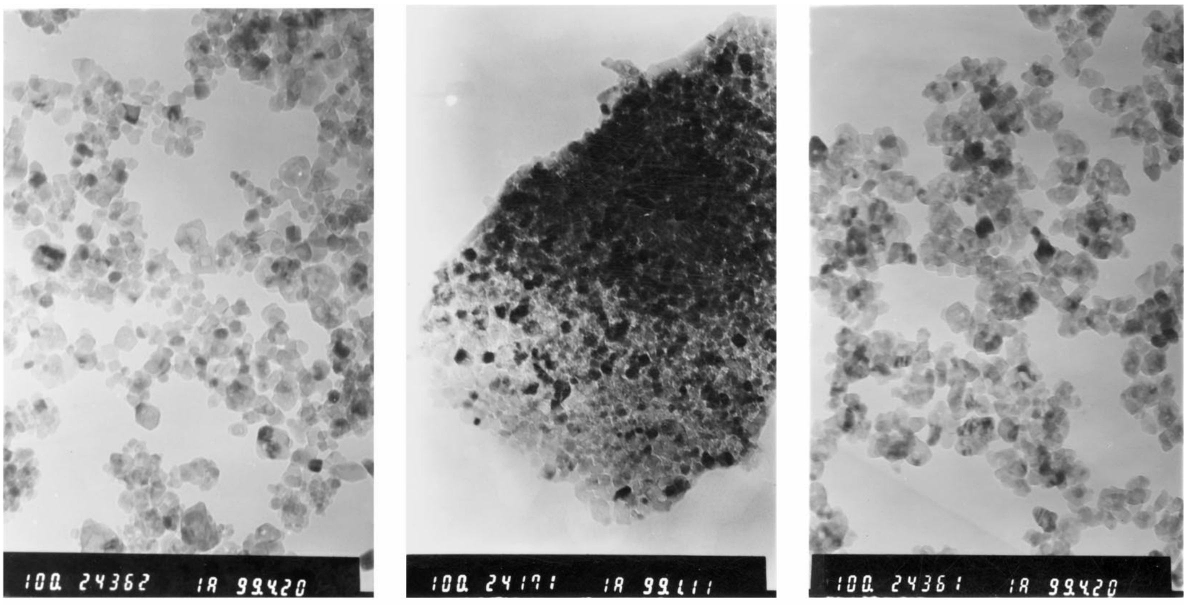
4. Conclusion

1. Nanosized anatase TiO_2 powder was successfully synthesized by a sol-gel method using $TiCl_4$ as a precursor.

2. The gelatinizing process was revealed as followings. At first, $TiCl_4$ reacted with ethanol to form $TiCl_x(OEt)_{4-x}$ species. Then, this species absorbed water to form $Ti(OH)_4$ inorganic polymerized gel.

3. The formation of inorganic gel and anatase TiO_2 nano particles can be promoted by increasing the gelatinizing time.

4. The size and activity of alcohol have obvious influence on the reacting progress and product. With the size of alcohol molecule increasing to be large enough,



(a) (b) (c)

Figure 9 The typical TEM photographs of TiO_2 powders gelatinizing in different alcohol solution and calcined for 1 hour at 400 °C. (a) synthesized with CH_3OH, high dispersitity, (b) synthesized with i-C_3H_7OH, big conglomeration, (c) synthesized with i-C_3H_7OH, small conglomeration.

the polymerization degree and mineralization degree of the precursor decrease, and the dispersivity of TiO_2 powders also decreases, but the grain sizes are almost the same.

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