研究简报

离子液体-水的混合溶剂中,合成条件对纳米 TiO_2 结晶度的影响

闫智英[1,2] 郑文君*,[1]
([1]南开大学化学学院材料化学系,天津 300071)
([2]云南大学材料与化学工程学院化学系,昆明 650032)

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Effect of Synthesis Conditions on Crystallinity of Nano Titania in Mixture Solvent of Ionic Liquid and Water

YAN Zhi-Ying[1,2] ZHENG Wen-Jun*,[1]
([1]*Department of Material Chemistry, Institute of Chemistry, Nankai University, Tianjin* 300071)
([2]*Department of Chemistry, Institute of Material and Chemical Engineering, Yunnan University, Kunming* 650032)

Abstract: The nanocrystalline TiO_2 was prepared in mixture solvent of ionic liquid (1-ethyl-3-methyl -imidazole acetate, $EmIm^+AcO^-$) and water by sol-gel low temperature hydrothermal treatment of tetrabutyl titanate. X-ray diffraction (XRD), transmission electron microscope (TEM), and Automatic nitrogen adsorption measurement techniques were employed to characterize the final products. The influences of various hydrothermal conditions, such as the amount of ionic liquid, reaction temperature and time, on the crystallinity of titania were investigated. Crystallinity was evaluated by crystallite size. The results showed that the crystallinity of sample prepared in mixture solvent is higher than that of sample from pure water; also, the size and crystallinity of titania particle can be controlled by alteration of the amount of ionic liquid. In addition, in the presence of ionic liquid, highly crystalline titania could be obtained at relatively low temperature and shorter time.

Key words: titania; ionic liquid; crystallinity

0 Introduction

Titania has been extensively used in a variety of applications such as gas sensors, dielectric ceramics, catalysts for thermal or photoinduced processes, photovoltaic solar cells, and pigments. One of the most important applications of titania is photodetoxification of water and air pollutants because of its high efficiency, stability, nontoxity, and low cost[1,2]. Titania has three crys talline polymorphs: anatase, rutile, and brookite. It is generally thought that anatase has a far higher photocatalytic activity than the rutile phase and brookite phase[3]. The performance of anatase in applications depends to a large extent on its physical and chemical properties. Fine particles are desired for high photoactivity due to high specific surface area. Besides, crystallinity of anatase was also experimentally shown to be an important factor in order to get

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*通讯联系人。E-mail:zhwj@nankai.edu.cn
第一作者:闫智英,女,36 岁,博士;研究方向:无机材料合成。

highly photocatalytic activity[4, 5].

Titania was mainly synthesized by sol-gel method using titanium alkoxides or chlorides [6 ~9], in the method, there are many factors influencing the size and morphology of the formed titania particles. These factors include the concentration of reactants, the pH of the solution, the temperature of hydrolysis and the property of the solvent. The low-temperature preparation of high crystalline titania with a large specific surface area have been a subject studied by many workers.

Ionic liquids (ILs) as "designer solvents" have been widely used in organic reactions and electrochemical processes[10, 11]. Recently, as template solvents in inorganic synthesis ionic liquid has been successfully used to synthesis porous metal oxides, molecule sieves[12~14] and nanoparticles[15]. Yoo et al.[12] indicat- ed that IL facilitated direct synthesis of crystalline titania at ambient condition by sol-gel method, but the product had poor crystallinity of 37%. We report the work here on the sol-gel low temperature hydrother-mal treatment of tetrabutyl titanate in the presence of ionic liquid, 1-ethyl-3-methyl-imidazole acetate ($EmIm^+AcO^-$), to synthesis nanocrystalline titania. Effect of the synthesis conditions on the crystallinity of nanocrystalline titania was investigated. The crystallinity of titania in this work was evaluated by crystallite size[16, 17].

1 Experimental

1.1 Synthesis

The synthetic procedure of $EmIm^+AcO^-$(IL) followed a reported route [18]. Titanium tetrabutoxide (98%, C.P.) was used as the precursors of titania without further purification and treatment. All other reagents used in the experiment were of analytical grade. Typically, 1.4 mL of titanium tetrabutoxide (TBT) was added dropwise to the mixture made of IL and water under rigorous stirring. Various IL/water by volume was chosen as listed in Table 1. The concentration of titanium species was kept to be 0.25 mol·L^{-3}. White precipitates of hydrous oxides were produced instantly, and the mixture was stirred for 2 h at room temperature. The resulting mixture was transferred to a 20 mL Teflon-lined stainless steel autoclave at 60~100 ℃ for one or two days. The product was then filtered, washed with deionized water, and dried at room temperature.

1.2 Characterization

Powder X-ray diffraction (XRD) measurements were performed on a Rigaku D/max 2500 diffraction using Cu $K\alpha$ radiation (λ=0.154 056 nm) at 40 kV and 120 mA by scanning at 2°·min^{-1}. The crystalline size of the TiO_2, D_{hkl} was calculated using the Scherrer formula: $D_{hkl}=0.9\lambda/B_{hkl}\cos\theta$, where B_{hkl}, the full width of the diffraction line at half of the maximum intensity, was determined on 101 X-ray diffraction lines of anatase phase. Transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) were obtained using a Tecnai G^2 20 S-Twin electron microscope at 200 kV. Samples were prepared by evaporating very dilute suspensions onto carbon-coated grids. The Brunauer - Emmett -Teller (BET) surface area was measured on a CHEMBET-3000 (America) using N_2 adsorption at −196 ℃ after drying in vacuum at 200 ℃.

2 Results and Discussion

Th e synthesis conditions, properties (crystallite size and specific surface area) of various nanocrysalline TiO_2 powders are given in Table 1.

Table 1 Synthesis conditions, properties of various nanocrystalline TiO_2 powders

Sample	$V_{IL}/(V_{IL}+V_{H_2O})$	Temperature / ℃	Crystallite size / nm	Specifie Surface area / ($m^2\cdot g^{-1}$)
1	0	100	7.3	251
2	0.25	100	13.2	115
3	0.5	100	21.4	78
4	1(pure ionic liquid)	100	amorphous	4
5	0.5	80	10	180

Continued Table 1

6	0.5	60	5	293
7*	0.5	100	10.3	238

*Reaction time is 24 h

2.1 Effect of the amount of IL

The samples were synthesized with various volume ratios of IL to water at 100 ℃ for 2 d. Fig.1 shows the X-ray powder diffraction pattern of titania (sample **1**, **2**, **3**, in Table 1) which can be assigned to anatase (JCPDS 21-1272). But the XRD pattern (Fig. 1a) of titania prepared from pure water shows clearly brookite phase at 2θ=31°. When IL is added to the system, brookite phase almost disappears (Fig.1 b, c).

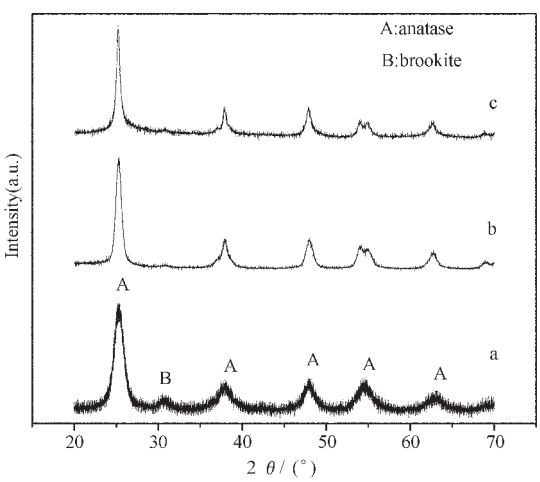

Fig.1　XRD patterns of sample **1** (a), sample **2** (b), sample **3** (c)

In addition, with the increase of IL the peak corresponding to anatase at 2θ=25.4° clearly increases and becomes sharper. The results indicate that IL is able to prevent from the production of brookite and favors the growth of anatase phase. According to the Scherrer formula, the size of anatase crystallite (D) for samples **1**, **2**, **3** was calculated to be about 7.3, 13.2, 21.4 nm, respectively. The relative TEM micrographs of samples are shown in Fig.2. From TEM images, it could be illustrated that the size and morphology change in samples with the increment of IL. By TEM observation, the average particle sizes are close to the diameters of these titania crystalline size estimated by XRD and gradually increase in turn of sample **1**, **2**, **3**. Grain boundaries for sample **3** are clearly observed in Fig.2 c, indicating that the nano particles are highly crystalline. In other words, the crystallinity of titania gradually improve with increase of IL. The change in the specific surface areas of samples is also listed in Table 1. Apparently, the specific surface area for sample **1**, **2**, **3** could be correlated to the crystallite size, i.e. smaller size crystallites have larger specific surface area.

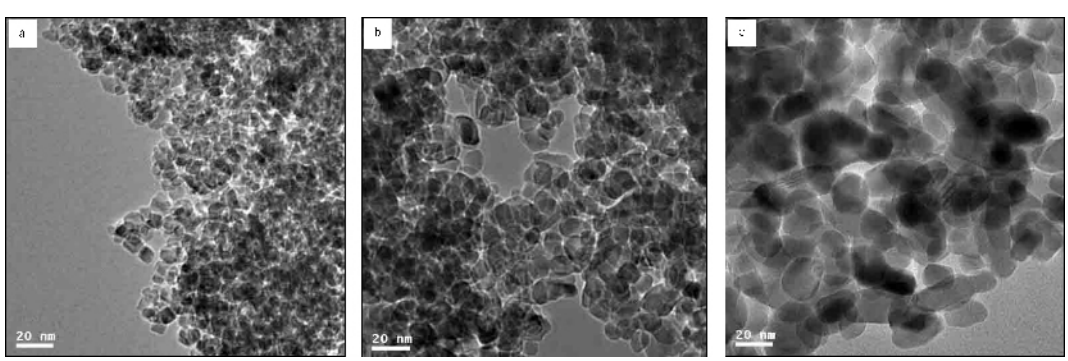

Fig.2　TEM images of sample **1** (a), sample **2** (b), sample **3** (c)

To further investigate the influence of IL on crystallization of titania, more experiments with $V_{IL}/(V_{IL}+V_{H_2O})$ more than 0.5 were performed. It was found that the crystallinity of anatase decreased, and amorphous phase produced when reaction was performed in pure IL. That is to say, in water-rich region, IL can promote the crystallinization of TiO_2 nanoparticles. As shown in Fig.3, particles size of prepared titania markedly increased with the increase of IL at the range of $V_{IL}/(V_{IL}+V_{H_2O})$ less than 0.5, and can be expressed as a similar linear relations with the amount of IL. Thus, it is suggested that the size and crys-

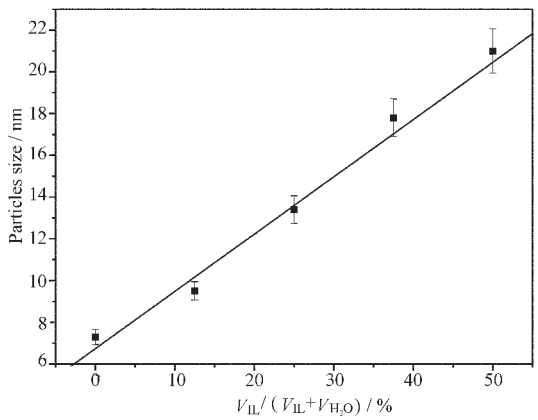

Fig.3 Plot of the particles size of product against the content of IL

tallinity of titania particles can be controlled by alteration of the amount of ionic liquid in reaction media.

In the present work, titanium tetrabutoxide was used as a titanium source; thus its hydrolysis requires the presence of water. We propose that the effect of IL is due to two characteristics of IL-water system. Firstly, the conductivity and viscosity of IL-water mixtures significantly depend on the amount of IL. As the amount of IL increases, it is the second characteristic that IL molecules form clusters of their own kind as in their pure IL state up to a threshold fraction [19]. From the characteristic of IL consisting virtually only of ions, we can induce that in the water-rich region the ionic strength is increasing with the IL added. Thus, the recrystallization process can be improved under IL-water system offering the environment of high ionic strength and conductivity. With the increase of IL, the high viscosity of system is the cause of decreasing diffusion coefficient. Then a higher growth speed can be obtained because of the higher concentration of reactants around TiO_2 particles. Whereas in the IL-rich region, the effect of ionic strength slowly reduces and the influence of viscosity grows stronger with the increase of IL molecule clusters; moreover, most of water molecules may be anchored to the anions and the cations of IL by forming hydrogen bonds; the reduction of free water molecules makes the hydrolysis of titanium tetrabutoxide to be confined.

2.2 Effect of reaction temperature

From the above studies, when $V_{II}/(V_{IL}+V_{H_2O})$ is 0.5, titania with high crystallinity was obtained at 100 ℃. Thus, to investigate the low crystallization temperature, experiments were performed with $V_{II}/(V_{IL}+V_{H_2O})$ of 0.5 at 60 ℃, 80 ℃ for 2 d, respectively. The XRD patterns of the products are given in Fig.4. It could be seen that the peak at 2θ =25.4° corresponding to anatase phase is getting lower and broader with the decrease of the temperature. The average crystallite sizes and surface area are listed in Table 1. The reaction temperature has a large effect on the crystallite. Anatase nanocrystals of about 10 and 5 nm are obtained at 80 and 60 ℃, respectively (sample **5**, **6**). Like the crystallite size, the surface areas also see a large change with temperature. The BET surface areas range from 170 $m^2 \cdot g^{-1}$ for the sample obtained at 80 ℃ to 293 $m^2 \cdot g^{-1}$ for the 60 ℃ sample, which is consistent with the decrease in grain size. It is a notable feature that at 60 ℃ the nanocrystalline anatase particles could be obtained. Its image and diffraction pattern are shown in Fig.5 and confirm a crystalline structure for this sample. Usually, the amorphous → anatase transformation may complete in the temperature range from 250~400℃. Yanagisawa et al.[20] have made a detailed investigation into crystallization of anatase from amorphous titania by using the hydrothermal technique and realized the transformation of amorphous to anatase at temperature of 120~250 ℃. Our results show that anatase is obtained at 60 ℃, indicating that use of IL can realize the lower temperature crystallization of titania. This result is similar to

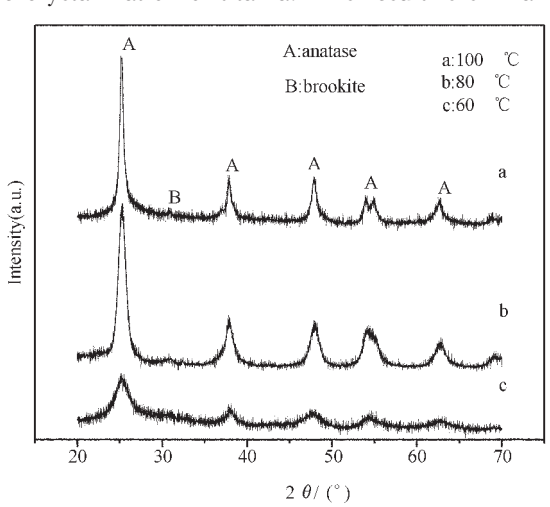

Fig.4 XRD patterns of sample 3 (a), sample 5 (b) and sample 6 (c)

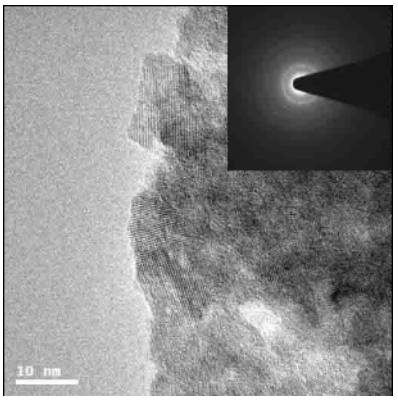

Fig.5　TEM micrographs of sample **6**

the observation by Zhou [13] and Yoo et al [12]. In their reports, titania was obtained by sol-gel method at 80 ℃, 100 ℃, respectively. These studies fully show that ionic liquid favors the crystallization of substance at low temperature.

2.3　Effect of reaction time

To quickly obtain the nanocrystalline TiO_2, we further examed the crystallinity of titania prepared in shorter time. It can be seen in Fig.6b that reducing reaction time to 24 h the highly crystalline titania may still be obtained. The crystalline size and specific surface area for sample **7** were listed in Table 1. Fig.7 shows the electron micrographs. It can be seen that the particles of the nanocrystalline titania have a narrow distribution range of particle size. The diffraction pattern of selected area electron diffraction (SAED) for the sample clearly indicates a highly crystalline structure. Many reports[21,22] on titania synthesis at low temperature suggested that the amorphous titania was converted into anatase for several week, even one year. Our results clearly show that the use of IL will favor the crystallization of titania in short time under compatible temperature.

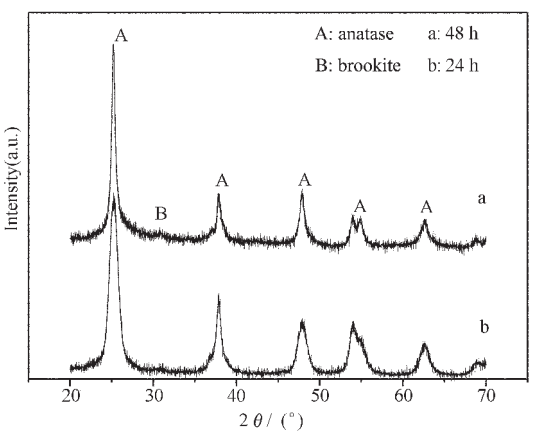

Fig.6　XRD patterns of sample **3** (a) and sample **7** (b)

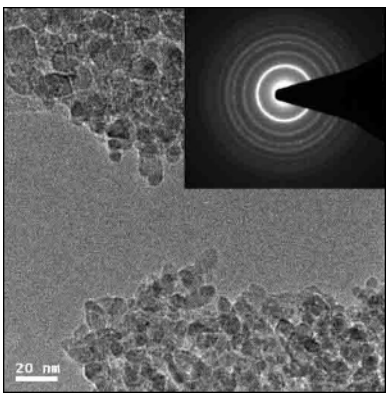

Fig.7　TEM image of sample **7**

3　Conclusions

The results show that the size and crystallinity of titania particle can be controlled by alteration of the amount of ionic liquid. In medium containing ionic liquid, highly crystalline anatase phase could be successfully prepared both at low temperature and in short time. Ionic liquid plays a key role in improving the crystallization of the final products. The product exhibits good crystallinity and needs no any subsequent heat treatment. In addition, the titania with high specific surface area is expected to be a good catalyst.

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